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SOURCES OF DIOXIN IN THE PRRI AREA

VOLUME I OF V

Prepared By:
TIERRA SOLUTIONS, INC.

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SOURCES OF DIOXIN IN THE PRSA AND PRRI AREAS

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- Ref. 2 - **The Inventory of Sources of Dioxin in the United States**. U. S. Environmental Protection Agency, Washington, DC. Dated April 1998.
- Ref. 3 - **Dioxin From Cradle To Grave**. By J. Thornton. Greenpeace USA. Dated April 1997.
- Ref. 4 - **A Literature Review of Formation and Release of PCDD/Fs from Gas Manufacturing: A Previously Unidentified Source?** By W. J. Walker and S. L. Huntley. Chemosphere, Vol. 35, No. 7, Page 1409. Dated 1997.
- Ref. 5 – EPA RCRA Waste Codes. Excerpts from 40 CFR Part 261, Identification and Listing of Hazardous Waste. Excerpts from 40 CFR Part 766, Dibenzo-Para-Dioxins/dibenzofurans.

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C12	4/21/93	Letter to Dale Webster, BASF from NJDEP
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E7	2/22/82	Hazardous Waste Investigation Findings by Inspector Tom Downey of BB&D
E8	5/16/84	Interoffice Memo from EPA Re: BB&D Sampling Results
E9	4/18/86	Soils and Ground Water Characterization; Bayonne Barrel and Drum Company; Prepared by Dan Raviv Associates, Inc
E10	6/2/88	RCRA Enforcement Inspection of BB&D; Prepared by Michael Ferriola, Environmental Scientist Source Monitoring Section
E11	10/24/88	U.S. Environmental Protection Agency; Preliminary Assessment of BB&D
E12	12/2/88	Site Inspection Review of BB&D submitted by Edward Gaven, NJDEP Bureau of Planning and Assessment
E13	9/30/92	Letter summarizing the Site Inspection Prioritization Evaluation of BB&D from Gary Bielen, Site Manager, John Rieckhoff, Pre-Remedial Program Manager and Dennis Stainken, Work Assignment Manager to Sandra Foose, USEPA
E14	3/26/97	Letter from William Lee, Environmental Project Manager, de maximis, inc., to Joseph Cosentino, USEPA enclosing Bayonne Barrel and Drum Site- Soil Investigation Report, by BBL
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E16	7/6/01	Letter from Richard Caspe, Director, Emergency and Remedial Response Division USEPA, to Recipients. Attached is a list of Potentially Responsible Parties.
E17	1946-1959	Correspondence from Passaic Valley Sewerage Commissioners documenting pollution of Harrison Creek.
E18	7/86	Soils and Ground Water Characterization prepared by Dan Raviv Associates, Inc.
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F4	1/27/76	Letter from J. F. Schwanhausser, Division Superintendent- Elizabeth PSE&G, to S.A. Lubetkin. Passaic Valley Sewerage Commissioners
F5	3/15/76	Memo from Passaic Valley Sewerage Commissioners concerning monthly reports for Jan. & Feb
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F9	3/20/91	Memo from NJ Department of Law and Public Safety, to Assistant Director for Enforcement Division of Water Resources & Assistant Director of Hazardous Waste Management. Attached is an investigation report of PSE&G.
F10	1950	Sanborn Map
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G4	10/31/84	Directive letter from NJDEP, to Milton Buck – Executive Director, Newark Redevelopment and Housing Authority Re: Violation
G5	2/6/85	Interoffice Memo from NJDEP to File Re: site inspection
G6	8/16/85	Letter from Riker, Danzig, Scherer, Hyland & Perreti, to Joseph Rogalski, Assistant Director- Div. Of waste management, NJDEP
G7	5/27/88	Letter from US Testing Company, Inc., to Betty Boros, NJDEP
G8	6/22/88	Letter from NJDEP to Thomas Spurkowsky, Site Manager Amer. Ref-fuel Re: Compliance Evaluation Inspection
G9	4/8/91	Letter from John Waffenschmidt-Asst. Director of Env. Compliance, Amer Ref-fuel, to Robert Oberthaler-NJDEP
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G14	3/25/95	Letter from Plant Manager, Amer. Ref-fuel, to NJDEP Re: Discharge Reports
G15	6/20/95	Letter from NJDEP, to Plant Manager Re: Compliance Evaluation Inspection. Attached is Discharge Surveillance Report
G16	10/83	Essex County Resource Recovery Project – Environmental Impact Statement

Thomasett/Hilton Davis Evidence Exhibits:

H1	7/30/56	Weekly Summary of Inspections for Thomasett Color Chemical Co.
H2	8/20/56	Weekly Summary of Inspections for Thomasett Color Chemical Co.
H3	1971	Annual Report by S.A. Lubetkin to the Passaic Valley Sewerage Commissioners
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H5	10/29/86	ECRA initial notice, General Information Submission Form from H.D. Lockwood, VP of Hilton-Davis, to NJDEP
H6	2/23/87	ECRA Site Evaluation Submission from Irving Cohen, President of Enviro-Sciences, Inc. to NJDEP
H7	6/18/96	Memo from Steve Huntley of Chem Risk, to Amanda Birrelll of Vinson & Elkins and Rick McNutt of Maxus. Attached is a report of PCB and PCDD/F discharge into Passaic by Hilton-Davis
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I9	05/05/42	Figure entitled Survey of 60-120 Lister Avenue
I10	01/07/65	Storm Sewer Map and Sanitary Sewer Map, #9G, 9H, by Porter Armstrong for Newark Housing Authority.
I11	9/4/70	City of Newark, Department of Public Works, "As-Is" Plans on Lister Avenue Sewer Improvements.
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I14	1971 – 1974	Excerpts from PVSC Annual Reports for 1971, 1972, 1973 and 1974, concerning Brown Street and Lockwood Street storm sewers.
I15		Excerpts from Chemical Waste Management Remedial Investigation Report – with associated documents, concerning on-site environmental conditions at the former Montrose/Chris Craft site.

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Givaudan Evidence Exhibits:

J1	1992	Givaudan Site Summary, taken from "Site Status Report" booklet, By NJDEP,
J2	4/2/75	Waste Effluent Survey of Givaudan Corporation for Passaic Valley Sewerage Commissioners, includes - Laboratory Analysis; sample from Givaudan Corp., from International Hydronics Corporation
J3	7/26/83	Letter from William Hyatt, Jr., Pitney Hardin Kipp & Szuch, to Michael Catania, NJDEP, enclosing Givaudan's information response re: trichlorophenol and hexachlorophene historical production.
J4	1/91	NJDEP Approved, TCDD Investigation Report and Limited Investigation Report
J5	12/13/91	Letter from David Sweeny of NJDEP, to Len Levy of Givaudan Corp.
J6	11/3/95	Letter from William Friedman of Brach, Eichler, Rosenberg, Silver, Bernstein, Hammer & Gladstone, to Robert Tavares, Chief Legal Counsel, Givaudan-Roure Corp.
J7	11/9/95	Letter from Leonard Levy, Director, Site Remediation Givaudan Corp., to Joseph Karpa, Division of Responsible Party Site Remediation NJDEP
J8	5/30/96	Letter from Leonard Levy of Givaudan Corp., to Maria Franco-Spera, Division of Responsible Party Site Remediation, NJDEP
J9	9/20/83	Report Chemical Sewer Investigation by CFM Inc. for Givaudan Corp.
J10	Various	Annual reports from PVSC re: sewer line breaks/incidents and related correspondence.
J11	1/29/92	Givaudan Site Map for Delineated TCDD Areas and Sample Locations produced by ERM, Inc.
J12	6/30/70	Plant Sewer System Map – Givaudan Corporation
J13	7/15/98	Phase III Remedial Investigation for Ground Water, Volume I, Givaudan-Roure Corp
J14	6/23/99	Letter from Richard Wroblewski of ERM, to Maria Franco-Spera of NJDEP, discussion of planned Remedial Action Report, and TCDD activity referenced in Appendix A.
J15	6/17/83	Executive Order #48B Re: Dioxin Emergency at Givaudan Clifton Site
J16	3/5/87	Administrative Consent Order- Ground Water
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J21	5/16/01	Letter from David Johnson, Givaudan, to Robert Schinn, NJDEP, re: sale of Givaudan plant site in Clifton.
J22	6/4/02	Letter from John Hogue, ERM, to Maria Franco-Spera, NJDEP, re: biennial certification/sale of Givaudan's Clifton property y.
J23	4/00	ERM Remedial Action Work Plan for Soils, (excerpts).
J24	3/1/00	ERM Draft Remedial Action Report, (excerpts)
J25	8/15/78	Killam Heavy Metal Source Determination Study
J26	April 1985	Givaudan's Plans for Discharge Prevention, Containment and Countermeasure and Discharge Cleanup and Removal.
J27	1983	Givaudan's Stormwater Drainage Patterns – details re: connection to County Street sewer.
J28	4/25/91	Letter from L.A. Levy, Givaudan, to Nicholas Eisenhauser, re: excess TCDD levels.
J29	6/22/83	NJDEP Internal Memorandum, D. Schrier to E. Liu re: review of Givaudan file concerning dioxin formation.
J30	2/00	ERM Sewer Decommissioning Report, (excerpts)
J31	9/4/96	Letter from L. Levy to Maria Franco-Spera, NJDEP.
J32		Annotated figure highlighted with on-site chemical, storm and sanitary sewer systems.

SOURCES OF DIOXIN IN THE PRRI AREA

INTRODUCTION AND INSTRUCTIONS

This report, Sources of Dioxin In The PRRI Area, is organized to present specific evidence compiled on certain Potentially Responsible Parties ("PRPs") and their association with sources of dioxin in the Passaic River Restoration Initiative ("PRRI") Area. The PRRI Area includes the Passaic River Study Area ("PRSA").

Report Organization

The contents of this report are organized into a set of five, (5), binders which serve to provide the following information:

- A narrative section which provides an overview and background on dioxin formation;
- A figure which provides the locations of the dioxin-associated PRPs identified to-date in the PRRI and PRSA areas;
- An overall Sources of Dioxin evidence summary chart;
- Select PRP case summaries with associated site location figures in the PRRI and PRSA;
- Analytical chemistry data obtained during sediment sampling and investigation activities conducted throughout the PRRI and PRSA areas;
- USEPA, trade and other technical reference materials relating to dioxin formation; and
- Tabbed sections containing copies of regulatory and other open source documentation that comprises the evidence associating each PRP with the formation of dioxin.

The background narrative section, dioxin reference materials, PRP locations figure, evidence summary chart, PRP case summaries, site figures and sediment chemistry data are all located in Volume 1 of this report.

The PRP-specific evidentiary materials have been organized for review in Volume 2 through Volume 5, inclusive, of this report.

Sources Of Information

It should be noted that the evidentiary materials have been compiled from various publicly available information sources. These open sources include, but are not limited to:

- The United States Environmental Protection Agency ("USEPA");
- The New Jersey Department of Environmental Protection ("NJDEP");
- Historical records of the Passaic Valley Sewerage Commissioners ("PVSC");

- Sewer infrastructure and discharge records of the City of Newark, the City of Clifton and Passaic County, NJ;
- Affidavits obtained from former employees of certain PRPs;
- Records obtained from online public and proprietary database information services; and
- General historical materials obtained from library sources in Newark, Clifton and Passaic, NJ.

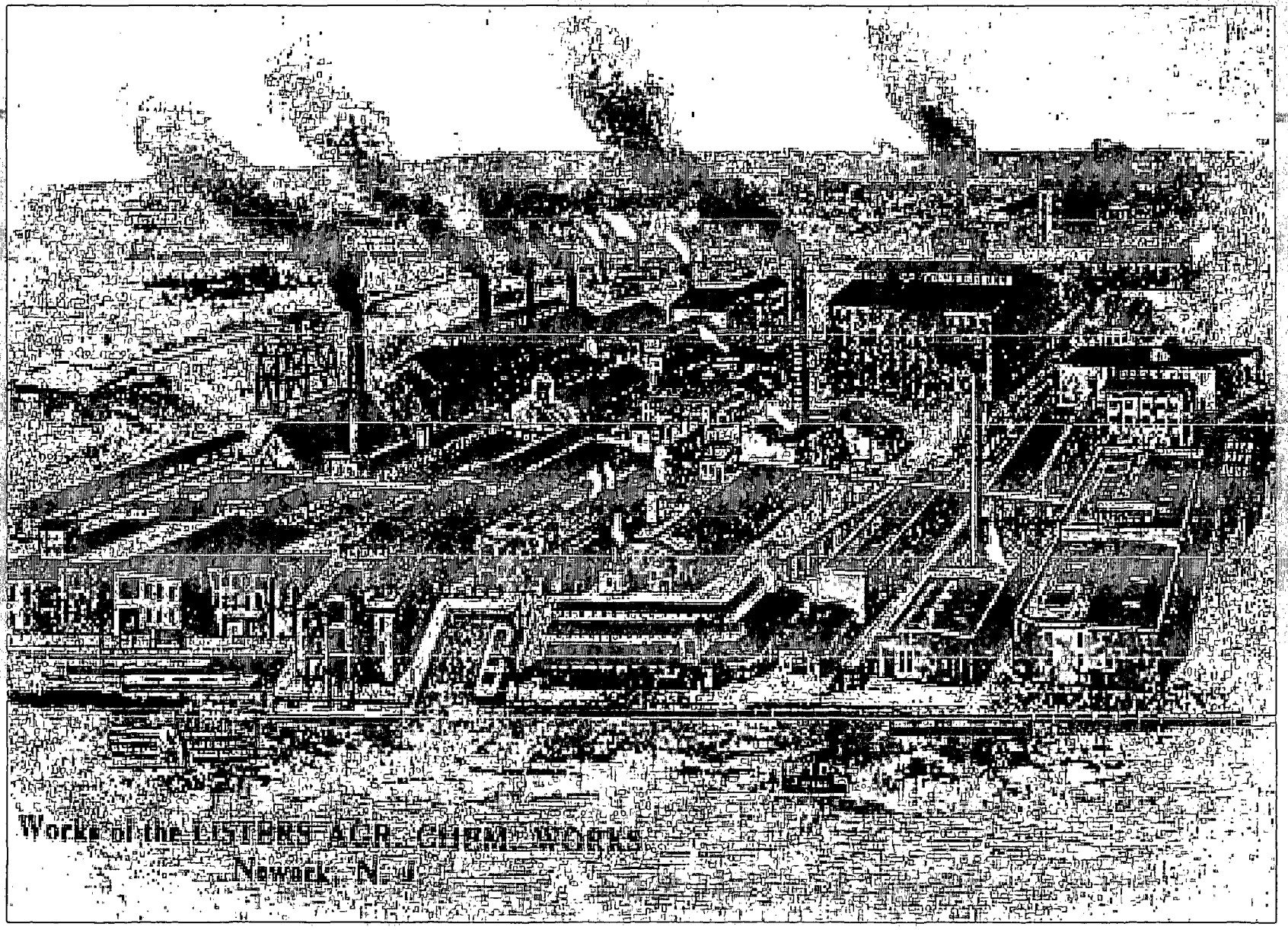
Summary

The evidence summary charts, associated figures, PRP case summaries, and dioxin association evidence are all arranged in a geographical progression, organized to read as if traveling from south to north in the PRSA and PRRI areas.

It is the objective of this report that the reader reviews the dioxin association information provided on the figures, case summaries, analytical data and evidence summary chart. The reader should then refer to the tabbed sections to review the detailed evidence compiled and presented for each PRP of interest.

This report serves to provide an interim compilation of those PRPs identified to-date, which are known to be associated with the formation of dioxin in the PRRI and PRSA areas. Ongoing efforts may serve to identify additional PRPs that are associated with dioxin formation.

Background and Case Examples



Works of the LISTERS AGR. CHEM. WORKS
Newark, N.J.

Presentation to USEPA on Sources of Dioxin In the PRRI Area

September 4, 2002

Facts Regarding Sources of Dioxin in the PRSA/PRRI Area

- There exist PRPs, which handled products and employed processes utilizing *chlorinated phenols* – just like the former Diamond site.
- There exist PRPs which handled chemicals and employed processes identified by USEPA as associated with the formation of dioxins.
- Sampling for dioxins on these sites has been limited; where sampling has been conducted dioxins have been detected.
- Many of these PRP sites have historical and/or present day discharge pathways to the PRRI.
- Additional investigation will be required.

Overview of Report on Sources of Dioxin in the PRRI Area

- Background on the formation of dioxin.
- Identification of more than 100 PRPs in the PRRI area associated with actual or likely dioxin generation to date.
- Evidence regarding 10 of these locations is provided in the report and exhibit binders.

Ten Dioxin PRP Case Studies

- Prentiss Drug & Chemical Company
- Alliance Chemical, Inc.
- BASF Corporation
- Arkansas Chemical Co./Hummel Chemical Co.
- Bayonne Barrel & Drum Co., Inc.
- PSE&G Essex Generating Station
- Essex County Resource Recovery Facility
- Thomasett Colors/Hilton-Davis Company
- Montrose Chemical Company/Chris Craft
- Givaudan-Roure Corporation

Background on the Formation of Dioxins

- USEPA has published extensively on this topic:
  - *Dioxins*, 1980, USEPA (Esposito, et al.)
  - *Estimating Exposure to Dioxin-Like Compounds*, 1994, USEPA (Exposure Assessment Group, OHEA)
  - *Locating and Estimating Air Emissions From Sources of Dioxins and Furans*, 1995, USEPA (Radian Corporation)
  - *The Inventory of Sources of Dioxin in the United States*, 1998, USEPA, (Exposure Analysis and Risk Characterization Group, Office of R&D).

Background on the Formation of Dioxins (Cont'd)

- USEPA classification of dioxin containing waste and dioxin-related compounds:
  - RCRA dioxin-containing hazardous waste codes (40 CFR 261, 766)
  - USEPA Dioxin Precursor compounds (40 CFR 766)

Background on the Formation of Dioxins

- Esposito (1980, USEPA) identified Classes of chemicals associated with the formation of dioxins:
  - Class I, II and III Organic Chemicals Related to Dioxin Formation
  - Classes I and II include polyhalogenated phenols and other chemicals "with a high probability of dioxin formation"
  - "The distinction between Classes I and II is arbitrary and does not indicate necessarily a difference in likelihood of dioxin formation."

Background on the Formation of Dioxins

CLASS I ORGANIC CHEMICALS (USEPA, 1980)	CLASS II ORGANIC CHEMICALS (USEPA, 1980)
4-Bromo-2,5-Dichlorophenol	Bromophenetole
2-Chloro-4-Fluorophenol	O-Bromophenol
Decabromophenoxybenzene	2-Chloro-1,4-Diethoxy-5-Nitrobenzene
2,4-Dibromophenol	5-Chloro-2,4-Dimethoxy-aniline
2,3-Dichlorophenol	Chlorohydroquinone
2,4-Dichlorophenol	O-Chlorophenol
2,5-Dichlorophenol	2-Chloro-4-Phenylphenol
2,6-Dichlorophenol	4-Chlororesorcinol
3,4-Dichlorophenol	2,5-Dibromo-4-Nitrophenol
Pentabromophenol	3,5-Dichlorosalicylic Acid
2,4,5-Tribromophenol	2,6-Diiodo-4-Nitrophenol
2,4,5-Trichlorophenol	3,5-Diiodosalicylic Acid
	O-Fluoroanisole
	O-Fluorophenol
	Tetrabromobisphenol
	Tetrachlorobisphenol

Background on the Formation of Dioxins

CLASS III ORGANIC CHEMICALS (USEPA, 1980)

3-Amino-5-Chloro-2-hydroxybenzenesulfonic acid
2-Amino-4-chloro-6-nitrophenol
O-Anisidine
Tetrachlorophthalic anhydride
Tetrafluoro-m-phenylenediamine
Tribromobenzene
1,2,4-Trichlorobenzene
2,4,6-Trinitroresorcinol
1-Phenol-2-sulfonic acid, formaldehyde condensate
Chloropentafluorobenzene
2,4-Dibromofluorobenzene
3,4-Dichloroaniline
2-Nitro-p-cresol
3,-4-Dichlorobenzotrichloride
Pentabromoethylebenzene
3,4-Dichlorophenylisocyanate
O-Phenetidine
Phthalic anhydride
Phenyl ether

2,5-Dihydroxybenzenesulfonic acid
2,5-Dihydroxybenzenesulfonic potassium salt
Benzaldehyde
Bromobenzene
O-Bromofluorobenzene
O-Chlorofluorobenzene
3-Chloro-4-fluoro-nitrobenzene
3-Chloro-4-fluorophenol
Maleic acid
Maleic anhydride
O-Nitroanisole
3,4-Dichlorobenzaldehyde
Pentabromochlorocyclohexane
1,2-Dichloro-4-nitrobenzene
Pentachloroaniline
O-Difluorobenzene
Picric Acid
Sodium picrate

Tetrabromophthalic anhydride
1,2,4,5-Tetrachlorobenzene
2,4-Dinitrophenol
2,4-Dinitrophenoxyethanol
3,5-Dinitrosalicylic acid
Fumaric acid
Hexabromobenzene
Hexachlorobenzene
Hexafluorobenzene
1,2-Dihydroxybenzene-3,5-disulfonic acid, disodium salt
O-Dichlorobenzene
O-Nitrophenol
3,4-Dichlorobenzotrifluoride
Pentabromotoluene
3,4-Difluoroaniline
Phenol (from chlorobenzene)
Pentafluoro aniline

Background on the Formation of Dioxins

- Esposito (1980, USEPA) also identified Classes of pesticide chemicals as "the most significant" groups of organic chemicals in relation to dioxin formation:
  - Class I Pesticide Chemicals are "highly likely" to be associated with dioxin formation.
  - Class II Pesticide Chemicals have a "reasonable but lesser probability" for association with dioxin formation. (Esposito, 1980, USEPA).

Background on the Formation of Dioxins

CLASS I PESTICIDE CHEMICALS (USEPA, 1980)

Methyl-5-[2,4-dichloroephenoxy]-2-nitrobenzoate	2,2-Dichloropropanoic acid 2-(2,4,5-trichlorophenoxy) ethyl ester
2,3,5,6-Tetrachloro-2,5-cyclorhexadiene-1, 4-dione	2,2'-Methylene bis (3,4,6-trichlorophenol)
2,4-Dichlorophenoxy acetic acid and esters and salts	2,2'-Methylene bis (3,4,6-trichloropenol), monosodium salt
2-4-Dichorophenoxybutyric acid and salts	2,4-Dichlorophenyl-p-nitrophenyl ether
3,6-Dichloro-2-methoxybenzoic acid	Pentachlorophenol and salts
3,6-Dichloro-2-methoxybenzoic acid, dimethyhlamine salt	Phosphorothioic acid, o, o-dimethyl O-(2,4,5-trichlorophenyl) ester
Phosphorothioic acid o-[2-chloro-4-nitrophenyl]o, o-dimethyl ester	2-(2,4,5-Trichlorophenoxy) propionic acid and esters and salts
	2,4,5-Trichlorophenol
Phosphorothioic acid o-2,4-dichlorophenyl o, o-diakyl ester	(2,4,5-Trichlorophenoxy) acetic acid
2,4-Dichlorophenoxyethyl sulfate, sodium salt	2,3,4,6-Tetrachlorophenol
2-[2,4-Dichlorophenoxy] propionic acid	

Background on the Formation of Dioxins

CLASS II PESTICIDE CHEMICALS (USEPA, 1980)

o-Benzyl-p-chlorophenol	3,5-Dibromo-4-hydroxybenzonitrile
Phosphorodithioic acid s-[[(4-chloro-phenyl)thio]methyl] o,o-diethyl ester	2,3,5,6-Tetrachloro-1,4-benzenedi-carboxylic acid dimethyl ester
2,3-Dichloro-1,4-napthalenedione	2,4-Dinitro-6-sec-butyl phenol, ammonium salt
3,5-Diiodo-4-hydroxybenzonitrile	1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer (lindane)
(4-Chloro-o-toloxy) acetic acid	4-(2-Methyl-4-chlorophenoxy) butyric acid
2-(4-Chloro-2-methylphenoxy) propionic acid	Phosphorothioic acid o,o-diethyl o-[4-nitrophenyl] ester
Pentachloronitrobenzene	Pipecolinopropyl-3,4-dichlorobenzoate
3-(2-Methylpiperidino)propyl-3,4-dichlorobenzoate	3,4-Dichloropropionanilide
1,2,4-Trichloro-5-[(4-chlorophenyl)-sulfonyl] benzene	2,3,6-Trichlorobenzoic acid
2,3,6-Trichlorophenylacetic acid and sodium salt	Triiodobenzoic acid

Background on the Formation of Dioxins

- EPA reports that certain chemicals can serve as "precursors" to dioxin. (40 CFR766)

- These dioxin precursor chemicals are not themselves contaminated with dioxin but, through further processing and under the correct conditions, can result in the formation of dioxin. (40 CFR 766)

Background on the Formation of Dioxins

Dioxin Precursor Chemicals Regulated by EPA (40 CFR 766)

Bromobenzene	1,4-Dichloro-2-nitrobenzene
o-Bromophenol	4-(2-Methyl-4-chlorophenoxy) butric acid
chlorobenzene	1,2,3,4,5-Pentabromo-6-chlorocyclohexane
5-Chloro-2, 4-dimethoxyaniline	Pentabromoethylbenzene
o-Chlorofluorobenzene	1,2,4,5-Tetrachlorobenzene
3-Chloro-4-fluoronitrobenzene	1,2,4,5-Tetrachloro-3-nitrobenzene
Chlorohydroquinone	1,3,5-Trichlorobenzene
4-Chloro-2-nitrophenol	1,2,3-Trichlorobenzene
o-Chlorophenol	1,2,4-Trichlorobenzene
2-Chloro-4-phenylphenol	1,3,5-Tribromobenzene
4-Chlororesorcinol	2,4,5-Trichlorobenzene
4-Chloro-o-tulouxy acetic acid	1,2-Dichloro-4-nitrobenzene
Dibromobenzene	2,6-Dichloro-4-nitroamine
2,6-Dibromo-4-nitroaniline	p-Dichlorobenzene
o-Dichlorobenzene	

Background on the Formation of Dioxins

- USEPA has classified dioxin-containing waste and dioxin-related compounds. These RCRA classifications include the following (40 CFR 261):
  - F020 Waste Code... hazardous constituents which include tetra- and pentachlorodibenzo- dioxins and furans; tri- and tetrachlorophenols and their chlorophenoxy derivatives.
  - F021 Waste Code... hazardous constituents which include penta- and hexachlorochlorodibenzo- dioxins and furans; pentachlorophenol and its derivatives.
  - F022 Waste Code... hazardous constituents which include tetra-, penta- and hexachlorochlorodibenzo- dioxins and furans.
  - F023 Waste Code... hazardous constituents which include tetra- and pentachlorochlorodibenzo- dioxins and furans; tri- and tetrachlorophenols and their chlorophenoxy derivatives.

Background on the Formation of Dioxins

- USEPA (1998) has identified, inventoried and categorized process sources for the formation and/or release of dioxin, including:
  - Chemical manufacturing, and processing sources
  - Combustion, incineration and other high temperature sources

Background on the Formation of Dioxins

Chemical Manufacturing/Processing Sources (EPA 1998)

- Aliphatic Chlorinated Compounds incl. 1,2-dichloroethane and tetrachloroethene
- 2,4-Dichlorophenoxy acetic acid
- Dyes, Pigments and Printing Inks incl. Dioxazine dyes/pigments, phthalocyanine dyes/inks
- Chlorine manufacture
- Chlorobenzenes
- Chlorophenols, mono- to tetra-
- Ethylene dichloride, vinyl chloride (monomer) and potentially PVC
- PCBs
- Pentachlorophenol
- Pulp and paper mills
- Railway and utility run-off
- Tall oil bases liquid soaps
- Textile and leather production (tanning)
- Wastewater treatment plants and municipal sludge

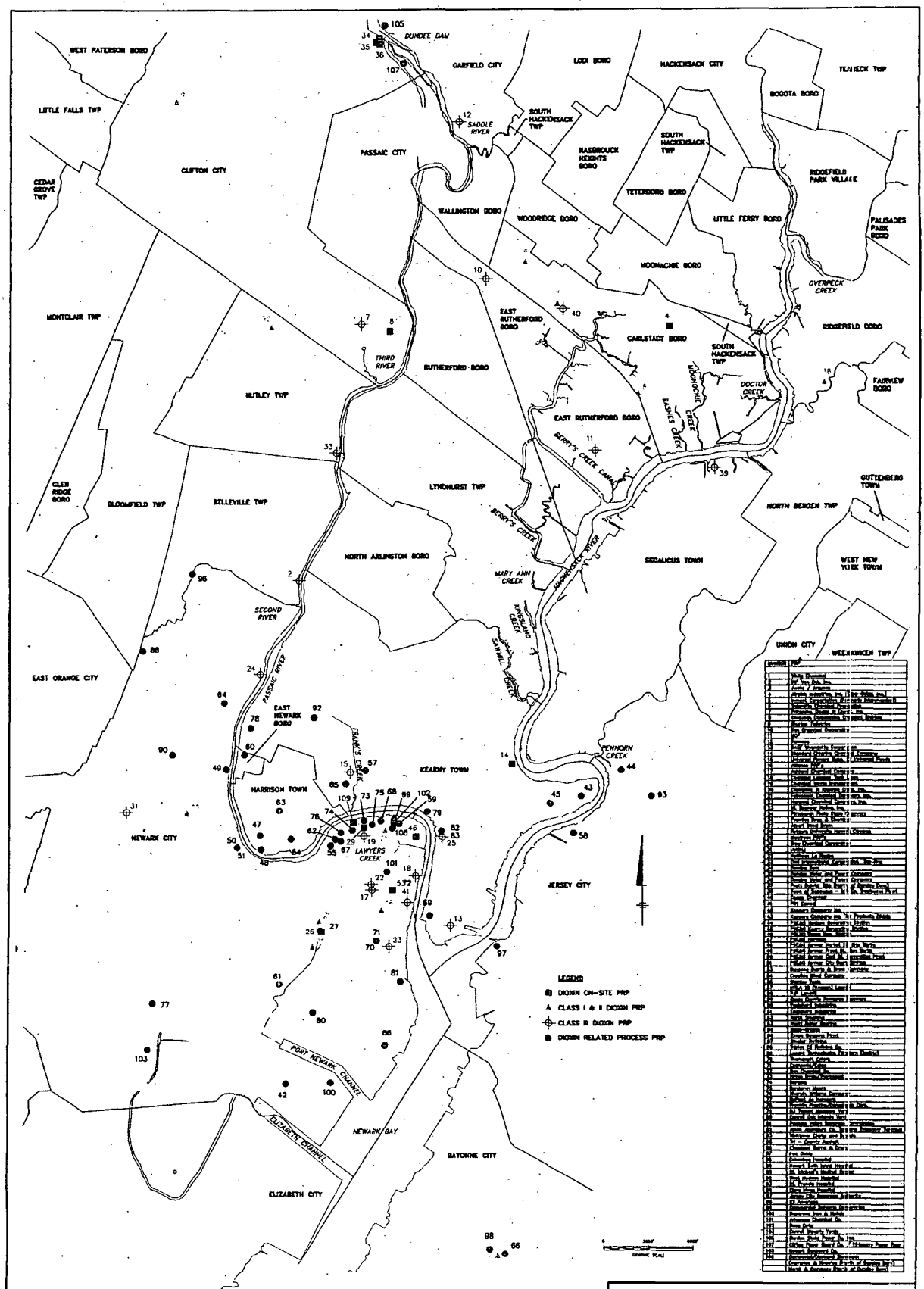
Background on the Formation of Dioxins

Combustion/High Temperature Sources (EPA 1998)

Asphalt mixing plants
Biogas combustion
Boilers/industrial furnaces
Carbon reactivation furnace
Cement kilns
Ceramic/glass production
Coal combustion
Coal gasification
Crematoria
Drum and barrel reclamation
Ferrous metal smelting/refining
Fires (buildings, etc.)
Hazardous waste incineration
Hospital/medical waste incineration
Industrial waste incineration
Kraft (black liquor) recovery boilers
Landfill fires
Lime production
Municipal Waste Incineration
Non-ferrous metal smelting/refining
Oil combustion
Petroleum refining/catalyst regeneration
Pulp and paper mill sludge incineration
Rubber production
Scrap electric wire recovery
Scrap metal reclamation and incineration
Sewage sludge incineration
Vehicle fuel combustion
Waste oil recycling
Wood burning

Sources of Dioxin in the PRSA/PRRI Area

- More than 100 potential source PRPs have been identified in the PRRI Area to date.
- These PRPs include:
  - PRPs with dioxin-contaminated soil on-site
  - Users/producers of Class I and II Organic Chemicals
  - Users/Producers of Class III Organic Chemicals
  - PRPs utilizing processes identified by USEPA as being associated with the formation of dioxins
- Additional investigation will be required



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IDENTIFICATION OF DIOXIN SOURCES

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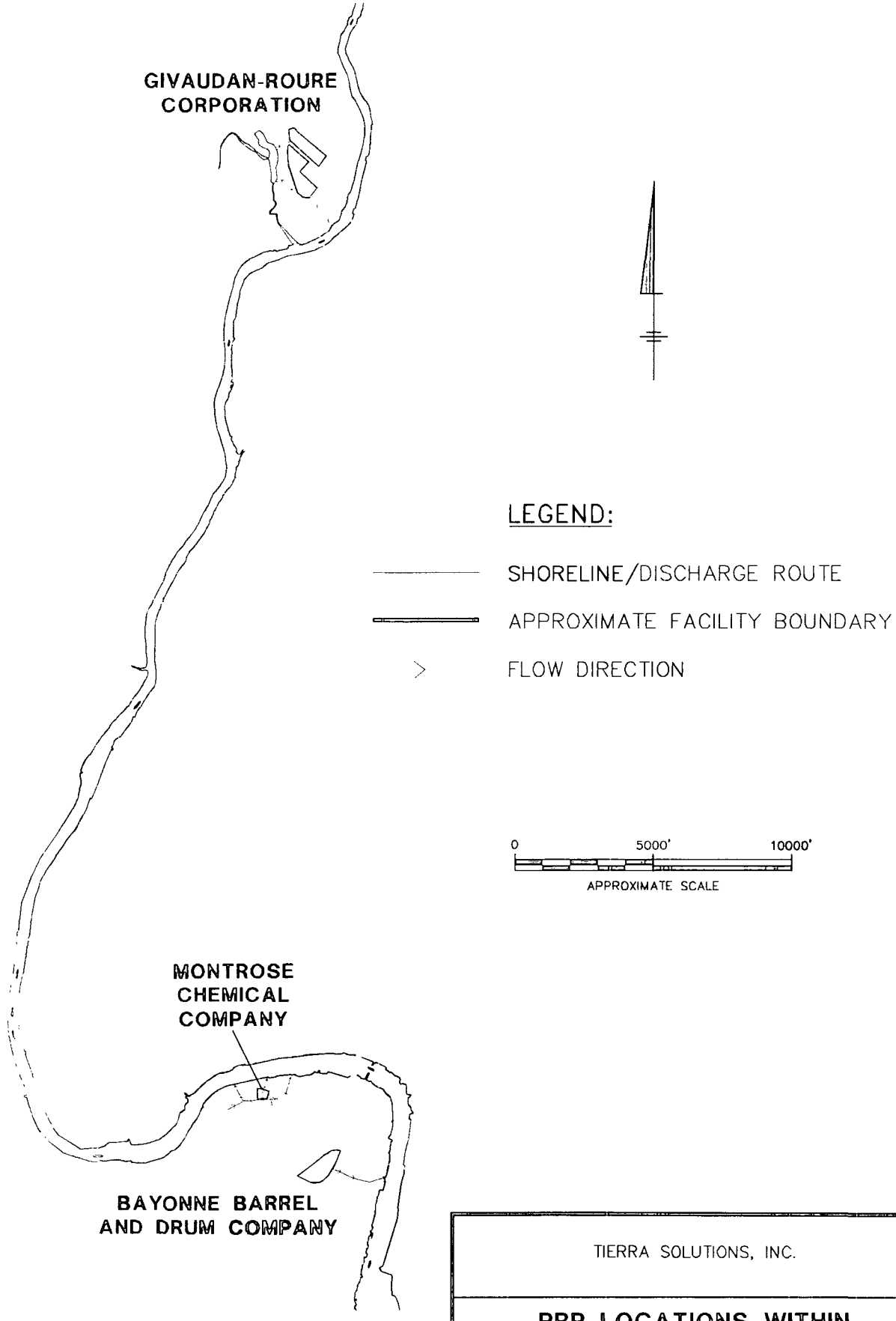
Dioxin PRP Case Studies

- The following three PRP case studies will…
  - Demonstrate the variety of source types in the PRRI/PRSA areas.
  - Demonstrate the types of evidence collected to date regarding these PRPs and the need for further investigation.
  - Demonstrate the need to sample for dioxin at these sites.

Montrose Chemical Company / Chris Craft Site

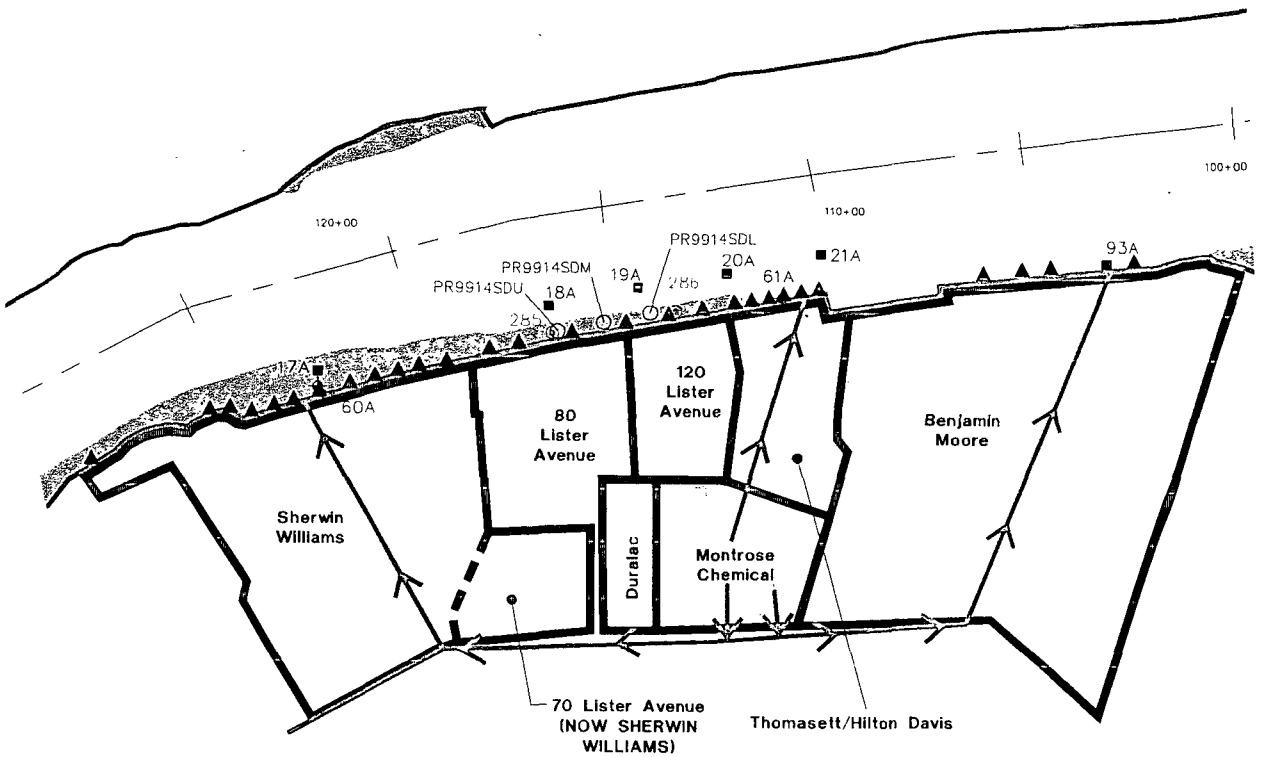
- The Montrose Chemical Company/Chris Craft (Montrose) Site is located at 120 Lister Avenue in Newark, Essex County, NJ. (See Exhibit I5)
- Montrose operated at 120 Lister Avenue from 1943 until 1974. (I3, I5, I6)
- Montrose is reported to have also operated at 70 Lister Avenue, Newark, NJ, from approximately 1937 through 1943. (I5)



TIERRA SOLUTIONS, INC.

PRP LOCATIONS WITHIN THE PRRI AREA

L: ON=*, OFF=*REF*
P: PAGESET/PLT-AP
8/27/02 SYR-54-LAF LAF
09994023/09994822.DWG



LEGEND

• 204	1995 RI-IWP CHEMICAL CORE LOCATION
○ 201	1995 RI-IWP GEOTECHNICAL CORE LOCATION
	SHORELINE/DISCHARGE ROUTE
	APPROXIMATE FACILITY BOUNDARY
	MUDFLATS (SURVEYED 1999)
	RIVER CENTERLINE
50+00	STATION DESIGNATION ABOVE DOWNSTREAM BOUNDARY OF THE PASSAIC RIVER STUDY AREA
○	SEDIMENT (LATE SUMMER/EARLY FALL 1999)
⊖	SEDIMENT (LATE SUMMER/EARLY FALL 1999 AND SPRING 2000)
■ 21A	1991 CORE SEDIMENT INVESTIGATION
⊕ 61A	1992 CORE SEDIMENT INVESTIGATION
■ 93A	1993 (JULY) CORE SEDIMENT INVESTIGATION
▲	HISTORICAL AND PRESENT DAY OUTFALLS

NOTES:

1. BASEMAP SOURCE: TOPO-METRICS, 1"=100', ORIGINAL MYLAR POSITIVES OF AERIAL PHOTOMETRICS SURVEY (1982) [ADJUSTED TO DIFFERENTIAL GLOBAL POSITIONING SYSTEM-SURVEYED MUDFLAT LOCATIONS, 1999.]
2. RIVER MILE DENOTES DISTANCE IN MILES ABOVE DOWNSTREAM BOUNDARY OF THE PASSAIC RIVER STUDY AREA.

TIERRA SOLUTIONS, INC.
PASSAIC RIVER STUDY AREA

SITE AREA CHEMISTRY FIGURE

BBL
BEASLAND, BOUCK & LEE, INC.
engineers & scientists

FIGURE
1

The Following Evidence Was Utilized to Develop These Findings Concerning Montrose/Chris Craft:

I1. 7/21/93 - Affidavit of former Montrose employee Oscar Randall.

I2. 7/21/93 - Affidavit of former Montrose employee Kelsey T. Brown.

I3. 7/27/93 - Affidavit of former Montrose employee S.H. Koved.

I4. 6/9/83 - Letter from former Montrose employee S. H. Koved, to R. Goldstein, Health Commissioner, NJ Department of Health, re: site hazards.

I5. 1937-1964 - Various Newark Industrial Directories.

I6. 1/25/93 - Chris Craft Industries' Response to EPA Information Request Letter.

I7. 12/15/93 - Chris Craft Industries' Response to Second EPA Information Request Letter.

These documents are included in Appendix I of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Montrose/Chris Craft:

I8. 10/1914 - Figure entitled Plan of Lister Agricultural Chemical Works.

I9. 05/05/43 - Figure entitled Survey of 60 – 120 Lister Avenue.

I10. 01/07/65 - Storm Sewer Map and Sanitary Sewer Map, Maps # 9G, 9H, by Porter Armstrong for Newark Housing Authority.

I11. 9/4/70 - City of Newark, Department of Public Works, "As-Is" Plans on Lister Avenue Sewer Improvements.

I12. 3/27/96 - Affidavit of former Hilton Davis employee Robert Malone.

I13. 1/9/78 - PVSC Industrial Sewer Connection Permit for Earthline Company, concerning Lister Avenue storm and sanitary sewer cross connections; with attached 12/8/77 letter from City of Newark to PVSC re permit application.

These documents are included in Appendix I of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Montrose/Chris Craft:

I14. 1971-1974 - Excerpts from PVSC Annual Reports for 1971, 1972, 1973 and 1974, concerning Brown Street and Lockwood Street storm sewers.

I15. Excerpts from Chemical Waste Management Remedial Investigation Report - with associated documents, concerning on-site environmental conditions at the former Montrose/Chris Craft site.

These documents are included in Appendix I of the Sources of Dioxin Report.

Montrose/Chris Craft Products

- Montrose manufactured chlorinated herbicides, pesticides, fuel and rubber additives, food and drug products, and chemical intermediates.
- Montrose products included:

DDT	1,2,4-Trichlorobenzene
2,4-D	Tricresyl phosphate
2,4,5-T	Bis (2-ethylhexyl) phthalate
Lindane	Other pesticides and herbicides

(See Exhibits I1, I2, I3, I4, I7)

Montrose's Dioxin Association

- Many raw materials and processes used by Montrose are identified by USEPA as being strongly associated with the generation of dioxin. (Esposito 1980, I3, I6, I7)
- 2,3,7,8-TCDD was generated by Montrose as a manufacturing by-product as evidenced by on-site soil contamination. (I15)

Montrose's Dioxin Association Continued

- Montrose manufactured USEPA Class I organic compounds 2,4-D and 2,4,5-T. (I3, I4)
- Montrose manufactured USEPA Class II pesticide chemical Lindane. (I1, I2)
- Montrose manufactured USEPA Class III organic compounds 1,2,4-trichlorobenzene, dichlorobenzene and hexachlorobenzene. (I2, I3)
- Chlorobenzene – utilized by Montrose as a raw material - is considered a dioxin precursor compound as regulated by USEPA. (40 CFR 766)

Montrose Site Contamination

- Site soil and groundwater are heavily contaminated with raw materials utilized and products manufactured by Montrose (I15):

  - DDT
  - 2,4-Dichlorophenol
  - 2,4,5-Trichlorophenol
  - Lindane & byproducts
  - Cresol
  - Bis(2-ethylhexyl)phthalate
  - Hexachlorobenzene
  - Dichlorobenzene
  - 1,2,4-Trichlorobenzene

- TCDD was detected at a concentration of 1.6 ppb *in one of three site soil samples analyzed for dioxin.* (I15)

Lister Avenue Area Historical Soil Sample Data

As of September 4, 2002

	Montrose Chemical	80 Lister	120 Lister	Sherwin Williams	Hilton Davis
Class I Organics:					
2,4-Dichlorophenol	23,000	1,400,000	800	210	NA
2,4,5-Trichlorophenol	160	1,700,000	3,500	ND	NA
2,4,6-Trichlorophenol	4,800	3,600	ND	ND	NA
Class I & II Pesticides:					
Pentachlorophenol	2,100	ND	ND	ND	NA
Alpha-BHC	2,3000,000	ND	50,000	NA	NA
Beta-BHC	100,000	130,000	28,000	NA	NA
Gamma-BHC (Lindane)	100,000	ND	ND	NA	NA
Delta-BHC	46,000	ND	ND	NA	NA
Dioxin Precursor Chemicals:					
Chlorobenzene	65,000	170,000	120	5,000,000	2,800
1,2,4-Trichlorobenzene	71,000,000	17,000	850	7,200	15,569
1,2-Dichlorobenzene	160,000	13,000	190	390,000	25,008
1,4-Dichlorobenzene	730,000	49,000	910	1,800,000	14,487
1,3-Dichlorobenzene	38,000	3,400	ND	NA	5,448
Class III Organics:					
Phenol	340,000	13,000	220	470	240,000
Hexachlorobenzene	10,000	620,000	44,000	1,400	947,459
Other PRP-related chemicals:					
Bis(2-ethylhexyl)phthalate	176,000	14,000	90,000	1,100	7,315
DDT	17,000,000	5,090,000	480,000	850	NA
DDE	520,000	297,000	7,500	170	NA
DDD	710,000	370,000	17,100	850	NA
Endosulfan	930	8,900	ND	NA	NA
PCB 1248	25,000	ND	ND	NA	ND
PCB 1260	50,000	ND	ND	NA	1.44
Total Cyanide (ppm)	176	34	2.14	NA	NA

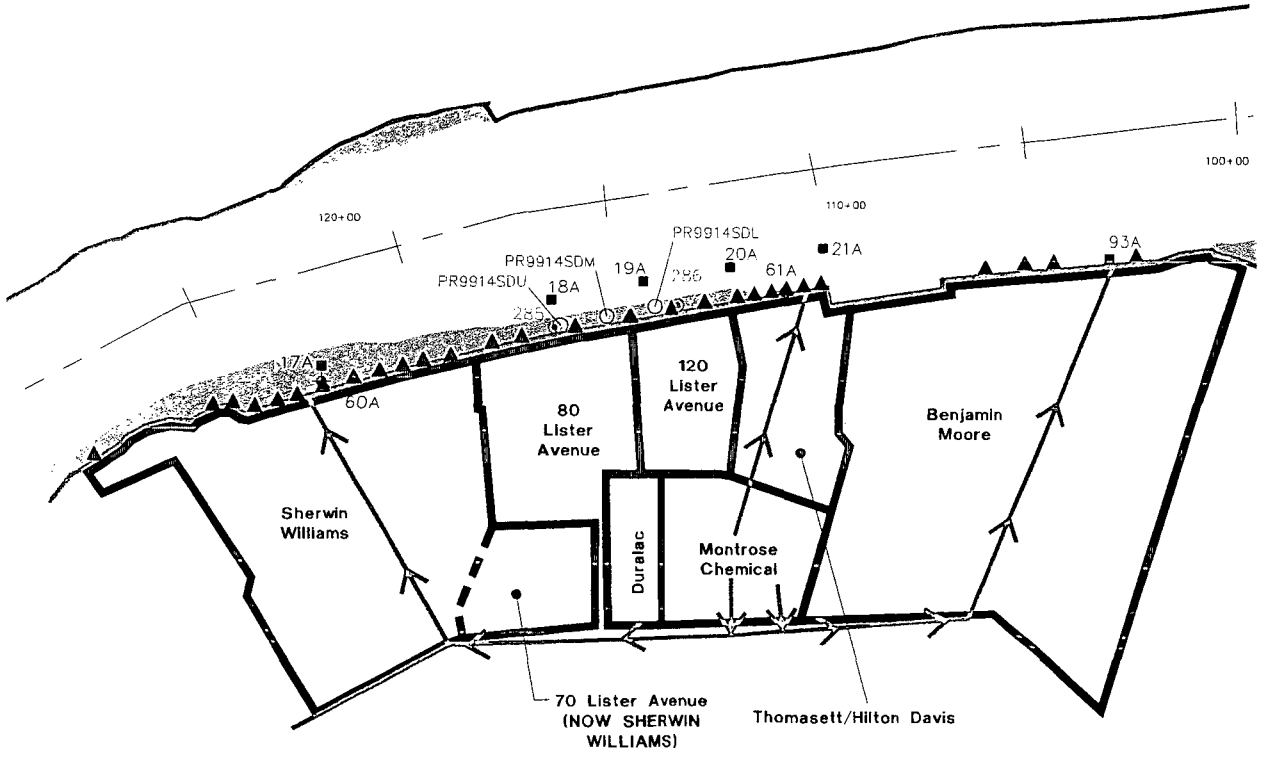
Volatile, Semivolatile, Pesticide/PCB, and Herbicide compounds are reported in PPB; NA = Not analyzed;
XX – Detected compounds used/produced by Montrose only; $\boxed{XX}$ – Detected compounds used/produced by both Montrose and Diamond.
Compounds listed by category designation include both listed compounds and related process wastes. Peak detected on-site concentrations listed.

Montrose Discharge Routes

- Direct discharges from the Montrose facility to the Passaic River occurred through the rear of the Lister Avenue Site, according to former employees. (I1, I12)

- On-site facility sewers have discharged to the municipal combined sewer line and the municipal storm sewer line. (I1, I3 & I11)

- On-site sewers from the Montrose facility discharged to the Passaic River via the Brown Street combined sewer outfall prior to the early-1970's, and via the Lockwood Street storm sewer outfall after the early 1970s. (I8, I9, I10, I11)



LEGEND

- 204 — 1995 RI-IWP CHEMICAL CORE LOCATION
- 201 — 1995 RI-IWP GEOTECHNICAL CORE LOCATION
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- APPROXIMATE FACILITY BOUNDARY
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- HISTORICAL AND PRESENT DAY OUTFALLS

NOTES:

1. BASEMAP SOURCE: TOPO-METRICS, 1"=100', ORIGINAL MYLAR POSITIVES OF AERIAL PHOTOMETRICS SURVEY (1982) [ADJUSTED TO DIFFERENTIAL GLOBAL POSITIONING SYSTEM-SURVEYED MUDFLAT LOCATIONS, 1999.]
2. RIVER MILE DENOTES DISTANCE IN MILES ABOVE DOWNSTREAM BOUNDARY OF THE PASSAIC RIVER STUDY AREA.

GRAPHIC SCALE

TIERRA SOLUTIONS, INC.
PASSAIC RIVER STUDY AREA

SITE AREA CHEMISTRY FIGURE

BBL® BLASLAND, BOUCK & LEE, INC. engineers & scientists

FIGURE 1

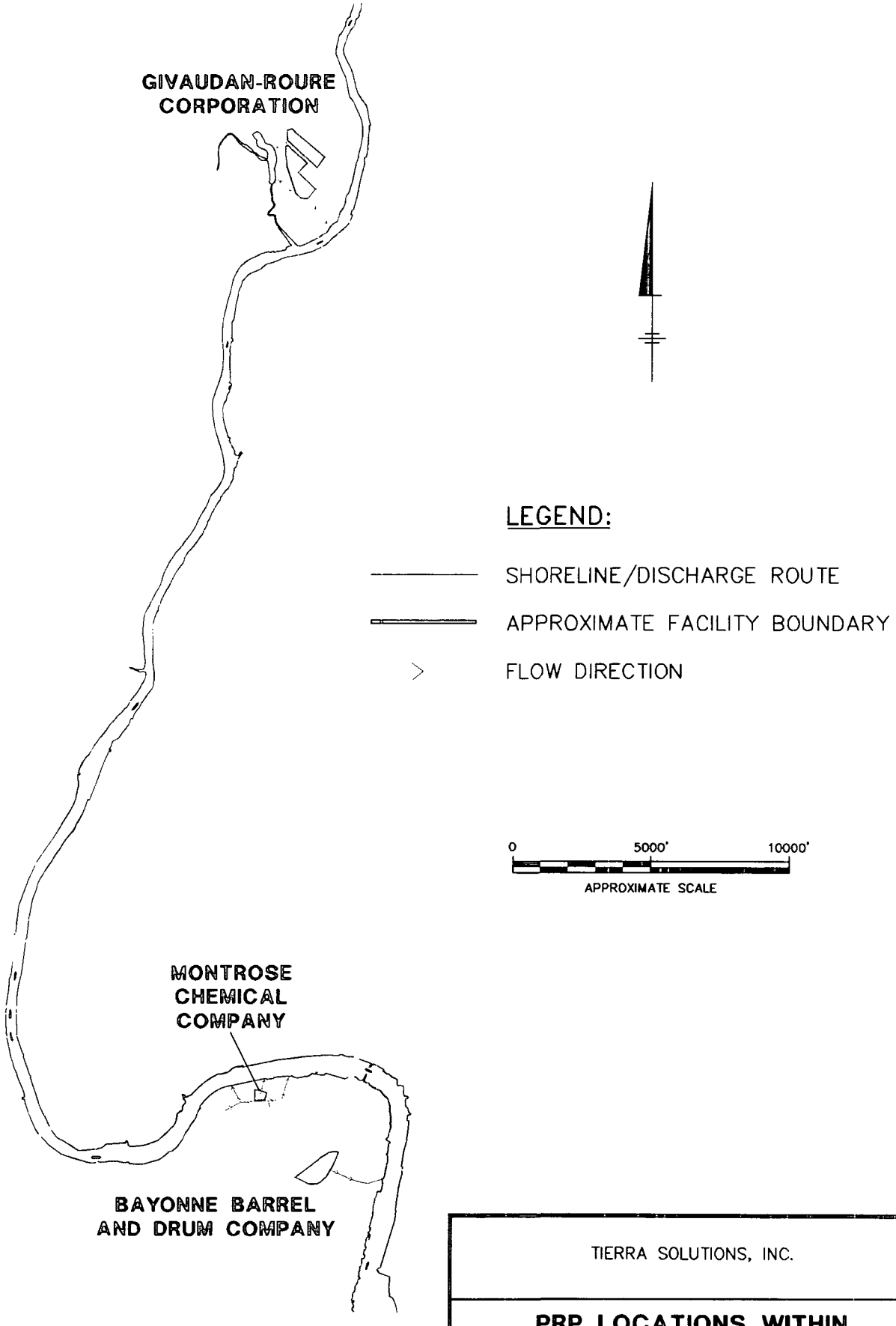
Montrose Sediment Chemistry

	Montrose On-Site	CORE # 60A	CORE # 285	CORE # 286	CORE # PR9914	CORE # 61A	CORE # 93A
Class I Organics:							
2,4-Dichlorophenol	23,000	ND	[illegible]	140,000	3200	ND	ND
2,4,5-Trichlorophenol	160	ND	[illegible]	360,000	3100	ND	ND
2,4,6-Trichlorophenol	4,800	ND	[illegible]	28,000	ND	ND	ND
Class I & II Pesticides:							
Pentachlorophenol	2,100	ND	ND	ND	ND	ND	ND
Alpha-BHC	2,3000,000	ND	ND	[illegible]	ND	ND	34.6
Beta-BHC	100,000	ND	ND	52.7	ND	56	[illegible]
Gamma-BHC (Lindane)	100,000	ND	ND	ND	ND	ND	ND
Delta-BHC	46,000	6.03	14.5	32	ND	ND	13.4
Dioxin Precursor Chemicals:							
Chlorobenzene	65,000	67	78,000	[illegible]	NA	ND	29,000
1,2,4-Trichlorobenzene	71,000,000	ND	[illegible]	110,000	220	ND	2100
1,2-Dichlorobenzene	160,000	ND	18,000	[illegible]	410	ND	17,000
1,4-Dichlorobenzene	730,000	ND	1600	[illegible]	1200	ND	35,000
1,3-Dichlorobenzene	38,000	ND	1100	9800	ND	ND	[illegible]
Class III Organics:							
Phenol	340,000	ND	2300	ND	[illegible]	ND	ND
Hexachlorobenzene	10,000	ND	1400	[illegible]	180	ND	ND
Other PRP-related chemicals:							
Bis(2-ethylhexyl)phthalate	176,000	52,000	220,000	220,000	15,000	98,000	1,700,000
DDT	17,000,000	968	7640	[illegible]	500	3150	1880
DDE	520,000	112	1170	1700	62.1	541	1690
DDD	710,000	267	156,000	11,700	93	2270	[illegible]
Endosulfan	930	ND	39.5	[illegible]	ND	ND	ND
PCB 1248	25,000	3200	3600	15,700	470	12,500	[illegible]
PCB 1260	50,000	ND	ND	ND	282	ND	ND
Total Cyanide (ppm)	176	ND	1.9	1.7	ND	ND	NA

Volatile, Semivolatile, Pesticide/PCB, and Herbicide compounds are reported in PPB; NA = Not analyzed;
XX – Detected compounds used/produced by Montrose only; XX – Detected compounds used/produced by both Montrose and Diamond.
Compounds listed by category designation include both listed compounds and related process wastes.
= Concentration is above mean based on the PRSA sediment sampling data. = Concentration is in the top 20 hits based on the PRSA sediment sampling data.
= Highest concentration detected in the PRSA, based on PRSA sediment sampling data.

Givaudan-Roure Corporation

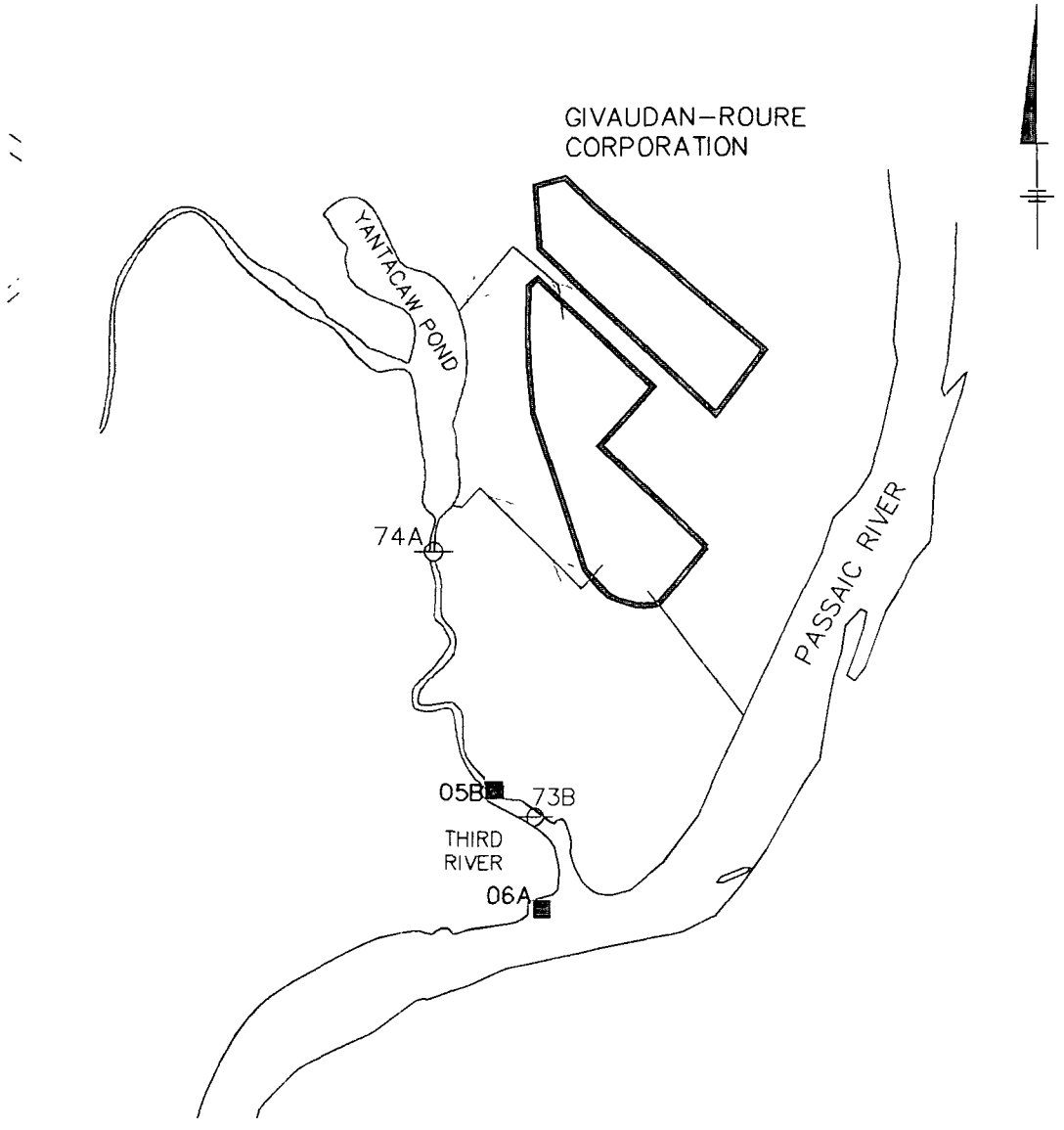
- The Givaudan-Roure Corporation (Givaudan) Site is located at 125 Delawanna Ave., Clifton, Passaic County, NJ. (See Exhibits J1, J13)
- Givaudan and its predecessors operated at the Clifton Site from approximately 1905 through 1998. (J13)



TIERRA SOLUTIONS, INC.

PRP LOCATIONS WITHIN THE PRRI AREA

L: ON=*, OFF=*REF*
P: PAGESET/PLT-AP
8/27/02 SYR-54-LAF LAF
09994023/09994822.DWG



LEGEND:

APPROXIMATE FACILITY BOUNDARY

SHORELINE/APPROXIMATE DISCHARGE ROUTE

05B ■ 1991 CORE SEDIMENT INVESTIGATION

74A ⊖ 1993 (MARCH) CORE SEDIMENT INVESTIGATION

0 1000' 2000'

GRAPHIC SCALE

SITE LOCATION MAP

GIVAUDAN-ROURE CORPORATION FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
8/27/02 SYR-54-GNS LAF LAF
09994023/09994B24.DWG

The Following Evidence Was Utilized to Develop These Findings Concerning Givaudan:

J1. 1992 - Givaudan Site Summary, taken from "Site Status Report" booklet, By NJDEP,

J2. 4/2/75 - Waste Effluent Survey of Givaudan Corporation for Passaic Valley Sewerage Commissioners, includes the 3 /25/75 - Laboratory Analysis; sample from Givaudan Corp., from International Hydronics Corporation.

J3 7/26/83 – Letter from William Hyatt, Jr., Pitney Hardin Kipp Szuch, to Michael Catania, NJDEP, enclosing Givaudan's information response re: trichlorophenol and hexachlorophene historical production.

J4. 1/91 -NJDEP Approved, TCDD Investigation Report and Limited Investigation Report

J5. 12/13/91- Letter from David Sweeny of NJDEP, to Len Levy of Givaudan Corp., re: offsite migration of 2,3,7,8 TCDD.

J6. 11/3/95 - Letter from William Friedman of Brach, Eichler, Rosenberg, Silver, Bernstein, Hammer & Gladstone, to Robert Tavares, Chief Legal Counsel, Givaudan-Roure Corp.

J7. 11/9/95 - Letter from Leonard Levy, Director, Site Remediation Givaudan Corp., to Joseph Karpa, Division of Responsible Party Site Remediation NJDEP.

J8. 5/30/96 - Letter from Leonard Levy of Givaudan Corp., to Maria Franco-Spera, Division of Responsible Party Site Remediation, NJDEP.

These documents are included in Appendix J of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Givaudan:

J9. 9/20/93 – Report Chemical Sewer Investigation by CFM Inc. for Givaudan Corp.

J10 Various –Annual reports from PVSC re: sewer line breaks/incidents and related correspondence.

J11. 1/29/92 – Givaudan Site Map for Delineated TCDD areas and sample locations produced by ERM.

J12. 6/30/70 – Plant sewer system map of Givaudan Corp.

J13. 7/15/98 - Phase III Remedial Investigation for Ground Water, Volume I,Givaudan-Roure Corp.

J14. 6/23/99 - Letter from Richard Wroblewski of ERM, to Maria Franco-Spera of NJDEP

J15. 6/17/83 - Executive Order #48B Re: Dioxin Emergency at Givaudan Clifton Site

These documents are included in Appendix J of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Givaudan Cont'd:

J16. 3/5/87 - Administrative Consent Order- Ground Water

J17. 3/5/87 - Administrative Consent Order TCDD

J18. 2/16/88 - Amended Administrative Consent Order TCDD

J19. Undated – City of Clifton Storm and Sanitary Sewer Maps

J20. 7/14/99 - Letter from Eugene Thomas, Givaudan, to Maria Franco-Spera, NJDEP, re: deed notice. and restrictions.

J21. 5/16/01 - Letter from David Johnson, Givaudan, to Robert Schinn, NJDEP, re: sale of Givaudan plant site in Clifton..

J22. 6/4/02 - Letter from John Hogue, ERM, to Maria Franco-Spera, NJDEP, re: Biennial Certification/sale of Givaudan's Clifton property.

J23. 4/00 - ERM Remedial Action Work Plan for Soils, (excerpts).

J24. 3/1/00 - ERM Draft Remedial Action Report, (excerpts)

J25. 8/15/78 - Killam Heavy Metal Source Determination Study

These documents are included in Appendix J of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Givaudan Cont'd:

J26. April 1985 - Givaudan's Plans for Discharge Prevention, Containment and Countermeasure and Discharge Cleanup and Removal.

J27. 1983 - Givaudan's Stormwater Drainage Patterns – details re: connection to County Street sewer.

J28. 4/25/91 - Letter from L.A. Levy, Givaudan, to Nicholas Eisenhauser, re: excess TCDD levels.

J29. 6/22/83 - NJDEP Internal Memorandum, D. Schrier to E. Liu re: review of Givaudan file concerning dioxin formation.

J30. 2/00 - ERM Sewer Decommissioning Report, (excerpts)

J31. 9/4/96 – Letter from L. Levy to Maria Franco-Spera, NJDEP.

J32. 6/30/70 - Annotated figure highlighted with on-site chemical, storm and sanitary sewer systems

These documents are included in Appendix J of the Sources of Dioxin Report.

Givaudan's Products

- Givaudan produced specialty, aromatic, flavor and fragrance chemicals at the Clifton Site. (J17)
- Givaudan conducted manufacturing processes that utilized distillations, extractions, organic synthesis and crystallizations.
- Givaudan utilized 2,4,5-Trichlorophenol as a raw material in the manufacture of Hexachlorophene (Isobac 20).

(Refer to Exhibits # J1, J29, J31)

Givaudan's Dioxin Association

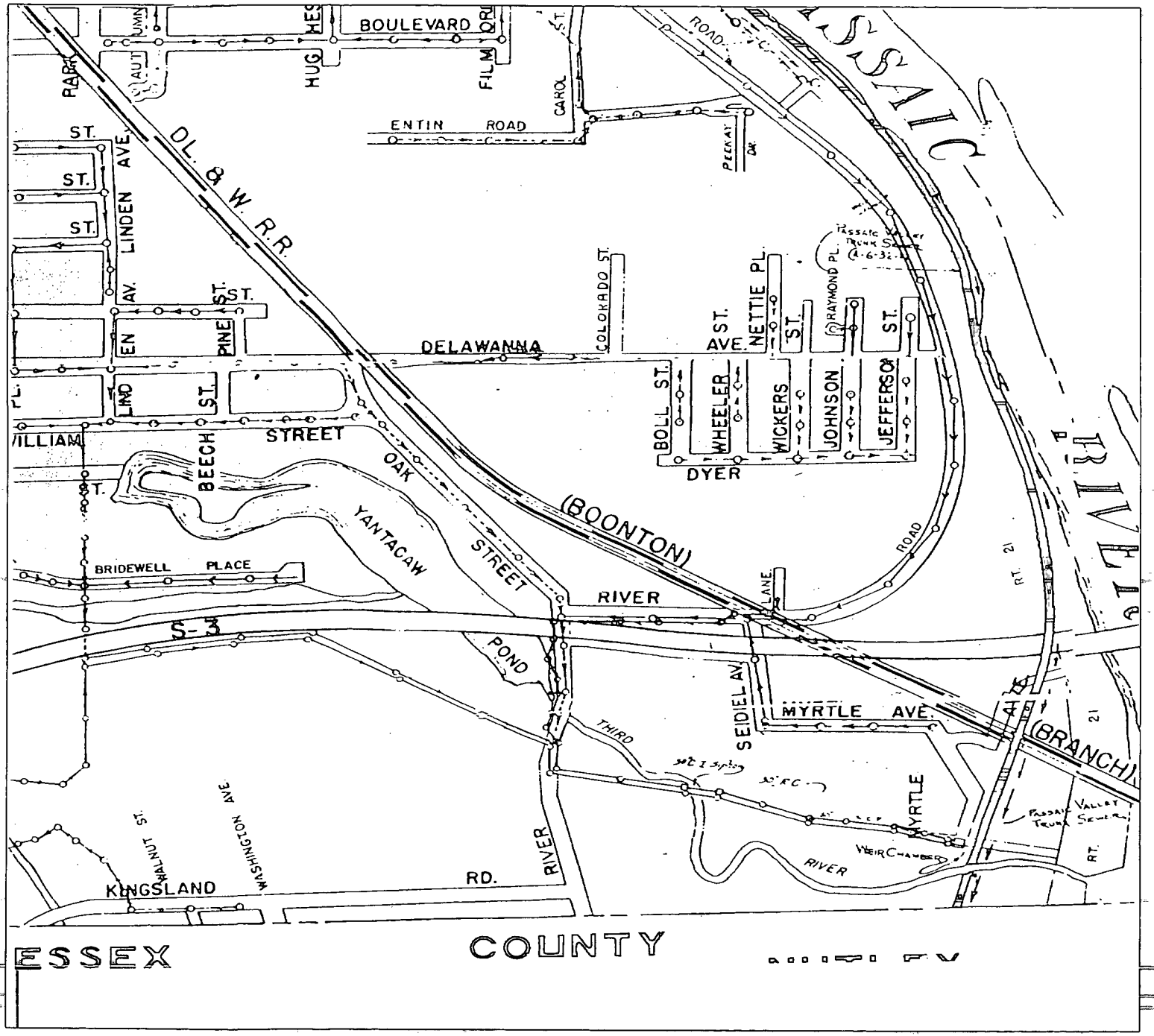
- Givaudan is known to have stored, used and or produced dioxin associated hazardous substances including:
  - USEPA Class I organic compound 2,4,5-Trichlorophenol was produced on-site from 1947 through 1949, and was used as a raw material in the on-site manufacture of Hexachlorophene (Isobac 20) from 1947 - 1984. (J8, J17, J21, J29, J31)
  - USEPA Class I organic compound 2,4-Dichlorophenol was identified as a contaminant in site soils. A "waste dichlorophenol pit" was also reportedly located near process buildings at the Givuadan facility. (J23, J29)

Givaudan Site Contamination

- Site soil and groundwater is heavily contaminated with raw materials utilized and products manufactured by Givaudan, including chlorinated organic compounds, semivolatile organic compounds and heavy metals. (J4, J11)
- Site soil and groundwater contamination has been identified in process areas, at facility wastewater collection ponds and adjacent to facility chemical sewers and storm sewers. (J4, J11)
- 2,3,7,8-TCDD has been identified in site soils at concentrations ranging up to 200 PPB. (J4, J11, J28)

Givaudan's Discharge Routes

- Direct process discharges occurred via the facility's chemical sewer system.
- TCDD levels were detected at concentrations up to 200 ppb in the vicinity of process buildings connected to the chemical sewer system. (J12, J14)
- Employee statements and municipal sewer maps indicate that the chemical sewer was plumbed to Yantacaw Pond which drained to the Third River and ultimately fed to Passaic River. (J19)
- EPA's help is needed here.


BOULEVARD
ENTIN ROAD
CAROL ST.
PEEKAY DR.
ROAD
PASSAIC
RIVER
DL. & W. R.R.
ST.
ST.
ST.
LINDEN AVE.
AV.
EN
PINE ST.
ST.
LIND
ST.
WILLIAM
STREET
BEECH
OAK
STREET
YANTACAW
POND
DELAWANNA
AVE.
COLORADO ST.
NETTIE PL.
ST.
RAYMOND PL.
ST.
BOLL ST.
WHEELER
WICKERS
JOHNSON
JEFFERSON
DYER
(BOONTON)
RIVER
BRIDEWELL PLACE
S-3
LANE
ROAD
RT. 21
SEIDIEL AV.
MYRTLE AVE.
(BRANCH)
THIRD
MYRTLE
RIVER
WEIR CHAMBER
PASSAIC VALLEY TRUNK SEWER
RT. 21
WALNUT ST.
WASHINGTON AVE.
KINGSLAND
RD.
RIVER
ESSEX
COUNTY

Givaudan's Discharge Routes Cont'd

- Direct discharges of process waste water in the 1970's were made from the facility to the Clifton sanitary sewer system. (J11, J12)
- Frequent breaks in the Clifton sanitary sewer lines immediately downstream from the Givaudan facility were reported to discharge process waste water to the Third River. (J10, J27)
- In investigating these incidents, the PVSC determined the cause of the sewer line breaks to be acidic waste discharges from Givaudan. (J10, J27)

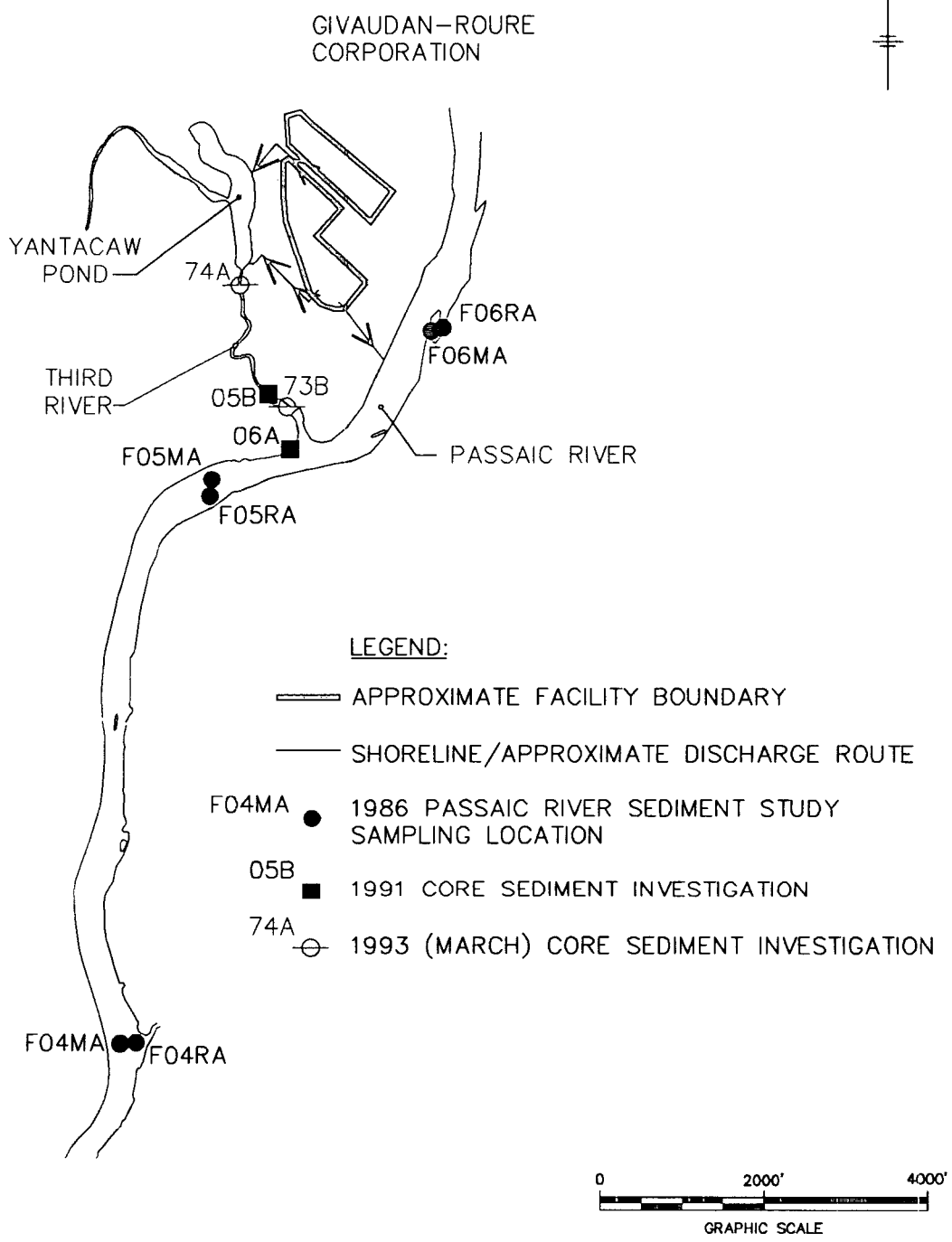
Givaudan's Discharge Routes Cont'd

- In an undated, post-1983, memorandum from Givaudan employee G. F. Talarico to P. Gross, it was stated:

> *"It is practically impossible to sustain the pH of our plant waste water effluent in the 5 to 9 range, prescribed by law, because our present system does not permit adequate neutralization or sufficient retention time of the flow. Passaic Valley Sewerage Commissioners are aware of our excursion from the required pH range and have been after us since 1978 when they discovered that the effluent from our plant caused the corrosion of the sewer line over the Third River."* (J27)

Givaudan's Discharge Routes Cont'd

- Facility documents indicate that storm water in southeastern portion of the site drains to a swale and storm drain system which discharges to the Passaic River. (J19)
- This southeastern portion of the site was found to be contaminated with up to 19 ppb of 2,3,7,8-TCDD. (J4, J11)



SITE LOCATION MAP

GIVAUDAN-ROURE CORPORATION FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
8/27/02 SYR-54-GNS LAF LAF
09994023/09994821.DWG

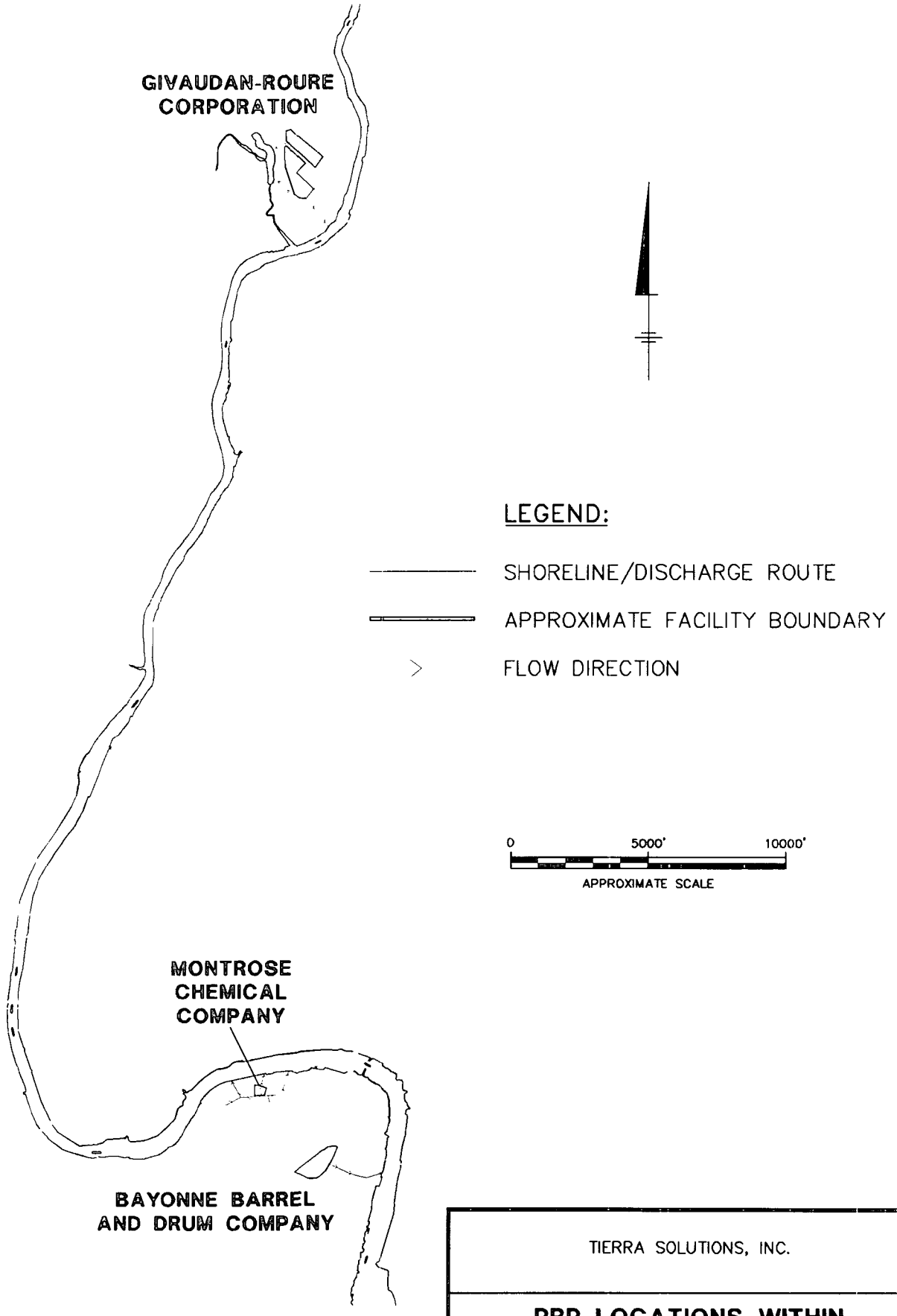
Givaudan Sediment Chemistry

HAZARDOUS SUBSTANCE (PPB)	CONC. IN SITE SOILS (+)	CORE # 5	CORE # 6	CORE # 73	CORE # 74	F04MA	FO4RA	FO5MA	FO5RA	FO6MA	FO6RA
2,4,5-Trichlorophenol	890,000	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
2,4-Dichlorophenol	230,000	ND	ND	ND	ND	NA	NA	NA	NA	NA	NA
Naphthalene	480,000	ND	320,000	ND	ND	NA	NA	NA	NA	NA	NA
Lead	3,870,000	413,000	197,000	47,800	368,000	NA	NA	NA	NA	NA	NA
Manganese	57,600	251,000	254,000	89,300	430,000	NA	NA	NA	NA	NA	NA
Zinc	211,000	394,000	No Data	65,200	488,000	NA	NA	NA	NA	NA	NA
2,3,7,8-TCDD (PPB)	214	0.720	0.015	0.002	0.086	2	2.6	ND	9.3	ND	0.092

ND = Not detected.
(+) = Highest detected concentrations in site soil.
= Concentration is above mean based on the PRSA sediment sampling data.
= Concentration is in the top 20 hits based on the PRSA sediment sampling data.
= Highest concentration detected in the PRSA, based on PRSA sediment sampling data.

Bayonne Barrel & Drum Company Superfund Site

- The Bayonne Barrel & Drum Company Superfund Site is located at 150-154 Raymond Blvd., Newark, Essex County, NJ. (See Exhibits E1, E3)
- BB&D and its predecessors operated at the Newark site from approximately 1931 until 1983. (E11, E13)
- USEPA cited BB&D in 1984 for non-permitted hazardous waste operations, filed suit against BB&D by 1988 for noncompliance, conducted Emergency Removal Actions in 1993 and 1994, and as of 1996, entered into a multi-party Administrative Consent Order to investigate soil contamination at the Site.



TIERRA SOLUTIONS, INC.

PRP LOCATIONS WITHIN THE PRRI AREA

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P: PAGESET/PLT-AP
8/27/02 SYR-54-LAF LAF
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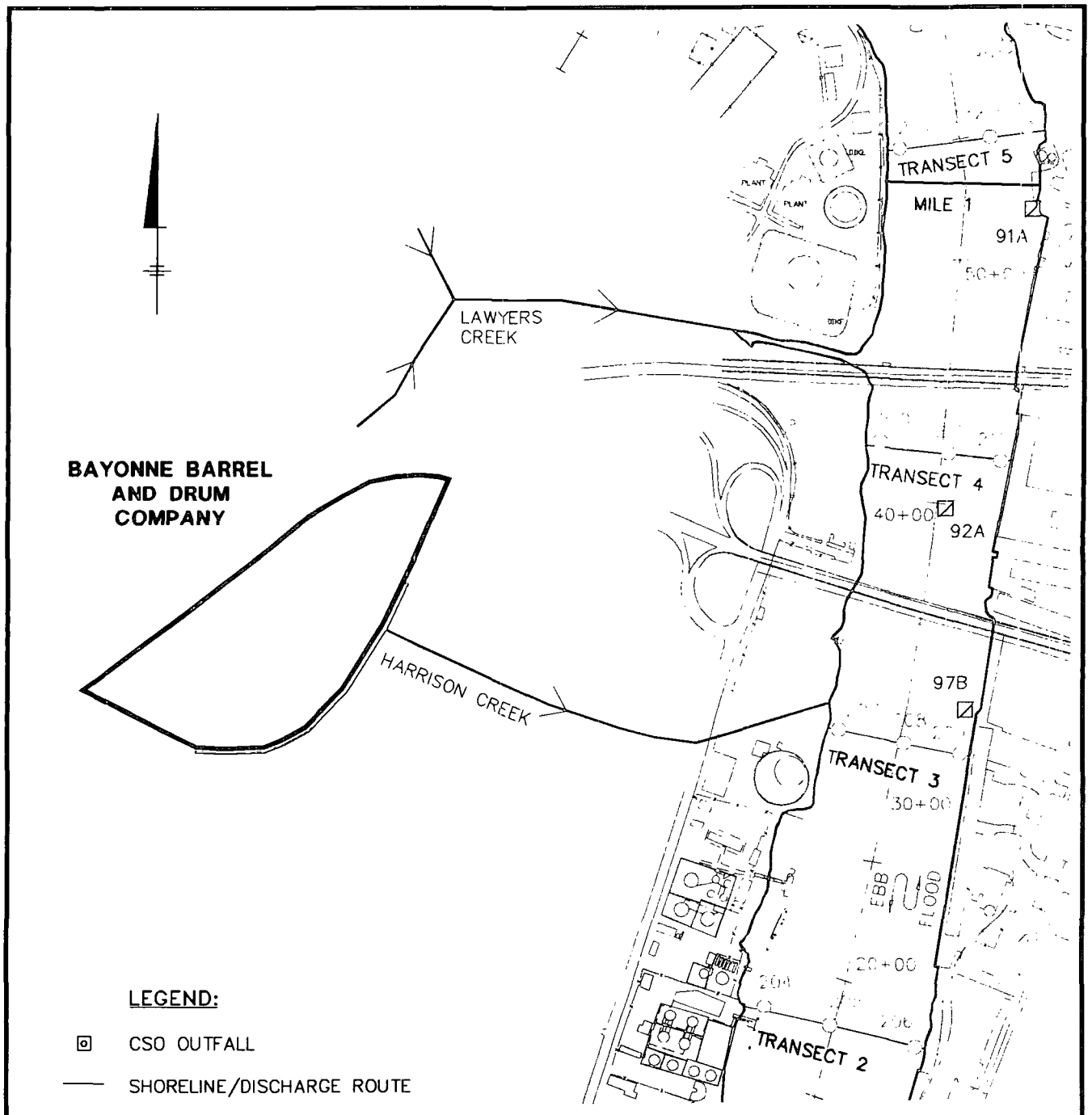


LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- SEDIMENT SAMPLING LOCATION
- 92A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- FLOW DIRECTION

0 600' 1200'
GRAPHIC SCALE

SITE LOCATION MAP

BAYONNE BARREL AND DRUM COMPANY FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
07/27/02 SYR-54-GMS LAF LAF
09994023/09994812.DWG

The Following Evidence Was Utilized to Develop These Findings Concerning Bayonne Barrel & Drum:

E1. 1/10/73 - Waste Effluent Survey of Bayonne Barrel & Drum Company for Passaic Valley Sewerage Commission

E2. 3/14/75 – BB&D Answer to Waste Effluent Survey for Passaic Valley Sewerage Commission

E3. 4/21/75 - Waste Effluent Survey of BB&D Company for Passaic Valley Sewerage Commission

E4. Undated - Schematic sketch of plant industrial waste piping showing various processes

E5. 1/27/76 - Letter from Carmen Della Pia, Industrial Department of Waste Effluent Survey of Bayonne Barrel & Drum Company for Passaic Valley Sewerage Commission, to Mr. Sal Russomanno, BB&D

E6. 1/28/76 - Letter from Sal Russomanno of BB&D to Carmen Della Pia of Passaic Valley Sewerage Commission

E7. 2/22/82 - Hazardous Waste Investigation Findings by Inspector Tom Downey of BB&D

E8. 5/16/84 - Interoffice Memo from EPA Re: BB&D Sampling Results

E9. 4/18/86 - Soils and Ground Water Characterization; Bayonne Barrel and Drum Company; Prepared by Dan Raviv Associates , Inc.

These documents are included in Appendix E of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Bayonne Barrel & Drum:

E10. 6/2/88 - RCRA Enforcement Inspection of BB&D; Prepared by Michael Ferriola, Environmental Scientist, Source Monitoring Section

E11. 10/24/88 - U.S. Environmental Protection Agency; Preliminary Assessment of BB&D

E12. 12/2/88 - Site Inspection Review of BB&D submitted by Edward Gaven, NJDEP Bureau of Planning and Assessment

E13. 9/30/92 - Letter summarizing the Site Inspection Prioritization Evaluation of BB&D from Gary Bielen, Site Manager, John Rieckhoff, Pre-Remedial Program Manager and Dennis Stainken, to Sandra Foose, USEPA

E14. 3/26/97 - Letter from from William Lee, Environmental Project Manager, de maximis, inc., to Joseph Cosentino, USEPA enclosing Bayonne Barrel and Drum Site- Soil Investigation Report, by BBL

E15. Undated - Figure showing Soil Sampling Locations of BB&D

E16. 7/6/01 - Letter from Richard Caspe, Director, Emergency and Remedial Response Division USEPA, to Recipients. Attached is a list Potentially Responsible Parties.

These documents are included in Appendix E of the Sources of Dioxin Report.

The Following Evidence Was Utilized to Develop These Findings Concerning Bayonne Barrel & Drum:

E17. 1946 – 1959 – Correspondence from Passaic Valley Sewerage Commissioners documenting pollution of Harrison Creek.

E18. 7/86 – Soils and Ground Water Characterization prepared by Dan Raviv Associates, Inc.

E19. 12/86 – Report by Louis Berger & Associates submitted to New Jersey Turnpike Authority, "Results of Preliminary Investigations ..."

These documents are included in Appendix E of the Sources of Dioxin Report.

Bayonne Barrel & Drum Site Operations and Site History

- BB&D reconditioned drums using caustic solutions, steel shot abrasive, fire blasting, on-site incineration and paint. (E1, E3, E7, E8, E14)
- The BB&D site, under USEPA direction, is undergoing a multi-party Superfund cleanup to address contaminated site soils, groundwater, ash and waste piles, and facility wastewater treatment and incinerator areas. (E14, E16)

Bayonne Barrel & Drum Site PRPs

- As of February 2001, USEPA has named the following 15 Potentially Responsible Parties for the Bayonne Barrel & Drum Superfund Site (E16):

  - Converters Ink Co. (c/o Zeneca, Inc.)
  - Hoffman-La Roche Corp.
  - National Starch & Chemical Co.
  - Reliance Universal (c/o Akzo Nobel)
  - Sherwin Williams Co.
  - BASF Corporation
  - Sequa Corp. (Sun Chemical Corp.)
  - Products Research & Chemical Corp. (c/o Courtaulds Aerospace, Inc.)
  - PPG Industries, Inc.
  - General Motors Corp.
  - S & W Waste, Inc.
  - Colonial Printing Ink, Inc.
  - Whittaker Corporation
  - E.I. DuPont de Nemours & Co.
  - Solvent Recovery Service of New Jersey, Inc

Bayonne Barrel & Drum's Dioxin Association

- USEPA has associated high temperature combustion processes with the generation of dioxin. (USEPA, 1998)

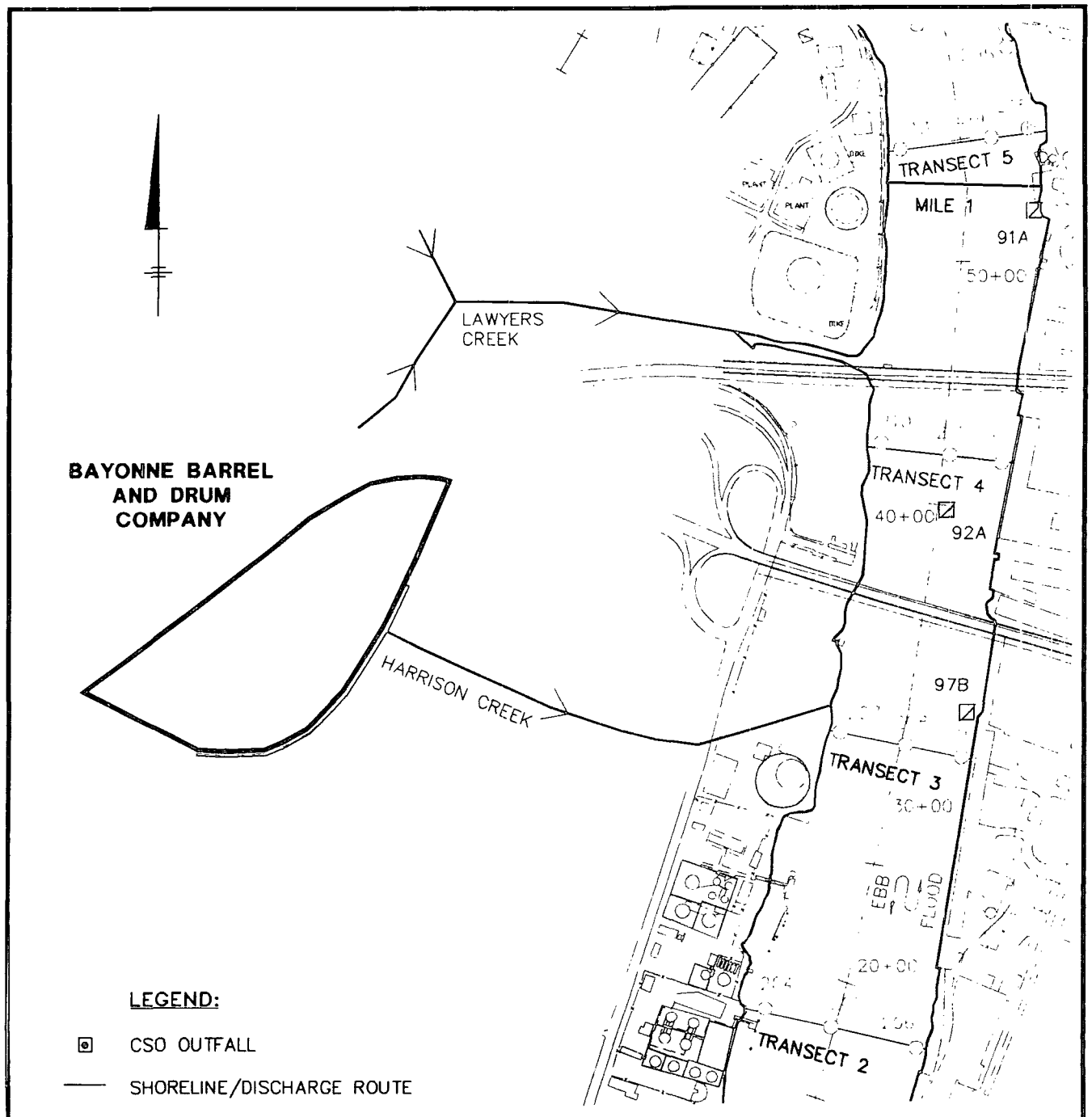
- Specific USEPA-recognized high temperature combustion processes known to have been utilized at the BB&D Site include drum and barrel reclamation, and incineration. (USEPA, 1998)

Bayonne Barrel & Drum Co.
Site Contamination

- Dioxin contamination has been identified *throughout the site* with peak concentrations of 2.83 ppb (2,3,7,8-TCDD) and 911.01 ppb (total TCDD equivalents). (E14, E15, E18)
- Contaminants derived from drum cleaning and other site operations have been detected at significant concentrations in site soil and groundwater. (E8, E9, E11, E14, E18, E19)
- Site contaminants include numerous pesticides, semivolatiles, metals and PCB's. (E8, E9, E11, E14, E18, E19)

Bayonne Barrel & Drum Discharge Route

- On-site ditches, wastewater lagoons and settling tanks were known to historically discharge to Harrison Creek, a tributary of the Passaic River. (E7, E11, E17)
- This occurred up to approximately 1973, when process wastewater from the BB&D facility was discharged to the PVSC sewer system. (E1, E3)
- USEPA reported in a 1984 site assessment that surface run-off from the BB&D Site drains to Harrison Creek. (E6, E7, E11, E12)
- Peak dioxin concentrations identified on site were detected along the eastern site boundary adjacent to these drainage areas. (E14, E16)



LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- 3C7 SEDIMENT SAMPLING LOCATION
- 92A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- FLOW DIRECTION

0 600' 1200'

GRAPHIC SCALE

SITE LOCATION MAP

BAYONNE BARREL AND DRUM COMPANY FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
07/27/02 SYR-54-GMS LAF LAF
09994023/09994B12.DWG

Bayonne Barrel & Drum Sediment Chemistry

Hazardous Substance (PPM)	CONC. IN SITE SOILS (+)	CORE # 207	CORE # 208	CORE # 209
Bis (2-ethylhexyl) phthalate	1500	140	60	200
Barium	6880	366	299	338
Cobalt	2690	19.5	17.1	16.3
Mercury	43.9	11.6	17.5	18.9
Alpha Chlordane	1.2	0.433	0.101	0.095
Gamma Chlordane	1.3	0.235	0.0835	0.086
DDD	1.4	2.300	0.075	0.779
DDE	6.4	1.790	0.181	0.496
DDT	0.860	379	17.2	431
Endrin Aldehyde	0.065	0.348	ND	0.043
Chlorobenzene	2.8	ND	ND	ND
Aroclor 1248	3400	5.310	2.570	4.320
Aroclor 1254	430	18.30	1.410	2.530
Aroclor 1260	120	2.110	ND	ND
2,3,7,8-TCDD (PPB)	2.85	8.45	1.91	17.4
Total TCDD Equivalents/TEQ (PPB)	911	No Data	No Data	No Data

ND = Not detected.
(+) = Highest detected concentrations in site soil.
= Concentration is above mean based on the PRSA sediment sampling data.
= Concentration is in the top 20 hits based on the PRSA sediment sampling data.
= Highest concentration detected in the PRSA, based on PRSA sediment sampling data.

Sources of Dioxin In The PRSA/PRRI Areas

- Evidence of the following 7 PRPs are provided in the exhibit binders for the Sources of Dioxin report:
  - Prentiss Drug & Chemical Company
  - Alliance Chemical, Inc.
  - BASF Corporation
  - Arkansas Chemical Co./Hummel Chemical Co.
  - PSE&G Essex Generating Station
  - Essex County Resource Recovery Facility
  - Thomasett Colors/Hilton-Davis Company

Sources of Dioxin in the PRSA & PRRI Areas

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
Dioxin On-site PRPs:					
4	Airwick Industries, Inc., (Ciba-Geigy, Inc.), 111-179 Commerce Road, Carlstadt, NJ	1962-1991 Moonachie Creek or Berrys Creek to Hackensack	44 ppt 2,3,7,8-TCDD in onsite drainage ditch sediments.	Hexachlorophene	Class I organic compound
8	Givaudan Corporation, Chemical Division, 110-125 Delawanna Ave., Clifton, NJ	1913-1999	200 ppb 2,3,7,8-TCDD onsite.	Hexachlorophene (Isobac 20); 2,4-Dichlorophenol; 2,4,5-Trichlorophenol	Class I organic compound
		Onsite chemical sewer to pond on Third River to Passaic	Peak concentration of 720 ppt in Third River sediments	Benzaldehyde; Fumaric acid	Class III organic compound
14	Standard Chlorine Chemical Co., 1015-1035 Belleville Turnpike, Kearny, NJ	1962-1995	2,3,7,8-TCDD detected in onsite lagoon sediments at 70 ppb. EPA Phase II sampling.	o-dichlorobenzene; 1,2,4-Trichlorobenzene; Maleic anhydride; Bromobenzene	Class III organic compounds
		Located on Hackensack River, site is underlain by system of drains, on-site lagoon that drain to River. NPDES permit for discharge to Dead Horse Creek to Hackensack.	2,3,7,8-TCDD was detected in both sediment cores 33A and 34A (up to 0.12 ppb) adjacent to the site in the Hackensack River.	Chlorinated benzene formulations	
26	Prentiss Drug & Chemical Co., Inc., 338 Wilson Avenue, Newark, NJ	1953-1982	2,3,7,8-TCDD was detected onsite at 200 ppb, and in Pierson's Creek sediments onsite at 0.9ppb.	Lindane	Class II pesticide compound

Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
	Pearson's Creek to Port Newark (North Channel)	Sampling of the North Channel of Port Newark detected concentrations ranging to 0.55 ppb (dredged area).	chlorophenol and mono- to tetra - manufacture/process	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
29	Montrose Chemical Corp./ Sobin Chemicals/ International Mineral & Chemical Corp./ Chris Craft Corp., 100 Lister Avenue, Newark, NJ	Direct discharges to Passaic River, also via discharges to Brown St. CSO and Lockwood St. Storm Sewer. 1942 - 1978	Low levels of 2,3,7,8-TCDD detected in limited onsite sampling.	2,4,-D and 2,4,5-T Manufacturing.	Class I oganic compounds.
			Significantly elevated concentrations of 2,3,7,8-TCDD detected in Passaic River sediments adjacent to site.	Propanil	Class II organic compound
				1,2,4-Trichlorobenzene	Class III organic compound
34	Dundee Dam (Owned by Dundee Water and Power Co.) - Extended from Dundee Canal at Ackerman Avenue to the canal's terminus at the Passaic River. Block 3.7/Lot 1 (site 11). Passaic, NJ	constructed in late 1880s Passaic River	2,3,7,8-TCDD detected at low levels in sediments		
35	Dundee Water and Power Company (Dundee Canal) - Block 54/Lot 1 (6 acres of canal and .1 land (site 2). Passaic, NJ	constructed in late 1880s Passaic River	2,3,7,8-TCDD detected at low levels in sediments		

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
36	Dundee Water and Power Company (Dundee Canal) - Extended from Dundee Canal at Passaic/Clifton border to Ackerman Avenue in Clifton. Block 4.14/Lot 1 (Site 9). Passaic/Clifton border.	constructed in late 1880s Passaic River	2,3,7,8-TCDD detected at low levels in sediments		
46	PSE&G Essex Generating Station, 155 Raymond Blvd., Newark, NJ	Site is adjacent to Passaic River.	Low levels of 2,3,7,8-TCDD detected onsite.	Boilers/Industrial Furnaces	
			2,3,7,8-TCDD was detected at up to 11.6 ppb in core 214 in the site vicinity.	Oil Combustion	
				Coal combustion	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
53	Bayonne Barrel & Drum Co. (BB&D), 150 and 154 Raymond Boulevard, Newark, NJ	Harrison Creek (site drainage and process discharges) to Passaic River.	Significant dioxin concentrations (TEQs) detected onsite; 2,3,7,8-TCDD peaks at	Drum & Barrel Reclamation	
			2,3,7,8-TCDD was detected at 8.45 ppb in sediment core 207 adjacent to the outfall of Harrison Creek to the Passaic River.		
Class I and II Organic Chemicals PRPs					
1	White Chemical Co., Hook Rd. and E. 22nd Streets, Bayonne, NJ	1961 - 1983	1983: USEPA Tier 1 dioxin testing at site inconclusive due to laboratory issues.	2,4-Dibromophenol; Pentabromophenol; 2,4,6-Tribromophenol	Class I organic compounds
		Documented: settling pond discharges to Platty Kill Creek to Kill Van Kull.	2,3,7,8-TCDD was detected in both sediment cores in the vicinity of the site in the Kill Van Kull - (up to 0.042 ppb)	Pentabromotoulene	Class III organic compound
3	Aceto/Arsynco, Foot of 13th Street, Carlstadt, NJ	Hackensack via NPDES Permit; Potential Berry's Creek discharger		3,5-Dichlorosalicylic acid	Class II organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
5	Inmont Corporation, 13th St., Carlstadt, NJ	Potential Berry's Creek discharger		3,5-Dichlorosalicylic acid	Class II organic compound
6	Scientific Chemical Processing Co., Inc., 216 Paterson Plank Road, Carlstadt, NJ	Direct discharges to Peach Island Creek to Berry's Creek to Hackensack.	Site not addressed by EPA dioxin sampling program.	2,4-Dichlorophenol identified in site soil.	Class I organic compound
			Peach Island Creek sediments contaminated; no dioxin sampling.	1,2,4-trichlorobenzene identified in site soil.	Class III organic compound
				NJDEP cites potential for dioxin generation via incomplete combustion of PCBs during 1970 fire.	
9	Shulton Toiletries, Inc., 697 Route 46, Clifton, NJ			o-chlorophenol	Class II organic compound
		NPDES-permitted discharge to Passaic river.		o-dichlorobenzene	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
16	Alliance Chemical Co,/ Pfister Chemical Co., Inc., 33 Avenue P, Newark, NJ	1945 - 2001	Limited sampling conducted in 1985 for 2,3,7,8-TCDD was N.D.	Site contaminants: 2, 4-Dichlorophenol, 2,4,5-Trichlorophenol.	Class I organic compound
		Plum Creek to Passaic from onsite wastewater lagoon; Roanoke Ave. CSO to Passaic post-1975.	2,3,7,8-TCDD was detected in core samples collected from Plum Creek and the Passaic River in vicinity of site outfalls/pathways.	Products: 2-chloro-1,4 diethoxy-5-nitrobenzene; 5-chloro-2,4-diethoxyaniline	Class II organic compound
				1,2,4-Trichlorobenzene	Class III organic compound
				unspecified dyes	
				Chlorophenols and mono -to - tetra manufacture/process	
				Manufacture of organic intermediates for use in the textile, paper and pigment industries.	
20	Crompton & Knowles Color, Inc., 52 Amsterdam Street, Newark, NJ	CSO case		o-chlorophenol	Class II organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
21	Fairmount Chemical Co., Inc., 117 Blanchard Street, Newark, NJ	Blanchard St. Storm Sewer	Low levels of 2,3,7,8-TCDD detected onsite during EPA Lister Ave. sampling.	2-Chloro-1,4-diethyoxy-5-nitrobenzene, Formulation of agricultural mixes.	Class II organic compound
			Significant concentrations of 2.3.7.8-TCDD detected in Passaic River sediments in vicinity of outfall.		
28	Rutgers University, Newark Campus, 360 Martin Luther King Boulevard, Newark, NJ	CSO case.		o-chlorophenol	Class II organic compound
30	Troy Chemical Corp., 1 Avenue L, Newark, NJ	1956 - Present	No dioxin sampling conducted at site. Creek sediments are heavily contaminated with site-derived contaminants.	o-chlorophenol	Class II organic compound
		Pearson's Creek to Port Newark (North Channel)	Sampling of the North Channel of Port Newark detected concentrations ranging to 0.55 ppb (dredged area).	1,2,4-Trichlorobenzene; 2,4-dinitrophenol	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
32	Hoffman La Roche Corp., 340 Kingsland Street, Nutley, NJ	CSO case, minor discharge to Third River from onsite POTW.		o-chlorophenol	Class II organic compound
				Picric acid; 2,4-dinitrophenol	Class III organic compound
				Medical Waste Incineration	
40	Cosan Chemical Corp., 400 14th St., Carlstadt	NPDES-permitted discharger to Hackensack.		2,4,6 - trichlorophenol	Class I organic compound
				Phthalic Anhydride, o - dichlorobenzene	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
Class III Organic Chemicals PRPs					
2	ISP Van Dyk, Inc., Main & William Streets, Belleville, NJ	1940-		Fumaric acid	Class III organic compound
7	Fritzsche, Dodge & Olcott, Inc., 85 Third St., Clifton, NJ	Potential Third River disharger		Benzaldehyde, Phenyl ether	Class III organic compound
10	Sun Chemical Corp., East Rutherford Pilot Plant, East Rutherford, NJ	NPDES permit to discharge to Hackensack River.		o-dichlorobenzene	Class III organic compound
11	Universal Oil Products Co. (UOP) NPL Site, Route 17 & Paterson Plank Road, East Rutherford, NJ	Bordered on southwest by Berry's Creek. Ackerman's Creek flows through the site and into Berry's Creek. Site is at approximately river mile 8. NPDES discharge to Hackensack		Benzaldehyde	Class III organic compound
12	Tenneco, 290-300 River Drive, Garfield, NJ	1969-1990		Benzaldehyde, Fumeric acid	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
13	BASF Wyandotte Corp., 50 Central Avenue, Kearny, NJ	1935 - 1964: United Cork. 1964 - 1990 BASF.	Site samples not analyzed for dioxin.	Phthalic anhydride; Benzaldehyde; 2,4-dinitrophenol.	Class III organic compound
		Located on Passaic River at Newark bay.	2,3,7,8-TCDD detected in core samples adjacent to the site (0.094 ppb) and in core samples upstream of the site (4.56 ppb) that are heavily contaminated with other compounds associated with this site.	Building fires in 1920s	
				Industrial waste incineration	
				Cork bleaching and/or steam pressing.	
				unspecified dyes	
				Manufacture of a avriety of chemical products including organic plasticizers, dyestuffs and chemical intermediates.	
15	Universal Flavors, Subs. Of Universal Foods Inc., 265 Harrison Avenue, Kearny, NJ	1984-		Phthalic Anhydride, Benzaldehyde	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
17	Ashland Chemical Company, 221 Foundry Street, Newark, NJ	1968 - 1988 Storm Sewers and drains to Passaic River via Roanoke Ave. Sewer.	No onsite dioxin sampling conducted. 2,3,7,8-TCDD detected in core samples collected in vicinity of Roanoke Ave. CSO.	Phthalic Anhydride, Phenyl ether, chlorobenzene, o-dichlorobenzene, maleic anhydride, 1,2,4-trichlorobenzene. Repackaging and shipping of chemicals, manufacture of alkyd resins, polyesters and plasticizers.	Class III organic compounds
18	Chemical Leaman Tank Lines, Inc., 80 Doremus Avenue, Newark, NJ	1970 - 1999 Site is located directly on the Passaic River, site drainage via Harrison Creek storm sewer and direct runoff.	No onsite dioxin sampling conducted. 2,3,7,8-TCDD detected @ 8.45 ppb in core samples (207) collected in vicinity of Harrison Creek outfall.	2,4-dinitrophenol	Class III organic compound
19	Chemical Waste Management, Inc., 107 Albert Avenue, Newark, NJ			2,4-dinitrophenol	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
22	Hummel Chemical Company, Inc., Foundry Street Complex, 185 Foundry Street, Newark, NJ	Roanoke Ave. Storm sewer, from drains on the Foundry St. complex site.	No onsite dioxin sampling conducted.	2,4-Dinitrophenoxy-ethanol; 3,5-Dinitrosalicylic acid; Hexachlorobenzene; Picric acid	Class III organic compound
			2,3,7,8-TCDD detected in core samples collected in vicinity of Roanoke Ave. CSO.	Numerous dioxin - associated compounds detected in site soil and sediment including 2,4 - dichlorophenol and 2,4,6 - trichlorophenol	
23	NL Spencer Kellog, Inc., 400 Doremus Avenue, Newark, NJ	Adjacent to Passaic river at Plum Creek outfall.	No dioxin sampling conducted at site.	Phthalic Anhydride	Class III organic compound
				unspecified dyes	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
24	Pittsburgh Plate Glass Company, Inc. (PPG), 29 Riverside Avenue, Newark, NJ	1921 - 1978		Phthalic Anhydride.	Class III organic compounds
		Adjacent to Passaic River at northern PRSA boundry.	2,3,7,8-TCDD was detected at relatively high levels in core 10 adjacent to the site (up to 32 PPB) and Transect 26 downstream from the site (up to 27 ppb.)	Unspecified Dyes and Pigments	
				Formulation and manufacture of various resins, pigments, linseed oil, paints, lacquer, enamels and varnishes.	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
25	Monsanto Corporation, Foot of Pennsylvania Ave., Kearny, NJ	Adjacent to Passaic River; site storm sewers drain to river; potential drainage from onsite wastewater lagoons.	No dioxin sampling conducted at site.	Maelic Anhydride, chlorobenzene	Class III organic compounds
			2,3,7,8-TCDD was detected at up to 4.4 ppb in sediment core 217 and at up to 0.83 ppb in core 77A in the site vicinity.	PVC production Product (STP) bleaching	
27	Albert Steel Drum, 338 Wilson Avenue, Newark, NJ	Rear of Prentiss Drug site.		Drum & Barrel Reclamation	
31	UMDNJ, Medical Building A-699, 100 Bergen Street, Newark, NJ	CSO case		2,4-dinitrophenol	Class III organic compound
33	Omi International Corp. Sel-Rex, 75 River Road, Nutley, NJ			2,4-dinitrophenol	Class III organic compound
39	Town of Secaucus - Mill Creek Treatment Plant, Koelle Boulevard, Secaucus, NJ			2,4-dinitrophenol	Class III organic compound
41	Pitt Consol Chemical Co., Inc./ Reilly Tar/ E. I. Dupont, 191 Doremus Avenue, Newark, NJ	1932 - 1981	No dioxin sampling conducted at site.	Picric acid	Class III organic compound

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
		Roanoke Ave. Sewer - illegal process discharges.	2,3,7,8-TCDD detected in core samples collected in vicinity of Roanoke Ave. CSO.	Asphalt mixing plant	
73	Hilton Davis/Thomasset, 120 Lister Avenue, Newark, NJ	Site is immediately adjacent to the Passaic River	No dioxin sampling conducted onsite.	Phthalic Anhydride, o-dichlorobenzene	Class III organic compound
			Significant dioxin contamination of sediments adjacent to site.	Phthalocyanine dyes	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
78	Franklin Plastics/Congoleum Corp., 113 Passaic Avenue, Kearny, NJ	Site is immediately adjacent to the Passaic River	No dioxin samping onsite.	PVC production	
			2,3,7,8-TCDD was detected at relatively high levels adjacent to the site in cores 284 and 296 -- within the top 20 PRSA hits. Other site contaminants were detected at similarly elevated concentrations in these samples.	Suspected use of fumaric acid and maleic anhydride based on Congoleum patents	Class III Organic Compounds
				Use of dyes, pigments and printing inks	
				Manuacturing builiding fires, use of waterproofing and fireproofing compounds	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
101	Arkansas Chemical Co., 185 Foundry St., Newark, NJ	Roanoke Ave. CSO to Passaic River	No dioxin sampling conducted at site.	Dyes, pigments and printing inks	
			2,3,7,8-TCDD detected in core samples collected in vicinity of Roanoke Ave. CSO.	Numerous dioxin - associated compounds detected in site soil and sediment including 2,4 - dichlorophenol and 2,4,6 - trichlorophenol. Additionally, pentachlorophenol and 1,2,4 trichlorobenzene were detectd in basement water.	Class III organic compounds

Process Sources Associated with Dioxin PRPs

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
42	Koppers Company,Inc., Maritime & Tyler Streets, Port Newark, NJ	Storm sewers to North channel of Port Newark.		Creosote and wood preservation operation	
43	Koppers Company,Inc., Tar Products Division, Fish House Rd., Kearny, NJ			Asphalt mixing plant	
44	PSE&G Hudson Generating Station, Duffield and Van Keuman Aves., Jersey City, NJ			Coal combustion	
45	PSE&G Kearny Generating Station, foot of Hackensack Avenue, Kearny, NJ	Site is adjacent to Hackensack River.		Coal combustion Oil Combustion	
46	PSE&G Essex Generating Station, 155 Raymond Blvd., Newark, NJ	Site is adjacent to Passaic River.	Low levels of 2,3,7,8-TCDD detected onsite. 2,3,7,8-TCDD was detected at up to 11.6 ppb in core 214 in the site vicinity.	Boilers/Industrial Furnaces Oil Combustion Coal combustion	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
47	PSE&G Harrison, South 4th Street, Harrison, NJ	Site is adjacent to Passaic River.	No dioxin sampling conducted at site. Admission of "suspected" dioxin onsite in PVSC application. 2,3,7,8-TCDD detected in cores in site vicinity.	Boilers/Industrial Furnaces Coal Combustion/gasification	
48	PSE&G former Market St. Gas Works, Market St., Newark, NJ	Site is adjacent to Passaic River.		Boilers/Industrial Furnaces Coal Combustion/gasification	
49	PSE&G former Front St. Gas Works, McCarter Highway, Newark, NJ	Site is adjacent to Passaic River.		Boilers/Industrial Furnaces Coal Combustion/gasification	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
50	PSE&G former Coal St. Generating Plant, Coal St., Newark, NJ	Site is adjacent to Passaic River.		Boilers/Industrial Furnaces Coal Combustion/gasification	
51	PSE&G former City Dock Station, Penn Station, Newark, NJ	Site is adjacent to Passaic River.		Boilers/Industrial Furnaces Coal Combustion/gasification	
52	PSE&G Bayonne Generating Station, Bayonne, NJ (former Hobart Ave. Gas Works)	Kill Van Kull		Coal combustion/gasification	
54	Crucible Steel Company, 1000 S. Fourth Street, Harrison, NJ			Foundry non-ferrous metal smelting and refining Electric Arc Furnaces	
55	Stanley Tools, 140 Chapel Street, Newark, NJ			Foundry	
56	Standard Tank, 1 Ingham Road, Bayonne, NJ			Hazardous waste incineration	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
57	MSLA 1B (Keegan) Landfill, Foot of Bergen Avenue, Kearny, NJ			Landfill fires	
58	PJP Landfill, 400 Sip Avenue, Jersey City, NJ			Landfill fires	
59	Essex County Resource Recovery, 66 Blanchard Street, Newark, NJ			Municipal Waste Incineration	
				Chlorobenzene, 1,2-Dichlorbenzene	Precursor, Class III Organic Compound
60	Englehard Industries, 1 West Central Avenue, East Newark, NJ			Non-ferrous metal smelting/refining	
61	Englehard Industries, 429 Delancy St., Newark			Non-ferrous metal smelting/refining	
62	Barth Smelting, Lister and Chapel Streets, Newark, NJ			Non-ferrous metal smelting/refining, foundries	
63	Hyatt Roller Bearing, 700 Frank E. Rodgers Blvd., Harrison, NJ			Non-ferrous metal smelting/refining, foundries	
64	Napp-Grecco, Route 21, Newark, NJ			Asphalt Mixing Plant	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
65	Exxon Bayway Refinery, Route 1, Linden, NJ			Petroleum Refining	
66	Exxon Bayonne Plant, Foot of East 22nd Street, Bayonne, NJ			Petroleum Refining	
67	Sinclair Refining, Chapel St., Newark, NJ			Petroleum Refining	
68	Triplex Oil Refining Co., Lister Ave., Newark			Petroleum Refining	
69	Lucent Technologies (Western Electric), 100 Central Ave., Kearny, NJ			Scrap electric wire recovery	
70	Thomasett Colors, 338 Wilson Ave., Newark, NJ			Dyes, pigments and printing inks	
71	Cyanamid/Calco, 358 Wilson Avenue, Newark, NJ			Dyes, pigments and printing inks	
72	Sun Chemical Co., 185 Foundry Street, Newark, NJ			Dyes, pigments and printing inks	
74	Duralac, 84 Lister Avenue, Newark, NJ			Dyes, pigments and printing inks	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
75	Benjamin Moore, 134 Lister Avenue, Newark, NJ			Dyes, pigments and printing inks	
76	Sherwin Williams Company, 60 Lister Avenue, Newark, NJ			Dyes, pigments and printing inks	
77	DuPont de Nemours, 256 Vanderpool Street, Newark, NJ			Dyes, pigments and printing inks	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
79	NJ Transit Meadows Yard, 1148 Newark Turnpike, Kearny, NJ	Site is immediately adjacent to Passaic river - Pumping station and Frank's Creek discharges.	No dioxin sampling onsite. Sediments in area of site are signifiantly contaminated with dioxins.	Runoff from railway and utility rights of way (to ditches)	
80	Conrail Oak Islands Yard, foot of Bay Ave. and Wheller Point Rd., Newark, NJ			Runoff from railway and utility rights of way (to ditches)	
81	Passaic Valley Sewerage Commission, 600 Wilson Ave., Newark, NJ	Direct outfall (bypass) to Newark Bay. Sludge loading, unloading and willful discharge.		Wastewater treatment plants / municipal sludge	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
82	Alcan Aluminum Co., Tomkins Tidewater Terminal, 1 Jacobus Ave., South Kearny, NJ	Site is immediately adjacent to Passaic River; historical discharge of process-related wastes.	No dioxin sampling conducted onsite.	PVC production, metal plating.	
			2,3,7,8-TCDD was detected at up to 17.4 ppb in sediment core 209 downriver from the site, as well as upriver of the site. Other site contaminants were found at top twenty levels in these same samples.		
83	Whittaker, Clarke and Daniels, Jacobus Ave., South Kearny, NJ			Phthaloncyanine Dyes	
84	Schering Corp., 60 Orange Street, Bloomfield,NJ			Hospital (medical waste) incineration	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
85	Tri - County Asphalt, foot of Sanford Ave., Kearny, NJ			Asphalt mixing plant	
86	Kingsland Barrel & Drum, Doremus Ave., Port Newark			Drum & Barrel Reclamation	
87	Iron Oxide, 125 Front Street, Elizabeth NJ			Ferrous metal smelting/refining	
88	Columbus Hospital, 495 North 13th Street, Newark, NJ			Hospital (medical waste) incineration	
89	Newark Beth Israel Hospital, 201 Lyons Avenue, Newark, NJ			Hospital (nedical waste) incineration	
90	St. Michael's Medical Center, 306 MLK Boulevard, Newark, NJ			Hospital (medical waste) incineration	
91	The Hospital Center at Orange, 188 South Essex Avenue, Orange, NJ			Hospital (medical waste) Incineration	
92	West Hudson Hospital, 206 Bergen Avenue, Kearny, NJ			Hospital (medical waste) incineration	
93	St. Francis Hospital, 25 McWilliams Place, Jersey City, NJ			Hospital (medical waste) inciineration	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
94	Irvington General Hospital, 832 Chancellor Avenue, Irvington, NJ			Hospital (medical waste) incineration	
95	East Orange General Hospital, 300 Central Avenue, East Orange, NJ			Hospital (medical waste) incineration	
96	Clara Maas Hospital, 1 Clara Mass Drive, Belleville, NJ			Hospital (medical waste) incineration	
97	Jersey City Sewerage Authority, Rt. 440 and Kellog St., Jersey City, NJ			Sewage Sludge Incineration Wastewater treatment plants/municipal sludge	
98	ICI Americas, 229 E. 22nd St., Bayonne, NJ			Hazardous Waste Incineration	
99	Commercial Solvents Corporation, Foot of Blanchard St., Newark, NJ			Scrap electric wire recovery/scrap metal reclamation	
100	Naporano Iron & Metals, 146 China St., Port Newark.			Scrap electric wire recovery/scrap metal reclamation	

	Name of PRP	Years of Operation / Discharge Routes	Dioxin Contamination (Site and Sediments)	Chemical and/or Process	Dioxin Relationship
102	Rose Color, Blanchard St., Newark, NJ			Dyes, pigments and printing inks	
103	Conrail Waverly Yards, Bessemer & Haynes Streets, Newark, NJ			Runoff from railway and utility rights of way (to ditches)	
104	Conrail Greenville - Tropicana Yards, 9 Linden Ave., Jersey City, NJ			Runoff from railway and utility rights of way (to ditches)	
105	Garden State Paper Co., Inc., 950 River Drive, Garfield NJ			Pulp / Paper mills	
106	Marcal Paper Mills, Inc. 1 Market St., Elmwood Park, NJ			Pulp / Paper mills	
107	Clifton Paper Board Co. / Whippany Paper Board Co., 1 Ackerman Ave., Clifton, NJ			Pulp / Paper mills	
108	Newark Boxboard Co., 17 Blanchard St., Newark, NJ			Pulp / Paper mills	

Dioxin Figures

Priority Case
Summaries & Figures

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A - Prentiss Drug & Chemical Company & Site Figures

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Prentiss Drug & Chemical Co.

LOCATION:

The Prentiss Drug & Chemical Company (Prentiss) site, approximately 9-acres in size, is located at 338 Wilson Avenue in Newark, Essex County, New Jersey.

OPERATIONS:

Commencing in 1956, the Prentiss operations at the site centered on the formulation and blending of a variety of pesticides, rodenticides and herbicides. These products included, but were not limited to, aldrin, chlordane, diazanone, DDT, DDVP, dieldrin, endrin, heptachlor, lindane, methoxychlor and warfarin. Prentiss was located at the site until circa 1982, when the company moved its Newark operations to Georgia.

The site was originally operated by American Cyanamid Company – and its predecessor Calco Chemical Company – starting from prior to 1939 through approximately 1950. Between 1951 and 1956, and at various time from that point to present, the site was utilized as a multi-tenant manufacturing complex.

Other historical, non-Prentiss, operators and operations at the site have included dye production (American Cyanamid), drum reconditioning (Albert Steel Drum), chemical manufacturing (Troy Chemical and also Welch Homes & Clark) and waste disposal and landfilling operations (Cuba Brothers, Fiore and also Courtesy Container). The City of Newark Housing and Redevelopment Authority reportedly has owned the property from 1977 to present.

DIOXIN RELATIONSHIP:

The production of halogenated hydrocarbon pesticides, such as those pesticides produced at the Prentiss facility, is often associated with the by-product production of dioxin.

For example, pentachlorophenol was utilized as a raw material in the pesticide production at the Prentiss facility. Pentachlorophenol is listed by the USEPA as USEPA as a Class I pesticide chemical. Further, Lindane, one of the pesticide final products produced at the Prentiss operation, is listed by the USEPA as a Class II pesticide chemical.

2,3,7,8-TCDD was historically generated as a manufacturing by-product from the Prentiss pesticide production operations and subsequently discharged to site soils and to the on-site Pearson's Creek surface waterway.

DISCHARGE ROUTES:

Direct Discharges to Pearson's Creek:
Documentation indicates that a network of concrete lined drainage trenches at the Prentiss facility were routed into an exterior drainage ditch which in turn was routed into Pearson's Creek. Of note, these concrete lined trenches were reportedly cracked in various locations. Process discharges, air emissions, spills and leaks collected via these concrete trenches would have been routed to the drainage ditch, then to Pearson's Creek and ultimately discharged into Newark Bay.

On-site Flooding:
The Prentiss site has been documented to have routinely flooded after rain events due to surface water backing up from the on-site Pearson's Creek waterway. The advancing and receding floodwaters from Pearson's Creek would have served to transport hazardous substances from site process areas, raw materials, stored products, and site soils into Pearson's Creek and ultimately to Newark Bay.

DIOXIN CONTAMINATION:

Sampling of soils at the Prentiss site has served to document the presence of 2,3,7,8-TCDD contamination at the site. The levels of TCDD contamination in the site soils ranged from non-detect to 214 PPB.

TCDD was also detected in the sediments of the Pearson's Creek waterway that traverses the Prentiss site. The concentration of TCDD in the Pearson's Creek sediments ranged from 0.2 to 0.9 PPB.

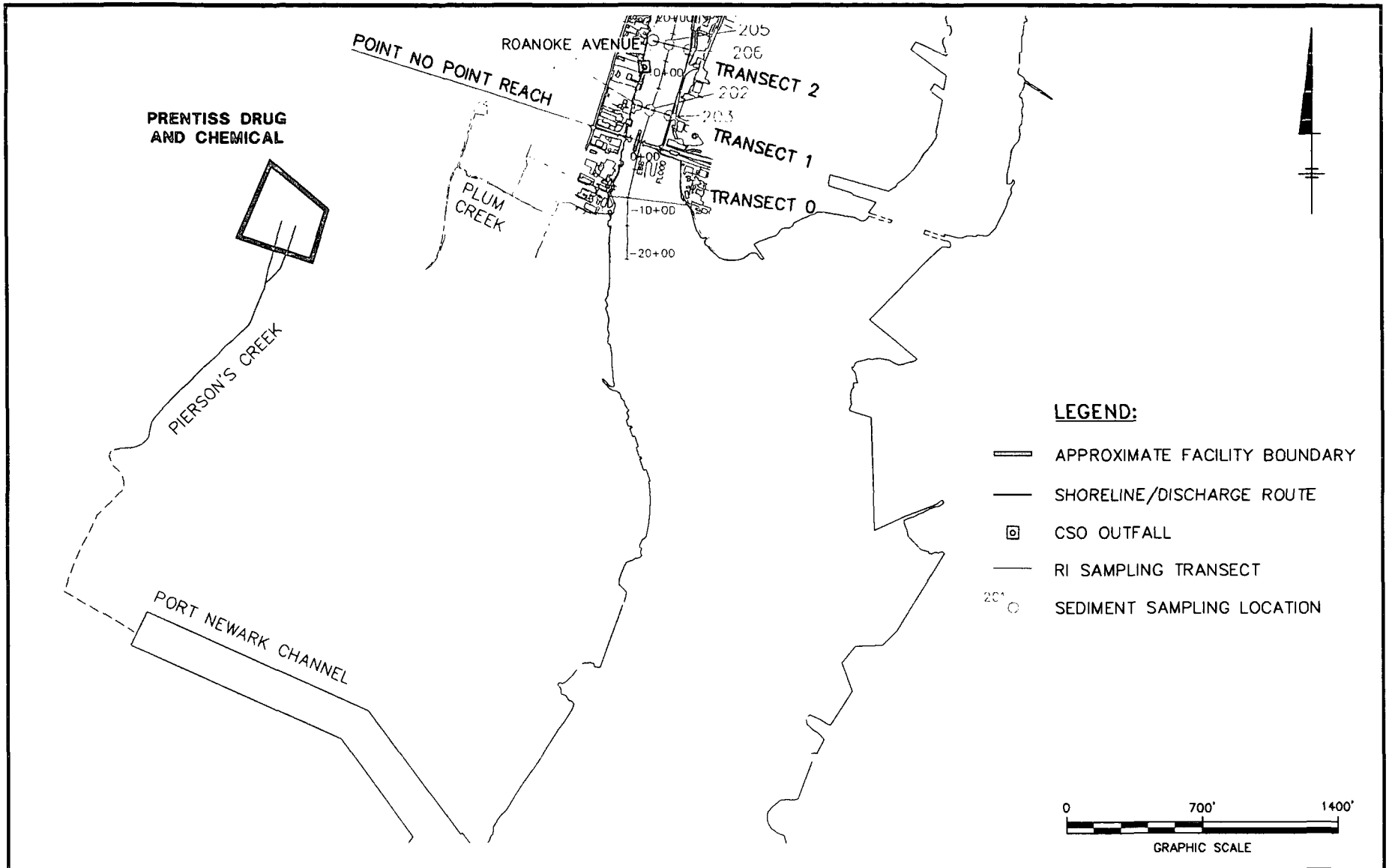
Further, TCDD has been identified to be present in the sediments of Newark Bay, located adjacent to the outfall of Pearson's Creek into the bay. TCDD contamination in the bay sediments near the Pearson's Creek outfall ranged from 0.18 to 0.55 PPB.

The presence of elevated concentrations of TCDD in the Prentiss site soils, in conjunction with known elevated TCDD sediment contamination in both Pearson's Creek and in Newark Bay, supports the historical transportation of hazardous materials from the Prentiss site to Newark Bay. Specifically, it documents that TCDD contamination from the historical Prentiss operations, has been transported via the Pearson's Creek waterway and deposited into Newark Bay.

Other hazardous substances known to be present in soils at the Prentiss site have been documented in sediments of the Pearson's Creek waterway and in Newark Bay. These hazardous substances include, but are not limited to, chlordane, dieldrin, DDE, endrin and PCBs. This fact further supports the historical transport of hazardous substances from Prentiss' operations to Newark Bay via Pearson's Creek.

REFERENCES: Please refer to Appendix A for the following:

Tab #	Date	Description
A1	7/17/80	Industrial Work Order for Prentiss Drug & Chemical
A2	8/12/80	Passaic Valley Sewerage Commissioners, Sewer Connection Application for Prentiss Drug & Chemical Co., Inc.
A3	8/15/80	Letter from Richard Miller, Executive VP of Prentiss, to Frank D'Ascensio, Supervisor of Industrial Waste, Passaic Valley Sewerage Commissioners
A4	2/13/81	Letter from Richard Miller of Prentiss, to Vincent Olivo, Technician for Passaic Valley Sewerage Commissioners
A5	2/20/81	Certified-Return Receipt of above letter
A6	9/1/83	Letter from Richard Miller of Prentiss, to Edward Stevenson, Manager, Industrial Survey Project, NJDEP. Attached is a selected substance report
A7	12/85	Phase II Dioxin Site Investigation Final Report, Prentiss Drug & Chem. Co., Inc. by NJDEP
A8	10/92	Feasibility Study Report for Albert Steel Drum/Prentiss and Chemical Site, submitted to NJDEP
A9	3/93	Phase II Remedial Investigation Report for Albert Steel Drum/Prentiss and Chemical Site, submitted to NJDEP
A10	Undated	Prentiss Drug and Chemical Company, General Information and Site History



SITE LOCATION MAP

PRENTISS DRUG AND CHEMICAL FACILITY

L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-GMS SDL LAF
09994023/09994819.DWG

B

Alliance Chemical Company / Pfister Chemical Company, Inc.

LOCATION: The Alliance Chemical Company Site is located at 33 Avenue P, Newark, NJ approximately ½ mile from the Passaic River.

OPERATIONS: Alliance manufactured specialty organic chemicals including: dyes, diazo compounds, zinc compounds and pigments from raw materials. Alliance reportedly began operations at the site in the 1930s time period. As of 1965, the Alliance Chemical Company was acquired by Pfister Chemical Company. From 1965, Alliance Chemical continued to operate at the Newark site as an operating division of Pfister Chemical. The Alliance operations were discontinued as of 2000.

DIOXIN RELATIONSHIP: Alliance is known to have stored, used and/or produced hazardous substances associated with the generation of dioxin.

- Alliance manufactured USEPA Class II organic compounds 2-chloro-1,4-diethoxy-5-nitrobenzene and 5-chloro-2,4-diethoxyaniline.
- Alliance utilized USEPA Class III organic compound 1,2,4-trichlorobenzene.
- USEPA Class I organic compounds; 2,4-dichlorophenol and 2,4,5-trichlorophenol were identified in site soil/sediment in the former process waste discharge area.

Chemical manufacturing processes utilized in the production of dyes, pigments and inks – including those processes known to have been utilized by Alliance – have been reported by the USEPA as being strongly associated with the by-product generation of dioxin and furan compounds.

DISCHARGE ROUTES: Alliance discharged process effluent to Plum Creek until 1970. Plum Creek is a tributary of the Passaic River. Unlined site trenches, wastewater lagoons and a facility pond were all reported as being part of an effluent collection system that is known to have historically discharged to the creek. As early as 1948, Alliance reportedly discharged an unspecified yellow-colored liquid to a storm ditch leading o Plum Creek. There are also numerous historical documented instances of Plum Creek flooding the Alliance site during storm events.

DISCHARGE ROUTES CONTINUED:

In 1970, Alliance was connected to the Passaic Valley Sewerage Commission (PVSC) sanitary sewer system. It is likely that even after the PVSC connection, effluent from Alliance continued to enter the Passaic River by way of overflow from the Roanoke Avenue combined sewer outfall.

DIOXIN CONTAMINATION:

Onsite sampling conducted on site in 1989 by NJDEP detected concentrations of 2,4,5-trichlorophenol, 2,4-dichlorophenol and 1,2,4-trichlorobenzene at depth in the area of the onsite lagoon and trench formerly used by Alliance for waste disposal. The samples were not analyzed for dioxin. Sampling conducted for dioxin in 1985, as requested by USEPA, was negative for locations elsewhere onsite. However, samples planned for the former lagoon area and trench were not collected.

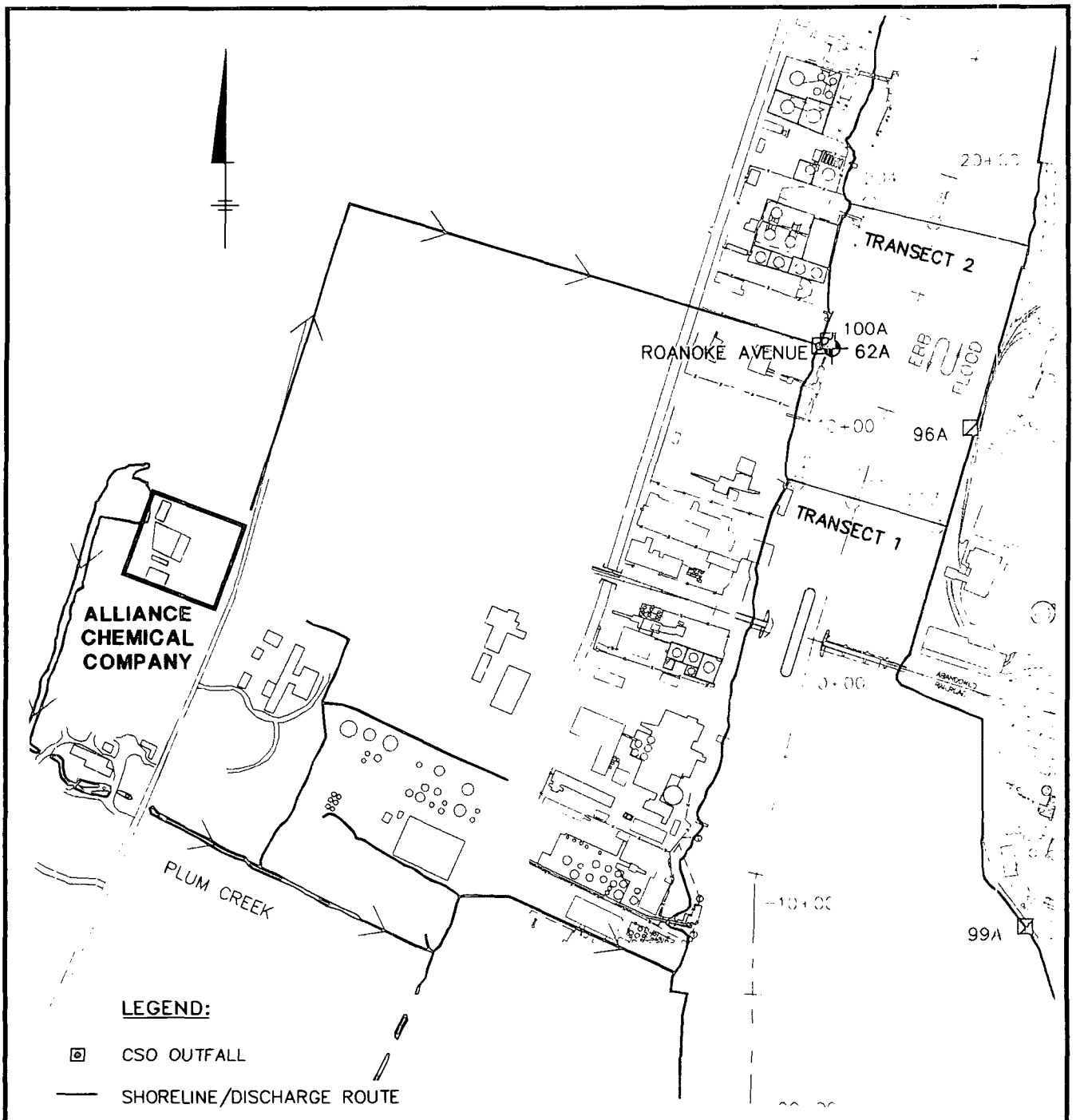
2,3,7,8-TCDD has been detected in samples for Plum Creek and the Passaic River in the vicinity of the Alliance site outfalls and discharge pathways. Additionally, significant concentrations of other site contaminants have been detected in Plum Creek and PRSA sediments, including a "top twenty" detect of 1,2,4-trichlorobenzene.

REFERENCES:

Please refer to Appendix B for the following:

Tab #	Date	Description
B1	1/11/66	Letter from Major F.R. Ulrich (A.C.E), to Alliance Color & Chemical Company
B2	1/20/66	Letter from Alliance Color & Chemical Co., to Major F.R. Ulrich (A.C.E)
B3	12/18/69	Letter from Passaic Valley Sewerage Commissioners, to Judson Merl (Plant Engineer) of Pfister Chemical Inc.
B4	12/24/69	Memo from Pfister Chemical Inc. to Jud Merl.
B5	3/21/72	Letter from Richard Leonard (Plant Manager – Alliance), to Sam Friscia, Director of Public Works, Newark
B6	3/27/72	Letter from Richard Leonard of Alliance to Edwin Barnhart of Hydroscience Inc.

B7	4/11/72	Requisition/Purchase Order from Richard Leonard of Alliance to Tim Sullivan of Hydroscience
B8	5/4/72	Letter from Tim Sullivan of Hydroscience, Inc. to Richard Leonard of Alliance
B9	5/10/72	Waste Effluent Survey from Passaic River Sewerage Commissioners noting Alliance Chemical Inc.'s water usage and plant waste.
B10	6/21/72	Letter from Richard Leonard of Alliance to Sam Friscia, Director of Public Works, Newark
B11	6/27/72	Letter from Richard Leonard of Alliance to The Mayor of Newark, Kenneth Gibson
B12	1/24/90	Summary - Alliance Color and Chemical Company, General Information and Site History
B13	1/28/94	Letter from Fredi Pearlmutter of Kerby, Cooper, English, Danis & Garvin, Counselors at Law to Lance Richman of the Emergency & Remedial Response Division of the U.S. Environmental Protection Agency
B14	8/8/01	Letter from Charles Ilsley, Jr. (Manager Environmental Affairs) of Pfister Chemical Inc., to Darryl Jennus (Chief Field Verification Section) of the Bureau of Discharge Prevention, NJDEP
B15	8/17/01	Letter from Charles Ilsley, Jr. of Pfister to Christopher Lucien (Project Engineer) of the Bureau of Discharge Prevention, NJ Department of Environmental Protection



LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- 201 SEDIMENT SAMPLING LOCATION
- 62A 1992 CORE SEDIMENT INVESTIGATION
- 96A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- FLOW DIRECTION

0 600' 1200'
GRAPHIC SCALE

SITE LOCATION MAP

ALLIANCE CHEMICAL COMPANY FACILITY

X: 09994+X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-GMS SDL LAF
09994023/09994811.DWG

BASF Wyandotte Corporation

LOCATION: Located at 50 Central Avenue, Kearny, New Jersey. The BASF site is on the east bank of the Passaic River at Newark Bay.

OPERATIONS: BASF operated at this site from 1966 to 1990. Prior to 1966, the site was operated by the United Cork Companies for the manufacture of cork and polystyrene products. The United Cork Companies was ultimately acquired by and merged into BASF. BASF manufactured a variety of chemical products, including plastics, dyestuffs and various chemicals and chemical intermediaries. The main product manufactured by BASF at this site was Phthalic Anhydride (PA).

DIOXIN RELATIONSHIP: Hazardous substances stored, used or produced at the facility include the following Class III organic compounds: phthalic anhydride, benzaldehyde and 2,4-dinitrophenol.

Onsite activities suspected to contribute to dioxin contamination include, building fires (1920s), industrial waste incineration, cork bleaching, steam pressing and the manufacture of unspecified dyes.

DISCHARGE ROUTES:

Municipal Sanitary Wastewater Discharges
BASF historically discharged its sanitary wastewaters to the municipal sanitary sewer system of the Town of Kearny.

Process Wastewater Discharges to Incinerator
From 1966-1971, BASF incinerated all process water and contaminated storm water in its on-site hazardous waste incinerator. Evaporation ponds were constructed in the southern end of the site and used from 1971-1976 to reduce the volume of wastewater materials incinerated in the on-site incinerator.

Facility Wastewater Treatment Plant
From 1976-1990, BASF completed and operated a Wastewater Pretreatment Facility (WPF) in the area of the evaporation ponds. Process wastewater from the Dye and PA plants, and contaminated storm water, was routed to the WPF for pretreatment prior to being discharged to the Kearny MUA. Effluent from the WPF was discharged to the Kearny MUA. The collected sludge from the WPF was incinerated on-site up until closure of the incinerator in 1989.

Non-Contact Cooling Water Discharges
Non-contact water generated from the facility's boiler room and PA plant was discharged directly to the Passaic River via a New Jersey Pollution Discharge Elimination System (NJPDES) permitted Discharge to Surface Water (DSW) permit.

DIOXIN CONTAMINATION:

On site samples were not analyzed for dioxins. Core samples adjacent to the site and upstream from the site indicate the presence of 2,3,7,8-TCDD in concentrations of 0.094 ppb and 4.56 ppb respectively.

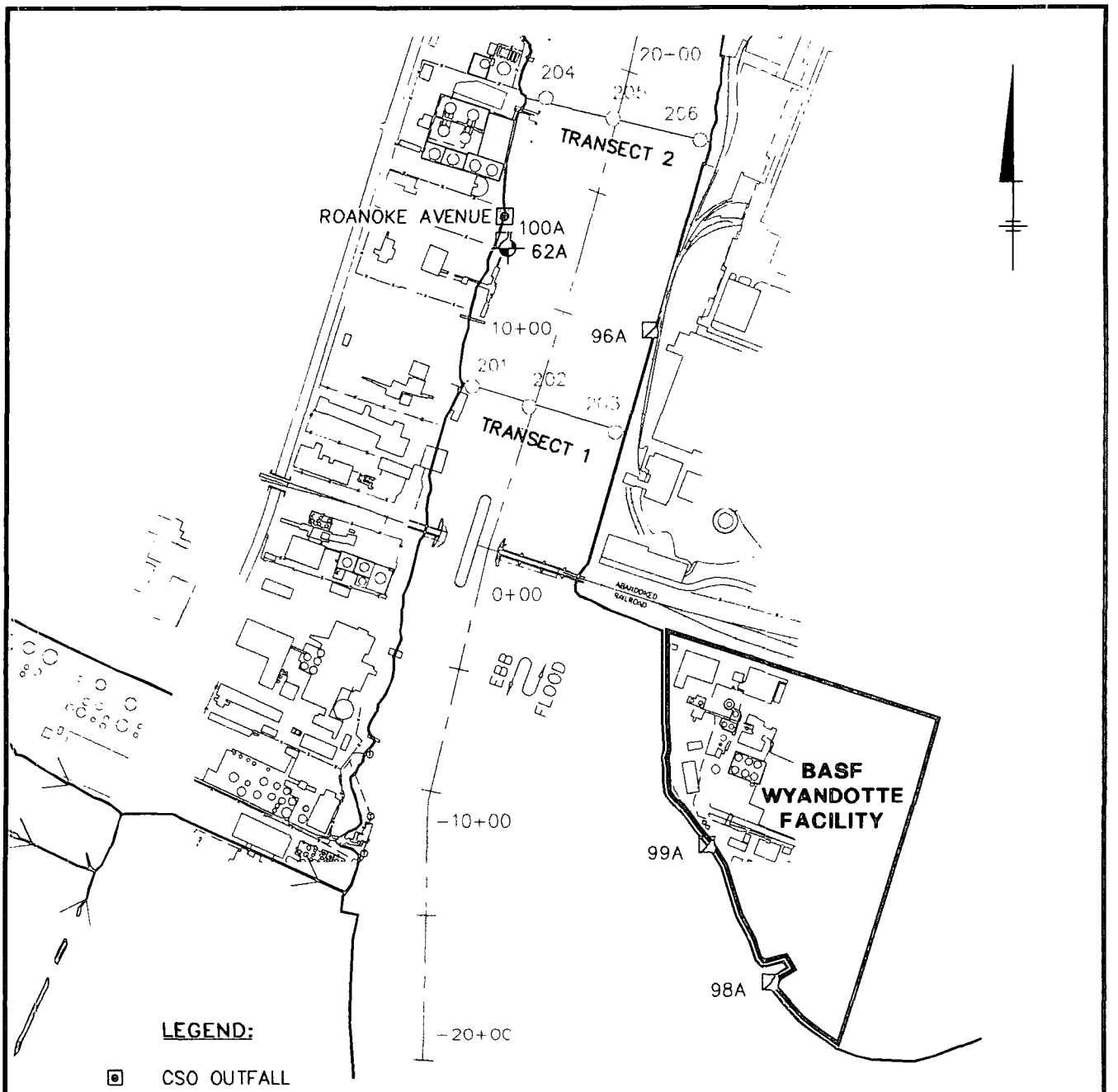
The areas where the core samples were taken are also heavily contaminated with other compounds associated with the site.

REFERENCES:

Please refer to Appendix C for the following:

Tab #	Date	Description
C1	1965	Poor's Register of Corporations, Directors and Executives, US & Canada.
C2	Undated	Data on Individual Products to be Manufactured.
C3	1972	List of Chemicals Used.
C4	Undated	Lists of Equipment; storage tanks, bed processing.
C5	Circa 1/30/74	Report on BASF history and methods of disposal.
C6	4/26/90	Hazardous Waste Generator Annual Report (1989) Certification Form -Report from BASF to the NJ Department of Environmental Protection.
C7	Circa 5/89	Notice of Final Denial of a Hazardous Waste Incinerator Permit Application from NJDEP to BASF.
C8	8/90	BASF Spill Location Plan, O'Brian & Gere Engineers, Inc.
C9	8/90	BASF Sanitary Sewer Plan, O'Brian & Gere Engineers, Inc.
C10	8/90	BASF Storm Sewer Plan, O'Brian & Gere Engineers.
C11	8/90	BASF Process Sewer Plan, O'Brian & Gere Engineers, Inc.
C12	4/21/93	Letter to Dale Webster, BASF from NJDEP.
C13	1/28/94	Letter to Lance Richman, Emergency and Remedial Response Division, U.S. EPA, from David Schneider of Bressler, Amery & Ross, Counselors at Law; attached is BASF Corporation's response to a request for information.

C14	11/30/95	Letter from Nancy Martin, Senior Attorney BASF Corporation to Lance Richman, Emergency and Remedial Response Division, U.S. EPA Attached is BASF's response to a request for Information from 11/6/95.
C15	10/98	Remedial Action Work Plan for BASF Corporation's Kearny, New Jersey Facility, Prepared by Dames & Moore.



LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- 201 SEDIMENT SAMPLING LOCATION
- 62A 1992 CORE SEDIMENT INVESTIGATION
- 96A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- FLOW DIRECTION

0 600' 1200'
GRAPHIC SCALE

SITE LOCATION MAP

BASF WYANDOTTE FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-GMS SDL LAF
09994023/09994B14.DWG

Arkansas Chemical/Hummel Chemical

LOCATION:

The Arkansas Chemical/Hummel Chemical site is located at the Foundry Street Complex, 185 Foundry Street, Newark, NJ at river mile 0.2. .

OPERATIONS:

From 1943-1983 Arkansas Chemical manufactured chemicals for the textile industry including dyes, pigments and printing inks on site.

Hummel Chemical Company operated a chemical warehouse and distribution center on-site from the mid 1950s to the late 1960s. Facility operations were reported to have also included the grinding of nitrates. Hummel supplied chemicals to the pyrotechnics industry. Though only limited information is available regarding Hummel's operations on site, it is probable that they included the reaction and mixing of chemicals in the powdered form.

DIOXIN RELATIONSHIP:

Chemical manufacturing processes known to have been utilized by both Arkansas Chemical and by Hummel – specifically those processes centering on the manufacture of dyes, pigments and inks – are reported to be strongly associated with the by-product generation of dioxin and furan compounds.

In 1980, USEPA reported the former Hummel Chemical facility at the Foundry Street Complex to have been a producer of several USEPA Class III organic compounds – specifically 2,4 -Dinitrophenoxyethanol; 3,5-Dinitrosalicylic acid; Hexachlorobenzene; and Picric acid.

Reportedly, on October 14, 1988, four soil samples were collected from the Foundry Street Complex and analyzed for 2,3,7,8-TCDD. However, and pertinent to the identification of dioxin sources, none of the October 1988 soil samples were collected from any areas believed to have been utilized as process areas by Hummel Chemical.

DISCHARGE ROUTES:

Arkansas Chemical reportedly discharged effluent to city storm sewers along Foundry Street via covered ditches. The Foundry Street storm sewers were, in turn, routed into the Roanoke Avenue sewer. The Roanoke Avenue sewer line historically served as a combined sewer outfall that allowed for the combined discharge of sanitary and storm waters directly to the Passaic River.

Via the Roanoke Avenue sewer line and outfall, the storm drains at the complex discharged to the Passaic River and allowed for the migration of chemicals spilled onsite to the river. Reportedly, storm drains on site would frequently flood during periods of heavy rain, redistributing contamination through out the site.

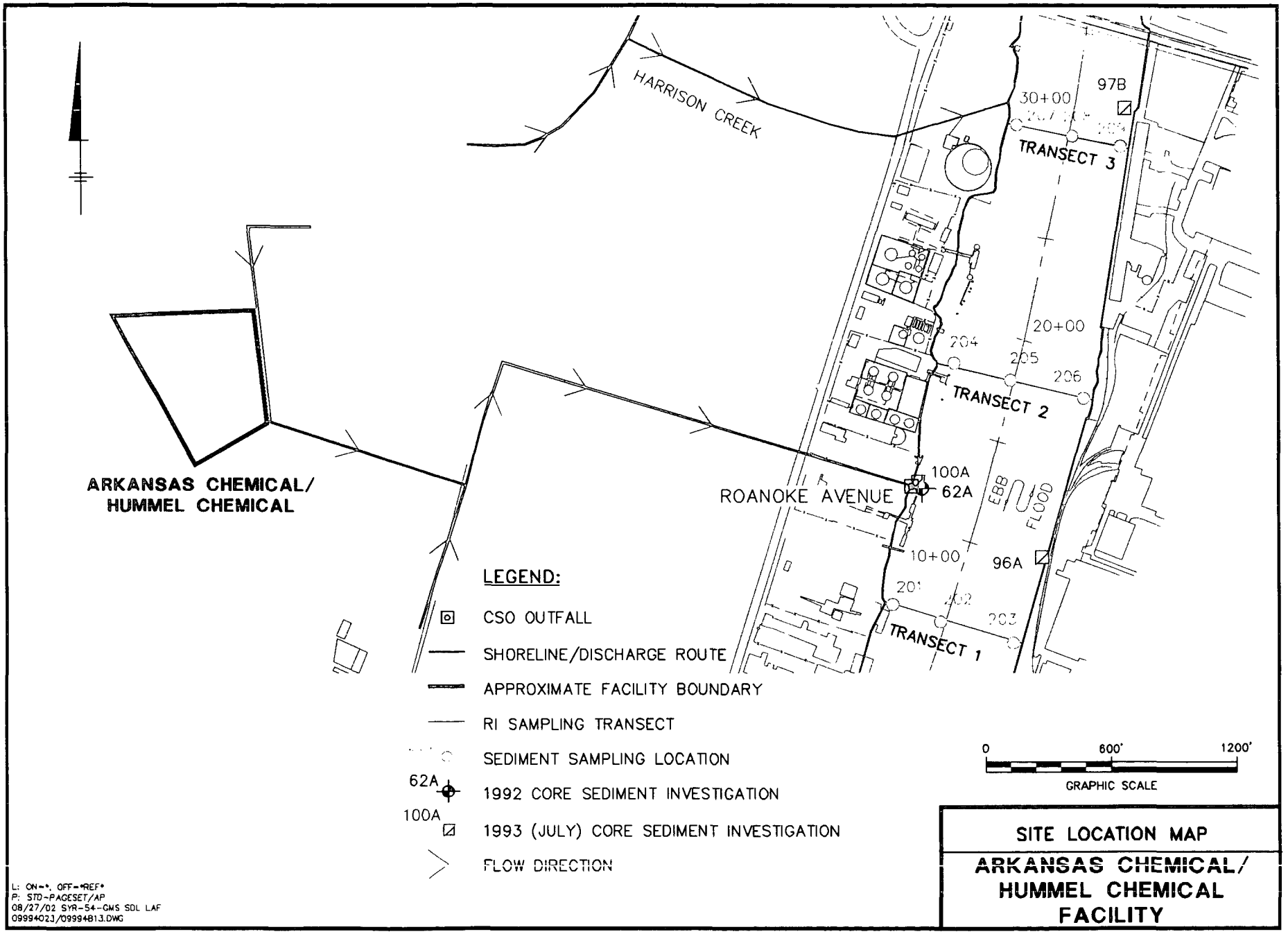
DIOXIN CONTAMINATION: Numerous dioxin-associated compounds - including 2,4-dichlorophenol and 2,4,6-trichlorophenol - were detected in sampling of site soils, groundwater and sediments.

Furthermore, USEPA Class III dioxin precursors, pentachlorophenol and 1,2,4-trichlorobenzene, were detected during sampling of on-site basement waters at the Arkansas site.

2,3,7,8-TCDD was detected in core samples taken in the vicinity of the Roanoke Avenue CSO. Other contaminants that were identified in sampling of site soils, groundwater and sediments were also identified in sediments sampled in the vicinity of the Roanoke Avenue outfall.

REFERENCES: Please refer to Appendix D for the following:

Tab #	Date	Description
D1	11/15/90	Memorandum from Paul Smith, NJDEP, to Foundry Street Complex File. In re: Site Inspection on 11/7/90.
D2	4/3/91	Memorandum from Doug Stewart, NJDEP, to Linda Grayson, NJDEP. In re: Responsible Party Investigation, Foundry Street Complex.
D3	5/20/91	NJDEP Case Transfer Report
D4	Undated	USEPA Preliminary Assessment- Potential Hazardous Waste Site.
D5	8/15/9	Memo from Paul Smith to File: Addendum to Foundry Street Complex Party Investigative Report.



SITE LOCATION MAP

ARKANSAS CHEMICAL/
HUMMEL CHEMICAL
FACILITY

L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-GMS SDL LAF
09994023/09994813.DWG

Bayonne Barrel & Drum Co.

LOCATION:

The Bayonne Barrel & Drum Company (BB&D) Superfund Site is located at 150-154 Raymond Boulevard, Newark, NJ. The site lies within 2000 feet of the Passaic River. Harrison Creek, a tributary to the Passaic River, historically flows along the eastern border of the property and discharges to the Passaic River.

OPERATIONS:

While BB&D began operations in the early 1940's, a predecessor drum conditioning concern was in operation at the site as of circa 1931. BB&D filed for bankruptcy in July 1982, and discontinued operations in September 1983. BB&D's operations consisted of the reconditioning of steel drums using caustic solution, steel shot abrasive, incineration, and paint.

DIOXIN RELATIONSHIP:

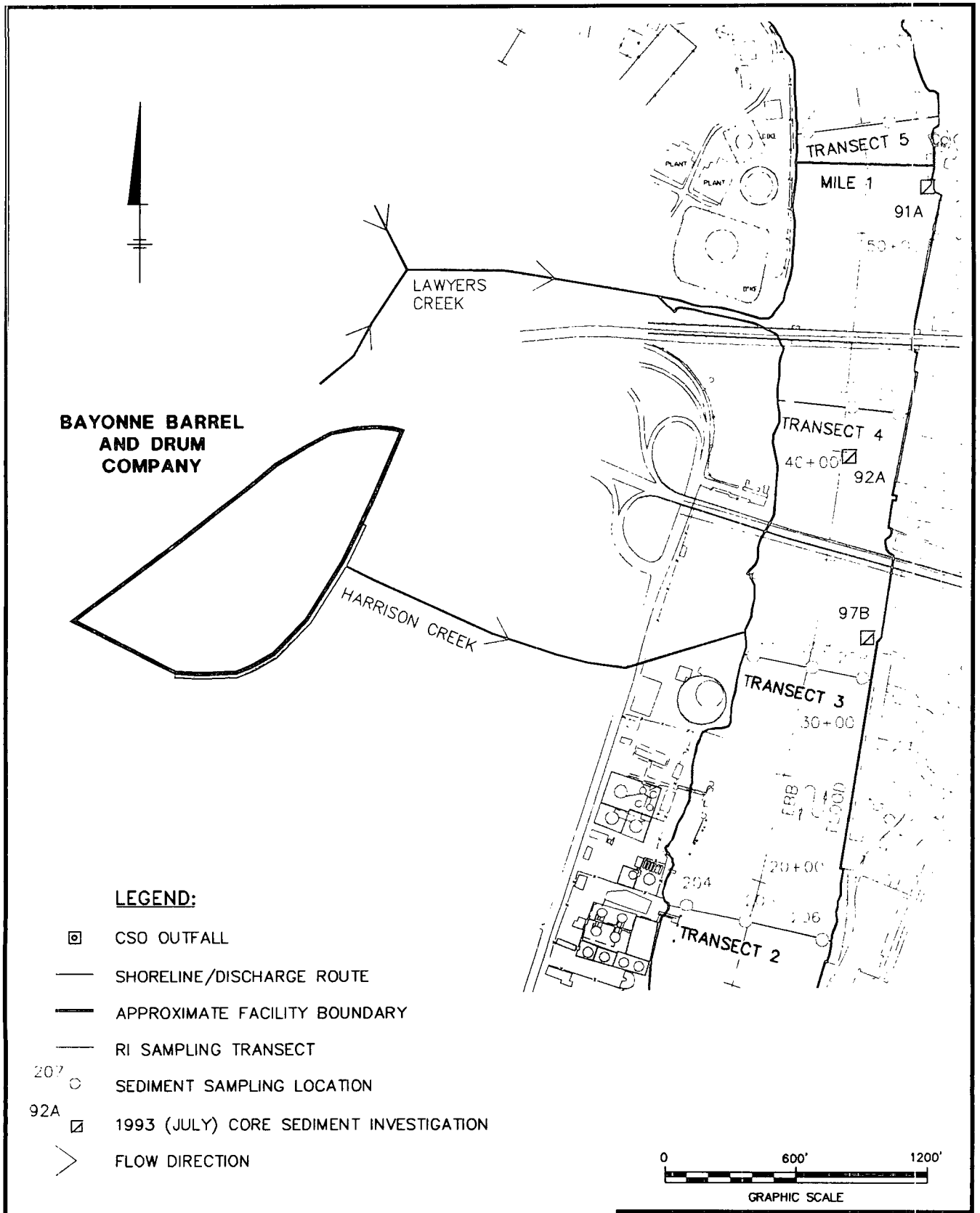
High temperature combustion processes historically utilized at the BB&D site – specifically those processes involved in drum and barrel reclamation – are reported to be strongly associated with the by-product production of dioxin and furan compounds. This association is strongly supported by the detection of numerous dioxin and furan compounds during USEPA-supervised soil and groundwater sampling activities at the BB&D NPL site.

DISCHARGE ROUTES:

Harrison Creek, a tributary to the Passaic River, originally ran through the BB&D property on a route adjacent to facility waste lagoons. On-site ditches and waste lagoons were historically routed and discharged to the creek. Harrison Creek was reportedly diverted in approximately January 1948 to the eastern border of the property, and may have been realigned again in the early 1950s when the NJ Turnpike Authority acquired parcels of the property from BB&D for construction of the NJ Turnpike. The settling lagoon was filled in and a wastewater settlement tank was constructed and in use as of 1957-1958. As of 1959, the waste lagoons were filled in and drainage ditches at the eastern edge of the site drained to a "liquid-filled trench" adjacent to the old lagoon location.

By January 1973, the BB&D operation's industrial wastewater was discharged to an 80 foot settling sluice and holding tanks before being released into the sanitary sewer to PVSC. A 1980 USEPA report noted that site run-off water drains to Harrison Creek and Lawyers Creek "which are now enclosed in storm water culverts." The approximate 1% slope towards the north/northeast allows collection of runoff to drain along the eastern border of the site.

E10	6/2/88	RCRA Enforcement Inspection of BB&D; Prepared by Michael Ferriola, Environmental Scientist Source Monitoring Section.
E11	10/24/88	U.S. Environmental Protection Agency; Preliminary Assessment of BB&D.
E12	12/2/88	Site Inspection Review of BB&D submitted by Edward Gaven, NJDEP Bureau of Planning and Assessment.
E13	9/30/92	Letter summarizing the Site Inspection Prioritization Evaluation of BB&D from Gary Bielen, Site Manager, John Rieckhoff, Pre-Remedial Program Manager and Dennis Stainken, Work Assignment Manager to Sandra Foose, USEPA.
E14	3/26/97	Letter from William Lee, Environmental Project Manager, de Maximis, inc., to Joseph Cosentino, USEPA enclosing Bayonne Barrel and Drum Site- Soil Investigation Report, by BBL.
E15	Undated	Figure showing Soil Sampling Locations of BB&D.
E16	7/6/01	Letter from Richard Caspe, Director, Emergency and Remedial Response Division USEPA, to Recipients. Attached is a list of Potentially Responsible Parties.
E17	1946 – 1959	Correspondence from Passaic Valley Sewerage Commissioners documenting pollution of Harrison Creek.
E18	7/86	Soils and Ground Water Characterization prepared by Dan Raviv Associates, Inc.
E19	12/86	Report by Louis Berger & associates submitted to New Jersey Turnpike Authority, "Results of Preliminary Investigations."



SITE LOCATION MAP

BAYONNE BARREL AND DRUM COMPANY FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
07/27/02 SYR-54-GMS LAF LAF
09994023/09994812.DWG

Public Service Electric & Gas (PSE&G) Essex Generating Station

LOCATION:

The PSE&G Essex Generating Station is located at 155 Raymond Boulevard, Newark, NJ 07101. The facility is situated on the west bank of the Passaic River at site study area river mile 1.0.

OPERATIONS:

PSE&G has operated the Essex Generating Station from approximately 1915 to present. The facility, described as an electrical generating station, has historically utilized the burning of coal, natural gas and/or oil to power electricity-producing turbine machinery at the site. The station originally used coal-fired boilers to power the turbines but switched to natural gas and oil (kerosene) in the 1960s – most likely 1963. Transformers are used at the station to transfer the energy from the turbine generators to distribution networks.

DIOXIN RELATIONSHIP:

Onsite activities that are suspected to have contributed to dioxin contamination include, the use of boilers and industrial furnaces, and the combustion of coal and oil. PSE&G has also admitted in documentation to the USEPA to the historical use of PCB-containing products at the Essex Generating Station.

Processes centering on high temperature combustion - such as those utilized at the PSE&G Essex facility in its (1) coal combustion; (2) boilers and industrial furnaces; (3) in its oil combustion; and (4) in the inadvertent combustion of PCB products - have all been reported as being strongly associated with the production of dioxin compounds.

DISCHARGE ROUTES:

The facility is known to have had a historical drainage ditch system that discharged to the Passaic River in addition to its five NPDES-permitted outfalls which discharge to the Passaic River. Non-contact cooling water, boiler blowdown, and storm water/surface run-off collected on-site are routed into these outfalls to the Passaic River.

Because the PSE&G Essex Generating Station is located directly on the Passaic River. Storm water and surface run-off serves as a mechanism for transporting contaminated media directly to the Passaic River. Site flooding conditions also serve as a mechanism for transporting contaminants spilled, leaked or discharged onto site soils into the Passaic River.

DIOXIN CONTAMINATION: Low levels of 2,3,7,8-TCDD contamination have been detected during limited soil sampling at the PSE&G Essex Generating Station site.

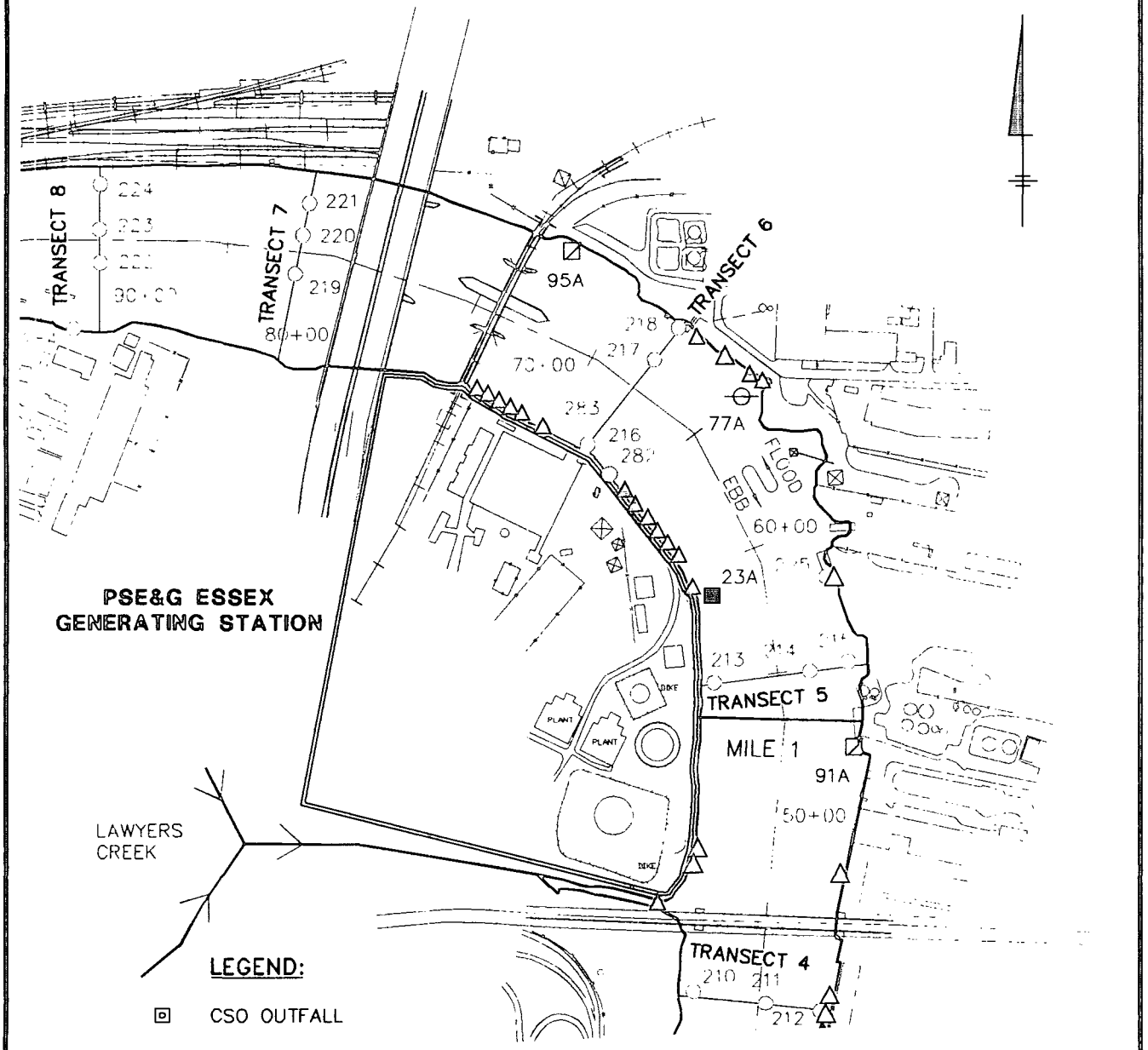
The 2,3,7,8-TCDD contamination - ranging in levels from non-detect to 3.2 PPB - was detected during soil sampling under the present-day NJ Turnpike bridge, but in an area that was formerly part of the PSE&G Essex facility until at least 1965. This limited sampling activity comprises the only known dioxin sampling at the PSE&G Essex site to date.

2,3,7,8-TCDD was detected at up to 11.6 ppb in core 214 in the vicinity of the PSE&G site.

REFERENCES: Please refer to Appendix F for the following:

Tab #	Date	Description
F1	1973	Annual Report by Chief Engineer S.A. Lubetkin to the Passaic Valley Sewerage Commissioners.
F2	1/14/76	Laboratory Report from Passaic Valley Sewerage Commissioners of PSE&G.
F3	1/21/76	Letter from S.A. Lubetkin of Passaic Valley Sewerage Commissioners, to C. E. Maginn, Jr., Division Superintendent – Essex, PSE&G.
F4	1/27/76	Letter from J. F. Schwanhausser, Division Superintendent- Elizabeth PSE&G, to S.A. Lubetkin, Passaic Valley Sewerage Commissioners.
F5	3/15/76	Memo from Passaic Valley Sewerage Commissioners concerning monthly reports for Jan. & Feb., 1976.
F6	2/26/80	Laboratory Report of PSE&G storm sewer, from Passaic Valley Sewerage Commissioners.
F7	1/28/91	NJDEP Communications Center Notification Report.
F8	1/31/91	Notice of Violation from NJDEP, to PSE&G.

F9	3/20/91	Memo from NJ Department of Law and Public Safety, to Assistant Director for Enforcement Division of Water Resources & Assistant Director of Hazardous Waste Management. Attached is an investigation report of PSE&G.
F10	1950	Sanborn Map.
F11	2/23/91	NJDEP Investigative Report.



LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- SEDIMENT SAMPLING LOCATION
- 23A 1991 (NOV/DEC) CORE SEDIMENT INVESTIGATION
- 62A 1992 CORE SEDIMENT INVESTIGATION
- 77A 1993 (MARCH) CORE SEDIMENT INVESTIGATION
- 91A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- HISTORIC AND PRESENT DAY OUTFALLS

0 600' 1200'

GRAPHIC SCALE

SITE LOCATION MAP

PSE&G ESSEX GENERATING STATION FACILITY

X: 09994X00L.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-CWS SDL LAF
09994023/09994817.DWG

Essex County Resource Recovery Facility/American Ref-Fuel, Inc.

LOCATION:

The Essex County Resource Recovery Facility (ECRRF) is located at 66 Blanchard Street in Newark, NJ on the south/western bank of the Passaic River.

OPERATIONS:

Operated by American Ref-Fuel, Inc., the ECRRF facility has served as a municipal waste incineration plant on the Blanchard Street site since approximately 1990.

Facility operations consist of the receipt, sorting, processing and incineration of municipal solid waste - with the ultimate sale of the resultant energy from the waste burning to PSE&G.

DIOXIN RELATIONSHIP:

As reported by the USEPA, high temperature combustion processes are reported to be strongly associated with the by-product production of dioxin and furan compounds. Relative to the ECRR facility, municipal waste incineration – an operation which centers on the use of high temperature combustion – is known to be associated with the generation of dioxin compounds.

As a permit requirement for operation of the municipal waste incinerator, ECRRF is required by the New Jersey Department of Environmental Protection ("NJDEP") to test for the presence of 2,3,7,8-TCDD in all ash piles generated from the incinerator.

DISCHARGE ROUTES:

Two onsite ditches, the Central Ditch and the West Ditch, discharge directly to the Passaic River. A portion of the site (the southeastern corner) is drained via Lawyer's Creek.

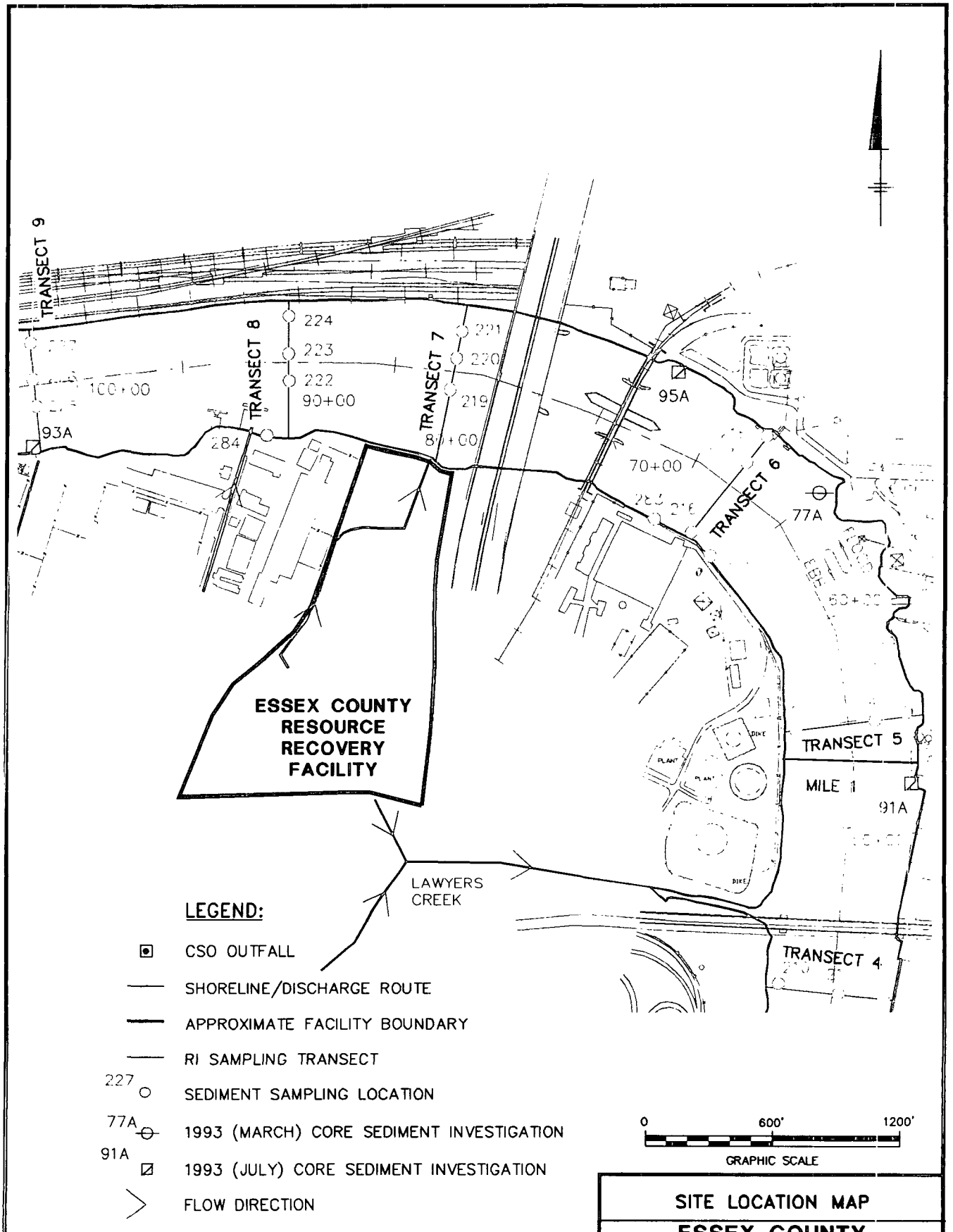
DIOXIN CONTAMINATION:

NJDEP has documented low levels of 2,3,7,8-TCDD in sampling of the ECRRF ash piles during testing conducted from 1995 to the present. During these ash pile-sampling events, concentrations of 2,3,7,8,TCDD have been detected at concentrations ranging from non-detect to 0.10 PPB.

Also of note, USEPA Class III dioxin precursor organic compounds, including chlorobenzene and 1,2-dichlorobenzene, have also been detected during historical soil and groundwater sampling activities at the site.

REFERENCES: Please refer to Appendix G for the following:

Tab #	Date	Description
G1	9/13/84	Memo from John Bielamowicz, Environmental Scientist NJDEP, to File-Essex County Resource Recovery Facility Application Re: Discharge Permits.
G2	Undated	Map of site.
G3	10/29/84	Interoffice Memo from Mark Gruzlovic NJDEP, to Vince Krisak Re: Recommendations & Case Status.
G4	10/31/84	Directive letter from NJDEP, to Milton Buck – Executive Director, Newark Redevelopment and Housing Authority Re: Violation.
G5	2/6/85	Interoffice Memo from NJDEP to File Re: site inspection.
G6	8/16/85	Letter from Riker, Danzig, Scherer, Hyland & Perreti, to Joseph Rogalski, Assistant Director- Div. Of waste management, NJDEP.
G7	5/27/88	Letter from US Testing Company, Inc., to Betty Boros, NJDEP.
G8	6/22/88	Letter from NJDEP to Thomas Spurkowsky, Site Manager Amer. Ref-fuel Re: Compliance Evaluation Inspection.
G9	4/8/91	Letter from John Waffenschmidt-Asst. Director of Environmental Compliance-Amer. Ref-fuel, to Robert Oberthaler-NJDEP.
G10	12/1/92	NJDEP Administrative Consent Order.
G11	6/21/93	Letter from NJDEP, to Assistant Director Env. Compliance for Amer. Ref-fuel Re: Compliance Evaluation Inspection.
G12	9/30/93	Letter from NJDEP, to American Fuel Co. of Essex, Re: Violation of Effluent Limits or Parameter Reporting Requirements.



SITE LOCATION MAP

ESSEX COUNTY RESOURCE RECOVERY FACILITY

X: 09994X00L.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54--GMS SDL LAF
09994023/09994815.DWG

H

Thomasett Color/Hilton Davis

LOCATION:

The Thomasett/Hilton Davis site is located at 120 Lister Avenue, adjacent to the Passaic River.

OPERATIONS:

Colorants that were marketed to the automotive, cosmetics, textile and drug industries were manufactured at this site. The primary products manufactured include phthalocyanine blue pigments, phthalocyanine green pigments, transoxides and drug and cosmetic grade pigments.

DIOXIN RELATIONSHIP:

Hazardous substances stored, used or produced at the facility include USEPA Class III organic compounds phthalic anhydride and o-dichlorobenzene.

The processes utilized by Thomasett/Hilton Davis in Newark for the manufacture of phthalocyanine dyes have been reported to be strongly associated with the by-product production of dioxins and furans compounds. This association is supported by findings published by EPA in 1986 that dioxin and furan by-products, in addition to PCBs, are in fact, known to be generated during the production of phthalocyanine dyes.

DISCHARGE ROUTES:

Direct discharges of process water to the Passaic River have historically occurred at the site, as documented by the Passaic Valley Sewerage Commissioners ("PVSC"). PVSC has documented a number of direct process wastewater discharges to the Passaic River that have historically occurred at the rear of the riverfront-located Thomasett/Hilton Davis site.

It is also documented in former employee witness affidavits that, during the 1950's time period, a "false sewer system" was installed onsite and historically utilized as a means to directly discharge process wastewater from the facility to the Passaic River.

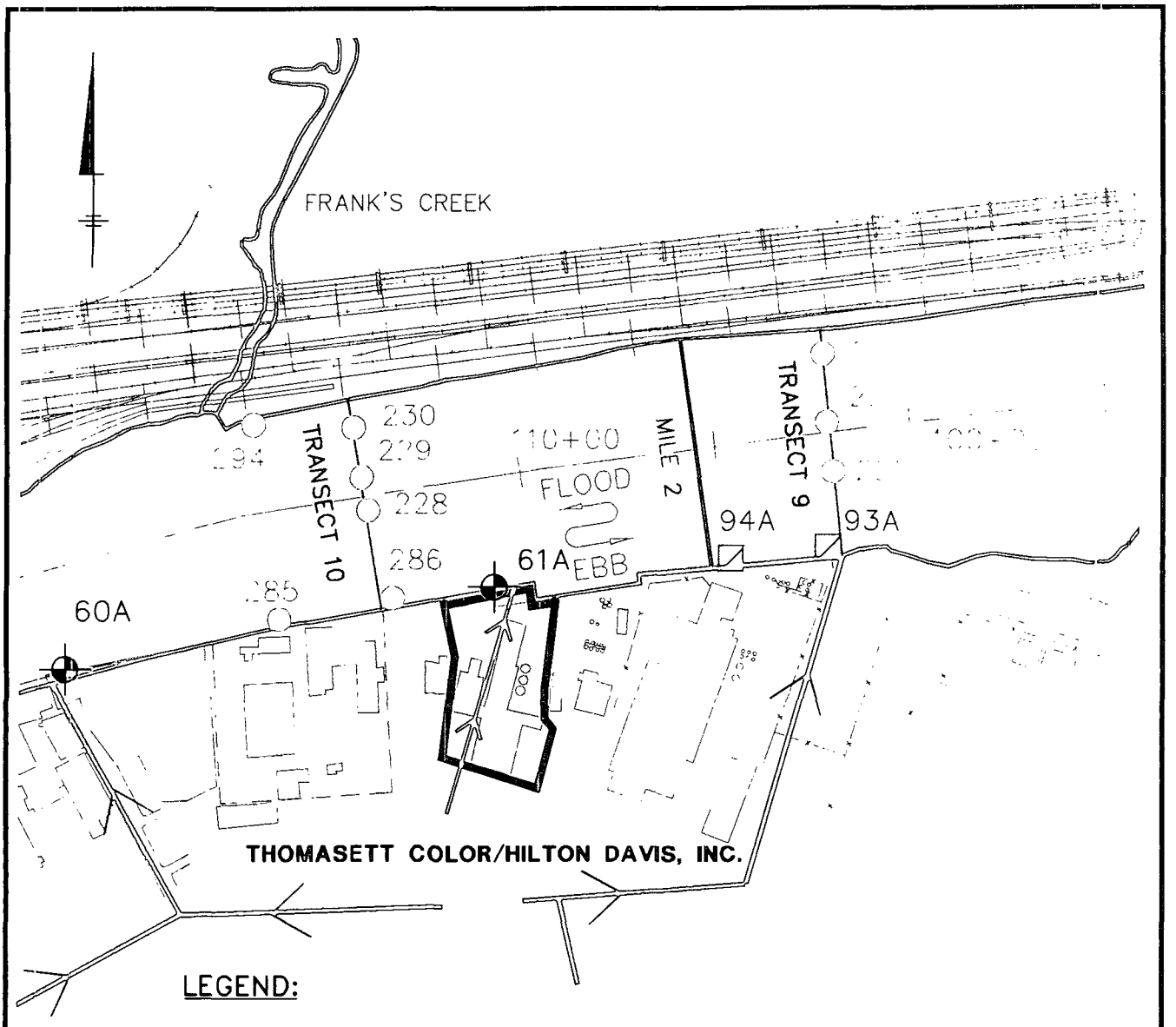
Process spills and leaks at the Thomasett/Hilton Davis facility reportedly discharged to the Passaic River via the municipal storm sewer system located on Lister Avenue. This storm sewer discharged to the Passaic River at the Brown Street outfall prior to the 1970s and at Lockwood Street after the early 1970s.

It is reported that during heavy rains, water would back up onto the Thomasett/Hilton Davis site through the facility catch basins. During these flood periods, the water would reportedly also discharge to the Passaic River through the City of Newark Storm Sewer on Lister Avenue.

DIOXIN CONTAMINATION: No dioxin soil sampling is known to have been conducted to-date at the site. However, there is evidence of significant dioxin contamination in the sediments of the PRSA located directly adjacent to the Thomasett/Hilton Davis Newark site.

REFERENCES: Please refer to Appendix H for the following:

Tab #	Date	Description
H1	7/30/56	Weekly Summary of Inspections for Thomasett Color Chemical Co.
H2	8/20/56	Weekly Summary of Inspections for Thomasett Color Chemical Co.
H3	1971	Annual Report by S.A. Lubetkin to the Passaic Valley Sewerage Commissioners.
H4	5/16/79	On-Site Material Storage.
H5	10/29/86	ECRA initial notice, General Information Submission Form from H.D. Lockwood, VP of Hilton-Davis, to NJDEP.
H6	2/23/87	ECRA Site Evaluation Submission from Irving Cohen, President of Enviro-Sciences, Inc. to NJDEP.
H7	6/18/96	Memo from Steve Huntley of Chem Risk, to Amanda Birrelll of Vinson & Elkins and Rick McNutt of Maxus. Attached is a report of PCB and PCDD/F discharge into Passaic by Hilton-Davis.
H8	6/19/96	Letter from Amanda Birrell of Vinson & Elkins, Attorneys, to Amelia Wagner of USEPA.
H9	Undated	List of Raw Materials Inventory for Hilton Davis.
H10	Undated	Hilton Davis Raw Materials Inventory.
H11	3/27/96	Affidavit of former Hilton Davis employee Robert Malone.



LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- SEDIMENT SAMPLING LOCATION
- 61A 1992 CORE SEDIMENT INVESTIGATION
- 94A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- FLOW DIRECTION

0 400' 800'
GRAPHIC SCALE

SITE LOCATION MAP

THOMASETT COLOR/ HILTON DAVIS, INC. FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-GWS SDL LAF
09994023/09994818.DWG

Montrose Chemical Company

LOCATION:

The Montrose Chemical Company site is located at 100 Lister Avenue, Newark, NJ. The site is bounded by industrial properties adjacent to the Passaic River on the north and by Lister Avenue to the south.

OPERATIONS:

Montrose Chemical - (parent company is Chris Craft, Inc.) - operated at the site from 1943 to 1974. The site is currently being operated by Chemical Waste Management of New Jersey, Inc. - (previously known as SCA Chemical, Inc.) - as a hazardous waste transfer, storage, recovery and treatment facility.

Montrose Chemical manufactured a variety of chemical products at the site, including chlorinated herbicides, pesticides, fuel and rubber additives, food and drug products and various chemical intermediates. Montrose products included, but were not limited to:

- 1,2,4-Trichlorobenzene
- 2,4,5-T
- 2,4-D
- Bis(2-ethylhexyl) phthalate
- DDT
- Dichlorobenzene
- Hexachlorobenzene
- Lindane
- Tricresyl phosphate
- Other pesticides and herbicides

DIOXIN RELATIONSHIP:

Many of the products used and manufactured at the Montrose site are associated with the formation of Dioxins.

- Montrose manufactured USEPA Class I organic compounds 2,4-D and 2,4,5-T.
- Montrose manufactured USEPA Class II pesticide chemical Lindane.
- Montrose manufactured USEPA Class III organic compounds 1,2,4-Trichlorobenzene; Dichlorobenzene and Hexachlorobenzene.
- Montrose utilized USEPA regulated dioxin precursor compound chlorobenzene as a raw material in its operations.

Reportedly 2,3,7,8-TCDD was generated as a manufacturing by-product and subsequently discharged along with the effluent from washing and settling steps utilized in on-site manufacturing processes.

DISCHARGE ROUTES:

Direct discharges to the Passaic River reportedly occurred at the rear of the facility and at the terminus of the local storm sewers at Brown and Lockwood Streets. Interviews with former employees indicate direct discharges to the Passaic River at the rear of the facility until approximately 1978. Employee interviews, as conducted by USEPA, and documentation indicates that wooden storm sewers onsite discharged to either the storm sewer, combined sewer or both located on Lister Avenue. This storm sewer discharged to the Passaic River at the Brown Street outfall prior to the 1970s and at the Lockwood Street outfall after the early 1970s.

Erosion of contaminated soil is likely to have occurred on site during Passaic River flooding. Advancing and receding floodwaters would serve as a mechanism for the transport of soil contamination from the site to the Passaic River.

DIOXIN CONTAMINATION:

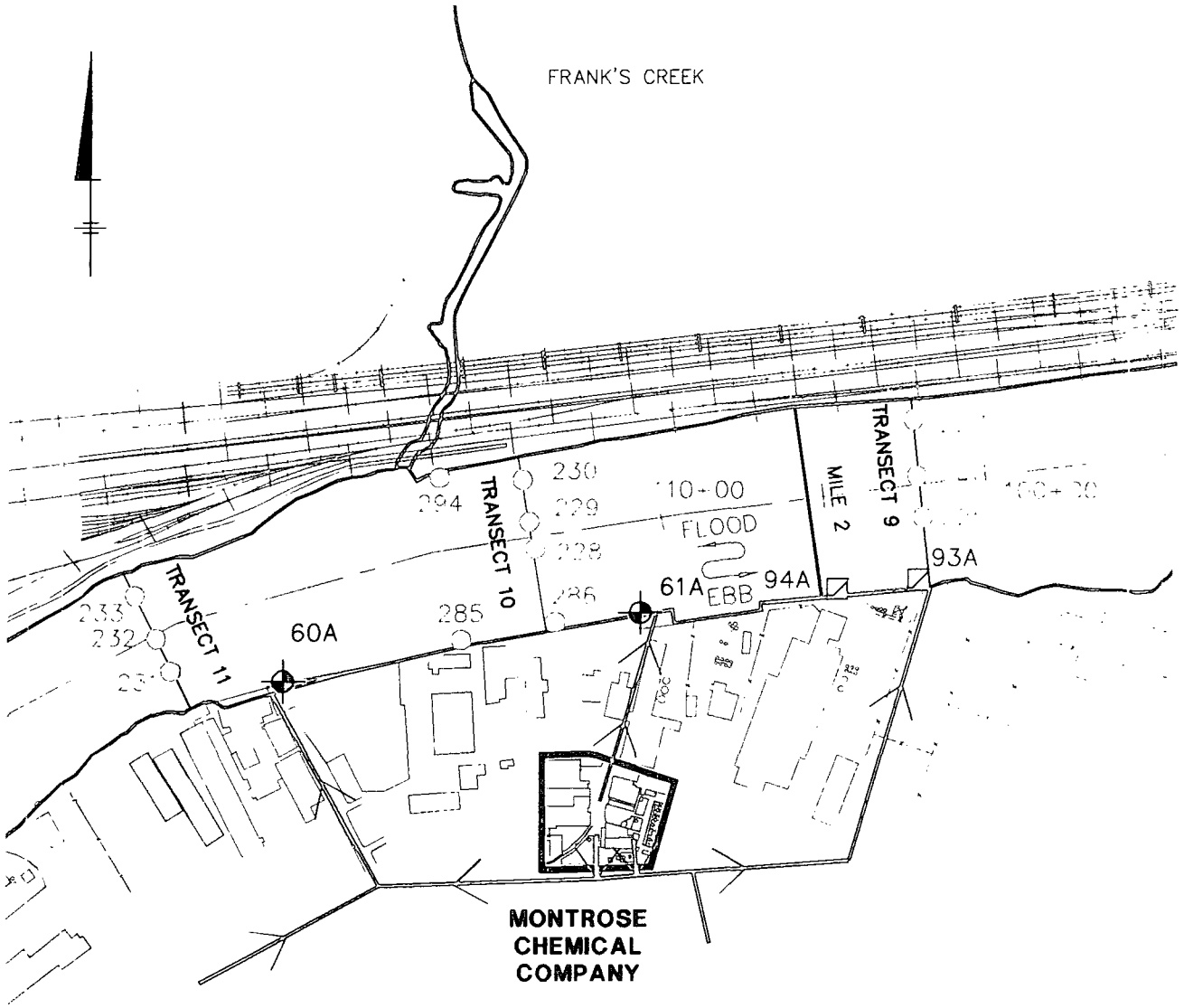
2,3,7,8-TCDD contamination was detected in PRSA sediments directly adjacent to the Montrose site at various levels ranging to 5300 ppb. A concentration of 240 ppb was detected in the vicinity of the Lockwood Street outfall.

REFERENCES:

Please refer to Appendix I for the following:

Tab #	Date	Description
I1	7/21/93	Affidavit of former Montrose employee Oscar Randall.
I2	7/21/93	Affidavit of former Montrose employee Kelsey T. Brown.
I3	7/27/93	Affidavit of former Montrose employee S.H. Koved.
I4	6/983	Letter from S. Koved to R. Goldstein, Health Commissioner, NJ Department of Health, re: site hazards.
I5	1937 - 1964	Various Newark Industrial Directories
I6	1/25/93	Chris Craft Industries' Response to EPA Information Request Letter.
I7	12/15/93	Chris Craft Industries' Response to Second EPA Information Request Letter.

I8	10/1914	Figure entitled Plan of Lister Agricultural Chemical Works.
I9	05/05/43	Figure entitled Survey of 60- 120 Lister Avenue.
I10	1/7/65	Storm Sewer Map and Sanitary Sewer Map, # 9G & 9H, by Porter Armstrong for Newark Housing Authority.
I11	1971(?)	City of Newark, Department of Public Works. "As-Is" Plans on Lister Avenue Sewer Improvements.
I12	3/27/96	Affidavit of former Thomasett/Hilton Davis employee Robert Malone.
I13	1/9/78	PVSC Industrial Sewer Connection Permit for Earthline Company, concerning Lister Avenue storm and sanitary sewer cross connections, with attached 12/8/77 letter from City of Newark to PVSC re: permit application.
I14	1971 - 1974	Excerpts from PVSC Annual Reports for 1971, 1972, 1973 and 1974 concerning Brown and Lockwood Street storm sewers.
I15		Excerpts from Chemical Waste Management Remedial Investigation Report – with associated documents concerning on-site environmental conditions at the former Montrose/Chris Craft site.



LEGEND:

- CSO OUTFALL
- SHORELINE/DISCHARGE ROUTE
- APPROXIMATE FACILITY BOUNDARY
- RI SAMPLING TRANSECT
- 227 SEDIMENT SAMPLING LOCATION
- 60A 1992 CORE SEDIMENT INVESTIGATION
- 94A 1993 (JULY) CORE SEDIMENT INVESTIGATION
- FLOW DIRECTION

0 500' 1000'

GRAPHIC SCALE

SITE LOCATION MAP

MONTROSE CHEMICAL COMPANY FACILITY

X: 09994x00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
08/27/02 SYR-54-GMS LAF LAF
09994023/09994B16.DWG

Givaudan-Roure Corporation

LOCATION:

The Givaudan Roure Company/Givaudan Chemical Company (Givaudan) site is located at 125 Delawanna Avenue in Clifton, Passaic County, New Jersey.

OPERATIONS:

From approximately 1905 through 1998, Givaudan has produced specialty, aromatic, flavor and fragrance chemicals at the Clifton site.

Givaudan began it operations at the site on a lease basis beginning in approximately 1905 and eventually purchased the entire property by the early-1930's time period. Of note, between 1947 and 1984, Givaudan produced the antibacterial chemical Hexachlorophene (under the "Isobac 20" product name) at the site. The Givaudan operations were discontinued at the Clifton site in approximately mid-1998.

DIOXIN RELATIONSHIP:

The historical manufacturing of Hexachlorophene/Isobac 20 and other products at the Givaudan Clifton facility was known to utilize hazardous substances associated with the formation of dioxin. These dioxin associated compounds include the following:

- USEPA Class I organic compound 2,4,5-Trichlorophenol (2,4,5-TCP) which was produced on-site from 1947 through 1949, and which was utilized as a raw material feedstock in the on-site manufacture of Hexachlorophene from 1947 through 1984.
- USEPA Class I organic compound 2,4-Dichlorophenol which was also utilized as a raw material at the site.
- USEPA Class III organic compounds Benzaldehyde and Fumaric acid.

DISCHARGE ROUTES:

Historical discharge mechanisms from the Givaudan site were reported to include the following:

1. Direct process discharges via the original "chemical sewer" system installed at the facility in 1947. Process wastewater was collected and treated on-site before being discharged to the chemical sewer and ultimately into a pond in the Third River, a tributary of the Passaic River. In 1985 a new chemical sewer, which included secondary containment, was installed and replaced part of the original chemical sewer system.

2. Direct discharges of process wastewater to the Clifton sanitary sewer system. Frequent sewer line breaks were reported to have occurred in this sewer line, historically resulting in the discharge of process wastewater to the Third River.

3. Majority of onsite storm water is collected and discharged into an on-site retention pond. This pond allows for the discharge of contaminants to site groundwater.

4. Storm water in a portion of the site historically discharged to a municipal Clifton storm sewer, and in turn, to the Third River.

5. Storm water in another portion of the site is directed via a trench into a Clifton storm sewer that discharges to the Passaic River.

DIOXIN CONTAMINATION:

Givaudan produced Hexachlorophene in Building #'s 58, 59, 60, 68, 168, (from late 1940's), and Building # 9, (since early 1970's). Trichlorophenol was produced in Building #'s 54 & 60.

Levels of 2,3,7,8 TCDD soil contamination were detected at concentrations ranging up to 200 ppb in the former process/production area, outside of Building # 54. This sampling location is situated above the chemical sewer line. Elevated concentrations of 2,3,7,8 TCDD were also found in areas of the eastern portion of the site, including immediately adjacent to the storm water retention pond.

2,3,7,8 TCDD was found at concentrations up to 18.79 ppb (estimated) under various site buildings, (Building #'s 93, 95, 168 & 60), with concentrations of 2,3,7,8 TCDD exceeding 2 ppb being detected in samples from as deep as 23- to 24-feet below ground surface.

The former drum storage area was located in the southeastern portion of the site, near Building #93, which showed 2,3,7,8 TCDD levels in excess of 7ppb. This area was adjacent to the storm water retention pond.

An Amended Consent Order was issued in February 1988, which, allowed Givaudan to perform limited excavation and remediation of contaminated soil within the Contaminated Process Area, Sample Area G-11, and to containerize contaminated soils on-site until appropriate treatment technologies became available

The 2,3,7,8 TCDD contamination detected in site soil - during those site investigations performed prior to ISRA-related site activities - was

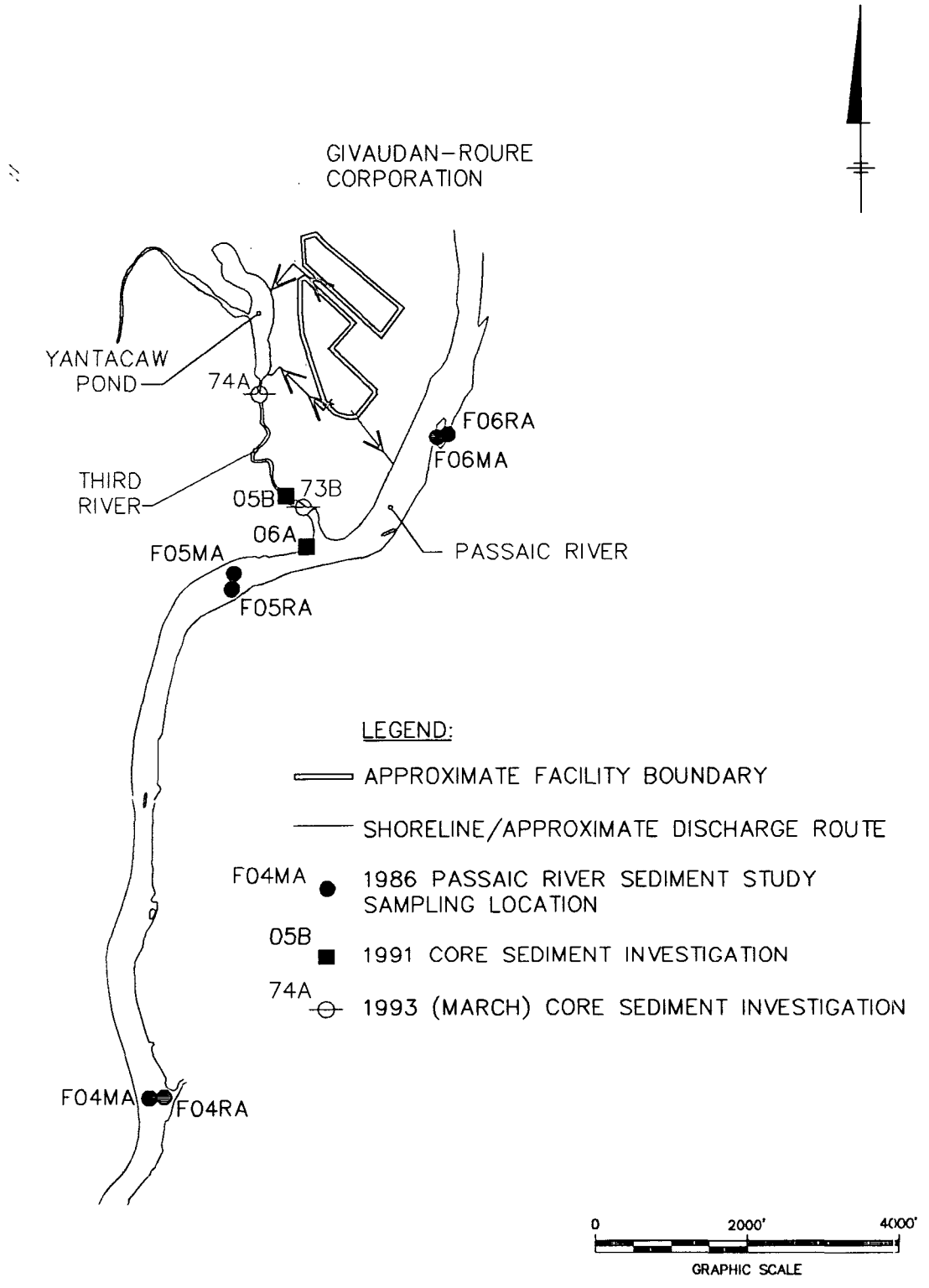
excavated (to 1 ppb) and placed in an on-site containment cell. That containment cell was completed in December 1996.

REFERENCES: Please refer to Appendix J for the following:

Tab #	Date	Description
J1	1992	Givaudan Site Summary, taken from "Site Status Report" booklet, By NJDEP.
J2	4/2/75	Waste Effluent Survey of Givaudan Corporation for Passaic Valley Sewerage Commissioners, includes Laboratory Analysis, sample for Givaudan Corp., from International Hydronics Corporation.
J3	7/26/83	Letter from William Hyatt, Jr., Pitney Hardin Kipp & Szuch, to Michael Catania, NJDEP, enclosing Givaudan's information response re: trichlorophenol and hexachlorophene historical production.
J4	1/91	NJDEP Approved, TCDD Investigation Report and Limited Investigation Report.
J5	12/13/91	Letter from David Sweeny of NJDEP, to Len Levy of Givaudan Corp.
J6	11/3/95	Letter from William Friedman of Brach, Eichler, Rosenberg, Silver, Bernstein, Hammer & Gladstone, to Robert Tavares, Chief Legal Counsel, Givaudan-Roure Corp.
J7	11/9/95	Letter from Leonard Levy, Director, Site Remediation Givaudan Corp., to Joseph Karpa, Division of Responsible Party Site Remediation NJDEP.
J8	5/30/96	Letter from Leonard Levy of Givaudan Corp., to Maria Franco-Spera, Division of Responsible Party Site Remediation, NJDEP.
J9	9/20/83	Letter from CFM Inc., to Givaudan Corp., enclosing Chemical Sewer Investigation Report for Givaudan Corp., 9/20/83. (second page of letter missing, report attached).
J10	Various	Annual reports from PVSC re: sewer line breaks/incidents and related correspondence.

J11	1/29/92	Givaudan site map for delineated TCDD Areas and sample locations produced by ERM, Inc.
J12	6/30/70	Plant sewer map-Givaudan Corp.
J13	7/15/98	Phase III Remedial Investigation for Ground Water, Volume I, Givaudan-Roure Corp.
J14	6/23/99	Letter from Richard Wroblewski of ERM, to Maria Franco-Spera of NJDEP.
J15	6/17/83	Executive Order #48B Re: Dioxin Emergency at Givaudan Clifton Site.
J16	3/5/87	Administrative Consent Order- Ground Water.
J17	3/5/87	Administrative Consent Order TCDD.
J18	2/16/88	Amended Administrative Consent Order TCDD.
J19	Undated	City of Clifton Storm and Sanitary Sewer maps.
J20	7/14/99	Letter from Eugene Thomas, Givaudan, to Maria Franco-Spera, NJDEP, re: deed notice and restrictions.
J21	5/16/01	Letter from David Johnson, Givaudan, to Robert Schinn, NJDEP, re: sale of Givaudan plant site in Clifton.
J22	6/4/02	Letter from John Hogue, ERM, to Maria Franco-Spera, NJDEP, re: biennial certification/sale of Givaudan's Clifton property.
J23	4/00	ERM Remedial Action Work Plan for Soils, (excerpts).
J24	3/1/00	ERM Draft Remedial Action Report, (excerpts).
J25	8/15/78	Killam Heavy Metal Source Determination Study.
J26	April 1985	Givaudan's Plans for Discharge Prevention, Containment and Countermeasure and Discharge Cleanup and Removal.
J27	1983	Givaudan's Stormwater Drainage Patterns – details re: connection to County Street sewer.

J28	4/25/91	Letter from L.A. Levy, Givaudan, to Nicholas Eisenhauser, re: excess TCDD levels.
J29	6/22/83	NJDEP Internal Memorandum, D. Schrier to E. Liu re: review of Givaudan file concerning dioxin formation.
J30	2/00	ERM Sewer Decommissioning Report, (excerpts).
J31	9/4/96	Letter from Leonard Levy of Givaudan Corp., to Maria Franco-Spera, NJDEP.
J32	6/30/70	Annotated figure highlighted with on-site chemical, storm and sanitary sewer systems.



SITE LOCATION MAP

GIVAUDAN-ROURE CORPORATION FACILITY

X: 09994X00.DWG
L: ON=*, OFF=*REF*
P: STD-PAGESET/AP
8/27/02 SYR-54-GWS LAF LAF
09994023/09994B21.DWG

Reference Sources

Ref. 1

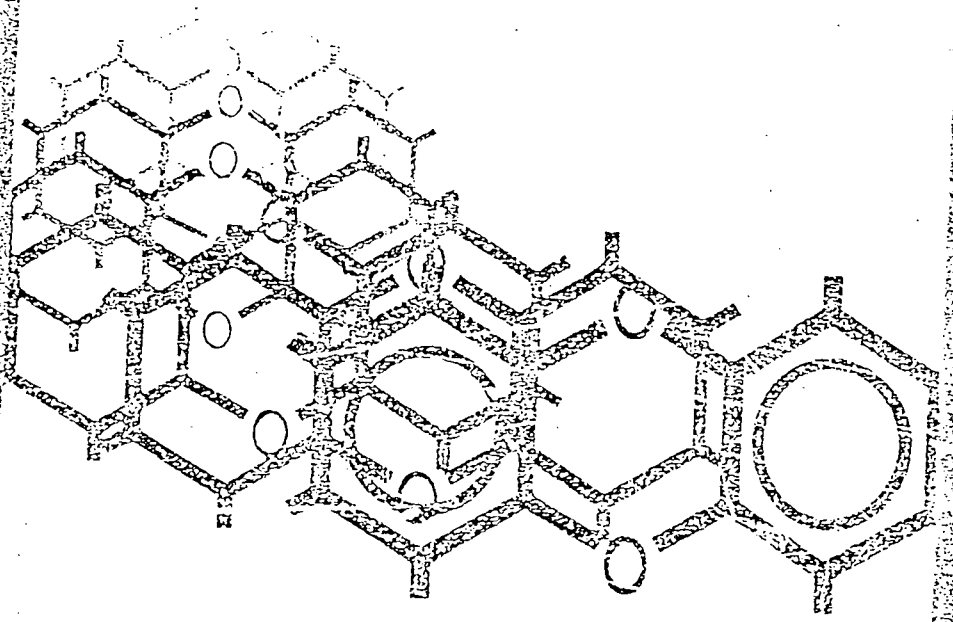
United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research & Development

PB82-136847

EPA Dioxins



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DIOXINS

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Forrest E. Dryden

Contract Nos. 68-03-2577
68-03-2659
68-03-2579

Project Officer
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Industrial Pollution Control Division
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INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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Other contributors were from the Brehan Laboratory and Chemistry Department of Wright State University and Walk, Haydel and Associates, Inc.

16. ABSTRACT

Concern about the potential contamination of the environment by dibenzo-p-dioxins through the use of certain chemicals and disposal of associated wastes prompted this study.

This report reviews the extensive amount of dioxin literature that has become available in recent years. Although most published reports deal exclusively with the highly toxic dioxin 2,3,7,8-TCDD, some include information on other dioxins. These latter reports were sought out so that a document covering dioxins as a class of chemical compounds could be prepared.

A brief description of what is known about the chemistry of dioxins is presented first. Chemical reaction mechanisms by which dioxins may be formed are reviewed, particularly those likely to occur within commercially significant processes. Various routes of formation are identified in addition to the classical route of the hydrolysis of trichlorophenol. Basic organic chemicals and pesticides with a reasonable potential for dioxin by-product contamination are surveyed as to current and past producers and production locations. Classifications are presented both for general organic chemicals and for pesticides that indicate likelihood of dioxin formation. Conditions are noted that are most likely to promote dioxin formation in various processes.

An analytical approach for use in quantifying part-per-trillion levels of TCDD's in various chemical wastes is included in this report. The Brehan Laboratory of Wright State University examined waste samples provided by the Environmental Protection Agency from plants manufacturing trichlorophenol, pentachlorophenol, and hexachlorophene, and from plants processing wood preservatives. The extraction procedure developed for isolating TCDD's from the various types of sample matrices is fully described. The analysis using highly specific and sensitive coupled gas chromatography-mass spectrometry (GC-MS) methods is also described in detail. TCDD's were detected and quantitatively determined in several of the samples at levels in the ppt to ppm range.

Incidents of human exposure to dioxins are reviewed and summarized. A review of the known health effects of 2,3,7,8-TCDD and other dioxins is presented. Many toxicological studies of the effects produced by chronic exposures to these toxicants and the possible mechanisms of action are described.

Reports on possible routes of degradation are characterized. Finally, current methods of disposal of dioxin-contaminated materials are described, and possible advanced techniques for ultimate disposal are outlined.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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SECTION 3
SOURCES OF DIOXINS

This section discusses in detail the possible sources of dioxins. The first subsection deals with the basic organic chemicals with the greatest potential for byproduct formation of dioxins. Subsequent subsections examine chlorophenols and their derivatives, hexachlorobenzene, dioxins in particulate air emissions from combustion, dioxins in plastic, and dioxins produced for research.

ORGANIC CHEMICALS

Because of the very large number of organic compounds and their varying proclivities to form dioxins, the compounds were screened initially on the basis of molecular structure, process sequence, and commercial significance.

As a means of focusing attention on those organic chemicals most likely to be associated with the formation of dioxins, they were placed in the following classifications:

Class I—Polyhalogenated phenols, primarily with a halogen ortho to the hydroxyl group, with a high probability of dioxin formation. Products with such compounds appearing as intermediates are also considered. Manufacture of these materials normally involves reaction conditions of elevated temperature plus either alkalinity or free halogen presence, either of which is conducive to formation of halogenated dioxins.

Class II—Ortho-halophenols and ortho-halophenyl ethers where the substituted groups are a mixture of halogens and nonhalogens. Processing conditions are similar to those defined for Class I and produce mixed substituted dioxins. The distinction between Classes I and II is arbitrary and does not indicate necessarily a difference in likelihood of dioxin formation.

Class III—Other chemicals having the possibility, but less likelihood, of dioxin formation. These include 1) ortho substituted aromatic compounds requiring an unusual combination of reaction steps to produce dioxins, 2) aromatic compounds that might form dioxins because of their production under semicombustion conditions, and 3) products that might contain dioxins by way of contamination of their starting materials.

Since only commercially significant products are of interest in this study, the listing is limited to those produced in quantities in excess of 1000 pounds per year and/or whose sales reach $1000 per year, as required for listing in the Stanford Research Institute Directory of Chemical Producers. The product lists are based on commercial production during the past 10 years.

Table 7 lists and classifies commercial organic chemicals selected as having a relationship to dioxin formation or presence. Structures are shown for Classes I and II, the chemicals of primary importance. Class III compounds are listed by name only. In addition, Tables A1-5 in Appendix A give further information on the producers and production sites of organic chemicals.

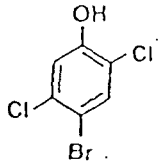
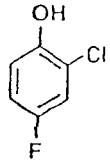
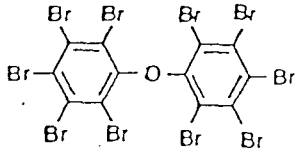
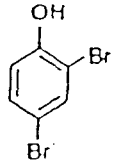
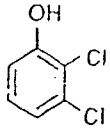
Most of the organic chemicals considered are used as manufacturing intermediates or at least are subjected to subsequent formulation or fabrication.

Thus further processing may introduce additional possibilities for dioxin formation, contamination, and exposure not contemplated within the scope of this study.

Toxicity of the many substituted dibenzo-*p*-dioxins varies widely. None are excluded from consideration here since disproportionation and other composition shifts may bring about changes from lower toxicity forms to higher (Buser 1976).

The intended reaction mechanisms for each Class I organic chemical are shown in Figures 2 through 12. The sequence is shown from left to right across the top of each figure, and the possible dioxin side reaction mechanism diverges to typical dioxin byproducts at the bottom of the figure. The specific dioxin products shown are those for which reasonably straightforward mechanisms can be postulated. In many cases more complex and secondary mechanisms may produce dioxins in addition to those shown.

TABLE 7. ORGANIC CHEMICALS RELATED TO DIOXIN FORMATION

Class I	
4-BROMO-2,5-DICHLOROPHENOL	
2-CHLORO-4-FLUOROPHENOL	
DECABROMOPHENOXYBENZENE	
2,4-DIBROMOPHENOL	
2,3-DICHLOROPHENOL	

(continued)

TABLE 7 (continued)

Class I (continued)

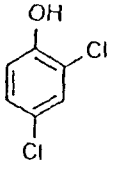
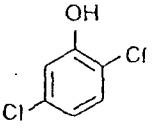
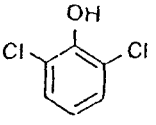
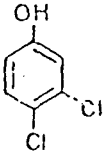
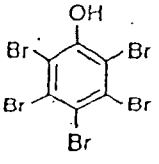
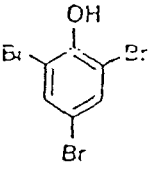
2,4-DICHLOROPHENOL	
2,5-DICHLOROPHENOL	
2,6-DICHLOROPHENOL	
3,4-DICHLOROPHENOL	
PENTABROMOPHENOL	
2,4,6-TRIBROMOPHENOL	

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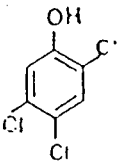
TABLE 7 (continued)

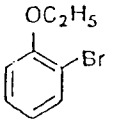
Class I (continued)

2,4,5-TRICHLOROPHENOL

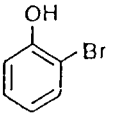


Class II

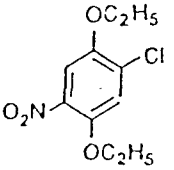
BROMOPHENETOLE



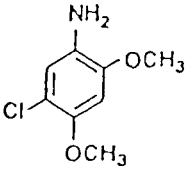
O-BROMOPHENOL



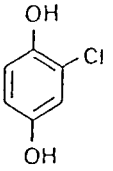
2-CHLORO-1,4-DIETHOXY-5-NITROBENZENE



5-CHLORO-2,4-DIMETHOXY-ANILINE



CHLOROHYDROQUINONE

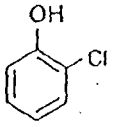


(continued)

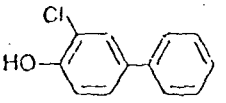
TABLE 7 (continued)

Class II (continued)

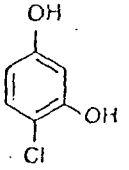
O-CHLOROPHENOL



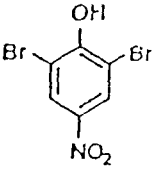
2-CHLORO-4-PHENYLPHENOL



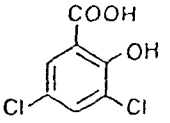
4-CHLORORESORCINOL



2,6-DIBROMO-4-NITROPHENOL



3,5-DICHLOROSALICYLIC ACID



2,6-DIIODO-4-NITROPHENOL

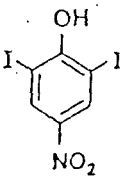


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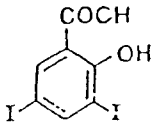
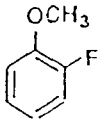
TABLE 7 (continued)

Class II (continued)

3 ,5-DIIODOSALICYLIC ACID



O-FLUOROANISOLE



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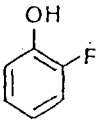
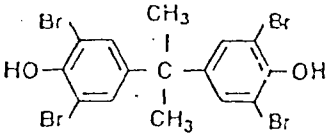
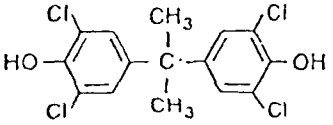


TETRABROMOBISPHENOL-A



TETRACHLOROBISPHENOL-A



Class III

3-Amino-5-chloro-2-hydroxybenzenesulfonic acid
2-Amino-4-chloro-6-nitrophenol
o-Anisidine
Benzaldehyde
Bromobenzene
o-Bromofluorobenzene

(continued)

TABLE 7 (continued)

Class III (continued)
o-Chlorofluorobenzene
3-Chloro-4-fluoro-nitrobenzene
3-Chloro-4-fluorophenol
4-Chloro-2-nitrophenol
Chloropentafluorobenzene
2,4-Dibromofluorobenzene
3,4-Dichloroaniline
o-Dichlorobenzene
3,4-Dichlorobenzaldehyde
3,4-Dichlorobenzotrichloride
3,4-Dichlorobenzotrifluoride
1,2-Dichloro-4-nitrobenzene
3,4-Dichlorophenylisocyanate
3,4-Difluoroaniline
o-Difluorobenzene
1,2-Dihydroxybenzene-3,5-disulfonic acid, disodium salt
2,5-Dihydroxybenzenesulfonic acid
2,5-Dihydroxybenzenesulfonic acid, potassium salt
2,4-Dinitrophenol
2,4-Dinitrophenoxyethanol
3,5-Dinitrosalicylic acid
Fumaric acid
Hexabromobenzene
Hexachlorobenzene
Hexafluorobenzene
Maleic acid
Maleic anhydride
o-Nitroanisole
2-Nitro-*p*-cresol
o-Nitrophenol
Pentabromochlorocyclohexane
Pentabromoethylebenzene
Pentabromotoluene
Pentachloroaniline
Pentafluoroaniline
o-Phenetidine.
Phenol (from chlorobenzene)
1-Phenol-2-sulfonic acid, formaldehyde condensate
Phenyl ether
Phthalic anhydride
Picric acid
Sodium picrate
Tetrabromophthalic anhydride
1,2,4,5-Tetrachlorobenzene
Tetrachlorophthalic anhydride
Tetrafluoro-*m*-phenylenediamine
Tribromobenzene
1,2,4-Trichlorobenzene
2,4,6-Trinitroresorcinol

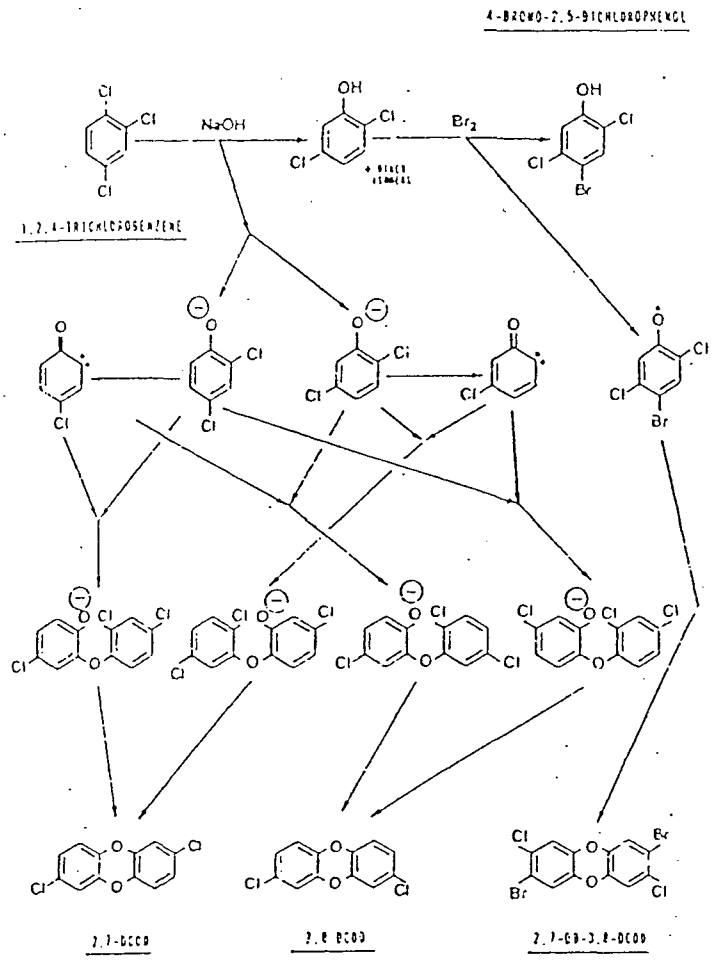


Figure 2. Proposed reaction mechanism for dioxin formation in the production of 4-bromo-2,5-dichlorophenol.

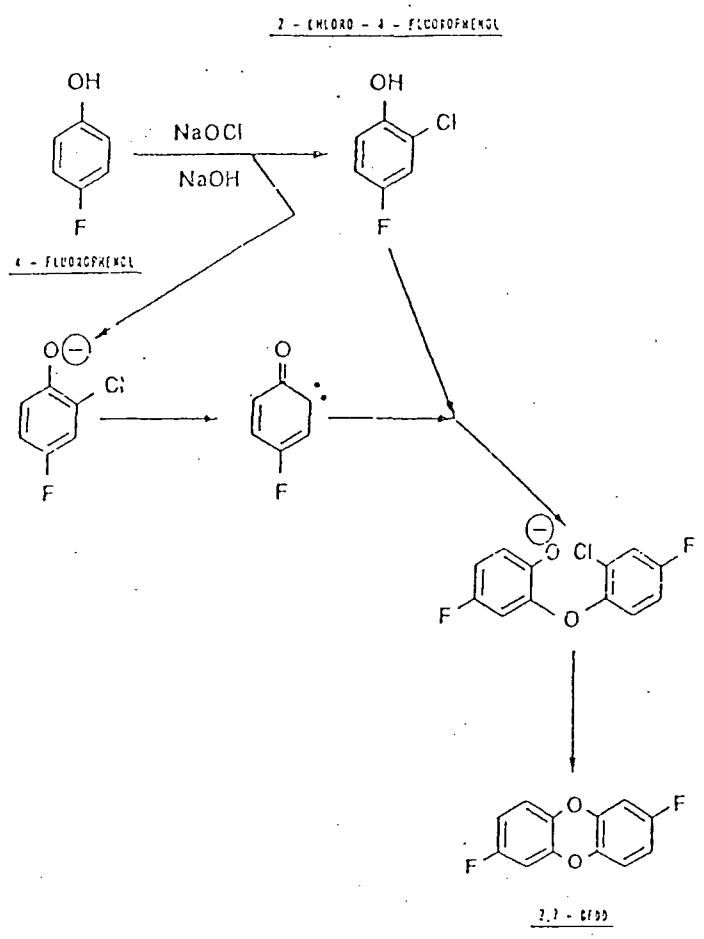


Figure 3. Proposed reaction mechanism for dioxin formation in the production of 2-chloro-4-fluorophenol.

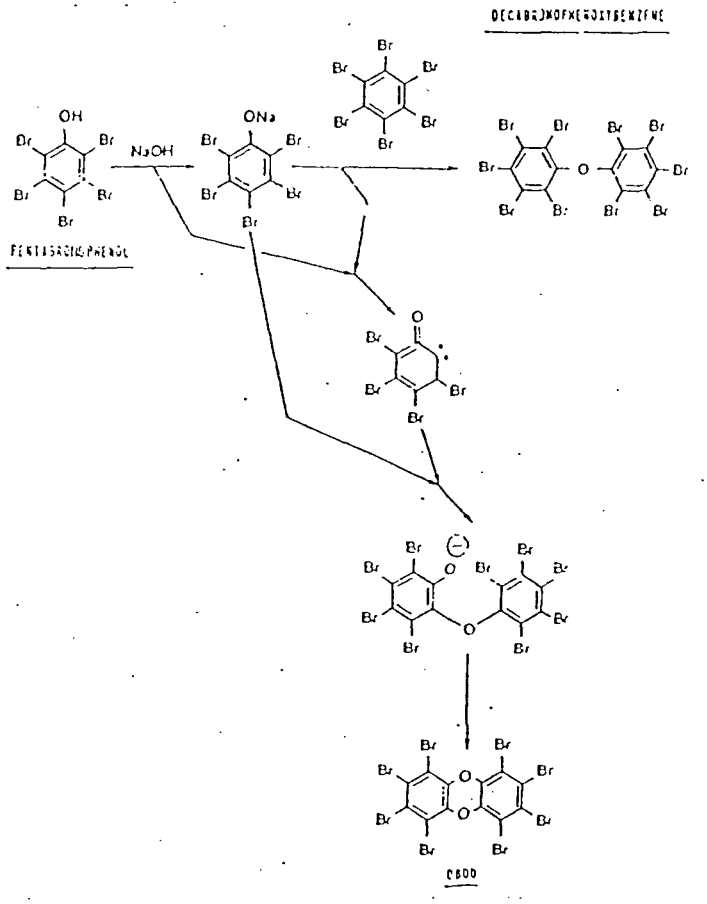


Figure 4. Proposed reaction mechanism for dioxin formation in the production of decabromophenoxybenzene.

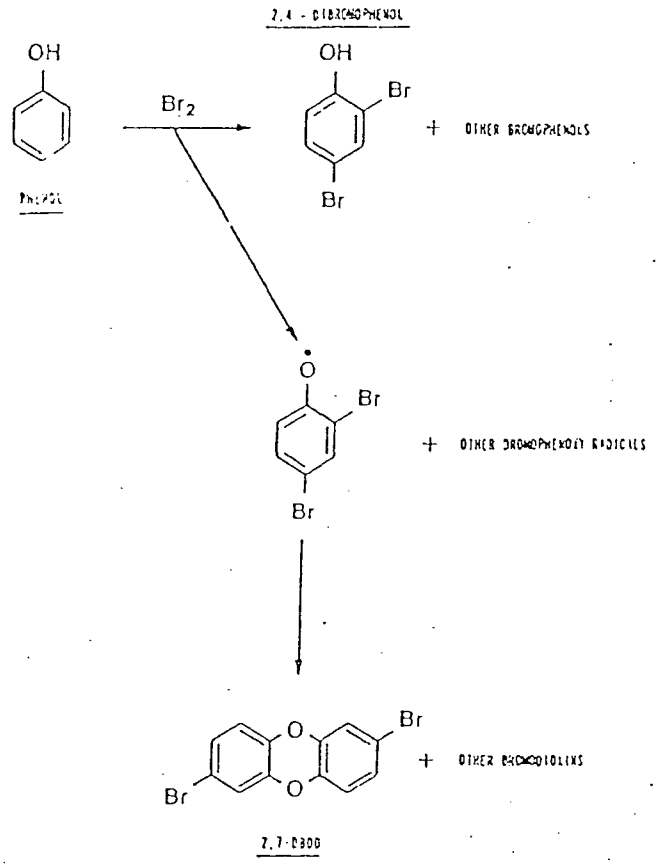


Figure 5. Proposed reaction mechanism for dioxin formation in the production of 2,4-dibromophenol.

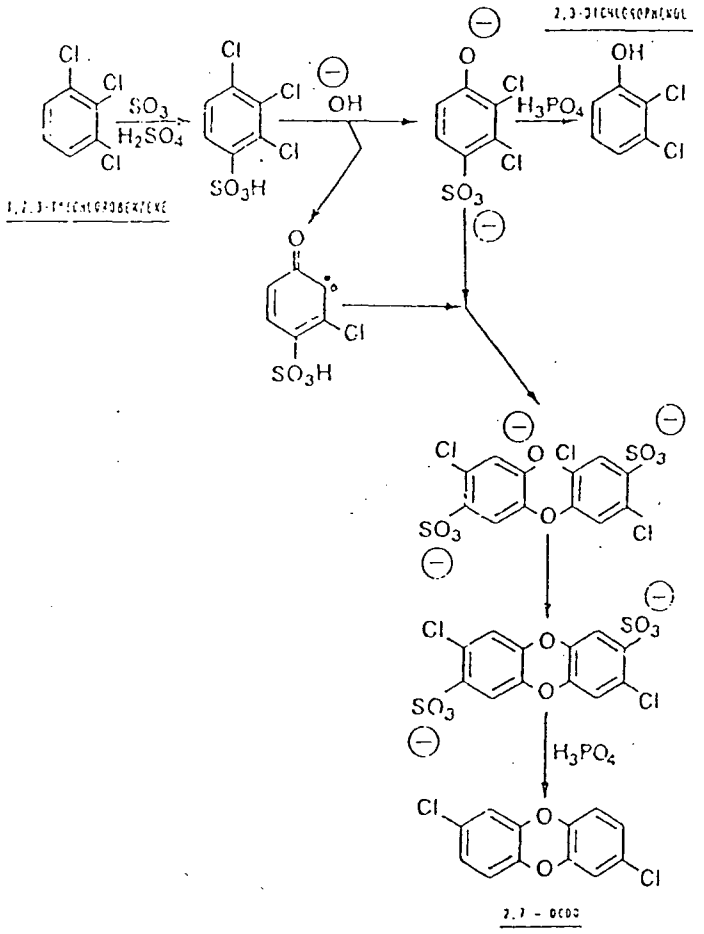


Figure 6. Proposed reaction mechanism for dioxin formation in the production of 2,3-dichlorophenol.

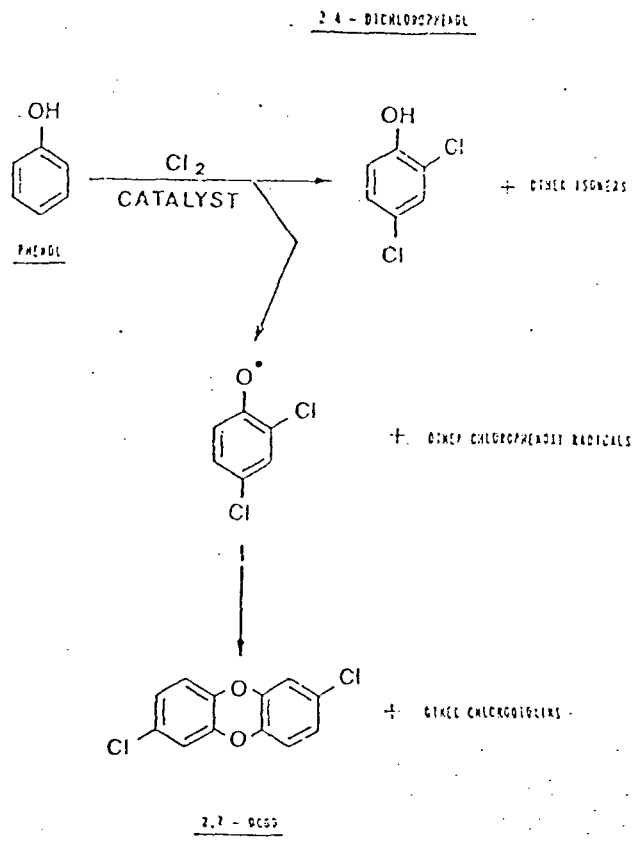


Figure 7. Proposed reaction mechanism for dioxin formation in the production of 2,4-dichlorophenol.

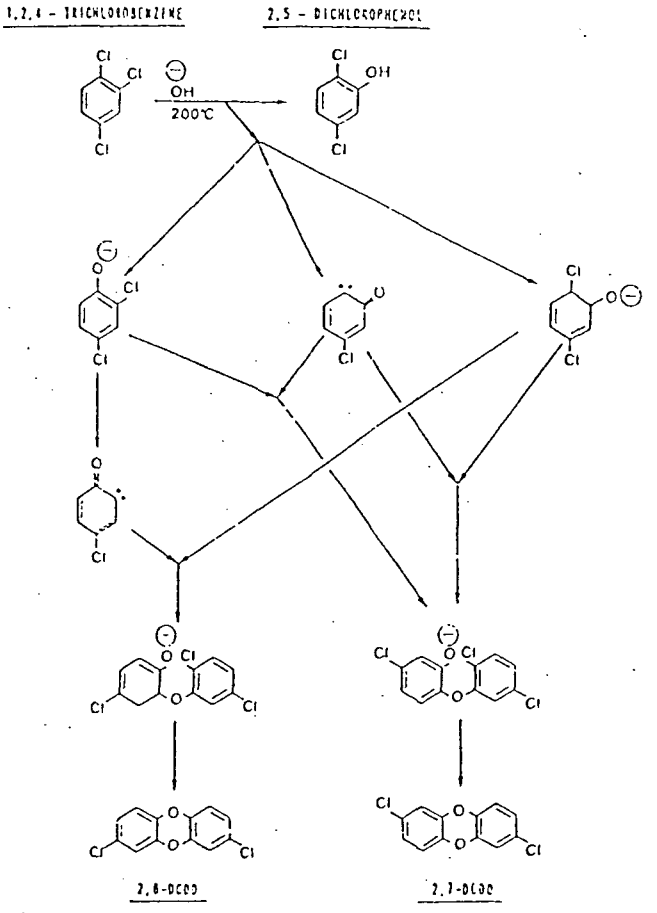


Figure 8. Proposed reaction mechanism for dioxin formation in the production of 2,5-dichlorophenol.

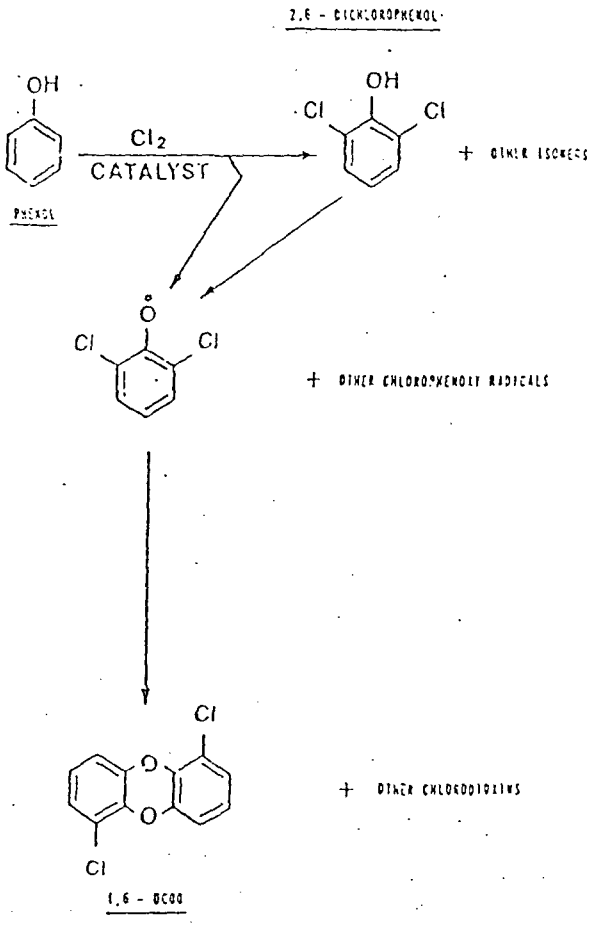


Figure 9. Proposed reaction mechanism for dioxin formation in the production of 2,6-dichlorophenol.

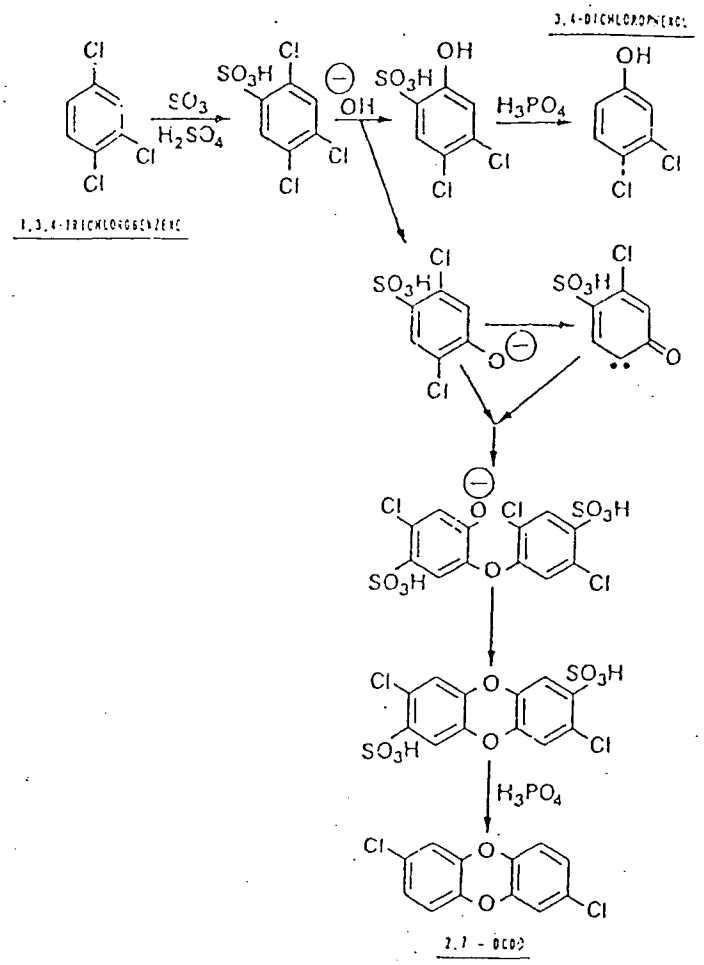


Figure 10. Proposed reaction mechanism for dioxin formation in the production of 3,4-dichlorophenol.

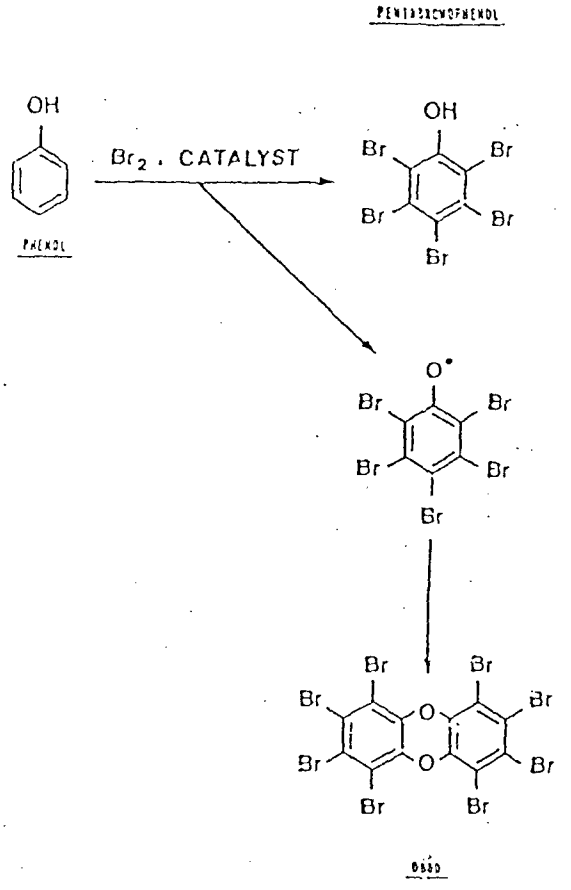


Figure 11. Proposed reaction mechanism for dioxin formation in the production of pentabromophenol.

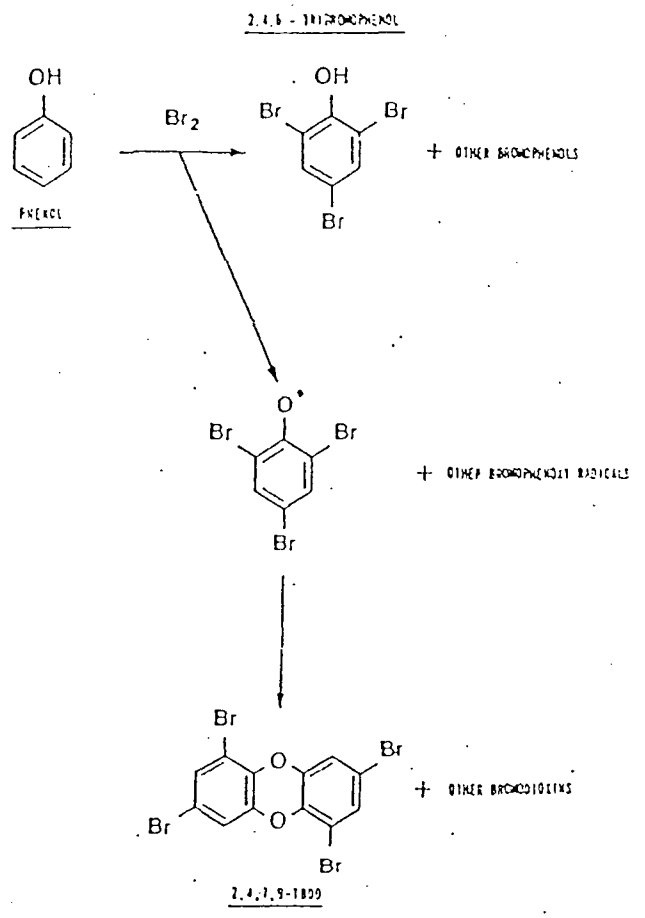


Figure 12. Proposed reaction mechanism for dioxin formation in the production of 2,4,6-tribromophenol.

PESTICIDE CHEMICALS

Pesticides are the most significant group of organic chemicals in relation to dioxin occurrence. This statement is based on the structure and reaction mechanism analogy, reaction conditions, detected presence of dioxins in a number of commercial pesticide products, and a history of environmental contamination problems, particularly with trichlorophenol and 2,4,5-T.

Chlorinated dibenzo-*p*-dioxins are known to be present in at least trace amounts in a number of pesticide chemicals. These include 2,4,5-T, silvex, 2,4-D, erbon, sesone, DMPA, ronnel, tetradifon, and the various chlorophenols (Fishbein 1973). In addition, the chemical structures, reactions, and process conditions for a number of others indicate dioxin content potential.

This study deals with production of the basic pesticide chemicals. Thus it does not address problems of dioxin formation possibly resulting from formulation, storage, distribution, and utilization of the pesticides. If exposure to alkaline formation media or elevated temperatures is encountered in any of the diverse procedures for handling and use of these pesticides, dioxin formation could be a significant problem.

Selection and Classification

The pesticide chemicals were selected for evaluation in this study on the basis of molecular structure, from those listed as commercial pesticides in the Farm Chemicals Handbook. The primary criterion was an ortho-halophenolic structure, or the derivative esters and salts thereof. Also considered were ortho dihalo aromatic structures, which conceivably could convert to phenols upon exposure to alkaline conditions.

A second criterion was a minimum commercial production level of 1000 pounds or $1000 value per year. These correspond to the minimum levels required for inclusion in the Stanford Research Institute Directory of Chemical Producers, which was a primary reference. The lists are based on production during the past 10 years.

The pesticide chemicals considered in this study are listed in Table 8. They are grouped into classes representing likelihood of dioxin formation, as follows:

Class I -- Highly likely to be associated with the presence of halogenated dibenzo-*p*-dioxins because of the presence of an ortho-halogenated phenol in the reaction sequence, with subjection to elevated temperature ($\geq$145° C+) plus either alkalinity or the presence of free halogen.

Class II - Reasonable but lesser probability of such dioxin association because of the presence of phenolic or aromatic structures related to dioxins; although not directly involving dioxin precursive conditions, such chemicals might form dioxins under irregular operating conditions.

TABLE 8. LIST OF PESTICIDE CHEMICALS

General name	Chemical name
Class I	
Bifenox	Methyl-5-(2,4-dichloroephenoxy)-2-nitrobenzoate
Chloranil	2,3,5,6-Tetrachloro-2,5-cyclorhexadiene-1,4-dione
(continued)	

TABLE 8. (continued)

General name	Chemical name
2,4-D and esters and salts	(2,4-Dichlorophenoxy) acetic acid and esters and salts
2,4-DB and salts	2,4-Dichlorophenoxybutyric acid and salts
Dicamba	3,6-Dichloro-2-methoxybenzoic acid
Dicamba, dimethylamine salt	3,6-Dichloro-2-methoxybenzoic acid, dimethylamine salt
Dicapthon	Phosphorothioic acid *o*-(2-chloro-4-nitrophenyl) *o,o*-dimethyl ester
Dichlofenthion	Phosphorothioic acid *o*-2,4-dichlorophenyl *o,o*-diakyl ester
Disul sodium (sesone)	2,4-Dichlorophenoxyethyl sulfate, sodium salt
2,4-DP	2-(2,4-Dichlorophenoxy) propionic acid
Erbon	2,2-Dichloropropanoic acid 2-(2,4,5-trichlorophenoxy) ethyl ester
Hexachlorophene	2,2′-Methylene bis (3,4,6-trichlorophenol)
Isobac 20	2,2′-Methylene bis (3,4,6-trichlorophenol), monosodium salt
Nitrofen	2,4-Dichlorophenyl-*p*-nitrophenyl ether
Pentachlorophenol (PCP) and salts	Pentachlorophenol and salts
Ronnel	Phosphorothioic acid, *o,o*-dimethyl O-(2,4,5-trichlorophenyl) ester
Silvex and esters and salts	2-(2,4,5-Trichlorophenoxy) propionic acid and esters and salts
2,4,5-T and esters and salts	(2,4,5-Trichlorophenoxy) acetic acid
—	2,3,4,6-Tetrachlorophenol
—	2,4,5-Trichlorophenol
Class II	
—	*o*-Benzyl-*p*-chlorophenol
Bromoxynil and esters	3,5-Dibromo-4-hydroxybenzonitrile

(continued)

TABLE 8. (continued)

General name	Chemical name
Carbonphenothion	Phosphorodithioic acid *s*-[[(4-chlorophenyl)thio]methyl] *o,o*-diethyl ester
DCPA	2,3,5,6-Tetrachloro-1,4-benzenedicarboxylic acid dimethyl ester
Dichlone	2,3-Dichloro-1,4-haphthalenedione
Dinitrobutylphenol, ammonium salt	2,4-Dinitro-6-*sec*-butyl phenol, ammonium salt
Loxynil	3,5-Diiodo-4-hydroxybenzonitrile
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer
MCPA	(4-Chloro-*o*-toloxy) acetic acid
MCPB	4-(2-Methyl-4-chlorophenoxy) butyric acid
Mecoprop	2-(4-Chloro-2-methylphenoxy) propionic acid
Parathion	Phosphorothioic acid *o,o*-diethyl *o*-(4-nitrophenyl) ester
PCNP	Pentachloronitrobenzene
—	Pipecolinopropyl-3,4-dichlorobenzoate
Piperalin	3-(2-Methylpiperidino)propyl-3,4-dichlorobenzoate
Propanil	3,4-Dichloropropionanilide
Tetradifon	1,2,4-Trichloro-5-[(4-chlorophenyl)-sulfonyl] benzene
—	2,3,6-Trichlorobenzoic acid
—	2,3,6-Trichlorophenylacetic acid and sodium salt
—	Triiodobenzoic acid

Chemical Reactions

Higher chlorinated dioxins have been detected in samples of a number of pesticides produced from 1950 to 1970. Data from these analyses were summarized by Fishbein (1973), as shown in Table 9.

TABLE 9. HIGHER CHLORINATED DIOXINS FOUND IN COMMERCIAL PESTICIDES[a]

Pesticide	Chlorodibenzo-p-dioxin detected[b]				Sample	
	Tetra-	Hexa-	Hepta-	Octa-	Number contaminated	Number tested
Phenoxyalkanoates						
2,4,5-T	++	++	-	-	23	42
Silvex	+	-	-	-	1	7
2,4-D	-	+	-	-	1	24
Erbon	-	-	-	++	1	1
Sesone	-	+	-	-	1	1
Chlorophenols						
Tri-	-	+	+	+	4	6
Tetra-	-	++	++	++	3	3
Penta- (PCP)	-	++	++	++	10	11
Others[c]	-	++	++	+	5	22

a—Fishbein 1973
b—Concentration range ++ = >10 ppm
+ = 0.5 to 10 ppm
- = <0.5 ppm
c—DMPA, ronnel, and tetradifon were found to contain chlorodioxin contamination.

Many of the dioxins present differ from those expected on the basis of the straightforward mechanisms hypothesized. Possible reasons for this may be that other mechanisms are at work or that substantial disproportionation is occurring among the dioxins initially formed, as has been suggested by Dow Chemical Company (Rawls 1979) and others (Buser 1976).

Reaction mechanisms for the Class I pesticide products are shown in the following figures. The intended product reaction sequence is from left to right across the top of each figure, and the possible dioxin side reaction mechanism diverges to typical dioxin byproducts at the bottom of the figure. The specific dioxin products shown are those for which reasonably straightforward mechanisms can be postulated. In many cases, more complex and secondary mechanisms may produce dioxins in addition to those shown, as evidenced by their analytical detection in a number of products (Fishbein 1973).

The initial reaction steps in producing many of the Class I pesticides are very similar and thus the pesticides are grouped by common mechanism. Similarity is noted in 2,4,5-T, silvex, ronnel, 2,4-D, erbon, sesone, dichlofenthion, dicapthon, bifenox, and dicamba. The final substitution pattern differs in each case, as does the precise halophenol or chlorobenzene starting structure.

The first step in production of 2,4,5-T, silvex, ronnel, and erbon is identical (Figures 13 through 16). Treatment of 1,2,4,5-tetrachlorobenzene with caustic yields 2,4,5-trichlorophenol. The reaction conditions are sufficiently drastic, including alkalinity and elevated temperature, to cause formation of the α-ketocarbene, which reacts with the chlorophenylate to give the predioxin, which then reacts to yield 2,3,7,8-TCDD. Continued alkaline processing, which occurs with each of these product items, also contributes to the same transient intermediates and consequently to formation of 2,3,7,8-TCDD.

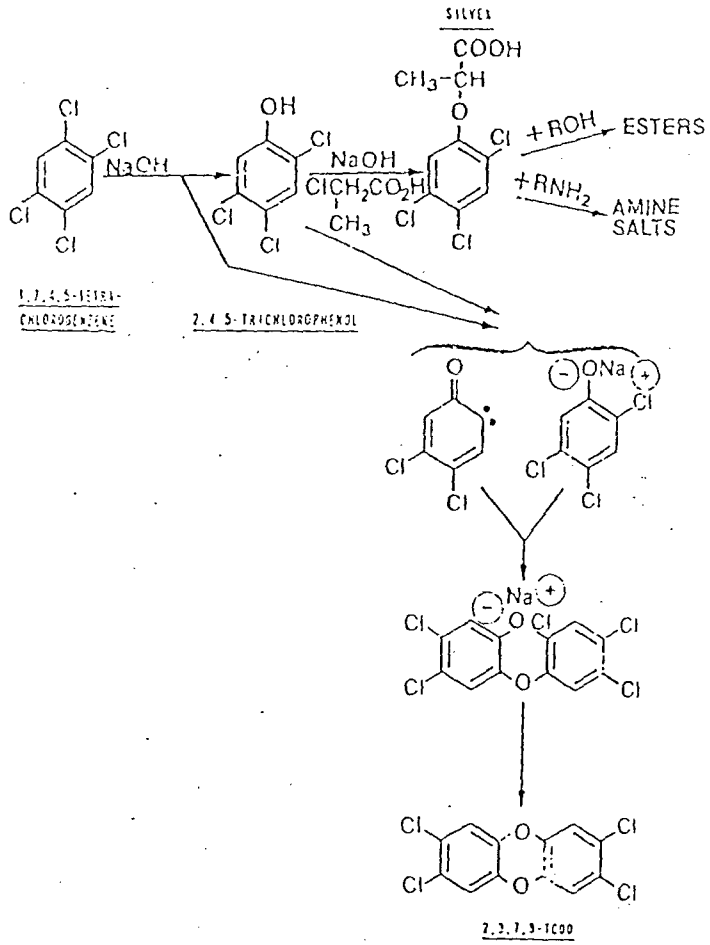


Figure 14. Silvex and esters and salts.

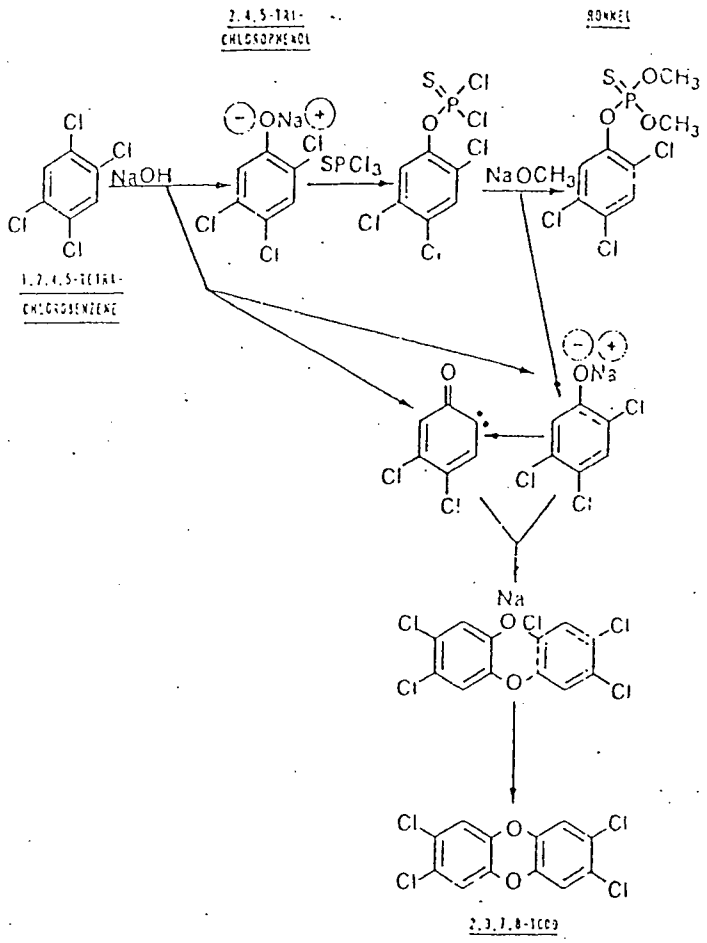


Figure 15. Ronnel.

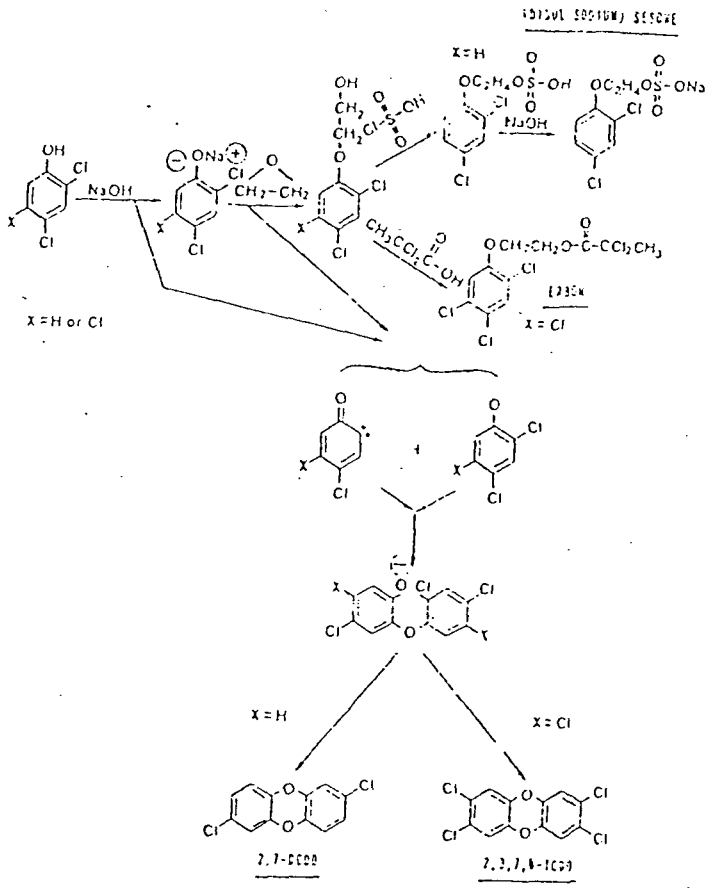


Figure 16. Erbon and sesone

The normal reaction sequences for 2,4-D, 2,4-DB, 2,4-DP, disul sodium (sesone), dichlofenthion, bitenox, and nitrofen (sequences shown in Figures 16 through 22) are analogous in their early steps to those of 2,4,5-T and others in the group just described, but occur via 2,4-dichlorophenol rather than 2,4,5-trichlorophenol. The dioxin formation sequence is likewise analogous but typically would produce 2,7-DCDD.

Note that the reaction mechanism for disul sodium is presented in the same figure (Figure 16) with that for erbon. This placement is not meant to imply that they are co-products, but rather is intended to demonstrate the analogous reaction patterns of typical pesticides differing as to halogenation and substitutions. Similar analogies can be drawn among nearly all of the pesticide chemicals studied.

Another point, important to dioxin formation, is demonstrated in Figure 17, showing the reaction for 2,4-D. The reaction sequence conventionally cited is chlorination of phenol to 2,4-dichlorophenol, followed by a reaction with chloroacetic acid in the presence of caustic to produce 2,4-D. This last step with the dichlorophenol under alkaline conditions can result in dioxin formation. An alternative process sequence cited in the patent literature (Manske 1949) reverses the order of chlorination, as shown in the upper tier reaction of Figure 16. This sequence would be expected to reduce the likelihood of dioxin formation. A commercially feasible yield in excess of 80 percent is noted, but the extent of commercial utilization is not known. This reaction sequence could possibly be adapted to other dihalogenated phenoxyalkanoates, with an expected reduction in dioxin formation.

Dicamba (Figure 23) with its dimethylamine salt presents one of the more complex dioxin derivation patterns because of the continued alkaline conditions under which various substitutions are made. First, preparation of 2,5-dichlorophenol and its subsequent further exposure to caustic results in transient intermediates and predioxins that form 2,7-DCDD and 2,8-DCDD. In addition, similar alkaline processing of the carboxyl and methyl substituted forms can result in variously substituted dioxins, only two of which, for simplicity, are shown in Figure 23.

Pentachlorophenol (PCP), a commercially high-volume chemical, can be manufactured by two basic methods. One involves direct chlorination of phenol (Figure 24) in the presence of an $AlCl_3$ catalyst. The presence of normal excess chlorine is conducive to formation of a free-radical intermediate, then of the predioxin, and ultimately of OCDD. The alternative process based on caustic treatment of hexachlorobenzene (Figure 25) produces chlorinated transient intermediates analogous to the 2,4,5-T series but fully chlorine substituted. These in turn form the predioxin and finally OCDD.

The comp[illegible]ee-radical mechanism by which chloranil is made (Figure 26) results in the [illegible] intermediates similar to those occurring as byproduct derivatives in PC[illegible] Therefore, OCDD should be expected as a dioxin contaminant.

Hexachlorophene [illegible] its sodium salt, Isobac 20 (Figure 27), are produced from 2,4,5-trichlorophenol whose preliminary production from 1,2,4,5-tetrachlorobenzene is carried out by reaction with caustic. This first step potentially forms dioxin precursors similar to the equivalent step in the manufacture of 2,4,5-T. Consequently, 2,3,7,8-TCDD is the anticipated byproduct dioxin.

The production of 2,3,4,6-tetrachlorophenol (Figure 28) by chlorination of phenol would be expected to yield trace byproducts of various isomeric hexachlorodibenzo-*p*-dioxins via a free-radical mechanism.

Again, because of the analytical evidence of many dioxins other than those hypothesized in these mechanisms, no specific dioxin presence should be presumed or excluded.

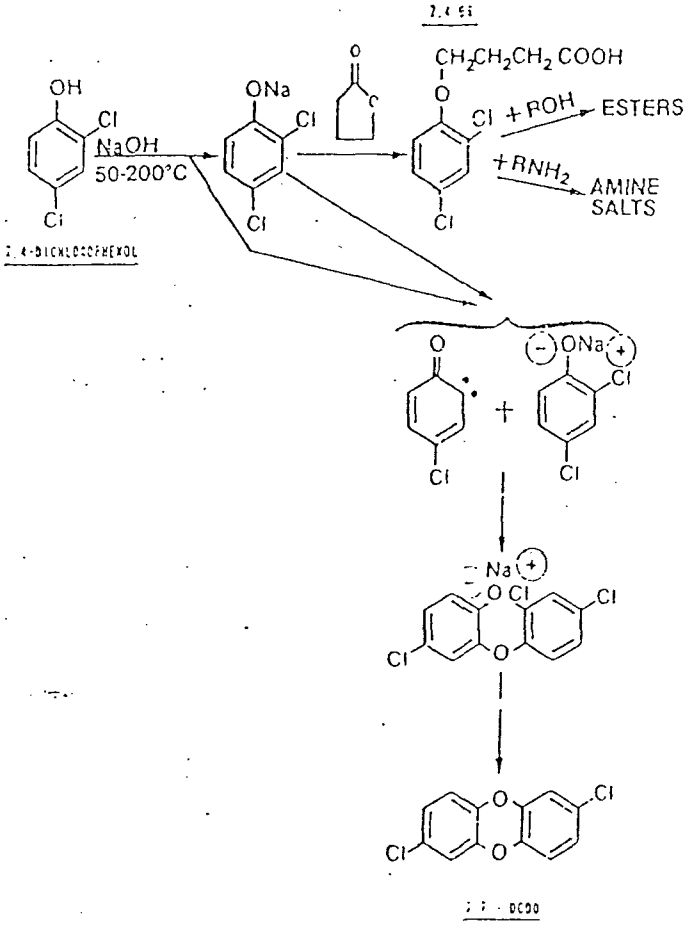


Figure 18. 2,4-DB.

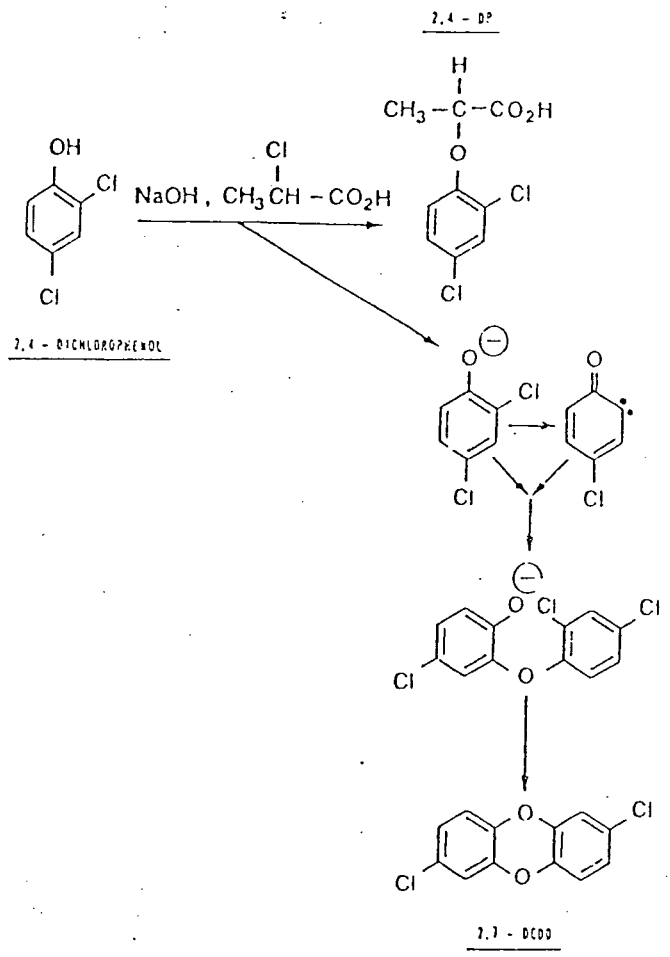


Figure 19. 2,4-DP

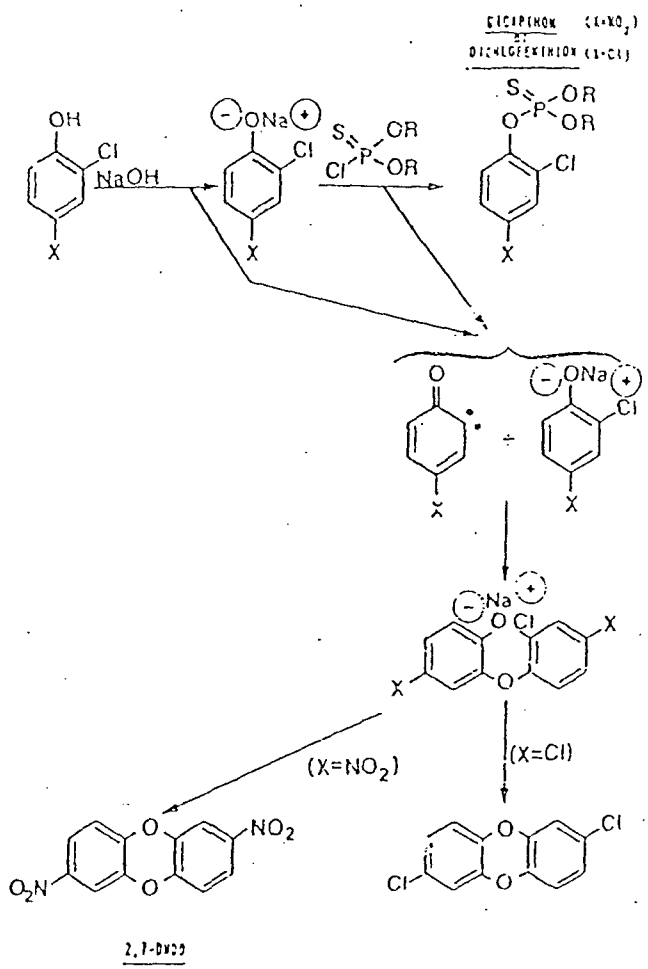


Figure 20. Dicapthon and dichlofenthion.

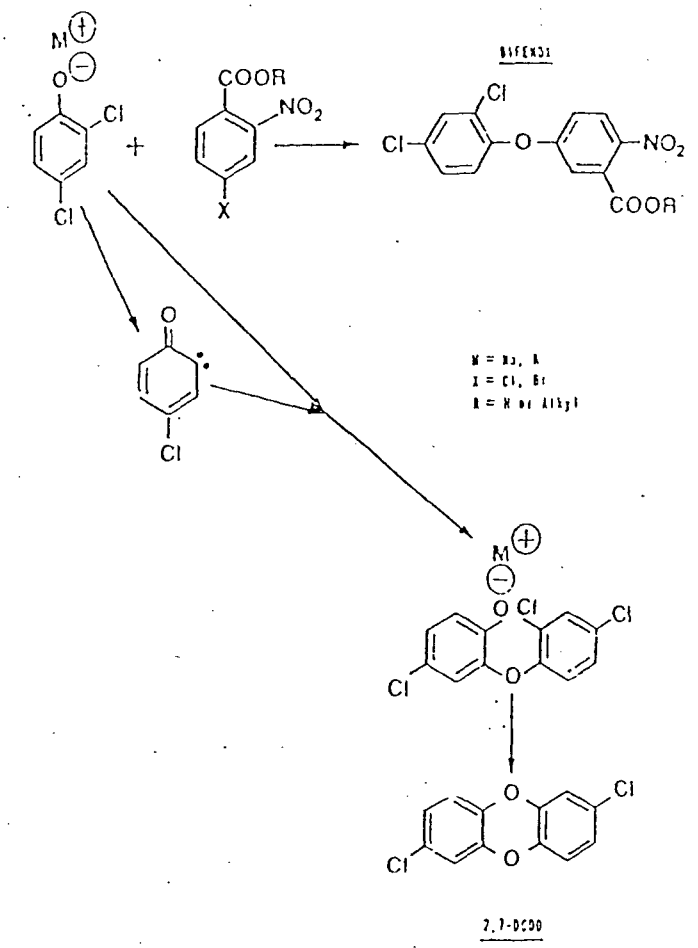


Figure 21. B fenox.

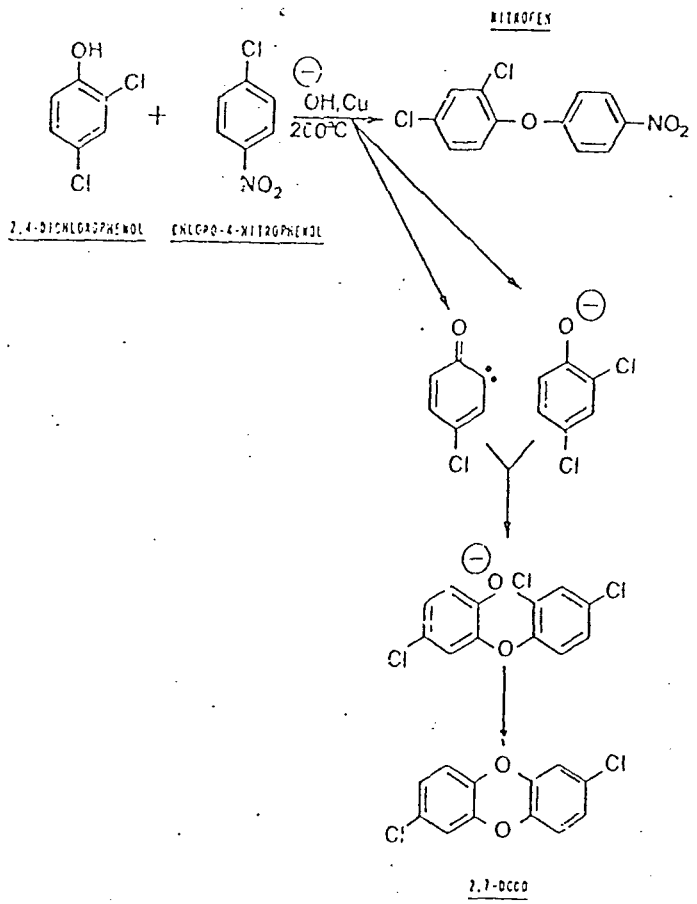


Figure 22. Nitrofen.

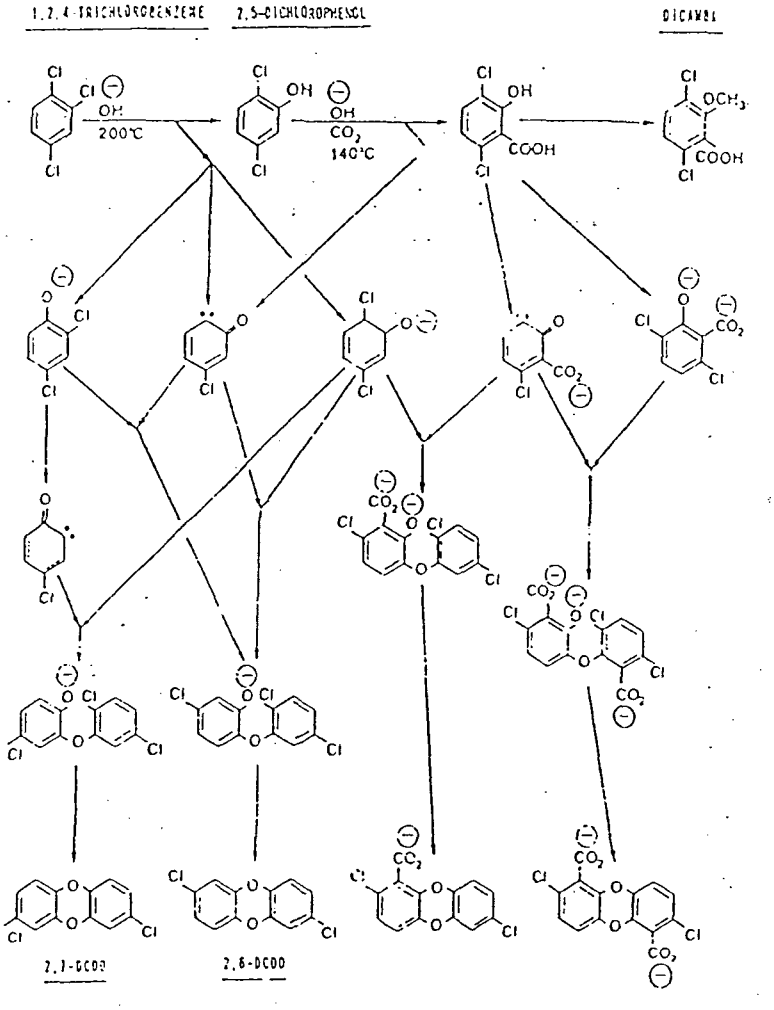


Figure 23. Dicamba.

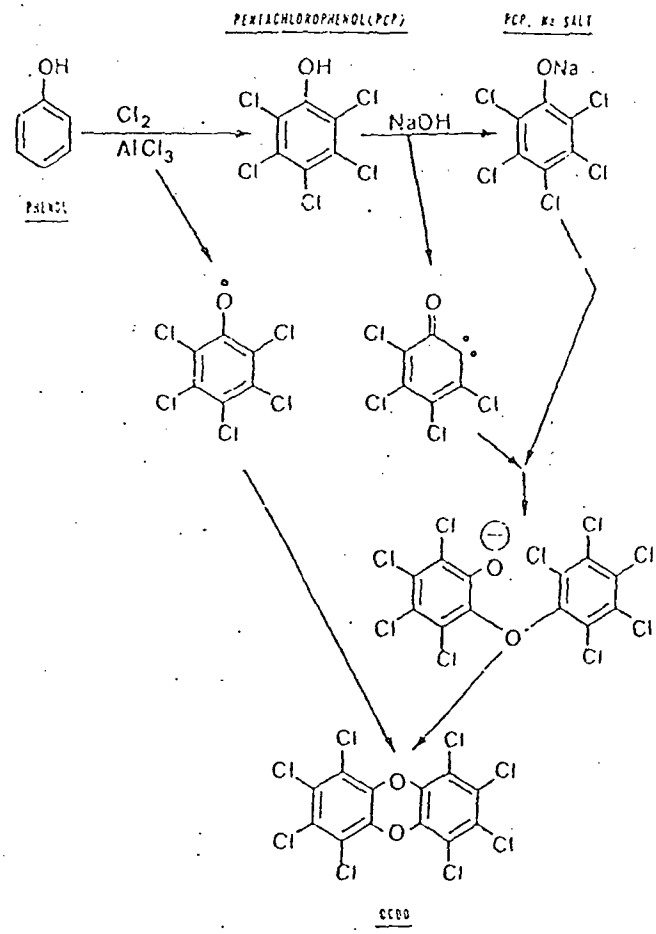


Figure 24. Pentachlorophenol (PCP) via phenol.

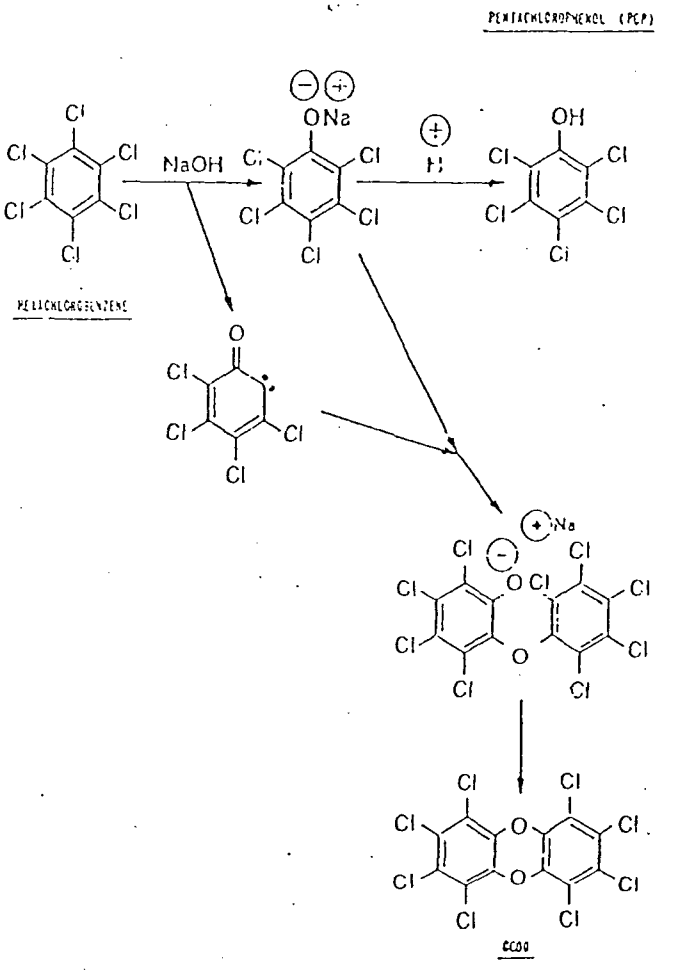


Figure 25. Pentachlorophenol (PCP) via hexachlorobenzene.

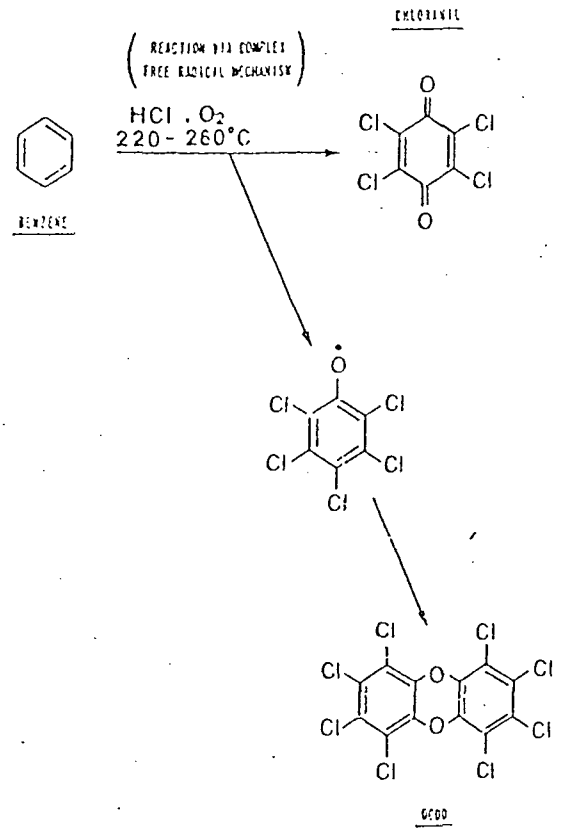


Figure 26. Chloranil.

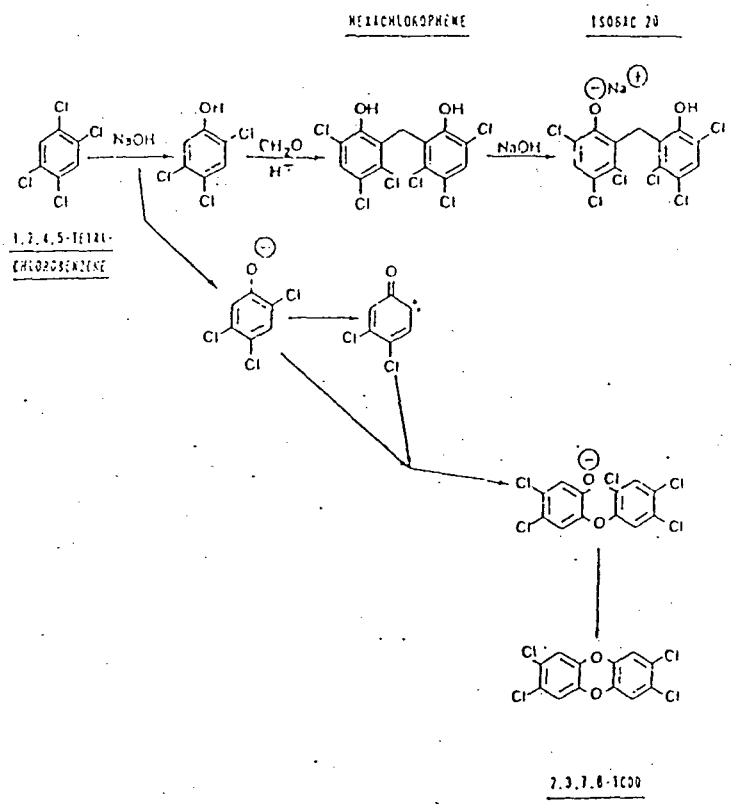


Figure 27. Hexachlorophene and Isobac 20.

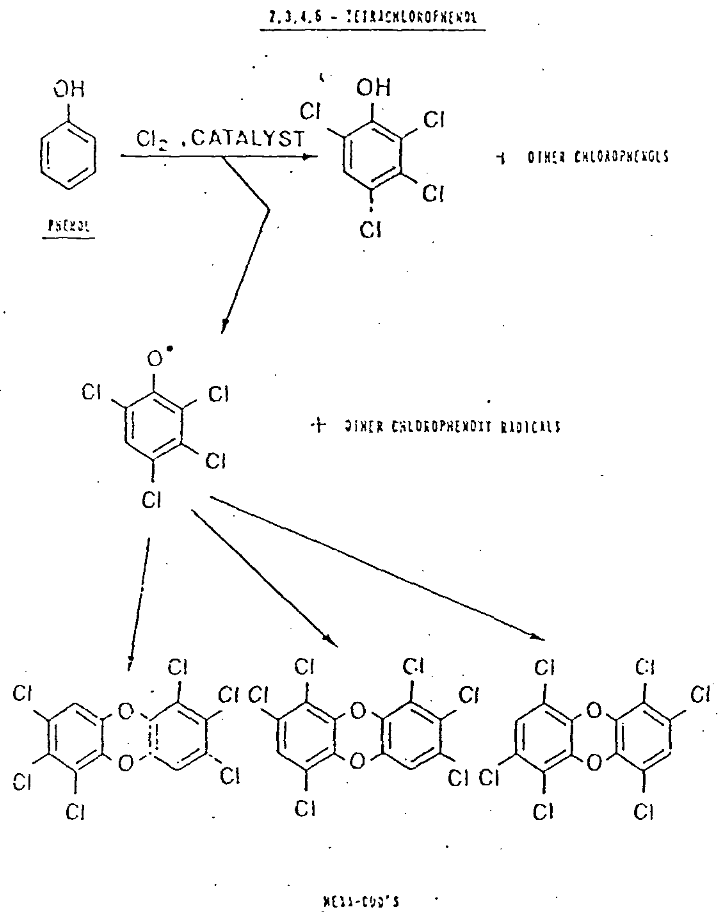


Figure 28. 2,3,4,6-Tetrachlorophenol.

Table 10 summarizes the primary raw materials involved in the production of the Class I pesticide chemicals.

A more complete discussion of many of these pesticides appears in the following subsections.

TABLE 10. PESTICIDE RAW MATERIALS

Pesticide product	Raw materials
Bifenox	2,4 Dichlorophenol 3-Halo-o-nitrobenzoic acid ester NaOH
Chloranil	Benzene Hydrogen chloride Oxygen
2,4-D and esters and salts	Phenol Chloroacetic acid NaOH Cl_2 Alcohols (for esters) Amines (for amine salts)
2,4-DB and salts	Phenol Cl_2 NaOH Butyrolactone Alcohols (for esters) Amines (for amine salts)
Dicamba	1,2,4-Trichlorobenzene NaOH CO_2 Dimethyl sulfate
Dicapthon	2-Chloro-4-nitrophenol NaOH Chlorodimethylthiophosphonate
Dichlorenion	2,4-Dichlorophenol NaOH Chlorodimethylthiophosphonate
Disul sodium (Jesone)	2,4-Dichlorophenol NaOH Ethylene oxide Chlorosulfonic acid
2,4 DP	2,4 Dichlorophenol 2-Chloropropionic acid NaOH

(continued)

TABLE 10. (continued)

Pesticide product	Raw materials
Erbon	1,2,4,5-Tetrachlorobenzene NaOH Ethylene oxide 2,2-Dichloropropionic acid
Hexachlorophene and Isobac 20	1,2,4,5-Tetrachlorobenzene NaOH Ethylene oxide
Nitrofen	2,4-Dichlorophenol Chloro-4-nitrobenzene KOH
Pentachlorophenol (PCP)	Phenol Cl_2 (Phenol route) or Benzene Cl_2 (Hexachlorobenzene route) NaOH
Ronnel	1,2,4,5-Tetrachlorobenzene NaOH Phosphorus sulfochloride $NaOCH_3$
Silvex and esters and salts	1,2,4,5-Tetrachlorobenzene NaOH Chloropropionic acid Alcohols (for esters) Amines (for amine salts)
2,4,5-T and esters and salts	1,2,4,5-Tetrachlorobenzene NaOH Chloracetic acid Alcohols (for esters) Amines (for amine salts)
2,3,4,6-Tetrachlorophenol	Phenol Cl_2
2,4,5-Trichlorophenol	1,2,4,5-Tetrachlorobenzene NaOH

DIOXINS IN COMMERCIAL CHLOROPHENOLS AND THEIR DERIVATIVES

Since most reports of dioxins are associated with chlorinated phenolic compounds, this section examines this group of organic materials with respect to their reported dioxin contaminants and their utilization, manufacture, production volumes, and derivatives. Similar information is presented, when available, for hexachlorobenzene, which has been found to contain dioxins, and also for a group of other related commercial chemicals that theoretically could contain dioxin contaminants, although no analyses have been reported. For each chemical, the discussions include the probable processing steps that may promote dioxin formation and also the mechanisms through which dioxins could appear in the associated process wastes or be retained within the chemical products.

Chlorophenols

Chlorinated phenols are a family of 19 compounds, consisting of a benzene ring to which is attached one hydroxyl group and from one to five chlorine atoms. The positions of the chlorine atoms with respect to the hydroxyl group and to each other provide the opportunity for three monochlorophenols, six each of dichloro- and trichlorophenols, three tetrachlorophenols, and one pentachlorophenol. Many researchers have established the presence of dioxins in these chemicals; Table 11 lists the results of several such studies.

Data in this table show that until recently dioxins have not been found in commercially produced mono- or dichlorophenols. The presence of 2,3,7,8-TCDD in low concentration was found in 1979 in a railroad tank car spill of *o*-chlorophenol. One or more samples of all chlorophenols with three or more chlorine atoms that have been examined have contained dioxins. TCDD's have been identified not only in the 2,4,5-trichloro isomer but also in the 2,4,6-trichloro isomer. One or more samples of trichlorophenol have contained dioxins with two to eight chlorine substituents. Only dioxins with six to eight chlorine substituents have been found in tetra- and pentachlorophenol. Numerous analyses have confirmed that dioxins with less than six chlorine substituents are not found in pentachlorophenol.

Most commercial chlorophenols are used as raw materials in the synthesis of other organic compounds. Some of the less highly chlorinated phenols are used with formaldehyde to make fire-resistant thermosetting plastics (Doedens 1964). Those containing three or more chlorine atoms are used directly as pesticide chemicals. 2,4,6-Trichlorophenol is effective as a fungicide, herbicide, and defoliant (Hawley 1971). It was formerly used in large quantities in the leather-tanning industry; however, its use in this industry has decreased substantially (U.S. Environmental Protection Agency 1978a), probably as a result of the improved effectiveness and mass production of 2,4,5-trichlorophenol, a substance of sufficient importance to warrant a special section in this report. 2,3,4,6-Tetrachlorophenol is used as a preservative for wood, latex, and leather, and also as an insecticide (Kozak et al. 1979).

Pentachlorophenol or its sodium salt is said to be the second most widely used pesticide in the United States. It is effective in the control of certain bacteria, yeasts, slime molds, algae, fungi, plants, insects, and snails. Because of its broad spectrum, pentachlorophenol is used in many ways:

- As a preservative for wood, wood products, leather, burlap, cordage, starches, dextrins, and glues
- As an insecticide on masonry for termite control

TABLE 11. CHLORODIOXINS REPORTED IN CHLOROPHENOLS

Chlorophenol sample	Chlorodioxins (-CDD's), ppm[a]								Data source
	mono-CDD's	DCDD's	tri-CDD's	TCDD's	penta-CDD's	hexa-CDD's	hepta-CDD's	OCDD	
Monochlorophenol									
2-chlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	Firestone 1972
o-chlorophenol	-	-	-	0.037 (2,3,7,8)[b]	-	-	-	-	Chemical Week 1979
Dichlorophenol									
2,4-dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	Firestone 1972
2,6-dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	Firestone 1972
Trichlorophenol									
2,4,5-trichlorophenol (1969)	ND	ND	ND	0.30 (1,3,6,8) 6.20 (2,3,7,8)	ND	ND	ND	ND	Firestone 1972
2,4,5-trichlorophenol (1970)	ND	ND	ND	ND	1.5	ND	ND	ND	Firestone 1972
2,4,5-trichlorophenol (1970)	ND	ND	ND	ND	ND	ND	ND	ND	Firestone 1972
2,4,5-trichlorophenol (1970)	ND	ND	ND	0.07 (2,3,7,8)	ND	ND	ND	ND	Firestone 1972
Na-2,4,5-trichlorophenol (1967)	ND	ND	ND	ND	ND	ND	ND	ND	Firestone 1972
Na-2,4,5-trichlorophenol (1969)	ND	0.72 (2,7)	ND	1.40 (2,3,7,8)	ND	ND	ND	ND	Firestone 1972
2,4,5-trichlorophenol	-	-	-	0.30 (2,3,7,8)	-	-	-	-	Elvidge 1971
2,4,6-trichlorophenol	ND	ND	93 (2,3,7)	49 (1,3,6,8)	ND	ND	ND	ND	Firestone 1972
trichlorophenol	-	-	-	ND (<5)	-	0.5-10	0.5-10	0.5-10	Woolson et al. 1972

(continued)

TABLE 11. (continued)

Chlorophenol sample	Chlorodioxins (-CDD's), ppm[a]								Data source
	mono-CDD's	DCDD's	tri-CDD's	TCDD's	penta-CDD's	hexa-CDD's	hepta-CDD's	OCDD	
Tetrachlorophenol									
2,3,4,6-tetrachlorophenol (Dowicide 6)	-	-	-	-	-	6	-	-	Buser 1975
2,3,4,6-tetrachlorophenol	ND	ND	ND	ND	ND	23	5.1	0.17	Firestone 1972
2,3,4,6-tetrachlorophenol (1967)	ND	ND	ND	ND	ND	4.1	ND	ND	Firestone 1972
2,3,4,6-tetrachlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	Firestone 1972
tetrachlorophenol	-	-	-	ND (0.5)	-	10-100	10-100	10-100	Woolson et al. 1972
Pentachlorophenol									
PCP (Dowicide 7)	-	-	-	-	-	9	235	250	Buser 1975
PCP	-	-	-	ND (0.5)	-	10-100	100-1000	100-1000	Woolson 1972
Na-PCP (1967)	ND	ND	ND	ND	ND	14	14.5	3.8	Firestone 1972
Na-PCP (1969)	ND	ND	ND	ND	ND	20	11.3	3.3	Firestone 1972
PCP (1970)	ND	ND	ND	ND	ND	39	49	15	Firestone 1972
PCP (1970)	ND	ND	ND	ND	ND	35	23	ND	Firestone 1972
PCP (1967)	ND	ND	ND	ND	ND	0.17	ND	ND	Firestone 1972
PCP (1969)	ND	ND	ND	ND	ND	13	47	ND	Firestone 1972
PCP (1970)	ND	ND	ND	ND	ND	0.91	2.1	5.3	Firestone 1972
PCP (1970)	ND	ND	ND	ND	ND	15	23	15	Firestone 1972
PCP (1978)	-	-	-	ND (0.1)	-	19	140	432	Dioxin in Industrial Sludges 1978
Pentachlorophenate	-	-	-	-	-	-	-	-	Jensen and Renberg 1972
PCP formulation	-	-	-	-	-	-	870	50-3300	Jensen and Renberg 1972
PCP (technical grade)	-	-	-	ND	-	33-42	19-24	7-11	Villanueva 1973
PCP (reagent grade)	-	-	-	ND	-	0.02-0.03	0.04-0.09	0.02-0.03	Villanueva 1973

(continued)

TABLE 11. (continued)

Chlorophenol sample	Chlorodioxins (CDD's), ppm[a]								Data source
	mono-CDD's	DCDD's	tri-CDD's	TCDD's	penta-CDD's	hexa-CDD's	hepta-CDD's	OCDD	
PCP (many samples)	-	-	-	ND	-	9-27	90-135	575-2510	PCP--A wood preservative 1977
PCP's (17)	-	-	-	-	-	0-23	-	0-3000	Crummett 1975
PCP or PCP Na (7)	-	-	-	-	-	0.03-10	0.6-180	5.5-370	Buser and Bosshardt 1978
PCP (Dowicide 7 1970)	-	-	-	-	-	4	125	2500	PCP Ad Hoc Study Report 12/78 SAB
PCP (Dowicide 7 1970) (distilled)	-	-	-	-	-	1.0	6.5	15	PCP Ad Hoc Study Report 12/78 SAB
PCP	-	-	-	-	-	9-27	-	575-2510	Johnson et al. 1973
Na-PCP (Dowicide G 1978)	-	-	-	-	-	ND-2	1-12	4-173	Dow Chemical Company 1978

a - Key to abbreviations and symbols: ND = Not detected (minimum detection level, ppm). Other numbers in parentheses indicate year chlorophenol sample was obtained or specific dioxin detected.
- = Not analyzed or not reported.

b - Presence of 2,3,7,8-TCDD confirmed but not quantitatively reported.

- As a fungicide/slimicide in pulp and paper mills, in cooling tower waters, and in evaporation condensors
- As a preharvest weed defoliant on seed crops
- As a preservative on beans (for replanting only)
- As a means of controlling slimes in secondary oil recovery injection water (in the petroleum industry)

By far the major use of pentachlorophenol is as a wood preservative. It was once reported to have been used in shampoos; however, this chemical does not now appear to be used as an ingredient in cosmetics or drugs, since it is not listed either in the CTFA Cosmetic Ingredient Dictionary (Cosmetic, Toiletry, and Fragrance Association, Inc. 1977), or in the Physicians' Desk Reference (1978).

Manufacture--

Through either process variations or separation of mixtures by fractional distillation, manufacturers selectively produce chlorophenols with specific numbers and arrangements of chlorine atoms. Table 12 shows that 13 of the 19 possible chlorophenols are currently sold commercially in sufficient volume to be listed in the 1978 Stanford Research Institute Directory of Chemical Producers. Seven of these are made in much higher volume than the other six. The high-volume products are all made by one of two major types of manufacturing processes, referred to herein as the hydrolysis method and the direct chlorination method.

As mentioned earlier, chlorophenols are benzene rings that contain one hydroxyl group and one or more chlorine atoms. The basic raw material in the manufacture of chlorophenols is benzene, and the two major manufacturing methods differ primarily in the order in which the substituents are attached to the benzene ring. In the hydrolysis method, chlorophenols are made by replacing one chlorine substituent of a polychlorinated benzene with a hydroxyl group. The hydrolysis method is the only practical method for producing some of the chlorophenols, such as the 2,4,5 isomer; this isomer is apparently the only one currently produced in large quantity by this method (Kozak 1979; Deinzer 1979; Chemical Engineering 1978). In the direct chlorination method, phenol (hydroxybenzene) is reacted with chlorine to form a variety of chlorophenols. Each manufacturing method is more fully described in the paragraphs below. In addition, a detailed description of the manufacture of 2,4,5-trichlorophenol (2,4,5-TCP) is outlined separately.

Hydrolysis method--The first step in the hydrolysis method is the direct chlorination of benzene. Through a series of distillations, rechlorinations, and other chemical treatments, several purified chlorobenzene compounds are obtained that contain from two to six chlorine substituents. Specific chlorophenols are then made by reacting one of the chlorine substituents with caustic, thereby replacing the chlorine atom with a hydroxyl group (see Figure 29). The reaction takes place in a solvent in which both materials are soluble, and the mixture is held at specific conditions of temperature and pressure until the reaction is complete. The product is then recovered from the reaction mixture. The solvent is usually an alcohol (most often methanol), although use of other solvents is possible.

A 1957 process patent describes the manufacture of pentachlorophenol from a starting material of hexachlorobenzene (U.S. Patent Office 1957c). Methanol is the solvent, and the reaction takes place at temperatures of 125° to 175° C and pressures of 125 to 300 psi. Reaction time is 0.2 to 3 hours. This method is known to have been used commercially (Arsenault 1976).

A variation of this process using ethylene glycol as the solvent also has been used commercially for the production of 2,4,5-trichlorophenol (Commoner and Scott 1976a; Whiteside 1977).

A process described in another 1957 patent uses water as the solvent in hydrolysis of dichloro- and trichlorobenzenes (U.S. Patent Office 1957c). Temperature is maintained from 240° C to 300° C under alkaline conditions at autogenous pressure. Reaction time varies from 0.5 to 3 hours. By this method, monochlorophenols are produced in yields greater than 70 percent from *o*-, *m*-, and *p*-dichlorobenzene. Metachlorophenol is formed as an impurity from the ortho- and para- starting materials through ring rearrangement mechanisms. Orthochlorophenol, which is the most likely dioxin precursor, is not formed by ring rearrangement but is produced in 86 percent yield from *o*-dichlorobenzene. Also, hydrolysis of 1,2,4-trichlorobenzene forms a mixture of dichlorophenol isomers in yields up to 95 percent.

TABLE 12. COMMERCIAL CHLOROPHENOLS AND THEIR PRODUCERS[a]

Chlorophenol	Manufacturer(s)
o-Chlorophenol	Dow Chemical Company Monsanto Company
m-Chlorophenol	Eastman Kodak Company Aldrich Chemical Company Specialty Organics, Inc. R.S.A. Corporation
p-Chlorophenol	Dow Chemical Company Monsanto Company
2,3-Dichlorophenol	Specialty Organics, Inc.
2,4-Dichlorophenol	Dow Chemical Company Monsanto Company Rhodia, Inc. Vertac, Inc.
2,5-Dichlorophenol	Velsicol Chemical Corporation
2,6-Dichlorophenol	Aldrich Chemical Company Specialty Organics, Inc.
3,4-Dichlorophenol	Aldrich Chemical Company
3,5-Dichlorophenol	Aldrich Chemical Company Specialty Organics, Inc.
2,4,5-Trichlorophenol	Dow Chemical Company Vertac, Inc.
2,4,6-Trichlorophenol	Dow Chemical Company
2,3,4,6-Tetrachlorophenol	Dow Chemical Company
Pentachlorophenol	Dow Chemical Company Vulcan Materials Company Reichold Chemicals

a - Source: Stanford Research Institute Directory of Chemical Producers, U.S. 1978

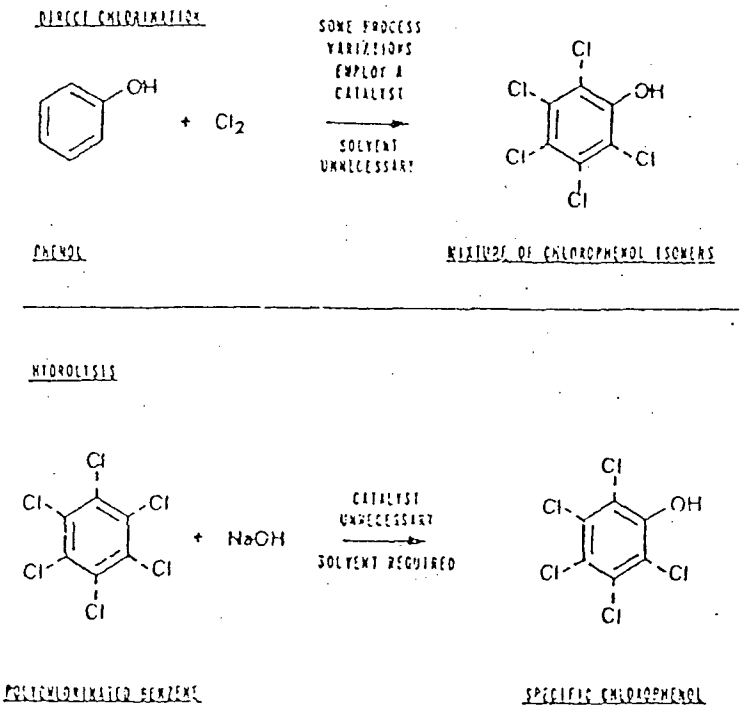


Figure 29. Basic chlorophenol reactions.

A 1967 patent describes the use of a combined methanol-water solvent system (U.S. Patent Office 1967b). Temperature is maintained at 170° to 200° C, under above-autogenous pressures. Reaction time is 1 hour or less.

A 1969 patent describes still another solvent, dimethylsulfoxide (DMSO) (U.S. Patent Office 1969). Use of this solvent in a mixture with water permits the reaction to take place at atmospheric pressure; caustic hydrolysis of hexachlorobenzene to pentachlorophenol occurs at approximately 155° C and is complete in about 3 hours. This process apparently has never been applied commercially.

When an alcohol is used as a solvent, the chemical mechanism that occurs involves an initial equilibrium reaction between the alcohol and caustic to form a sodium alkoxide, which is the reagent that actually attacks the chlorobenzene. The compound formed first is the alcohol ether of the chlorophenol. On standing, rearrangement of the compound occurs to form the chlorophenate plus any of several side reaction products (Sidwell 1976). This mechanism is significant because it explains the "aging" step that is a distinct phase in commercial hydrolysis sequences, and it also explains the substantial quantity of byproduct impurities that are derived from the alcohol solvents.

In all these processes, the product is recovered through either of two methods. In one, extraction into benzene separates the organic materials from water, salt, and excess caustic. Subsequent vacuum distillation recleans the benzene for recycle and also separates the chlorophenols into purified fractions. Extraction with benzene (or a similar solvent) is probably the preferred product recovery method for chlorophenols of lower molecular weight, especially the mono- and dichloro-products, since they are more easily distilled than the heavier products.

The alternative product recovery method is to filter the reaction mixture, perhaps after partial neutralization or evaporation and subsequent cooling, to reclaim unreacted polychlorobenzenes. The solution is then acidified and filtered again to collect the solid products. This variation is probably best suited to recovery of tri-, tetra-, and pentachlorophenols because these products and their raw materials are solids at room temperature and therefore can be removed more easily in the filtration operations.

Chlorophenols can be purified by distillation to separate high-boiling impurities. Technical feasibility has been reported in three 1974 patents, in which purified pentachlorophenol is recovered in good yield by high vacuum distillation in the presence of chemical stabilizers (U.S. Patent Office 1974a, 1974b, 1974c). Purification of 2,4,5-trichlorophenol by distillation has also been reported (World Health Organization 1977).

The high-temperature, high-pressure, and strongly alkaline conditions of the hydrolysis process are conducive to the formation of dioxin compounds. Although not in present U.S. commercial use, the hydrolysis manufacture of pentachlorophenol was especially favorable for the formation of octachlorodibenzo-*p*-dioxin (OCDD)(Figure 25, p. 72). As described in more detail later in this section, the commercial hydrolysis method is known to produce 2,3,7,8-TCDD from 1,2,4,5-tetrachlorobenzene.

Direct chlorination method—Direct chlorination begins by the addition of a hydroxyl group to benzene to form hydroxybenzene or phenol. This compound is manufactured in specialized plants, usually through sulfonation, chlorination, or catalytic oxidation of benzene. Dioxins have not been reported as resulting from this portion of the process; this study is therefore concerned only with the second part of the process in which phenol is reacted with chlorine to form various chlorophenols.

The reaction of phenol with chlorine actually forms a mixture of chlorinated phenols (see Figure 29), although certain compounds are formed preferentially. Direct chlorination is practical, therefore, only if the desired product is one of the high-yield compounds. Except for low-volume specialty isomers and the high-volume 2,4,5 isomer, all commercial chlorophenols made in this country are those that are formed preferentially by this process (Buser 1978; Kozal 1979; Deinzer 1979; Chemical Engineering 1978). These include mono- and dichlorophenols that are substituted at positions 2 and 4, the symmetrical 2,4,6-trichlorophenol isomer, 2,3,4,6-tetrachlorophenol, and pentachlorophenol.

Chlorination of phenol can be accomplished in batch reactors, but is best suited to the continuous process shown in simplified form in Figure 30 (U.S. Patent Office 1960, Sittig 1969). Liquid phenol and/or lower chlorinated phenols are passed countercurrently with chlorine gas through a series of reaction vessels. Trace amounts of aluminum chloride catalyst are added, usually as a separate feed into an intermediate vessel. Equipment is sized so that all the chlorine is absorbed by the phenol, the last phenol-containing vessel is usually built as a scrubbing column to ensure complete chlorine absorption. Gas leaving the scrubber is anhydrous hydrogen chloride, which is either used in other chemical operations or dissolved in water to form substantially pure hydrochloric acid as a byproduct.

The chlorophenol compound created in greatest amount by this process is established by the ratio of feed rates of chlorine and phenol. Because all chlorine is consumed, it is fed at rates 1 to 5 times the molecular proportion of phenol, depending on the principal product desired. To prevent excessive oxidation that produces nonphenolic chlorinated organic compounds, temperatures are carefully regulated; the usual temperatures are 130° to 190° C for pentachlorophenol and 170° C for 2,4-dichlorophenol. Pressure is atmospheric, and reaction time is 5 to 15 hours (U.S. Patent Office 1960).

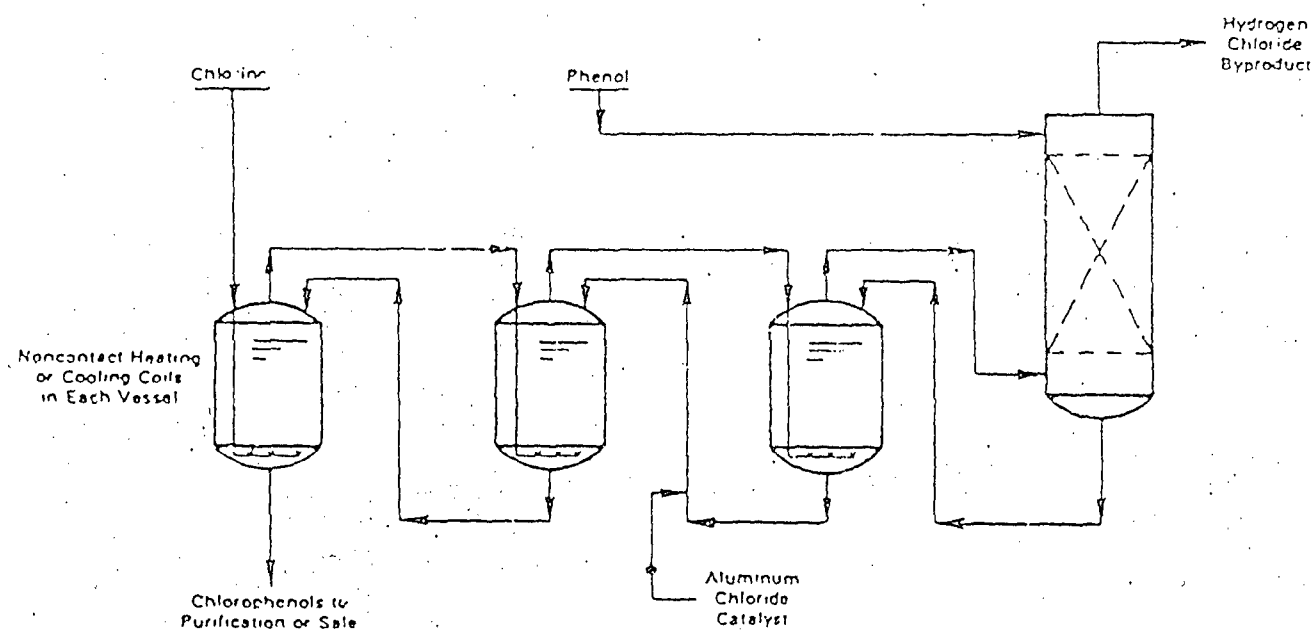


Figure 30. Direct chlorination of phenol

The mixture from the first reaction vessel can be vacuum-distilled to separate the various compounds. Unreacted phenol and any undesired less-chlorinated phenols would be recycled. To make some products for which purity standards are rather flexible, very little purification is necessary, and some processes may include no final distillation or other treatment. Also, a chlorinated product may be withdrawn from the scrubber (usually a mixture of 2- and 4-mono- or 2,4-dichlorophenol) and may be either distilled, with portions recycled to the first reactor for further chlorination, or sold as is. 2,4-Dichlorophenol may be further processed to the phenoxy herbicide 2,4-D.

Supplemental processing steps may be necessary to remove contaminants such as "hexachlorophenol" (hexachlorocyclohexadiene-1,4-one-3), dioxins, and furans from PCP made by this process. Hexachlorophenol may be formed during the process by overchlorination of the reaction mass (U.S. Patent Office 1939). Dioxins may be formed during distillation by the condensation of PCP with itself or with hexachlorophenol (see Table 5; see also Figure 24, p. 71).

Dioxins have been reported in numerous samples of PCP, as shown in Table 8. Although hexa-CDD's, hepta-CDD's, and OCDD are known to be present in commercial PCP, 2,3,7,8-TCDD has never been found (Chemical Regulation Reporter 1978; U.S. Environmental Protection Agency 1978e).

All PCP made in the United States is produced by the direct chlorination of phenol; apparently the method involving the hydrolysis of hexachlorobenzene has never been used commercially for PCP production (American Wood Preservers Institute 1977). Dow reportedly changed its production process in 1972 to produce a PCP with lower dioxin content; the other two producers of PCP apparently have not followed Dow's lead (Chemical Regulation Reporter 1978). Details of Dow's process change were not reported.

Production—

Production figures for di- and tetrachlorophenols are not available. Although current figures for pentachlorophenol production are also not available, it is estimated from production capacity information (Table 13) that U.S. manufacturers are producing as much as 53 million pounds of PCP annually. Annual U.S. trichlorophenol production is probably also in the range of 50 million pounds (Crosby, Moilanen, and Wong 1973).

As Table 12 indicates, chlorophenols are apparently manufactured by at least 11 companies, which represent two diverse groups of chemical producers. Of the 13 commercial chlorophenols, 7 are made by Dow Chemical Company in Midland, Michigan. Except for 2,4,5-trichlorophenol, all of the isomers made by Dow are those formed preferentially through direct chlorination of phenol. Competitive with Dow in the sale of these seven chlorophenols are four other companies:

Monsanto Company—Sauget, Illinois

Reichold Chemicals, Inc.--Tacoma, Washington

Vulcan Materials Company--Wichita, Kansas

Rhodia, Inc.--Freeport, Texas

All of these companies are engaged for the most part in the mass production of organic chemicals for which market demand is relatively constant. These companies are geared to heavy chemical production, and their products are made to commercial standards of purity and are usually sold at relatively low prices.

The other six chlorophenols are made by five companies that generally manufacture fine or specialty chemicals:

Velsicol Chemical Corp.--Beaumont, Texas

Eastman Kodak Company--Rochester, New York

TABLE 13. 1977 PENTACHLOROPHENOL PRODUCTION CAPACITY[a]

Company	Production location	1977 Capacity (millions of pounds)
Dow Chemical Company[b]	Midland, MI	17
Monsanto Company[c]	Sauget, IL	26
Reichold Chemicals	Tacoma, WA	20
Vulcan Materials Company	Wichita, KN	16
	Total capacity	79

a—Source: American Wood Preservers Institute 1977. These figures presumably do not include production of sodium or potassium salts of pentachlorophenol.
b—Dow ceased production of the sodium salt of PCP (Dowicide G) in April 1978 (Dow Chemical Company 1978).
c—Monsanto stopped all PCP production as of January 1, 1978 (Dorman 1978).

Aldrich Chemical Co., Inc.—Milwaukee, Wisconsin
Specialty Organics, Inc.—Irwindale, California
P.S.A. Corporation—Ardsley, New York

Products from these manufacturers are often batch-produced under contract with specific industrial customers, sometimes to high standards of purity. They are manufactured in much smaller quantities than those described above, often intermittently, and they are sold at a relatively high price. Often, the products from these companies are used in the manufacture of pharmaceuticals, photographic chemicals, and similar high-quality chemical materials. Without exception, the chlorophenols made by these companies are those not formed preferentially through direct chlorination of phenol.

Any chlorophenol with a chlorine atom at position 2 (ortho to the hydroxyl group) may be a precursor for dioxin formation. Nine of the 11 companies are reported to make at least one chlorophenol of this description. Potential for the occurrence of dioxins is therefore not limited to the manufacture of chlorophenols for pesticide use.

It is not known, however, whether the hydrolysis method, which is especially conducive to dioxin formation, is used to make the lower-volume chlorophenols. In many instances, this method probably is not used because the parent polychlorobenzenes needed for raw materials usually cannot be directly synthesized by conventional chlorination techniques. For production of *m*-chlorophenol in high yields, for example, general chemical references describe a synthesis route that involves chlorination of nitrobenzene, followed by reduction, diazotization, and hydrolysis of the nitrate group (Vinopal, Yamamoto, and Casida 1973). Multistep batch processes of this type are necessary to cause the substituents to attach to the ring at unnatural positions (Kozak 1979). These specialized production methods are not addressed in this report.

The primary chemical producers described above are not the only commercial sources of chlorophenols. Other companies purchase chlorophenols from primary producers, combine them with other ingredients, and market the formulated

products. Still others deal only in distribution of the chemicals or chemical mixtures. Most often the trade name of the product changes each time it is bought and sold.

2,4,5-Trichlorophenol

In 1972, hexa-, hepta-, and octachlorodioxins were found at concentrations of 0.5 to 10 ppm in four of six trichlorophenol samples analyzed. Tetrachlorodioxins were not detected (0.5 ppm level of detection). The research report implies that the 2,4,5 isomer of trichlorophenol was being analyzed (Woolson, Thomas, and Ensor 1972).

Also in 1972, another study showed dioxins in trichlorophenols (Firestone et al. 1972). Isomers identified in 2,4,5-trichlorophenol (or its sodium salt) at ppm levels were 2,7-di-, 1,3,6,8-tetra-, 2,3,7,8-tetra-, and pentachlorodioxins. High levels of 2,3,7-trichlorodioxin (93 ppm) and 1,3,6,8-tetrachlorodioxin (49 ppm) were found in the 2,4,6 isomers of trichlorophenol. The investigator analyzed for, but could not detect, mono-, hexa-, hepta-, and octachlorodioxins in these trichlorophenol samples. Data from these two studies are included in Table 11 on page 79.

A U.S. EPA position document on 2,4,5-TCP (U.S. Environmental Protection Agency 1978i) was prepared to accompany the August 2, 1978, *Federal Register* notice of rebuttable presumption against continued registration of 2,4,5-TCP products. The position document gives the following description of the known uses of this chemical:

> The largest use of 2,4,5-TCP is as a starting material in the manufacture of a series of industrial and agricultural chemicals, the most notable of which is the herbicide 2,4,5-T and its related products including silvex [2-(2,4,5-trichlorophenoxy) propionic acid], ronnel [0,0-dimethyl 0-(2,4,5-trichlorophenyl)-phosphorothioate], and the bactericide hexachlorophene.
>
> 2,4,5-TCP and its salts are used in the textile industry to preserve emulsions used in rayon spinning and silk yarns, in the adhesive industry to preserve polyvinyl acetate emulsions, in the leather industry as a hide preservative, and in the automotive industry to preserve rubber gaskets. The sodium salt is used as a preservative in adhesives derived from casein, as a constituent of metal cutting fluids and foundry core washes to prevent breakdown and spoilage, as a bactericide/fungicide in recirculating water in cooling towers, and as an algicide/slimicide in the pulp/paper manufacturing industry.
>
> There are some minor uses of 2,4,5-TCP and its salts in disinfectants which are of major importance relative to human exposure. These include use on swimming-pool-related surfaces; household sickroom equipment; food processing plants and equipment; food contact surfaces; hospital rooms; sickroom equipment; and bathrooms (including shower stalls, urinals, floors, and toilet bowls).

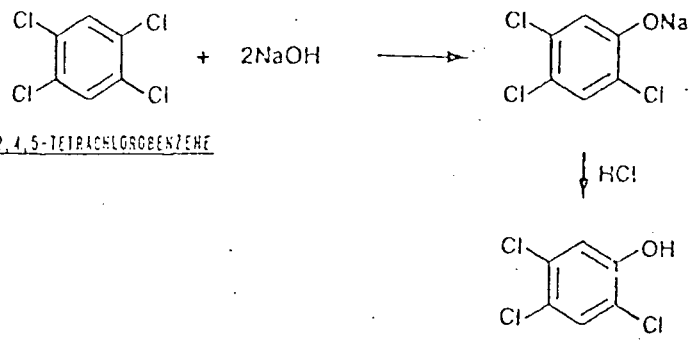
It is apparent, therefore, that all the uses of 2,4,5-TCP exploit the poisonous character of the compound and its derivatives. As a pesticide, it is subject to EPA registration in all of its applications except those associated with food processing.

Manufacture—

Only trace amounts of 2,4,5-trichlorophenol are created by direct chlorination of phenol. It can be made in about 50 percent yield by rechlorination of 3,4-dichlorophenol (U.S. Patent Office 1956c). Neither of these production methods is in commercial use in this country.

Domestic commercial production is accomplished through hydrolysis of 1,2,4,5-tetrachlorobenzene, which is a principal isomer produced by rechlorination of *o*-dichlorobenzene. Conversion of this chemical to the sodium salt of 2,4,5-TCP is

a batch reaction with caustic soda. Subsequent neutralization with a mineral acid forms the product. The basic process is a typical application of the hydrolysis method of chlorophenol production described earlier. The reaction sequence is given below:



1,2,4,5-TETRACHLOROBENZENE

2,4,5-TRICHLOROPHENOL

At least three variations of the basic process have been described in process patents specifically for production of 2,4,5-TCP, differing only in the solvents used and therefore in the conditions needed to drive the reaction to completion. The first patented process (U.S. Patent Office 1950) uses a solvent of ethylene glycol or propylene glycol at preferred temperatures of 170° to 180° C and pressures up to 20 psi. A second patent, the most recent (U.S. Patent Office 1967b), describes the use of methanol as a solvent, with temperatures ranging from 160° to 220° C and with pressure less than 350 psi (probably 50 to 200 psi). Both of these alcohol-based processes require 1 to 5 hours to complete.

A third patent (U.S. Patent Office 1957b) describes the use of water as the reaction solvent. Use of water necessitates the most severe operating conditions: operating temperatures from 225° to 300° C and pressures from 400 to 1500 psi. This method permits greater production, since reaction time is reduced to no more than 1.5 hours and in some instances to as little as 6 minutes. In addition to its production efficiency, the water-based process eliminates the side reactions between caustic and the alcohol solvents, which form undesired impurity compounds. The process also improves product yield and eliminates solvent costs. It appears, however, that the high-temperature, high-pressure, and strongly alkaline conditions of the water-based process promote a continuation of the reaction, in which 2,4,5-TCP combines with itself to form 2,3,7,8-TCDD (see Figure 13, p. 59).

The patent examples cited above are fairly old, and details of the current 2,4,5-TCP production methods are difficult to obtain. A 1978 EPA report on 2,4,5-TCP briefly describes present-day 2,4,5-TCP manufacture as a reaction of tetrachlorobenzene with caustic in the presence of methanol at 180° C under pressure. Although a final product purification step is described in the most recent patent example (U.S. Patent Office 1967b), the EPA report does not describe it.

A more detailed estimate of current production methods is derived from fragmentary descriptions of both U.S. and foreign operations (Sidwell 1976; World Health Organization 1977; Fuller 1977; Whiteside 1977; Fadiman 1979; D. R. Watkins 1980). (One plant from which much of this information was derived ceased production of 2,4,5-TCP in 1979.) Figure 31 is a flow chart prepared from

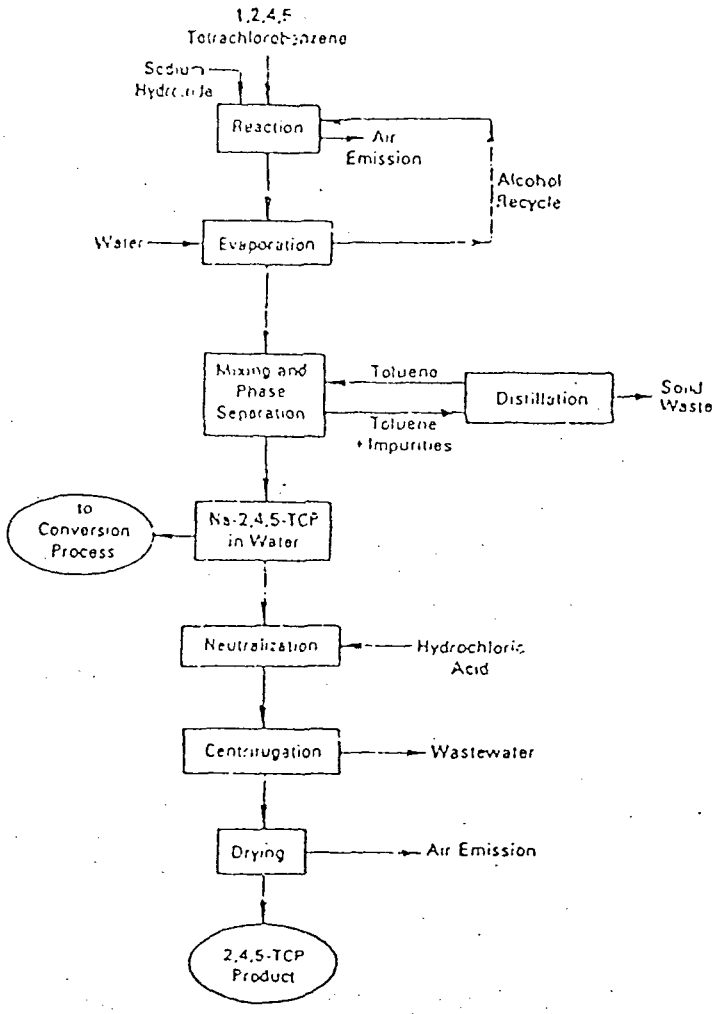


Figure 31. Flow chart for 2,4,5-TCP manufacture.

these sources, showing the most likely process details. In this processing scheme, alcohol and caustic are mixed and heated. Tetrachlorobenzene is added, an exothermic reaction begins, and cooling water is turned onto the reactor coils. After all the tetrachlorobenzene has been added, the batch is "aged"; during the aging period, sodium-2,4,5-trichlorophenate (Na-2,4,5-TCP) is formed. Volatile compounds such as dimethyl ether also are formed during the aging step; these are vented from the reactor, along with small amounts of vaporized methanol. According to Vertac, Inc., dimethyl ether is absorbed by a water scrubber, in which it is highly soluble. The presence of these flammable vapors presents a fire or explosion hazard, and the reaction vessel is usually enclosed in blastproof walls to minimize physical damage from any accident that may occur during the aging step.

On completion of the reaction, the methanol is evaporated, condensed, and recycled. At the same time, water is added to keep the batch contents in solution.

In this process, a toluene washing step is conducted to purify the product by removing some of the high-boiling impurities. Toluene condensed from the overhead of an auxiliary still is mixed into the cooled water solution of Na-2,4,5-TCP. The mixture is then allowed to stand quietly so that the water and organic phases can separate into layers. The organic layer, containing impurities, is decanted and returned to the toluene still as feed. The water layer containing partially purified Na-2,4,5-TCP, can be used directly to manufacture a herbicide derivative. Alternatively, hydrochloric acid can be added to neutralize the mixture. Acidic 2,4,5-TCP precipitates and is separated from the liquid by centrifugation.

Many of the impurities created during this process, including 2,3,7,8-TCDD, accumulate in the bottom of the toluene still. Still bottoms are removed periodically to be discarded. Toluene still bottoms have been identified as the source of at least one exposure of the public to dioxins, and also as the source of one of the highest concentrations of 2,3,7,8-TCDD (40 ppm) ever discovered in such wastes (Watkins 1979, 1980; Richards 1979a). (Analysis of this waste sample is fully described in Section 4 of this report.)

As shown in Figure 31, the acidic 2,4,5-TCP is dried and either packaged for sale or used to manufacture other derivative products. One reference shows one or more stages of purification of the product after it is centrifuged from the water solution (World Health Organization 1977). One stage of high-vacuum distillation is conducted to create what is described as "agricultural grade 2,4,5-TCP." A second stage of distillation removes additional impurities to form "pharmaceutical grade 2,4,5-TCP." It is believed that all U.S. hexachlorophene is made from a distilled grade of this chemical.

Process details concerning the only remaining 2,4,5-TCP plant in the United States have not been released. It was reported in 1967 that this plant (Dow Chemical Company, Midland, Michigan) was using the water-based process described in its 1955 patent (Scounce 1959; U.S. Patent Office 1957b), but this probably is not the case today. Another report states that the process is conducted with very careful temperature control to prevent the formation of dioxins (Sittig 1974). This source also indicates that still bottoms from the manufacture of 2,4,5-T at this plant are being discarded by incineration; therefore, a distillation is presumably being performed. It is not known whether these still bottoms are from a toluene washing still or from a product still.

Production—

Dow Chemical Company is apparently the only current producer of both 2,4,5-TCP and Na-2,4,5-TCP. Merck and Company has recently begun producing Na-2,4,5-TCP (Stanford Research Institute 1979). Current records related to the EPA Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) indicate that 42 companies, including Dow, are marketing 94 registered commercial products containing 2,4,5-TCP or its salts (U.S. Environmental Protection Agency 1978i). According to EPA sources, most, if not all, of these companies obtain the basic chemical from Dow (Reece 1978c).

Former 2,4,5-TCP manufacturing sites are listed in Table 14 by location and owner. Details of the processes used by these former producers are not known; however, "still bottoms" were said to be the source that created a dioxin exposure at Verona, Missouri (see Section 5). The methanol-based process with a toluene washing stage was used by Verlac, Inc. (Watkins 1980).

Current U.S. production figures for 2,4,5-TCP and its salts are not available (U.S. Environmental Protection Agency 1978i). In 1970, the estimated level of domestic production for 2,4,5-TCP and its derivatives was 50 million pounds (Crosby, Moilanen, and Wong 1973). In 1974, the reported annual world

TABLE 14. FORMER 2,4,5-TCP MANUFACTURING SITES[a]

Plant location	Owner
Niagara Falls, NY	Hooker Chemicals and Plastics (approximately 45 years;[b]
Jacksonville, AR	Reasor-Hill Corp (1948-61);[c] Hercules, Inc (1961-71)[c] Transvaal, Inc (1971-78)[c]
Verona, MO	North Eastern Pharmaceuticals and Chemicals Co.
Monmouth Junction, NJ	Rhodia, Inc.
Linden, NJ	GAF Corp.
Chicago, IL	Nalco Chemical Co.
Cleveland, OH	Diamond Shamrock Corp

a--Unless otherwise noted, the information in this table was derived from Stanford Research Institute Directory of Chemical Producers, United States 1976-79 and U.S. International Trade Commission Synthetic Organic Chemicals, U.S. Production and Sales 1968, 1974, 1976-78
b--Chemical Week 1978a
c--Richards 1979a

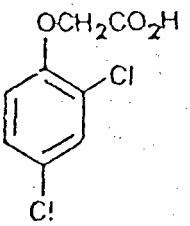
production of all chlorophenols and their salts was estimated to be 100,000 tons, or 200 million pounds (Nilsson et al. 1974).

Chlorophenol Derivatives with Confirmed Dioxin Content

The wide utilization of chlorophenols in chemical synthesis makes it virtually impossible to identify all the potential derivatives of this class of compounds. The following paragraphs outline the manufacture of derivatives that, upon analysis, have been reported to contain chlorinated dioxins. The products are all pesticides, which are usually made as only partially purified chemicals and are intended to be distributed rather broadly into the environment.

2,4-D, 2,4-DB, 2,4-DP, and 2,4-DEP—

The compound 2,4-dichlorophenoxyacetic acid (2,4-D) is a widely used herbicide and a close chemical relative of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) described later in this section. A 50:50 mixture of these two chemicals, known as "Herbicide Orange" (earlier called "Agent Orange"), was used as a defoliant during the Vietnam conflict. The chemical formula of 2,4-D is shown below.



2,4-D

The herbicide 2,4-DB is 4-(2,4-dichlorophenoxy) butyric acid; 2,4-DP is 2-(2,4-dichlorophenoxy) propionic acid, and 2,4-DEP is tris [2 - (2,4-dichlorophenoxy) ethyl] phosphite; all are closely related chemically to 2,4-D.

In 1972, Woolson, Thomas, and Ensor found hexachlorodioxin in one sample of 2,4-D at a level between 0.5 and 10 ppm. No other dioxins were observed. Twenty-three other 2,4-D samples, as well as three 2,4-DB and two 2,4-DEP samples, were analyzed, but no dioxins were found at a 0.5 ppm limit of detection. Apparently, only tetra-, hexa-, hepta-, and octachlorodioxins were sought in these analyses. The samples apparently were not analyzed for dichlorodioxins, which should be more likely to occur (see Figure 17, p. 64).

According to the World Health Organization (1977), 2,4-D is widely used as a herbicide for broadleaf weed control in cereal crops (wheat, corn, grain sorghum, rice, other small grains), sugar cane, and citrus fruits (lemons), and on turf, pastures, and noncrop land. Food-related uses account for 58 percent of all 2,4-D used in the United States in 1975.

Two manufacturing processes have been described for 2,4-D, only one of which starts with a chlorinated phenol. One process is a direct chlorination of phenoxyacetic acid (U.S. Patent Office 1949). The other process is a reaction between 2,4-dichlorophenol and chloroacetic acid (U.S. Patent Office 1958a). The second process is similar to the 2,4,5-T manufacturing process described in the following section and is also similar to the process used to make 2,4-DB (U.S. Patent Office 1963).

Since many companies make 2,4-D and its esters and salts, both production processes may be in use, although it is claimed that chlorination of phenoxyacetic acid produces a higher yield and is a simpler process. In a batch reactor, phenoxyacetic acid is melted by heating it to 100° C. With continuous agitation, chlorine is bubbled through the molten chemical and the temperature is increased slowly to 150° C. A stream of dry air is passed through the reactor to sweep away the hydrogen chloride byproduct. When the calculated amount of chlorine has been added, the resulting mass is cooled, pulverized, and packaged. No solvent is used, no special recovery operation is needed, and product purification is unnecessary. If dioxins are created during this process, the mechanism of their formation is unknown.

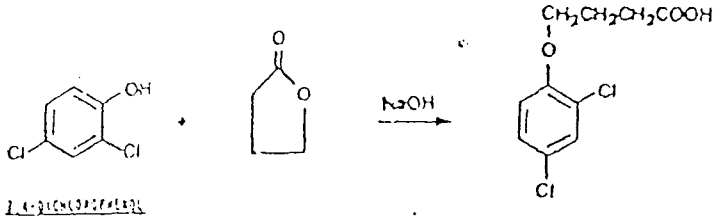
The second process involves reaction of 2,4-dichlorophenol with chloroacetic acid in a solvent mixture of water and sodium hydroxide. This process is said to be used by at least one large manufacturer (Sittig 1974). Heat is applied to the vessel, and the water is evaporated from the mixture. When the temperature begins to rise, indicating that most of the water has evaporated, heating is stopped and a fresh charge of cold acidified water is added. The product can be filtered from the mixture and dried; this procedure would form an impure product.

Alternatively, the product can be extracted from the cooled mixture with a water-immiscible solvent and then separated from the solvent by distillation. This latter recovery method would probably create anhydrous organic wastes and therefore is probably in use by at least one company that has been reported to incinerate waste tars from 2,4-D manufacture (Sittig 1974).

This chlorophenol-based process for making 2,4-D could create dioxins because it provides for an alkaline mixture of a dioxin precursor chemical in contact with hot heating surfaces. If the product is only filtered from the reaction mixture, the dioxin contaminants would be captured along with the product. If solvent extraction is employed, part of the dioxin would probably appear in wastes from the process and part would probably be captured with the product.

The process for manufacture of 2,4-DB uses 2,4-dichlorophenol and gamma butyrolactone in a solvent mixture of dry butanol and nonane, with sodium hydroxide as a reaction aid. The chemical reactions are shown on the following page.

The ingredients are mixed and heated to a temperature of about 165° C for a



2,4-DB

period that may range from 1 to 24 hours. On completion of the reaction, dilute sulfuric acid is added and 2,4-DB precipitates; the precipitate is centrifuged from the mixtures, dried, and packaged. Liquids from the centrifuge are allowed to stand quietly and separate into two liquid layers. The water fraction is discarded, and the organic layer is recycled to the subsequent reaction batch. Any water that is brought into the reactor is removed by distillation before the next reaction is started.

It is possible that dioxins could be produced by this process by the mixture of 2,4-dichlorophenol with sodium hydroxide being brought into contact with a hot surface (see Figure 18, p. 65). Product recovery methods are such that any dioxins formed would either be removed as solids along with the product or be recycled to the succeeding batch.

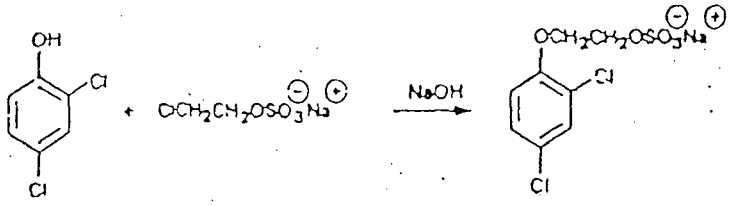
Commercial production of 2,4-D in the United States started in 1944 and by the mid-1960's had peaked at 36 million kg (World Health Organization 1977). After the use of Herbicide Orange was discontinued, production dropped. Production in 1974 is estimated to have been 27 million kg (World Health Organization 1977). Production figures for 2,4-DB and 2,4-DEP are not available.

The current basic producers of 2,4-D and 2,4-DB acids, esters, and salts as reported by Stanford Research Institute in 1978 are listed in Table 15. Former producers or production sites are listed in Table 16. No current producers of 2,4-DEP are listed in the Stanford Research Institute publication of 1978.

Sesone—

The chemical name for the pesticide sesone is 2-(2,4-dichlorophenoxy) ethyl sodium sulfate. The only sample known to have been analyzed for dioxins contained 0.5 to 10 ppm hexachlorodioxin (Helling et al. 1973). No tetra-, hepta-, or octachlorodioxins were detected (0.5 ppm detection level). Analysis apparently was not performed for di-, tri-, or pentachlorodioxins.

Sesone is made from 2,4-dichlorophenol by boiling it for several hours in a water solution of beta-chloroethyl-sodium sulfate and sodium hydroxide. The following are the chemical reactions of the process:



2,4-C

SESONE

TABLE 16. CURRENT BASIC PRODUCERS OF 2,4-D AND 2,4-DB ACIDS, ESTERS, AND SALTS[a]

Pesticide	Company	Production location
2,4-D and esters and salts	Dow Chemical Company	Midland, MI
	Fallek-Lanzro Corp	Tuscaloosa, AL
	Imperial, Inc	Shenandoah, IA
	North American Philips Corp., Thompson-Hayward Chemical Co., subsidiary	Kansas City, KS
	PBI-Gordon Corp	Kansas City, KS
	Rhodia, Inc	Portland, OR St. Joseph, MO Chicago Heights, IL
	Riverdale Chemical Co	Chicago Heights, IL
	Union Carbide Corp., Amchem Products, Inc., subsidiary	Ambler, PA Fremont, CA
	Vertac, Inc., Transvaal, Inc., subsidiary	Jacksonville, AR
2,4-DB and salts	Rhodia, Inc	Portland, OR
	Union Carbide Corp., Amchem Products, Inc., subsidiary	Ambler, PA

a—Source: Stanford Research Institute 1978

In more detail, the straight-chain reactant is made by combining ethylene chlorohydrin and chlorosulfonic acid in a refrigerated water solution (U.S. Patent Office 1958c). After partial neutralization with sodium hydroxide, 2,4-dichlorophenol is added and the mixture is boiled for about 15 hours. According to the patent example, the mixture is probably not purified; it is simply spray-dried to form a usable product. It could be purified by repeated extractions with hot alcohol to separate the sodium sulfate impurity.

The manufacture of sesone meets all of the requirements for promotion of the formation of 2,7-DCDD (see Figure 16, p. 62). Both the raw material and the final product contain a chlorine atom ortho to a ring-connected oxygen atom, and the mixture is heated in the presence of sodium hydroxide. Although overall reaction temperature is only slightly above 100° C, it could be higher at the heating surfaces.

The volume of sesone produced annually is not known. Only nine commercial products containing the herbicide are currently registered as pesticides with EPA.

TABLE 16. FORMER BASIC PRODUCERS OF 2,4-D AND 2,4-DB ACIDS, ESTERS, AND SALTS[a]

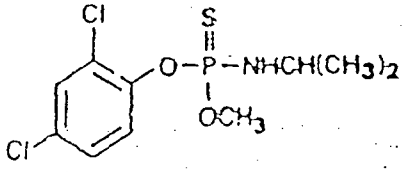
Pesticide formerly reported produced	Company	Production location
2,4-D acid, esters, and salts	Chempar	Portland, OR
	Miller Chemical, subsidiary of Alco Standards	Whitelord, MD
	Rhodia, Inc.	North Kansas City, KS St. Paul/Minneapolis, MN
	Thompson Chemical	St. Louis, MO
	Woodbury, subsidiary of Comutrix	Orlando, FL
2,4-DB and salts	Rhodia, Inc.	North Kansas City, MO St. Paul/Minneapolis, MN

a--Source: Dinsdale et al. 1980

DMPA—

The chemical name for DMPA is O-(2,4-dichlorophenyl) O-methyl isopropylphosphoramidothioate (Merck Index 1978). Some of the relatively higher chlorodioxins (hexa-, hepta-, and/or octachlorodioxins) were detected at ppm levels in at least one DMPA sample analyzed in 1972 (Helling et al. 1973).

The following is the structure for DMPA.



DMPA

Synthesis of this molecule involves the methanolysis of O-(2,4-dichlorophenyl) phosphorodichlorothioate, which is made through the phosphorylation of dichlorophenol (U.S. Patent Office 1960; Blair, Kaner, and Kenaga 1963).

DMPA is known commercially as Zytron, K-22023, and Dow 1329 (Merck Index 1978). It is useful as an insecticide, especially against houseflies (Blair, Kaner, and Kenaga 1963). It is also useful as a herbicide for controlling the growth of undesirable plants (U.S. Patent Office 1963; Merck Index 1978). DMPA is not believed to be produced in large amounts. Currently three companies – Dow

Silvex is available either as the acid or esters and salts of the acid. The low-volatility esters are probably the form most widely used.

TCDD's were detected (1.4 ppm) in one of seven silvex samples manufactured between 1965 and 1970 and analyzed in 1972; no other dioxins were detected (Woolson, Thomas, and Ensor 1972; Kearney et al. 1973b).

The following are recent producers of silvex as listed in the 1978 Stanford Research Institute Directory of Chemical Producers:

Dow Chemical Company—Midland, Michigan

North American Phillips, Thompson Hayward Chemical, subsidiary—Kansas City, Kansas

Riverdale Chemical—Chicago Heights, Illinois

Vertac, Inc., Transvaal, Inc., subsidiary—Jacksonville, Arkansas

Hercules, Inc., of Wilmington, Delaware, is a former producer (U.S. Tariff Commission 1965). The 1978 EPA pesticide files indicate that more than 300 products or formulations containing silvex are registered (U.S. Environmental Protection Agency 1978f).

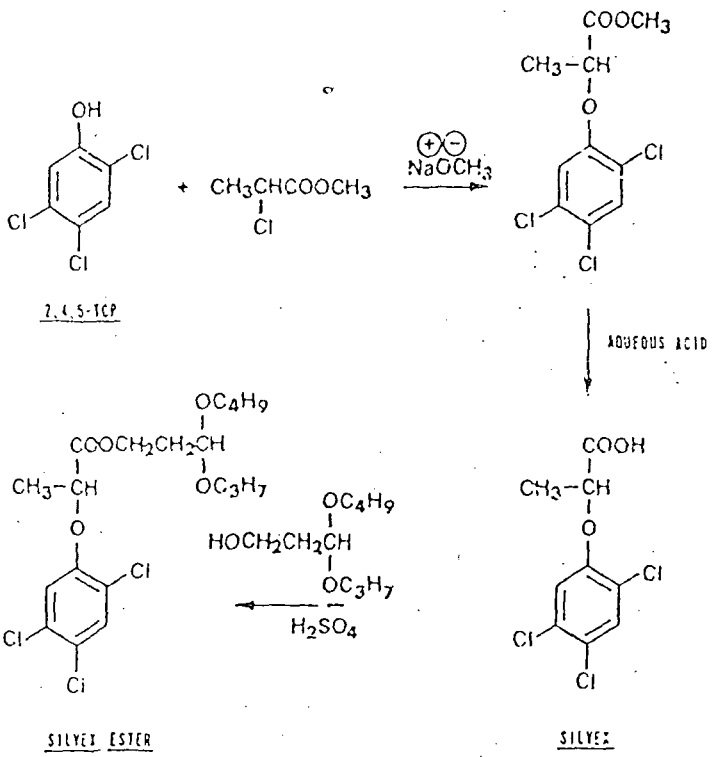
Silvex manufacture is more complex than that of other 2,4,5-TCP derivatives. The compounds sold commercially are usually complex esters, made from a specialized alcohol and silvex acid. The final manufacture of the ester is well documented in a process patent (U.S. Patent Office 1956a), as is the manufacture of the specialized alcohol. No definitive information has been found, however, on manufacture of the silvex acid, probably because compounds of this type can be manufactured by a long-established chemical reaction that is used in many categories of the organic chemical industry (J. Am. Chem. Soc. 1960). Silvex acid would be the source of any dioxins in commercial silvex products (see Figure 14, p. 60). The figure on the following page illustrates the most likely chemical reaction that would form the silvex acid and also shows the subsequent esterification, as described in the patent.

In the first step, 2,4,5-TCP is probably brought into reaction with the methyl ester of 2-chloropropionic acid, with methanol as the solvent and sodium methoxide as a reaction aid. This reaction would occur approximately at the boiling temperature of methanol, which is 65° C. The resulting compound would probably be separated from the reaction mixture by treatment with acidified water followed by extraction with a chlorinated hydrocarbon.

The addition of more acidified water to the extractant and a subsequent evaporation at a temperature near 108° C would hydrolyze the intermediate compound and also would drive off the chlorinated hydrocarbon for recycle and the methanol by-product to be reclaimed for other uses. The resulting compound is 2-(2,4,5-trichlorophenoxy) propionic acid, which is known to be a reactant in the subsequent processing (U.S. Patent Office 1956a).

Other methods could be used to prepare this intermediate acid, but none of them would utilize high temperatures or unusual solvents. The use of a strongly alkaline hydrolysis step, rather than an acidic medium, is possible. In any method, the last step is probably another solvent extraction using 1,2-dichloroethane to prepare the mixture for the next operation.

Silvex acid can be converted to various esters by using selected ether alcohols. The esterification steps are identical except for variations in the alcohol raw material. In a solvent of 1,2-dichloroethane, with concentrated sulfuric acid as a reaction aid, the intermediate acid is mixed with an ether alcohol. In the following example, butoxypropoxypropanol is used. The mixture is held at about 95°C for about 7 hours. During this period, the water formed in the reaction is removed by passing the reflux condensate through a decanter. At the end of the reaction, the product is present as an insoluble precipitate, which is filtered from the mixture, washed with sodium carbonate solution, and vacuum-dried at about 90° C.



Although complete data are unavailable, no information indicates that temperatures greater than 100° C would occur at any step in the manufacture of acidic silvex or its esters. It is therefore unlikely that dioxin compounds would be created as side reaction products.

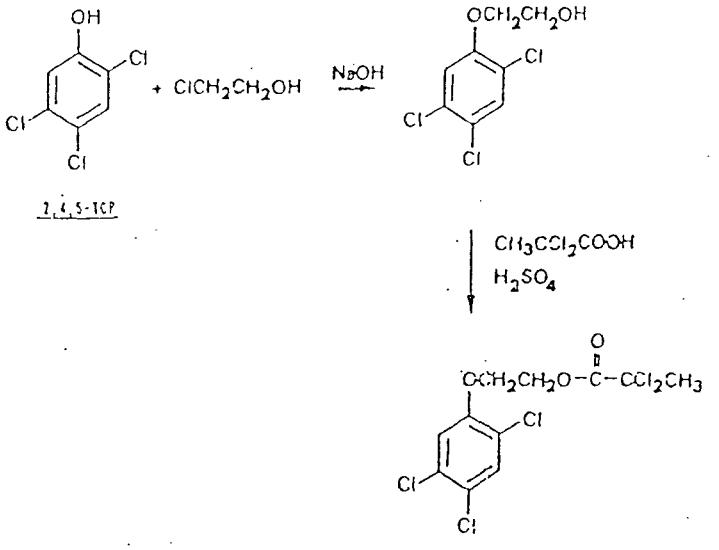
Absence of detailed information makes it impossible to establish whether dioxin contamination would carry through from the 2,4,5-TCP raw material into the final product. Theoretical considerations do not permit an estimation of the degree of purification required by the various intermediate compounds. Probably, as noted above, at least two solvent extraction operations are used to separate the principal processing materials from water solutions. Since TCDD's are very slightly soluble in chlorinated organic solvents, some could be carried through these operations, but most should be rejected.

Erbon—Very little information is available on erbon, which is derived from 2,4,5-trichlorophenol. Analysis of one erbon sample produced in 1970 indicated more than 10 ppm octachlorodioxin (Woolson, Thomas, and Ensor 1972). Tetra-, penta-, hexa-, and heptachlorodioxins were not detected (0.5 ppm limit of detection).

In 1978, nine companies had registered 17 products containing erbon (U.S. Environmental Protection Agency 1978). Dow is probably the only producer of the basic chemical. The other companies are most likely formulators who obtain their basic erbon ingredient from Dow. The volume of erbon produced annually is not known.

This herbicide is an ester based on 2,4,5-TCP. Although the initial manufacturing step is not reported, the first intermediate is almost identical to that

used to make sesin. General organic chemical references indicate that it is probably made by an initial reaction of 2,4,5-TCP with ethylene chlorohydrin (March 1968). Water is the most likely solvent, made strongly alkaline with sodium hydroxide, and the intermediate probably precipitates on addition of acid and is filtered from the solution and dried. A process patent (U.S. Patent Office 1956b) discloses that the second reaction step is a combination of the intermediate with 2,2-dichloropropionic acid in a solution of ethylene dichloride (1,2-dichloroethane), with addition of a small amount of concentrated sulfuric acid to remove the water formed in the reaction. These chemical reactions are shown by the following sequence drawing:



ESION

The resulting reaction mixture is partially purified by washing with water and is then fractionally distilled under vacuum to recover ethylene dichloride for recycle and possibly to separate the product from any impurities.

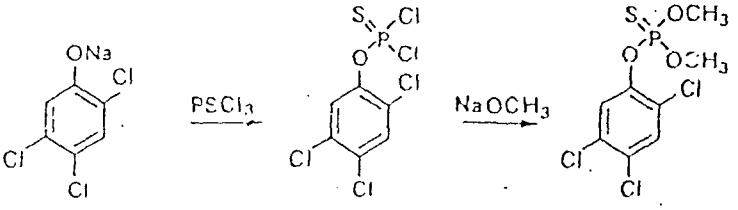
The first step of the reaction is the one that could possibly form dioxins (see Figure 16, p. 62). Both the raw material and the resulting intermediate contain a chlorine atom ortho to a ring-connected oxygen atom, and the mixture is heated with sodium hydroxide. Temperatures are not high, however, since water is probably the solvent used and this simple reaction ordinarily does not require application of pressure. Dioxin formation could occur at the surface of steam coils if high-pressure steam is used for distillation.

Apparently no operation other than the final distillation would remove any dioxin contamination from this material. Since the most likely impurities would be more volatile than the final ester, even the distillation may not serve to isolate dioxins into a waste stream. Most dioxins either formed by the process or present in the raw material would probably be collected with the final product.

Ronnel—The chemical name of ronnel is 0,0-dimethyl 0-(2,4,5-trichlorophenyl) phosphorothioate. This insecticide is also known by such names as fenchlorfos, Trolene, Etrolene, Nankor, Korlan, Viozene, and Fetoral (Merck Index 1978).

Ronnel is effective in the control of roaches, flies, screw worms, and cattle grubs (Merck Index 1978). In 1972, highly chlorinated dioxins were detected at ppm levels in an unknown number of ronnel samples (Woolson, Thomas, and Linsor 1972).

The manufacture of ronnel is a two-step process (U.S. Patent Office 1952) in which Na-2,4,5-TCP is reacted first with thiophosphoryl chloride, then with sodium methoxide. The chemical reactions are shown below:



Na-2,4,5-TCP

RONNEL

In the first step, dry Na-2,4,5-TCP is added to an excess of thiophosphoryl chloride (2 to 4 times the theoretical amount) and heated slightly, perhaps to 80° C. Sodium chloride is formed as an insoluble precipitate; it is filtered from the mixture and discarded. The clear filtrate is vacuum-distilled to recover the excess thiophosphoryl chloride for recycle and to fractionally separate the intermediate from side reaction impurities.

In a separate reaction vessel, metallic sodium is mixed with methanol. Hydrogen gas is liberated, creating a methanolic solution of sodium methoxide. This solution is mixed slowly with the purified intermediate while the mixture is maintained at approximately room temperature with noncontact cooling water.

When measured amounts of both reactants have been combined, the mixture is held for a period of time to ensure completion of the reaction. A nonreactive organic solvent is then used to extract the product from a mixture of methanol, excess sodium methoxide, and byproduct sodium chloride. Suitable extraction solvents are carbon tetrachloride, methylene dichloride, and diethyl ether. The extraction solvent is decanted from the mixture, washed with water solutions of sodium hydroxide, and fractionally vacuum-distilled to separate the extraction solvent for recycle and to separate ronnel from side reaction byproducts.

Throughout this process, the temperature probably does not exceed 150° C. The highest temperature probably occurs in the base of the final distillation column. In theory, additional dioxins are not likely to be created by this process because of the absence of high temperature and pressure, although all other conditions meet the requirements for formation of 2,3,7,8-TCDD (see Figure 15, p. 61).

It appears even less likely that dioxins originally present in the Na-2,4,5-TCP raw material would be carried through into the product. If all the steps outlined above are properly conducted, some of the operations might isolate dioxins into waste streams. The solubility of dioxins in thiophosphoryl chloride is unknown; if they are insoluble, they would be removed with the first filtration. Because the solubility of dioxins in chlorinated methanes is very slight (0.37 g/liter for TCDD in chloroform), much of the dioxin present would not be captured by the extraction solvent and would be carried away with the methanol reaction solvent. Distillations afford two other opportunities to isolate dioxin contaminants into waste organic fractions. Although the probability of dioxins carrying through into the final product appears slight, definitive information is not recorded.

Ronnel is reportedly produced by only one company—Dow Chemical Company, Midland, Michigan (Stanford Research Institute 1978). Annual production volume is not known. It is found in over 300 pesticide formulations registered by more than 100 companies.

Chlorophenol Derivatives with Unconfirmed Dioxin Content

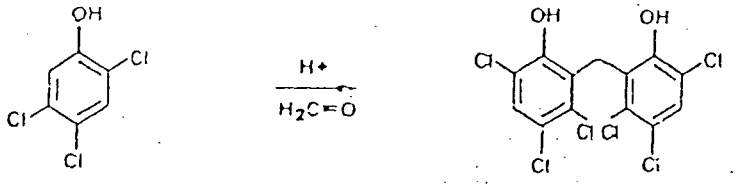
This subsection deals with several other chlorophenol derivatives that may contain dioxins. The compounds discussed include those that have been analyzed for dioxin content with negative results and also those for which analytical data have not been reported.

Hexachlorophene—

Hexachlorophene is known chemically as either bis-(3,4,6-trichloro-2-hydroxyphenyl) methane, or 2,2'-methylene-bis (3,4,6-trichlorophenol). It is also known commercially as G-11 (Cosmetic, Toiletry, and Fragrance Association, Inc. 1977). Hexachlorophene is an effective bactericide and fungicide. Prior to 1972 it was widely advertised and distributed as an active constituent of popular skin cleansers, soaps, shampoos, deodorants, creams, and toothpastes (Wade 1971; U.S. Dept. HEW 1978). Although its use has been considerably restricted by the Food and Drug Administration, it still may be used as a preservative for cosmetics and over-the-counter drugs; the concentration is restricted to 0.1 percent in these products. Skin cleansers containing higher levels may also be sold but only as ethical pharmaceuticals, available by medical prescriptions (U.S. Code of Federal Regulations Title 21 1978). As an agricultural pesticide, hexachlorophene is a constituent of formulations used on three vegetables and on some ornamental plants for control of mildew and bacterial spot. It is also used in limited industrial and household applications as a disinfectant.

The grade of hexachlorophene produced today is reported to contain less than 15 μg/kg (< 15ppb) 2,3,7,8-TCDD (World Health Organization 1977). In a 1972 analysis, dioxins could not be detected in hexachlorophene at a detection limit of 0.5 mg/kg (0.5 ppm) (Helling et al. 1973).

Four process patents have been issued on manufacture of hexachlorophene, and all are variations of the following chemical reaction.



2,4,5-TCP

Hexachlorophene

Hexachlorophene is formed by reacting one molecule of formaldehyde with two molecules of 2,4,5-TCP at elevated temperatures in the presence of an acid catalyst (Moye 1972). The patented processes differ in temperature, reaction time, order of reagent additions, reaction solvents, and other physical parameters.

In the first process, patented in 1941, methanol is the solvent and large amounts of concentrated sulfuric acid are used to bind the water that is formed as a reaction byproduct; the process takes place at 0° to 5°C over a 24-hour period (U.S. Patent Office 1941). A second patent issued in 1948 discloses that the methanol solvent is

eliminated and the reaction is conducted with paraformaldehyde at an elevated temperature (135° C) over a 30-minute period (U.S. Patent Office 1948). A 1957 patent reintroduces a solvent, which is one of several chlorinated hydrocarbons (U.S. Patent Office 1957d). Temperature is 50° to 100° C, and reaction time is 2 to 3 hours. Oleum (sulfuric acid plus SO_3) is used as the catalyst and concentrated sulfuric acid is recovered as the byproduct. Finally, a 1971 patent revises the order of reagent addition and also emphasizes the chemical reaction mechanism (U.S. Patent Office 1971). The last-mentioned process is probably the one in present use; its processing sequence is shown in Figure 32.

Patent information indicates that older manufacturing methods probably reclaimed the product from the reaction mixture by neutralizing the sulfuric acid with sodium hydroxide, which would have created a rather large amount of brine waste. In modern processes, conditions are probably maintained so that the residual sulfuric acid separates as a distinct liquid layer when agitation of the mixture is stopped after completion of the reaction. This acid, which contains the water formed during the reaction, is decanted from the mixture; it is strong enough to be used elsewhere in the plant complex, although it probably cannot be used in subsequent hexachlorophene batches.

In the patent examples, the organic layer that remains after the acid is removed is mixed with activated carbon, which is then filtered from solution. The purpose of this treatment is to remove colored impurities. The clear filtrate is then chilled to approximately 0° C; crystals of hexachlorophene precipitate and are filtered from solution, dried, and packaged. The filtrate, which would contain some hexachlorophene, is probably directly recycled for use in succeeding batches.

There is no indication that dioxins would be formed during the production of hexachlorophene, since highly acidic conditions are maintained throughout the process and temperatures are well below those known to be needed for dioxin reactions (Hambrough 1974). If dioxins are found in hexachlorophene, the most likely explanation for their presence is that contamination in the 2,4,5-TCP raw material is carried through into the final product (see Figure 27, p.74). In a situation identical to that of the 2,4,5-T process, the patent descriptions show the possibility of activated carbon adsorption, which could cause accumulation of dioxins into an extremely hazardous waste. If carbon adsorption is not used in commercial practice or if it is not totally effective, any dioxins in the raw material will either appear in the hexachlorophene product or be recycled to succeeding batches. Although dioxins are not known to be soluble in sulfuric acid, they might be carried out of the process with the acid byproduct; if this were the case, dioxins could then appear in other products of the plant in which the sulfuric acid is utilized.

Givaudan Corporation in Clifton, New Jersey, is apparently the only active U.S. producer of hexachlorophene. Until 1976, the 2,4,5-TCP for hexachlorophene manufacture was produced by Givaudan's ICMESA plant in Seveso, Italy, and shipped to New Jersey for conversion. In 1976, Wright State University analyzed two representative samples of this trichlorophenol and found 1.8 and 1.9 ppb TCDD's (Hiernan 1976). An accident in 1976 closed the ICMESA plant and eliminated Givaudan's primary supply of 2,4,5-TCP. (For further details of the ICMESA incident see Section 5, p. 168). It is now believed that all the 2,4,5-TCP for hexachlorophene manufacture is supplied by Dow Chemical Company and that Givaudan specifies an extremely low dioxin content. In 1978, five waste samples from the Clifton plant were analyzed for chlorinated dioxins. None were found at a 0.1 ppm level of detection (U.S. Environmental Protection Agency 1978d). Subsequent analysis of three of these samples found no TCDD's at 0.1 or less ppb (see Section 4 of this report).

About 400 commercial products containing hexachlorophene have been marketed recently, in pesticide, drug, cosmetic, and other germicidal formulations. The annual production volume of the germicide is not reported.

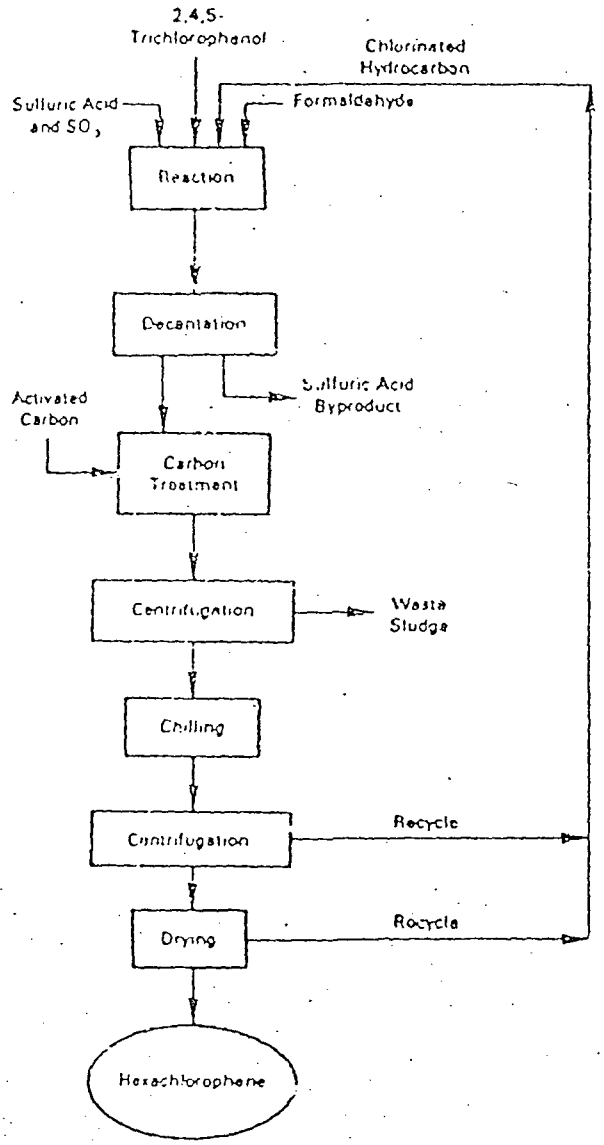
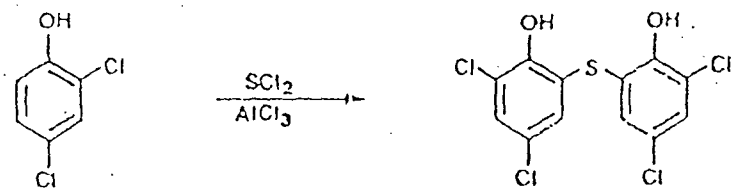


Figure 32. Flow chart for hexachlorophene manufacture

Bithionol—

Bithionol (2,2'-thio-bis[4,6-dichlorophenol]) is an antimicrobial agent that was approved at one time for drug use by the U.S. Food and Drug Administration. This approval was withdrawn in October 1967 because the chemical was found to produce photosensitivity among users (Kimbrough 1974, Merck Index 1978). The U.S. EPA continues to approve its use as a pesticide in three animal shampoo formulations. These formulated bithionol products may no longer be actively marketed, however, because the single basic source of this chemical (Sterling Drug's Dilton-Davis Chemical Co.) apparently no longer produces it (Chem Sources 1975; Stanford Research Institute 1977).

The manufacture of bithionol is a one-step reaction between 2,4-dichlorophenol and sulfur dichloride (U.S. Patent Office 1962, U.S. Patent Office 1958b). Carbon tetrachloride is used as the solvent and a small amount of aluminum chloride serves as the catalyst. Bithionol is formed in a reaction at about 50° C; batch time is about 2 hours. The chemical reaction is shown below.



BITHIONOL

Two methods of product recovery are outlined in one process patent (U.S. Patent Office 1958b). In one method, water is added and impure bithionol precipitates. To form a crude product, it is necessary only to filter the solids from the mixture and wash them several times in water and cold carbon tetrachloride. They are then dried and packaged.

Alternatively, to recover a purified product, water is added and the mixture is distilled to remove the carbon tetrachloride for recycle. Bithionol collects as an organic sediment, which is separated from the water solution by decantation, washed with water and sodium bicarbonate, vacuum-dried, redissolved in hot chlorobenzene, filtered, chilled to precipitate bithionol, and again filtered.

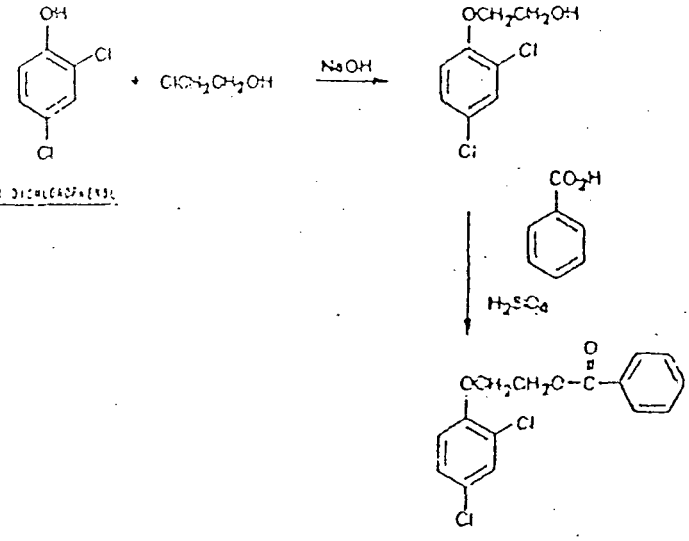
A separate patent outlines a procedure for forming metallic salts of bithionol, which are compounds that permanently impregnate cotton fabrics with disinfectant properties (U.S. Patent Office 1962). The process uses sodium hydroxide and various metallic salts in room-temperature reactions with water as the solvent.

This manufacturing operation apparently provides no potential for production of dioxins by the known process of dioxin formation. In the manufacture of crude bithionol, there is no opportunity to react any dioxins that may be present in the 2,4-dichlorophenol raw material. They would be carried through into the final product.

If bithionol is purified by the process outlined above, one filtration operation would remove compounds that are insoluble in hot chlorobenzene. Some dioxins, however, are slightly soluble in this solvent and thus might persist even in purified bithionol or its salts.

Sesin —

Sesin is an ester based on 2,4-dichlorophenol. The manufacture is similar to that of erbon, a 2,4,5-TCP-based herbicide described earlier. Although details of the first process step have not been reported, general organic chemical references indicate that sesin manufacture probably begins by a reaction between 2,4-dichlorophenol and ethylene chlorohydrin, as shown in the reaction sequence that follows (March 1968). Water is the most likely solvent, made strongly alkaline with sodium hydroxide, and the intermediate probably precipitates on addition of acid and is filtered from solution and dried.



2,4-DICHLOROPHENOL

SESIN

A process patent discloses that the second reaction step is a combination of the intermediate with benzoic acid (U.S. Patent Office 1956d). Xylene is the solvent, and a small amount of sulfuric acid is used to remove the water formed in the reaction.

The resulting reaction mixture is neutralized with sodium carbonate and is then fractionally distilled under vacuum to recover the xylene for recycle and possibly to separate the product from any impurities.

The first step of the reaction is the one that could possibly form dioxins. Both the raw material and the resulting intermediate contain a chlorine atom ortho to a ring-connected oxygen atom, and the mixture is heated with sodium hydroxide. High temperature is not present, however. Since water is probably the solvent, this simple reaction would not ordinarily require application of pressure. Dioxin formation could occur at the surface of steam coils if high-pressure steam is used for distillation.

Apparently no operation other than the final distillation would remove any dioxin contamination from this material. Even this distillation may not isolate dioxins into a waste stream. Most dioxins either formed by the process or present in the raw material would probably be collected with the final product.

Trichlorophenol Piperazine--

A pharmaceutical compound can be made from commercial 2,4,5-trichlorophenol for use as an anthelmintic (deworming medication) (U.S. Patent Office 1961a, Short and Ebinger 1962). The research and animal tests of this drug were conducted prior to 1962 with unpurified commercial-grade 2,4,5-TCP. The drug was made by dissolving the chlorophenol in warm benzene and adding a measured quantity of piperazine. The resulting solution was filtered to remove insoluble matter, diluted with petroleum ether, and chilled. Crystals of the drug precipitated and were filtered from the mixture, washed with petroleum ether, dried, and packaged in gelatin capsules.

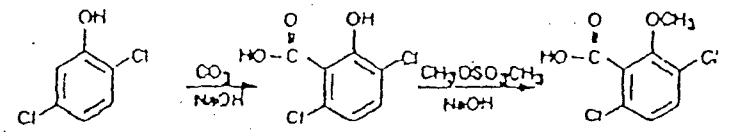
If this drug is being manufactured, the volumes are very low because it is not listed in most pharmaceutical trade references. Manufacture would probably be by the same process used in the laboratory, probably in very small batches, and with equipment not much larger than standard laboratory apparatus.

Any dioxins present in the TCP raw material are probably discharged in plant wastes rather than being concentrated into the pharmaceutical. Most of the dioxin probably is filtered from the benzene solution as part of the insoluble matter. Since some dioxins are slightly soluble in both benzene and petroleum ether, a portion might remain in solution and be transferred to solvent recovery distillation columns. The remaining dioxin would be discarded as part of an anhydrous tar from the base of these columns. The pharmaceutical industry usually incinerates both solid organic residues and solvent recovery tars.

Dicamba--

The herbicide dicamba is a derivative of salicylic acid known chemically as 3,6-dichloro-2-methoxybenzoic acid. In 1972, analysis of eight samples indicated no tetra-, hexa-, or hepta-CDDs at a detection level of 0.5 ppm (Woolson, Thomas, and Ensor 1972). The presence of DCDDs is theoretically possible, however (see Figure 23, p. 70).

Dicamba is made by acylation of 3,6-dichlorosalicylic acid, which in turn is made from 2,5-dichlorophenol. The chemical reactions are shown below.



2,5-Dichlorophenol

Dicamba

The first step is known as the Kolbe-Schmitt reaction and is also used to make unsubstituted salicylic acid from unsubstituted phenol in addition to halogenated derivatives (U.S. Patent Office 1955a). Operating temperature is probably below 200° C, and operating pressure is probably greater than 8 atmospheres. The chlorinated salicylic acid is mixed into water and sodium hydroxide and treated with dimethyl sulfate (U.S. Patent Office 1967a). The reaction is conducted initially with refrigeration to retard the otherwise violent reaction, the mixture is then heated for a few hours at reflux temperature (slightly above 100° C).

On completion of the reaction, the mixture is acidified with hydrochloric acid. Dicamba precipitates and is filtered from the mixture, rinsed with water, and dried. Recrystallization from an organic solvent such as ether is possible, but probably is not conducted in commercial practice.

Except for high temperature, all conditions necessary for formation of chlorinated dioxins are present. It is likely that at high temperature dicamba would

lose carbon dioxide in a reversal of the initial manufacturing reaction, and any dioxins formed would not contain carboxyl groups.

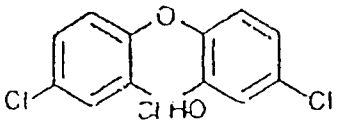
Dicamba is reported to be made by Velsicol Chemical Corporation in Beaumont, Texas, under the trade name Banvel (Stanford Research Institute 1978). It is commercially available in many formulated pesticide products.

Other Chlorophenol Derivatives -

Compounds other than the products listed above are also potential dioxin sources, but are made and used in smaller volumes.

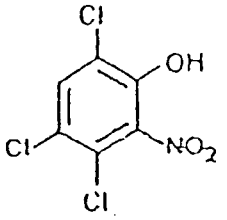
A compound with the trade name of Irgasan DP300 is used as a bacteriostat and a preservative. Often described by the generic abbreviation TCS, it is an acid-amide derivative of a chlorinated salicylic acid, made by first reacting 2,4-dichlorophenol with sodium hydroxide and carbon dioxide at high pressure, then reacting the resulting intermediate with 3,4-dichloroaniline (U.S. Patent Office 1955a).

The pesticide Irgasan DP-300 is a predioxin that was once sold in this country by Ciba-Geigy Corporation. As outlined in Section 2, it was used in some of the research of chlorinated dioxin chemistry, and dioxins were formed readily on heating of this compound. Its chemical formula is as follows:



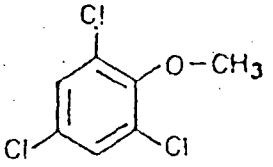
This compound is a derivative of 2,4-dichlorophenol, although the process of manufacture has not been reported.

The formulation called Dowlap was once used in the Great Lakes to control the sea lamprey, an eel-like fish. The active ingredient of the formulation was 3,4,6-trichloro-2-nitrophenol, whose chemical formula is as follows:



This compound was made by direct nitration of 2,4,5-trichlorophenol using concentrated nitric acid in a solvent of glacial acetic acid (Merck Index 1978).

A dye assistant chemical for use with polyester fibers was once made with the trade name Tyrene (Merck Index 1978). Its chemical name is 2,4,6-trichloroanisole or 2,4,6-trichloromethoxybenzene, with a structural formula as follows:



It was probably made by acylation of 2,4,6-trichlorophenol with dimethyl sulfate.

Dioxins in Chlorophenol Production Wastes

Although the dioxin content of many products containing chlorophenols or their derivatives has been reported in the literature, little information is available on dioxins in the industrial wastes created by chlorophenol manufacture. One unpublished report (U.S. Environmental Protection Agency 1978d) describes analysis for dioxins in 20 samples of liquid wastes from plants manufacturing trichlorophenol, pentachlorophenol, and hexachlorophene. The limit of detection was 0.1 ppm. No TCDD's were detected in any of the samples. Hexa-, hepta-, and octachlorodioxins were found in the pentachlorophenol wastes. The report does not indicate clearly whether any of the higher chlorodioxins were found in the hexachlorophene wastes.

Considerations of solubility and volatility suggest that large concentrations of dioxins will be found in the still bottom wastes from 2,4,5-TCP manufacture. Direct analytical evidence to this effect, though limited, is affirmative. Waste oils identified as early 1970 still residues from a former 2,4,5-TCP manufacturing plant in Verona, Missouri, have been analyzed and reported to contain ppm quantities of 2,3,7,8-TCDD (Johnson 1971, Commoner and Scott 1976a). A toluene still bottom waste taken from Transvaal's plant in Jacksonville, Arkansas, has recently been found to contain 40 ppm of TCDD'S (Watkins 1979, also see Section 4 of this report).

The effect of biological treatment on removal of dioxins from liquid industrial wastes is not known. In 1978, the Dow Chemical Company reported that no 2,3,7,8-TCDD could be detected in 13 of 14 grab and composite samples from the secondary and tertiary outfall of its manufacturing plant, which produces large quantities of 2,4,5-TCP, 2,4,5-T, and other chlorophenolic compounds; one sample was questionable. The reported level of detection ranged from 1 to 8 ppt. No information is given on the dioxin content of the untreated waste stream or on the treatment methods.

Apparently it has been common practice for chemical manufacturers to dispose of dioxin-contaminated wastes or other toxic chemical wastes by landfill. Either liquid or solid forms of the wastes are placed in drums and stored or buried. Dioxin wastes disposed of in this manner would be expected to be quite concentrated. Recently ppt to ppb levels of TCDD's were reported in environmental samples from two landfills in Niagara Falls, New York (Chemical Week 1979). Hooker Chemical reportedly has dumped a total of 3700 tons of 2,4,5-trichlorophenol wastes over the past 45 years in these two dumps (Hyde Park and Love Canal) and in one other disposal site on the company's Niagara Falls property. The report estimated that the wastes buried in these landfills could contain over 100 pounds of TCDD'S.

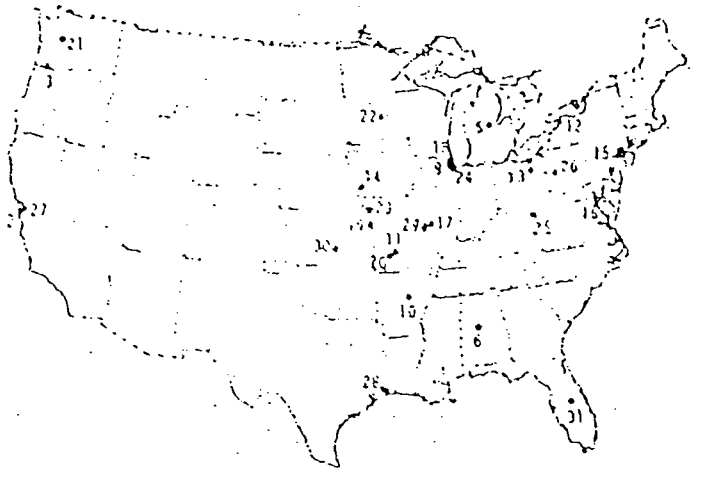
At the Transvaal pesticide plant in Jacksonville, Arkansas, more than 8000 barrels of dioxin-contaminated wastes are stored on the plant property (Eadsman 1979). The total quantity of TCDD present in the wastes has not been estimated.

No other known information describes the quantities of dioxins that might be buried elsewhere in the United States. In an effort to identify areas where landfills are most likely to contain large dioxin wastes, Figure 33 illustrates the locations where chlorophenols and their derivatives are now or were formerly produced. A list of these locations is presented in Table 19; note that this list does not include locations of the many companies that are believed only to formulate or otherwise merchandise the chlorophenols or their derivatives.

A detailed discussion of the methods used for disposal of dioxins is presented in Section 8. Additional information related to the environmental effects of dioxin disposal is presented in the subsection on Water Transport in Section 7.

HEXACHLOROBENZENE

In 1974, a technical paper reported the presence of OCDD in samples of commercial hexachlorobenzene (Villanueva et al. 1974). Three samples were



1. Philadelphia, PA
2. San Mateo, CA
3. Portland, OR
4. Cleveland, OH
5. Midland, MI
6. Tuscaloosa, AL
7. Linden, NJ
8. Clifton, NJ
9. Naperville, IL
10. Jacksonville, AR
11. Springfield, MO
12. Niagara Falls, NY
13. Dover, OH
14. Shenandoah, IA
15. Rahway, NJ
16. Whitelord, MD
17. Sauget, IL
18. Chicago, IL
19. Kansas City, KS
20. Verona, MO
21. Tacoma, WA
22. St. Paul, MN
23. St. Joseph, MO
24. Chicago Heights, IL
25. Nitro, WV
26. Amelor, PA
27. Fremont, CA
28. Port Neches, TX
29. St. Louis, MO
30. Wichita, KS
31. Orlando, FL

Figure 33. Locations of current and former producers of chlorophenols and their derivatives

TABLE 19. LOCATIONS OF CURRENT AND FORMER PRODUCERS OF CHLOROPHENOLS AND THEIR DERIVATIVES[a]

Producer	Location	Chemical Type
Alco Chemical Corp	Philadelphia, PA	2,4-D
J. H. Baxter and Company	San Mateo, CA	PCP
Champar	Portland, OR	2,4,5-T 2,4-D
Diamond Shamrock Corp	Cleveland, OH	2,4,5-TCP 2,4,5-T 2,4-D
Dow Chemical Company	Midland, MI	2,4,5-TCP 2,4,6-TCP 2,3,4,6-Tetrachlorophenol 2,4-D 2,4,5-T Silvex Bonnel Erbon DIMPA
Fallei-Lankro Corp	Tuscaloosa, AL	2,4-D
GAF	Linden, NJ	2,4-D
Givaudan Corporation, Chemicals Division	Clifton, NJ	Hexachlorophene
Guth Corp.	Naperville, IL	2,4-D
Hercules, Inc.[b]	Jacksonville, AR	2,4-D Silvex 2,4,5-TCP
Hoffman-Taff, Inc	Springfield, MO	2,4,5-T
Hooker Chemical Corp Occidental Petroleum Corp., subsidiary	Niagara Falls, NY	2,4,5 TCP
ICC Industries, Inc. Dover Chemical Corp., subsidiary	Dover, OH	PCP
Imperial, Inc	Shenandoah, IA	2,4-D
Merck and Co., Inc.	Rahway, NJ	2,4,5-TCP
Miller Chemicals, Alco Steel subsidiary	Whiteford, MD	2,4-D

(continued)

TABLE 19. (continued)

Producer	Location	Chemical Type
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, IL	PCP 2,4,5-T 2,4-D
Nalco Chemical Co.	Chicago, IL	PCP 2,4,5-TCP
North American Phillips Corp., Thompson-Hayward Chemical Co., subsidiary	Kansas City, KS	2,4-D 2,4,5-T Silvex
North Eastern Pharmaceuticals	Verona, MO	2,4,5-TCP
PBI-Gordon Corporation[c]	Kansas City, KS	2,4-D 2,4,5-T
Private Brands, Inc.[c]	Kansas City, KS	2,4-D 2,4,5-T
Reichhold Chemicals, Inc.	Tacoma, WA	PCP
Rhodia, Inc. Agricultural Division	Portland, OR St. Paul, MN St. Joseph, MO	2,4-D 2,4-DB
Riverdale Chemical Co.	Chicago Heights, IL	2,4-D 2,4,5-T Silvex
Roberts Chemicals, Inc.	Nitro, WV	2,4,6-TCP
Rover-Amchem Amchem Products, Inc., Division[d]	Ambler, PA Fremont, CA St. Joseph, MO	2,4,5-T 2,4-D
Sanford Chemicals	Port Neches, TX	2,3,4,6-Tetrachlorophenol PCP
Thompson Chemicals	St. Louis, MO	2,4,5-T 2,4-D
Union Carbide Corp. Agricultural Products Division Amchem Products, Inc., subsidiary[e]	Ambler, PA Fremont, CA St. Joseph, MO	2,4-D 2,4,5-T
Vertac, Inc Transvaal, Inc., subsidiary[b]	Jacksonville, AR	2,4,5-TCP 2,4-D 2,4,5-T Silvex

(continued)

TABLE 19. (continued)

Producer	Location	Chemical Type
Vulcan Materials Co. Chemicals Division	Wichita, KS	PCP
Woodbury Comutrix subsidiary	Orlando, FL	2,4-D

a—Sources: Stanford Research Institute Directory of Chemical Producers, United States 1976, 1977, 1978, and 1979. U.S. Tariff Commission. Synthetic Organic Chemicals, United States Production and Sales 1968. U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales 1974, 1976, 1977, and 1978.

b—Hercules, Inc., was a former owner of the Jacksonville, AR, facility now owned by Vertac, Inc.

c—Private Brands, Inc., is believed to be a former owner of the Kansas City, KS, facility now owned by PBI-Gordon Corp.

d—Former Rover-Amchem facilities in Ambler, PA; Fremont, CA; and St. Joseph, MO, are now owned by Union Carbide Corp.

analyzed, two of which contained OCDD in concentrations of 0.05 and 211.9 ppm. All three contained octachlorodibenzofuran (OCDF) in concentrations of 0.34, 2.33, and 58.3 ppm. One sample contained a trace amount of heptachlorodibenzofuran. It was established that the principal impurity in these samples was pentachlorobenzene in amounts ranging from 0.02 percent to 8.1 percent. When the samples were examined qualitatively, 11 other impurities having polychlorinated ring-type structures were identified:

Octachlorobiphenyl
Decachlorobiphenyl
1-Pentachlorophenyl-1,2,3-dichloroethylene
Decachlorobiphenyl
Octachlorobiphenylene
Octachloro-1,1-bicyclopentadienylidene
Hexachlorocyclopentadiene
Nonachlorobiphenyl
Decachlorobiphenyl
Pentachloroiodobenzene
Heptachloropilium

It is significant that this list includes no phenolic compounds and no predioxins or isopredioxins. In fact, the only compounds in these samples that contain oxygen are dioxins and dibenzofurans.

Uses

Hexachlorobenzene is a registered pesticide formerly used to control a fungus infection of wheat. It is also a waste byproduct from manufacturing plants that produce chlorinated hydrocarbon solvents and pesticides (Villanueva 1974; U.S. Environmental Protection Agency 1978g). It can be used as a raw material in the manufacture of pentachlorophenol, but is not so used in this country.

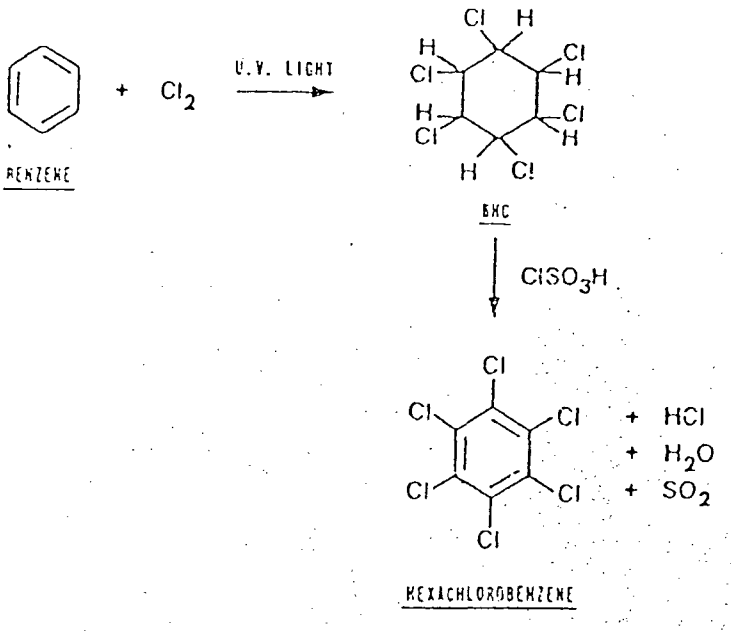
Hexachlorobenzene is not the same compound as benzene hexachloride. The empiric formula of hexachlorobenzene (HCB) is C_6Cl_6, and its structure is that of benzene in which all of the hydrogen atoms have been replaced with chlorine.

Benzene hexachloride (BHC) is the common name of hexachlorocyclohexane. Its empiric formula is $C_6H_6Cl_6$, and its structure results from direct addition of chlorine to benzene rather than from replacement of hydrogen. One stereoisomer of BHC, the gamma form, is a powerful insecticide, and its use in this country is severely restricted. It is still made, however, because BHC is an intermediate in the most common synthesis method of producing HCB.

Manufacture

In the manufacture of HCB, the first step is a photochlorination, in which chlorine gas is bubbled through benzene (Wertheim 1939; U.S. Patent Office 1955b). This occurs in a specialized reaction vessel fitted with a strong source of ultraviolet light. In a low-temperature reaction, the light catalyzes the conversion of approximately 25 percent of the benzene into a mixture of BHC isomers. This mixture is "crude" BHC, consisting of about 65 percent of the alpha isomer, 10 percent beta, 13 percent gamma, 8 percent delta, and 4 percent epsilon. It is separated by distilling off most of the excess benzene for recycle and then filtering the BHC crystals from the mixture.

All stereoisomers of BHC are equally suitable for the manufacture of HCB. The continuation of the process consists of mixing BHC with chlorosulfonic acid or sulfuryl chloride and holding the mixture at approximately 200° C for several hours (U.S. Patent Office 1957a). This step removes the hydrogen from BHC and thereby restores the unsaturated benzene ring. When the mixture is cooled, HCB precipitates and is separated by filtration, rinsed with water, dried, and packaged. The following shows the overall chemical reactions of the process.



Descriptions of these process steps provide no indication that dioxins are formed. The raw materials are benzene, chlorine, and chlorosulfonic acid, none of

which are likely sources of dioxins. The only reactant that could contribute the oxygen needed to complete the dioxin ring is chlorosulfonic acid, but in this compound the oxygen is tightly bound in a linkage with sulfur.

There is, however, a supplemental process that contributes other chemicals that may lead to dioxin formation. This extra step may be conducted at some plants, or may have been conducted in earlier years. If a market exists for the sale of gamma-BHC as an insecticide, this material is extracted from the mixture of crude BHC and benzene after most of the excess benzene has been distilled off for recycle. To this concentrated solution, water is added, along with other chemicals. The objective is to form an emulsion that will entrain part of the BHC. The solution is then filtered, the emulsion passes through the filter, while the solids that were not emulsified are captured. Since gamma-BHC accumulates preferentially in the emulsion, the solids from this first filtration are used for HCB manufacture and the filtrate is treated with salt to break the emulsion and then refiltered. The second crop of solids contains up to three times as much gamma-BHC as the crude product and is dried and sold separately (U.S. Patent Office 1955b).

As indicated by the process patent, chemicals added during this supplemental step include a wide range of organic detergents and solvents, but none of those listed are phenolic or have been shown to create dioxins. Detergents of the anionic type are preferred, especially salts of sulfonated succinic esters, although any of the common surface-active agents are suitable. Supplemental solvents may not be employed, since benzene alone is said to be preferred, but other suitable solvents include dioxanes, any of the aliphatic substituted benzenes, any of the common chlorinated paraffin hydrocarbons, kerosenes, and ethyl ether. Dioxane is the one compound listed that might contribute to dioxin formation, although the reaction is not reported in published literature.

Production

Current information on the volume of production of hexachlorobenzene is uncertain. Annual production estimates range from 420,000 to 750,000 pounds. Stauffer was the only reported domestic producer in 1974. Dover Chemical Company of Niagara Falls, New York, was the only reported producer in 1977 (U.S. Environmental Protection Agency 1978g). Dioxins have not been reported in any other chlorobenzene compounds.

OTHER PHENOLIC COMPOUNDS WITH DIOXIN-FORMING POTENTIAL

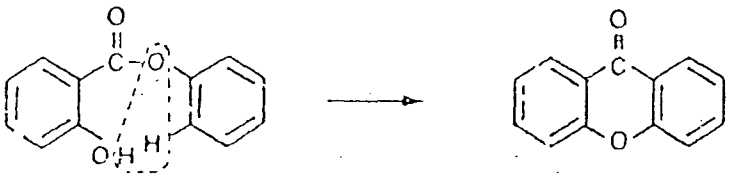
Several compounds with a phenol nucleus that do not contain chlorine are now being manufactured or were manufactured at one time. Four such compounds or classes of compounds are examined for their dioxin-forming potential in this section. (See also Table 7, page 38)

Brominated Phenols

Three brominated phenolic compounds were once manufactured, and may still be. Because brominated dioxins have been made in laboratory experiments, they may be created during the manufacture of these compounds.

Published data describe the production method for tetra-bromo-cresol, which is made by direct bromination of *o*-cresol in a solvent of carbon tetrachloride with aluminum and iron powders as catalysts (U.S. Patent Office 1943). The following reaction is conducted at room temperature, and it requires about 24 hours to complete a batch

into phenol and carbon dioxide, but also into smaller amounts of phenyl salicylate, which in turn condenses to xanthone:



PHENYL SALICYLATE XANTHONE

Since the ortho carbon is held weakly in the salicylic acid molecule, and since the triple-ring xanthone structure has been identified, the formation of dioxins may also be possible, especially if oxygen is present.

Both salicylic acid and xanthone are widely distributed in nature. Salicylic esters are responsible for some plant fragrances, and xanthone is a yellow pigment in flowers.

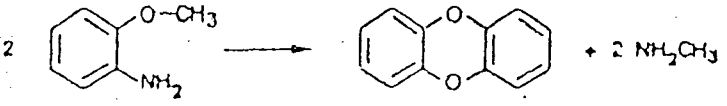
Salicylic acid is manufactured by four companies in this country:

Dow Chemical Company - Midland, Michigan
Monsanto Company - St. Louis, Missouri
Hilton-Davis Chemical Company - Cincinnati, Ohio
Tenneco Chemicals, Inc. - Garfield, New Jersey

The combined capacity of these four plants is 24 million kilograms annually.

Aminophenols

The o-aminophenols could conceivably form dioxins through condensation with loss of ammonia. These are not high-volume chemicals and are not known to be made with halogen substituents. A class of related compounds is used in much larger quantity; these are the derivatives of o-anisidine (methoxyaminobenzene), which in several forms are important dye intermediate chemicals. These might condense in appropriate environments into the dioxin structure through loss of methylamine. The environments would probably be acidic.

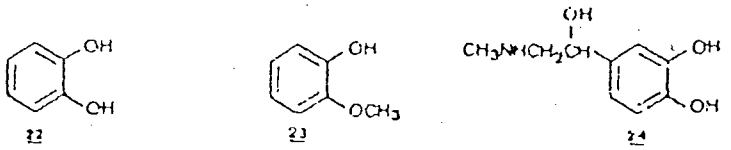


Although this reaction is possible, it is unlikely because the amine group is tightly bound to the benzene ring. Aminophenols or similar compounds are not likely sources of dioxin contamination.

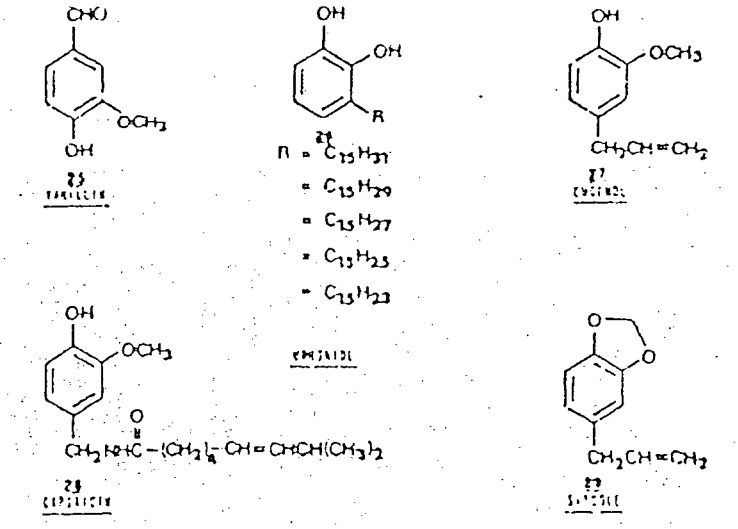
DIOXINS IN PARTICULATE AIR EMISSIONS FROM COMBUSTION SOURCES

Recent reports by chemists at the Dow Chemical Company maintain that dioxin formation is a natural consequence of combustion (Dow 1978). There are

numerous naturally occurring compounds that could, during the complex process of combustion, serve as precursors of dioxins. Combustion of these compounds in the presence of chlorine-containing compounds (e.g., DDT or polyvinyl chloride) could lead to the formation of chlorinated dioxins. Examples of such naturally occurring "potential" dioxin precursors are given below.

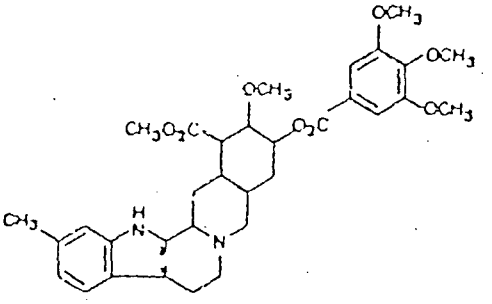


Catechol (22) occurs in nature as the product of phenol biodegradation and as a major product of tannin pyrolysis (Wertheim 1939). Guaiacol (23) occurs as the major phenolic component in several hardwood trees and is also prepared synthetically for use as an ingredient in cough syrups (Merck 1978; U.S. EPA Draft 1979). Adrenaline (24) is a naturally occurring mammalian hormone and is also prepared synthetically for use in many drug formulations (U.S. EPA Draft 1979). Other naturally occurring compounds that contain the orthohydroxy or alkoxy groups include vanillin (25), which is the flavoring ingredient in vanilla extract, urushiol (26), a mixture of compounds that are the toxic constituents of poison ivy, eugenol (27), the pungent principle of cloves; capsaicin (28) the pungent principle of various peppers; and safrole (29), the major volatile constituent of sassafras.



Among many plant alkaloids that include the structure are reserpine (30), glaucine (31), and colchicine (32). Other potential dioxin precursors are found in the fomecin (33) series of antibiotics, produced by a fungus, and also in one of the active ingredients of creosote.

A constituent of animal urine is 4-hydroxy-3-methoxymandelic acid (Merck Index 1978). Since the structure is so common in living organisms, it is also often used in synthetic medicinal compounds, including phenisomone, isoproterenol, estil (an anaesthetic), methocarbanol, and the high-volume drugs guaifenesin and methyldopa (U.S. Environmental Protection Agency 1979)



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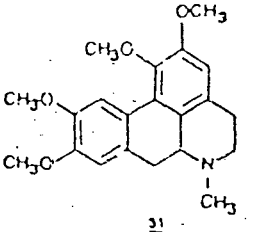
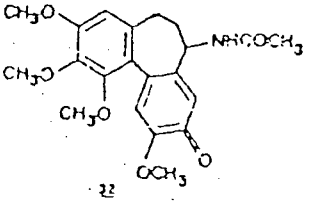
RESERPINE



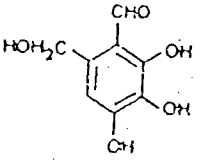
31

GLAUCINE



32

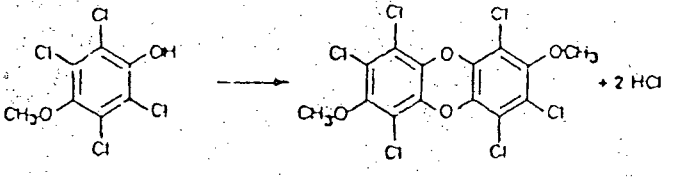
COLCHICINE



33

FOMECIN

At least one natural compound may be by itself a precursor for a chlorinated dioxin. A microorganism species creates a defensive chemical known as drosophylin A (34), (p-methoxytetrachlorophenol) (Merck Index 1978). In theory it could, when heated, form a substituted hydroxy or methoxy chlorinated dioxin, one possibility of which is:



34

DROSOPHYLLIN A

Several reports describe the occurrence of dioxins in fly ash and flue gases from municipal incinerators and industrial heating facilities. In 1977, analysis of samples of fly ash from three municipal incinerators in the Netherlands showed 17 different dioxins (5 TCDD's, 5 penta-CDD's, 4 hexa-CDD's, 2 hepta-CDD's, and OCDD) (Olie, Vermeulen, and Hutzinger 1977). Although the specific number of isomers was not stated, the same dioxins were found in flue gas from one of the incinerators. In addition, large amounts of di-, tri-, and tetrachlorophenols were found in flue gases, and high levels of chlorobenzenes, especially hexachlorobenzene, were detected in all fly ash samples.

Another team of investigators reported finding the same dioxins in Switzerland (Huser and Hosshardt 1978). This study quantitatively determined that the total amount of polychlorinated dibenzo-*p*-dioxins in the fly ash from a Swiss municipal incinerator and industrial heating facility were 0.2 ppm and 0.6 ppm, respectively. High-resolution gas chromatography was then used to identify 33 specific dioxin isomers found in the fly ash samples. The dioxin isomers known to be most toxic, which are 2,3,7,8-TCDD, 1,2,3,7,8-penta-CDD, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD, were only minor constituents of the total dioxins found.

Later in 1978, researchers at Dow Chemical Company reported finding ppb levels of chlorinated dioxins in particulate matter from air emissions of two industrial refuse incinerators, a fossil-fueled powerhouse, and other combustion sources such as gasoline and diesel autos and trucks, two fireplaces, a charcoal grill, and cigarettes. (See Table 29.) All of these sources are believed to be located on or near the Dow facilities in Midland, Michigan. Tetra-, hexa-, hepta-, and octachlorodioxins were found. Concentrations of 2,3,7,8-TCDD were minor relative to concentrations of other dioxins. Dow concluded from the study that their Midland facility was not a measurable source of the dioxins found in fish from nearby rivers, and that, in fact, chlorinated dibenzo-*p*-dioxins may be ubiquitous in combustion processes. A preliminary data analysis by the EPA does not entirely agree with Dow's conclusions. The EPA continues to believe that Dow's Midland plant is the major and possibly the only source of the dioxins contaminating fish in nearby rivers. The EPA has asked Dow for further clarification of the company's findings and analytical methods (Merenda 1979).

In contrast to the Dow finding of 38 ppb TCDD's in powerhouse emissions, Kimble and Gross (1980) report finding no TCDD's in fly ash from a typical commercial coal-fired power plant in California; the detection limit was 1.2 ppt. Crummett of Dow Chemical Company asserts that these studies could not have found 2,3,7,8-TCDD to be present because the solvents used for the extraction techniques in preparation for the analytical analysis were not appropriate.

In 1980 Wright State University chemists analyzed emissions from a U.S. municipal incinerator for chlorodioxins (Tiernan and Taylor 1980). TCDD's were detected in all seven samples. Isomer-specific analyses indicate that 2,3,7,8-TCDD is a minor product, and evidence was obtained for the presence of 1,3,6,8-, 1,3,7,9-, 1,3,7,8-, 1,3,6,7-, and at least six other TCDD isomers.

The formation of dioxins from the thermal decomposition of chlorophenols and their salts (chlorophenates) is well documented. In 1971, Milne reported finding no evidence of formation of lower chlorinated dioxins from the thermal decomposition of dichlorophenols; all six dichlorophenol isomers were studied. However, Andine (1973) found that pyrolysis of 2,3,4,6-tetrachlorophenate produced two hexa-CDD isomers. Later, Stehl et al. (1973) found that burning paper treated with sodium pentachlorophenate produced OCDD, but burning either wood or paper treated with pentachlorophenol did not produce the dioxin. In 1975, a series of pyrolysis experiments was conducted with 2,3,4-, 2,3,5-, 2,4,5- and 2,5,6-tri, 2,3,4,5-, 2,3,5,6- and 2,3,4,6-tetra, and pentachlorophenates to obtain samples of many tetra-, penta-, hexa-, and hepta-CDD's for study (Buser 1975). In 1977, 2,3,7,8-TCDD was found as a combustion product of many 2,4,5-trichlorophenoxy compounds, but the amount of this dioxin was very small relative to the

TABLE 20. DIOXINS IN SELECTED SAMPLES*
(ppb except as noted)

Source	TCDD's				
	2,3,7,8-TCDD	Other TCDD Isomers	Hexa CDD's	Hepta CDD's	OCDD
Soil inside plant	0.3-100	0.8-15	7-280	70-3200	490-20,500
Dust samples from Dow Research Building	0.7-2.6	0.5-2.3	9-35	140-1200	650-7500
Soil and dust from Midland and metro areas	0.03-0.04		0.09-0.4	0.3-3.9	0.4-31
Soil and dust from major metro area	0.005-0.03		0.02-0.14	0.10-3.3	0.35-22
Soil and dust from urban area	none	none	0.03-1.2	0.035-1.6	0.05-2.0
Soil and dust from rural area	none	none	none	0.02-0.05	0.10-0.35
Dow stationary tar incinerator particulates	none	none	1-20	27-160	190-440
Dow rotary kiln incinerator with supplementary fuel	none	none	1.4-5.0	4-110	9-950

(continued)

TABLE 20. (continued)

Source	TCDD's: 2,3,7,8-TCDD	TCDD's: Other TCDD isomers	Hexa-CDD's	Hepta-CDD's	OCDD
Dow rotary kiln incinerator without supplementary fuel	110-6200	1800-12,000	1300-65,000	2000-510,000	3000-810,000
Dow townhouse fired with fuel oil/coal	none	38	2	4	24
Automobiles					
catalytic - carbon	none	0.1	0.5-2.0	2-14	8-72
catalytic - rust	0.4	4.0	0.7	3	28
noncatalytic	none	4.0	none	3	10-16
diesel trucks	3.0	20.0	4-37	35-110	190-280
Fireplaces (scrapings)	0.1	0.27	0.23-3.4	0.07-16	0.89-75
Cigarettes (tars)	none	none	4.2-8.0	8.5-30	18-50
Charcoal-grilled steaks	none	none	none	3-7	5-79
Residential electrostatic precipitator	0.6	0.40	34	430	1300
Particulates from rotary kiln scrubber water with supplemental fuel	46		200	970	1200
without supplemental fuel	2500		3400	20,000	42,000

(continued)

TABLE 20. (continued)

Source	TCDD's		Hexa-CDD's	Hepta-CDD's	OCDD
	2,3,7,8-TCDD	Other TCDD isomers			
Filtered scrubber water	0.0028		0.005	0.024	0.026
Cooling tower residues	1.8-6.0		10	12-25	56-119
Sewer waters before treatment (concentration - ppt)	1-4		N.A.[b]	N.A.[b]	3-1500

a--Source: Dow Chemical Company 1978
b--N.A. = not applicable

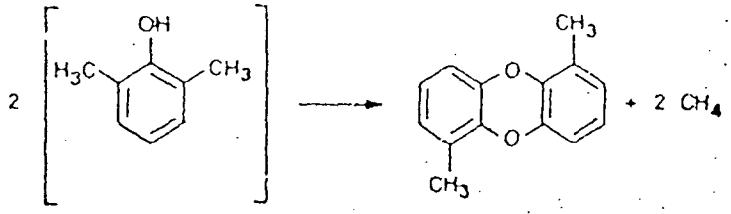
amount of the 2,4,5-trichlorophenoxy compound that was burned (Stehl and Lamparski 1977). Results of the study showed that only 1.2×10^{-9} to 5×10^{-7} percent by weight of the 2,4,5-trichlorophenoxy species was converted to 2,3,7,8-TCDD by combustion.

The origin of the dioxins in airborne particulates from combustion is not yet clarified. Rappe et al. (1978) suggest that polychlorinated dibenzo-*p*-dioxins can be formed during combustion by dimerization of chlorophenates, by dechlorination of more chlorinated polychlorinated dibenzo-*p*-dioxins, and by cyclization of predioxins. Dow Chemical Company (1978) suggests that because of the complex nature of the materials being burned and the complex chemistries of fire, the formation of chlorinated dioxins occurs in all combustion processes, i.e., that the formation is not necessarily limited to combustion in the presence of chlorophenates or chlorophenols. The presence of biosynthesized compounds with characteristics of dioxin precursors may give some credence to this contention.

An alternative explanation for the observed presence of dioxins in the fly ash of refuse incinerators is that the dioxins enter intact as contaminants of the wastes being burned. For example, silvex-treated grass clippings, sawdust or other wastes from PCP-treated wood (landscape timber, railroad ties), and "empty" PCP, silvex, or other pesticide containers from home or industrial use might be direct sources of the dioxins detected in municipal incinerator fly ash. If this were the case, seasonal variations in fly ash dioxin content would be expected, with larger amounts in spring and summer.

DIOXINS IN PLASTIC

In 1965, it was reported that dioxin is an impurity in the preparation of polyphenylene ethers (Cox, Wright, and Wright 1965). No reports further substantiating this finding are known. "PPO" is a trademark of General Electric Company for a polyphenylene thermoplastic derived from 2,6-dimethylphenol (Hawley 1971). The dioxin configuration one would expect from condensation of the dimethylphenol is as follows:



2,6-DIMETHYLPHENOL 1,6-DIMETHYLDIBENZO-P-DIOXIN

Because PPO is highly resistant to acids, bases, detergents, and hydrolysis, it may be used in hospital and laboratory equipment, and in pump housings, impellers, pipes, valves, and fittings in the chemical and food industries.

DIOXINS PRODUCED FOR RESEARCH PURPOSES

Many investigators have reported the sources of purified dioxin standards used in their studies. Some of these dioxin sources and the names of the dioxins provided are listed in Table 24.

In addition to these, Dow Chemical Company has recently published methods for preparing all of the TCDD isomers (Nestrick, Lamparski, and Stehl 1979).

TABLE A5. PRODUCERS OF PESTICIDE CHEMICALS, CLASSES I AND II

Chemical	Producer	Location
Class I		
Bifenox	Mobil	Mt. Pleasant, TN
Chloranil	Arapahoe	Boulder, CO*
	Uniroyal	Naugatuck, CT*
2,4-D and esters and salts	Amchem	Ambler, PA
		Fremont, CA
		St. Joseph, MO
	Chemical Insecticide Corp.	Matuchen, NJ*
	Chempar	Portland, OR*
	Diamond Shamrock	Newark, NJ*
	Dow	Midland, MI
	Fallek-Lankro	Tuscaloosa, AL
	Guth Chem.	Hillside, IL*
	Imperial	Shenandoah, IA
	Miller Chem.	Whitelord, MD*
	Monsanto	Sauget, IL*
	PBI-Gordon	Kansas City, KS
	Rhodia	N. Kansas City, MO*
		Portland, OR
		St. Joseph, MO
		St. Paul, MN*
	Riverdale	Chicago Hgts., IL
	Thompson Chem.	St. Louis, MO*
	Thompson-Hayward	Kansas City, KS
	Transvaal	Jacksonville, AR
	Woodbury	Orlando, FL*
2,4-DB and salts	Amchem	Ambler, PA
	Rhodia	N. Kansas City, MO*
		Portland, OR
		St. Joseph, MO
		St. Paul, MN*
Dicamba	Velsicol	Beaumont, TX
		Chattanooga, TN*
Dicapthon	American Cyanamid	Warners, NJ*
Dichlofenthion	Mobile	Charleston, SC*
		Mt. Pleasant, TN*
Dimethylamine salt of dicamba	PBI-Gordon	Kansas City, KS
Disul sodium (sesone)	Amchem	Ambler, PA*
		Fremont, CA*
		Linden, NJ*
		St. Joseph, MO*

(continued)

TABLE A6. (continued)

Chemical	Producer	Location
	GAF	Linden, NJ*
	Union Carbide	Institute and South Charleston, WV*
2,4-DP	Rhodia	Portland, OR
	Transvaal	Jacksonville, AR
Erbon	Dow	Midland, MI*
Hexachlorophene	Givaudan	Clifton, NJ
Isobac 20	Givaudan	Clifton, NJ
Nitrofen	Rohm and Haas	Philadelphia, PA
Pentachlorophenol (PCP) and and salts	Dow	Midland, MI
	Merck	Hawthorne, NJ*
	Monsanto	Sauget, IL
	Reichhold	Tacoma, WA
	Sanford Chemical	Port Neches, TX*
	Vulcan Materials	Wichita, KS
Ronnel	Dow	Midland, MI
Silvex and esters and salts	Dow	Midland, MI
	Guth Chemical	Hillside, IL*
	Millmaster Onyx	Berkeley Hgts., NJ*
	Riverdale	Chicago Hgts., IL
	Thompson-Hayward	Kansas City, KS
	Transvaal	Jacksonville, AR
2,4,5-T and esters and salts	Amchem	Ambler, PA
		Fremont, CA
		St. Joseph, MO
	Chemical Insecticide Corp	Metuchen, NJ*
	Chempar	Portland, OR*
2,4,5-T and esters and salts (continued)	Diamond Shamrock	Newark, NJ*
	Dow	Midland, MI
	Guth Chemical	Hillside, IL*
	Hercules	Brunswick, GA*
	Millmaster Onyx	Berkeley Hgts., NJ*
	PBI-Gordon	Kansas City, KS
	Riverdale	Chicago Hgts., IL
	Thompson Chemical	St. Louis, MO*
	Thompson-Hayward	Kansas City, KS
	Transvaal	Jacksonville, AR
2,3,4,6-Tetrachlorophenol	Dow	Midland, MI
	Sanford	Port Neches, TX*

(continued)

TABLE A6. (continued)

Chemical	Producer	Location
2,4,5-Trichlorophenol and salts	Chemical Insecticide Corp.	Metuchen, NJ*
	Diamond Shamrock	Newark, NJ*
	Dow	Midland, MI
	GAF	Linden, NJ*
	Hercules	Brunswick, GA*
	Hooker	Niagara Falls, NY*
	N. Eastern Pharmacy	Verona, MO*
	Transvaal	Jacksonville, AR
2,4,6-Trichlorophenol	Dow	Midland, MI
Class II		
o-Benzyl-p-chlorophenol	Monsanto	Saugus, IL
	Reichhold	Tacoma, WA
Bromoxynil and esters	Amchem	Ambler, PA
	Rhodia	Portland, OR
		St. Joseph, MO
Carbochenothion	Stauffer	Cold Creek, AL*
		Henderson, NV
Chlorothalonil	Diamond Shamrock	Greens Bayou, TX
DCPA	Diamond Shamrock	Greens Bayou, TX
Dichlone	Aceto	Flushing, NY*
	FMC	Middleport, NY
	Uniroyal	Naugatuck, CT*
Dinitrobutylphenol, ammonium salt	Dow	Midland, MI
4,6-Dinitro-o-cresol and sodium salt	Blue Spruce	Bound Brook, NJ
Ioxynil	Amchem	Fremont, CA*
	Rhodia	Portland, OR*
Lindane	Hooker	Niagara Falls, NY
	Prentiss	Newark, NJ
MCPA and derivatives	Diamond Shamrock	Newark, NJ*
	Dow	Midland, MI
	Fallek-Lankro	Tuscaloosa, AL
	Guth Chemical	Hillside, IL*
	Monsanto	Nitro, WV*
	Rhodia	Portland, OR

(continued)

TABLE A7. ALPHABETICAL LIST OF PESTICIDE CHEMICAL PRODUCERS

Producer	Location	Chemical (class)
Acato Chem. Co., Inc.	Flushing, NY	Dichlone (II)*
Alco Standard Corp. (see Miller Chem.)		
Amcham Products, Inc. Brookside Av. P.O. Box 33 Ambler, PA 19002 (Subsidiary of Union Carbide)	Ambler, PA	2,4-D and esters and salts (I)
		2,4-DB and salts (I)
		Disul sodium (II)*
		2,4,5-T and esters and salts (I)
		Bromoxynil and esters (II)
		MCPB (II)
		2,3,6-Trichlorobenzoic acid and salt (II)
		Triiodobenzoic acid (II)
	Fremont, CA	2,4-D and esters and salts (I)
		Disul sodium (II)*
		2,4,5-T and esters and salts (I)
		Ioxynil (II)*
		MCPB (II)*
		2,3,6-Trichlorophenyl acetic acid, sodium salt (II)
	Linden, NJ	Disul sodium (II)*
	St. Joseph, MO	2,4-D and esters and salts (I)
		Disul sodium (II)*
		2,4,5-T and esters and salts (I)
		MCPB (II)
		2,3,6-Trichlorobenzoic acid (II)
		2,3,6-Trichlorophenyl acetic acid, sodium salt (II)
American Cyanamid Co. Berdan Av. Wayne, NJ 07470	Warners, NJ	Dicapthon (I)*
		Parathion (II)*
American Potash and Chem. Corp. Kerr-McGee Chem. Corp. Kerr-McGee Center Oklahoma City, OK 73125	Hamilton, MS	Parathion (II)*
	Los Angeles, CA	Parathion (II)*
Arapahoe Chem. Div., Syntex Corp. 3401 Hillview Av. Palo Alto, CA 94304	Boulder, CO	Chloranil (I)*
Blue Spruce Co. Stirling, NJ 07980	Bound Brook, NJ	4,6-Dinitro-o-cresol and sodium salt (II)
		Propanil (II)

(continued)

TABLE A7. (continued)

Producer	Location	Chemical (class)
Chemical Insecticide Corp 30 Whitman Av Metuchen, NJ 08840 (1971 address)	Metuchen, NJ	2,4-D and esters and salts (I)* 2,4,5-T and esters and salts (I)* 2,4,5-Trichlorophenol (I)*
Champar Chem. Co., Inc (address not available)	Portland, OR	2,4-D and esters and salts (I)* 2,4,5-T and esters and salts (I)*
W. A. Cleary 1049 Somerset St Somerset, NJ 08873	Somerset, NJ	Macoprop (II)
Diamond Shamrock Corp 1100 Superior Av. Cleveland, OH 44114	Greens Bayou, TX Newark, NJ	Chlorothalonil (II) DCPA (II) 2,4-D and esters and salts (I)* 2,4,5-T and esters and salts (I)* 2,4,5-Trichlorophenol and salts (I)* MCPA (II)*
Dow Chemical U.S.A.	Midland, MI	2,4-D and esters and salts (I) Dinitrobutylphenol ammonium salt (II) Erbon (I)* MCPA and derivatives (II) MCPB (II)* Pentachlorophenol and salts (I) Ronnel (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I) 2,4,5-Trichlorophenol (I) 2,4,6-Trichlorophenol (I)
E. I. du Pont de Nemours and Co., Inc 1007 Market St Wilmington, DE 19898	Deepwater, NJ	2,3,6-Trichlorobenzoic acid and salts (II)*
Eagle River Chemicals Co Helena, AR 72342 (Subsid. of Vertac, Inc.)	Helena, AR	Propanil (II)
Eli Lilly and Co. 740 S. Alabama St. Indianapolis, IN 46206	Indianapolis, IN Lafayette, IN	Piperalin (II)* Piperolinopropyl-3,4-dichlorobenzoate (II) Piperalin (II)

(continued)

TABLE A7. (continued)

Producer	Location	Chemical (class)
FMC Corp One Illinois Center 200 East Randolph Dr. Chicago, IL 60601	Baltimore, MD Middleport, NY	Tetradifon (III)* Dichlone (I)
Fallek-Lankro Corp P.O. Box H Tuscaloosa, AL 35401 (Joint venture of Fallek Chem. Corp. and Lankro Chem. Group Ltd. (UK))	Tuscaloosa, AL	2,4-D and esters and salts (I) MCPA and derivatives (II) Mecoprop (II)
GAF Corp. 140 West 51st St. New York, NY 10020	Linden	Disul sodium (I)* 2,4,5-Trichlorophenol and salts (I)*
Givaudan Corp. 100 Delawanna Av Clifton, NJ 07014 (Affiliate of L. Givaudan and Cie (Switz.))	Clifton, NJ	Hexachlorophene (I) Isobac 20 (I)
Guth Chemical Co P.O. Box 302 Naperville, IL	Hillside, IL	2,4-D and esters and salts (I)* Silvex and esters and salts (I)* 2,4,5-T and esters and salts (I)* MCPA (II)*
Gulf Oil Corp. (see Millmaster Onyx)		
Hercules, Inc 910 Market St. Wilmington, DE 19899	Brunswick, GA	2,4,5-T and esters and salts (I)* 2,4,5-Trichlorophenol and salts (I)*
Hooker Chemical Corp. 1900 St. James Pl. Houston, TX 77027 (Subsid. of Occidental Petroleum Corp.)	Niagara Falls, NY	2,4,5-Trichlorophenol and salts (I)* Lindane (II)
Imperial, Inc West 6th and Grass Streets Shenandoah, IA	Shenandoah, IA	2,4-D and esters and salts (I)
Mallinckrodt, Inc 675 Brown Rd. P.O. Box 5840 St. Louis, MO 63134	Raleigh, NC	Triiodobenzoic acid (III)*

(continued)

TABLE A7. (continued)

Producer	Location	Chemical (class)
Merck and Co., Inc. 126 East Lincoln Av. Rahway, NJ 07065	Hawthorne, NJ	Pentachlorophenol and salts (I)*
Miller Chem. and Fertz. Corp Subsid. of Alco Standard Corp. Valley Forge, PA 19481	Whitoford, MD	2,4-D and esters and salts (I)*
Millmaster Onyx Group 99 Park Av. New York, NY 10016 (Part of Gulf Oil Corp.)	Berkeley Hgts., NJ	Silvex and esters and salts (I)* 2,4,5-T and esters and salts (I)*
Mobil Chem. Co. Phosphorus Div. P.O. Box 26638 Richmond, VA 23261 (Div. of Mobil Corp.)	Charleston, SC Mt. Pleasant, TN	Dichlofenthion (I)* Bifenox (I) Dichlofenthion (I)*
Monsanto Co. 800 North Lindbergh Blvd. St. Louis, MO 63166	Anniston, AL Luling, LA Nitro, WV Sauget, IL	Parathion (II) Propanil (II)* MCPA (II)* 2,4-D and esters and salts (I)*
Monsanto Co. (continued)		Pentachlorophenol and salts (I) o-Benzyl-p-chlorophenol (II) MCPB (II)* PCNB (II)*
Morton Chem. Co. Div. of Morton-Norwich Products, Inc. 100 North Wacker Dr. Chicago, IL 60606	Ringwood, IL	Mecoprop (II)*
North Eastern Pharmaceutical and Chem. Co. P.O. Box 270 Stamford, CT 06904	Verona, MO	2,4,5-Trichlorophenol and salts (I)*
Occidental Petroleum Corp. (see Hooker)		
Olin Corp. 120 Long Ridge Rd. Stanford, CT 06904	Leland, MS McIntosh, AL Rochester, NY	PCNB (II) PCNB (II) PCNB (II)*

(continued)

TABLE A7. (continued)

Producer	Location	Chemical (class)
PBI-Gordon Corp 300 South Third St. Kansas City, KS 66118	Kansas City, KS	Dimethylamine salt of dicamba (I) 2,4,5-T and esters and salts (I) Mecoprop (III)
Prentiss Drug and Chem. Co., Inc. 363 Seventh Av. New York, NY 10001	Newark, NJ	Lindane (III)
Reichhold Chem., Inc RCI Bldg. White Plains, NY 10603	Tacoma, WA	Pentachlorophenol and salts (I) o-Benzyl-p-chlorophenol (III)
Rhodia, Inc. 600 Madison Av. New York, NY 10022 (Subsid. of Rhone-Poulenc SA (France))	N. Kansas City, MO	2,4-D (I)* 2,4-DB (I)* Ioxynil (III)*
	Portland, OR	2,4-D (I) 2,4-DB (I)
Rhodia, Inc. (continued)		2,4-DP (I) Bromoxynil and esters (II) MCPA and derivatives (II) MCPB (II) Mecoprop (III)
	St. Joseph, MO	2,4-D and esters and salts (I) 2,4-DB and salts (I) Bromoxynil and esters (II) MCPA and derivatives (II) MCPB (II) Mecoprop (III)
	St. Paul, MN	2,4-D and esters and salts (I)* 2,4-DB (I)*
Riverdale Chem., Inc. 220 East 17th St. Chicago Hgts., IL 60411	Chicago Hgts, IL	2,4-D and esters and salts (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I)
Sobin Chem., Inc. International Minerals and Chem. Corp. IMC Plaza Libertyville, IL 60048	Newark, NJ	Propanil (III)*
Sonford Chem. Co. Pure-Atlantic Hwy. Port Neches, TX 77651	Port Neches, TX	Pentachlorophenol and salts (I)* 2,3,4,6-Tetrachlorophenol (I)*
Stauffer Chem. Co. Westport, CT 06880	Cold Creek, AL Henderson, NV Mt. Pleasant, TN	Carbophenothion (III)* Carbophenothion (III) Parathion (III)*

(continued)

TABLE A7. (continued)

Producer	Location	Chemical (class)
Syntex Corp (see Arapahoe)		
Tenneco Chems Co Park 80 Plaza West Sedolo Brook NJ 07662 (Part of Tenneco, Inc.)	Fords, NJ	2,3,6-Trichlorobenzoic acid and salts (II)* (2,3,6-Trichlorophenyl) acetic acid and sodium salt (II)*
Thompson Chems Corp 3028 Locust St St Louis, MO 63103	St Louis, MO	2,4-D and esters and salts (I)* 2,4,5-T and esters and salts (I)*
Thompson-Hayward Chem Co 5200 Speaker Rd. P O Box 2383 Kansas City, KS 66110 (Subsid. of North American Philips Corp.)	Kansas City, KS	2,4-D and esters and salts (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I)
Transvaal, Inc. Marshall Rd P.O. Box 69 Jacksonville, AR 72076 (Subsid of Vertac, Inc.)	Jacksonville, AR	2,4-D and esters and salts (I) 2,4-DP (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I) 2,3,4,6-Tetrachlorophenol (I) 2,4,5-Trichlorophenol and salts (I)
Union Carbide Corp. 270 Park Av. New York, NY 10017 (see also Alcham)	Institute and South Charleston, WV	Disul sodium (I)*
Uniroyal, Inc. 1230 Av. of the Americas New York, NY 10020	Naugatuck, CT	Chlorani (I)* Dichlone (II)*
Velsicol Chem. Corp. 341 East Ohio St. Chicago, IL 60611 (Subsid of Northwest Industries, Inc.)	Bayport, TX Beaumont, TX	Parathion (II)* Dicamba (I)
Vertac, Inc. (see Transvaal and Eagle River)		
Vulcan Materials Co. P.O. Box Birmingham, AL 35223	Wichita, KS	Pentachlorophenol and salts (I)

(continued)

TABLE A7. (continued)

Producer	Location	Chemical (class)
Woodbury Chems. Subsid of Comutrix Corp 8373 N E 2nd Av Miami, FL 33138	Orlando, FL	2,4-D and esters and salts (I)

*No longer produced at this location

Ref. 2

United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

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External Review Draft

EPA

The Inventory of Sources of Dioxin in the United States

Review Draft (Do Not Cite or Quote)

Notice

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

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3. COMBUSTION SOURCES OF CDD/CDF: WASTE INCINERATION

Incineration is the destruction of solid, liquid, or gaseous wastes through the application of heat within a controlled combustion system. The purposes of incineration are to reduce the volume of waste that needs land disposal and to reduce the toxicity of the waste, making it more sterile. In keeping with this definition, incinerator systems can be classified by the types of wastes incinerated: municipal solid waste incineration; medical and pathological waste incineration; hazardous waste incineration; sewage sludge incineration; tire incineration; and biogas flaring. Each of these types of incinerators are discussed in this chapter. The purposes of this chapter are to: characterize and describe waste incineration technologies in the United States and to derive estimates of annual releases of CDDs and CDFs into the atmosphere from these facilities for reference years 1987 and 1995.

Combustion research has developed three theories on the mechanisms involved in the emission of CDDs and CDFs from combustion systems: (1) CDD/CDFs can be introduced into the combustor with the feed and pass through the system unchanged, (2) CDD/CDFs can be formed during combustion, or (3) CDD/CDFs can be formed via chemical reactions in the post-combustion portion of the system. The total CDD/CDF emissions are likely to be the net result of all three mechanisms; however, their relative importance is often uncertain. To the extent practical with the available data, the combustors in each source category were divided into classes judged to have similar emission factors. This classification effort attempted to reflect the emission mechanisms described above. The emission mechanisms suggest that the aspects of combustor design and operation that could affect CDD/CDF emissions are furnace design, composition of the waste feed, temperature in the post-combustion zone of the system, and type of air pollution control device (APCD) used to remove contaminants from the flue gases. Therefore, incineration systems that are similar in terms of these factors should have similar CDD/CDF emissions. Accordingly, this chapter proposes classification schemes that divide combustors into a variety of design classes based on these factors. Design class, as used here, refers to the combination of furnace type and accompanying APCD.

3.1. MUNICIPAL SOLID WASTE INCINERATION

As discussed previously, CDD/CDF emission theory suggests that CDD/CDF emissions can be related to several factors, including furnace design, composition of the waste feed, temperature in the post-combustion zone of the system, and type of APCD used to remove contaminants from the flue gases. Accordingly, this chapter proposes a classification scheme that divides municipal solid waste incinerators (MSWIs) into a variety of design classes based on those factors. Some APCDs are operated at different temperatures; therefore, operating temperature is used to define some design classes. Because the theory also suggests that feed can influence CDD/CDF emissions, the proposed furnace classification system distinguishes refused-derived fuel from normal municipal solid waste (MSW). This section begins with a description of the MSWI technology and then proposes the design classification scheme. Using this scheme, the MSWI industry is characterized for the reference years 1987 and 1995. Finally, the procedures for estimating emissions are explained, and results summarized.

3.1.1. Description of Municipal Solid Waste Incineration Technologies

For purposes of this report, MSWI furnace types are divided into three major categories: mass burn, modular, and refuse-derived fuel. Each of these furnace types is described below, followed with a description of the APCDs used with these systems.

Furnace Types

Mass Burn: Historically, this furnace type derived its name because it burned MSW as received (i.e., no preprocessing of the waste was conducted other than removal of items too large to go through the feed system). Today, a number of other furnace types also burn unprocessed waste (as described below). Mass burn furnaces are distinguished from these others because they burn the waste in a single stationary chamber. In a typical mass burn facility, MSW is placed on a grate that moves through the combustor. The 1995 inventory indicates that the combustion capacity of facilities ranges from 90 to 2,700 metric tons of MSW per day. Three subcategories of mass burn (MB) technologies are described below:

- Mass burn refractory-walled (MB-REF) systems represent an older class of MSWIs (generally built in the late 1970s to early 1980s) that were designed only to reduce the volume of waste in need of disposal by 70 to 90 percent. These facilities

usually lacked boilers to recover the combustion heat for energy purposes. In the MB-REF design, the MSW is delivered to the combustion chamber by a traveling grate and/or a ram feeding system. Combustion air in excess of stoichiometric amounts (i.e., more oxygen is supplied than needed for complete combustion) is supplied both below and above the grate.

- Mass burn waterwall (MB-WW) facilities represent enhanced combustion efficiency, as compared with MB-REF incinerators. Although it achieves similar volume reductions, the MB-WW incinerator design provides a more efficient delivery of combustion air, resulting in sustained higher temperatures. Figure 3-1 is a schematic of a typical MB-WW MSWI. The term 'waterwall ' refers to a series of steel tubes, running vertically along the walls of the furnace. The tubes contain water, which when heated by combustion, transfer energy from the heat of combustion to the water. The water reaches boiling temperature, and steam is produced. The steam is then used to drive an electrical turbine generator or for other industrial needs. This transfer of energy is termed 'energy recovery.'

- Mass burn rotary kiln combustors (MB-RC) use a water-cooled rotary combustor, which consists of a rotating combustion barrel configuration mounted at a 15-20° angle of decline. The refuse is charged at the top of the rotating kiln by a hydraulic ram (Donnelly, 1992). Preheated combustion air is delivered to the kiln through various portals. The slow rotation of the kiln (i.e., 10 to 20 rotations/hour) causes the MSW to tumble, thereby exposing more surface area for complete burnout of the MSW. These systems are also equipped with boilers for energy recovery. Figure 3-2 is a schematic of a typical MB-RC MSWI.

Modular Incinerator: This is the second general type of MSWI furnace used in the United States. As with the mass burn type, modular incinerators burn waste without preprocessing. Modular MSWIs consist of two vertically mounted combustion chambers (i.e., a primary and secondary chamber). In the 1995 inventory, modular combustors' combustion capacity ranged from 4 to 270 metric tons/day. The two major types of modular systems, "excess air" and "starved air," are described below.

- The modular excess-air system consists of a primary and secondary combustion chamber, both of which operate with air levels in excess of stoichiometric requirements (i.e., 100 to 250 percent excess air). Figure 3-3 illustrates a typical modular excess-air MSWI.

- Starved (or controlled) air is a newer type of modular system, which is easier and less expensive to operate than the excess-air systems. In these systems, air is supplied to the primary chamber at sub-stoichiometric levels. The products of incomplete combustion entrain in the combustion gases that are formed in the primary combustion chamber, then pass into a secondary combustion chamber. Excess air is added to the secondary chamber, and combustion is completed by elevated temperatures sustained with auxiliary fuel (usually natural gas). The high

and uniform temperature of the secondary chamber, combined with the turbulent mixing of the combustion gases, results in low-levels of particulate matter and organic contaminants being formed and emitted. Therefore, many existing modular units lack post-combustion air pollution control devices. Figure 3-4 is a schematic view of a modular starved-air MSWI.

Refuse-Derived Fuel (RDF): The third major type of MSWI furnace technology is designed to combust refuse-derived fuel (RDF). RDF is a general term that describes MSW from which relatively noncombustible items are removed, thereby enhancing the combustibility of the MSW. RDF is commonly prepared by shredding, sorting, and separating out metals to create a dense MSW fuel in a pelletized form, having a uniform size. Three types of RDF systems are described below.

- The dedicated RDF system burns RDF exclusively. Figure 3-5 shows a typical dedicated RDF using a spreader-stoker boiler. Pelletized RDF is fed into the combustor through a feed chute, using air-swept distributors; this allows a portion of the feed to burn in suspension and the remainder to burn out after falling on a horizontal traveling grate. The traveling grate moves from the rear to the front of the furnace, and distributor settings are adjusted so that most of the waste lands on the rear two-thirds of the grate. This allows more time to complete combustion on the grate. Underfire and overfire air are introduced to enhance combustion, and these incinerators typically operate at 80 to 100 percent excess air. Waterwall tubes, a superheater, and an economizer are used to recover heat for production of steam and/or electricity. The 1995 inventory indicates that dedicated RDF facilities range in total combustion capacity from 227 to 2,720 metric tons/day.

- Cofired RDFs burn both RDF and normal MSW.

- The fluidized-bed RDF (FB-RDF) burns the waste in a turbulent and semi-suspended bed of sand. The MSW may be fed into the incinerator either as unprocessed waste or as a form of RDF. The RDF may be injected into or above the bed through ports in the combustor wall. The sand bed is suspended during combustion by introducing underfire air at a high velocity, hence the term "fluidized." Overfire air at 100 percent stoichiometric requirements is injected above the sand suspension. Waste-fired FB-RDFs typically operate at 30 to 100 percent excess air levels and at bed temperatures around 815°C (1,500°F). A typical FB-RDF is presented as Figure 3-6. Technology has two basic design concepts: (1) a bubbling-bed incineration unit and (2) a circulating-bed incineration unit. The 1995 inventory indicates that fluidized-bed MSWIs have capacities ranging from 184 to 920 metric tons/day. These systems are usually equipped with boilers to produce steam.

Air Pollution Control Devices (APCDs)

MSWIs are commonly equipped with one or more post-combustion APCDs to remove various pollutants prior to release from the stack (e.g., particulate matter, heavy metals, acid gases, and/or organic contaminants) (U.S. EPA, 1992d). These APCDs include:

- Electrostatic precipitator (ESP),
- Fabric filter (FF),
- Dry scrubber (DS),
- Dry sorbent injection (DSI), and
- Wet scrubber (WS)

Electrostatic Precipitator: The ESP is generally used to collect and control particulate matter that evolves during MSW combustion, by introducing a strong electrical field in the flue gas stream; this, in turn, charges the particles entrained in the combustion gases (Donnelly, 1992). Large collection plates receive an opposite charge to attract and collect the particles. CDD/CDF formation can occur within the ESP at temperatures in the range of 150 to about 350°C. As temperatures at the inlet to the ESP increase from 150 to 300°C, CDD/CDF concentrations have been observed to increase by approximately a factor of two for each 30°C increase in temperature (U.S. EPA, 1994f). As temperature increases beyond 300°C, formation rates decline. Although ESPs in this temperature range efficiently remove most particulates and the associated CDD/CDFs, the formation that occurs can result in a net increase in CDD/CDF emissions. This temperature related formation of CDD/CDF within the ESP can be applied to distinguish hot-side ESPs from cold-side ESPs. For purposes of this report, ESPs are classified as follows:

- A cold-side ESP operates at or below 230°C.
- A hot-side ESP operates at an inlet temperature greater than 230°C.

Fabric Filters (FF): FFs are also particulate matter control devices, which remove dioxins associated with particles and any vapors that adsorb to the particles. Six- to 8-inch diameter bags, made from woven fiberglass material, are usually arranged in series. An induction fan forces the combustion gases through the tightly woven fabric. The porosity of the fabric allows the bags to act as filter media and retain a broad range of particles

sizes (i.e., down to less than 1 micrometer in diameter). The FF is sensitive to acid gas; therefore, it is usually operated in combination with spray dryer adsorption of acid gases.

Dry Scrubbers (DS): DSs, also called spray dryer adsorption, involve both the removal of acid gas and particulate matter from the post-combustion gases. By themselves, these units probably have little effect on dioxin emissions. In a typical DS system, hot combustion gases enter a scrubber reactor vessel. An atomized hydrated lime slurry (water plus lime) is injected into the reactor at a controlled velocity (Donnelly, 1992). The hydrated lime slurry rapidly mixes with the combustion gases within the reactor. The water in the hydrated lime slurry quickly evaporates, and the heat of evaporation causes the combustion gas temperature to rapidly decrease. The neutralizing capacity of hydrated lime reduces the combustion gas content of acid gas constituents (e.g., hydrogen chloride gas, and sulfur dioxide gas) by greater than 70 percent. A dry product, consisting of particulate matter and hydrated lime, settles to the bottom of the reactor vessel. DS technology is used in combination with ESPs. The DS reduces ESP inlet temperatures to make a cold-side ESP. DS/FFs have achieved greater than 95 percent reduction and control of CDD/CDFs in MSWI emissions (U.S. EPA, 1992d).

Dry Sorbent Injection (DSI): DSI is used to reduce acid gas emissions. By themselves, these units probably have little effect on dioxin emissions. DSI involves the injection of dry hydrated lime or soda ash either directly into the combustion chamber or into the flue duct of the hot post-combustion gases. In either case, the reagent reacts with and neutralizes the acid gas constituents (Donnelly, 1992).

Wet Scrubber (WS): WS devices are designed for acid gas removal, and are more common to MSWIs in Europe than in the United States. They should help reduce emissions of dioxin in both vapor and particle forms. WS devices consist of two-stage scrubbers. The first stage removes HCl, and the second stage removes SO_2 (Donnelly, 1992). Water is used to remove the HCl, and caustic or hydrated lime is added to remove SO_2 from the combustion gases.

In addition to the APCDs described above, some less common types are also used in some MSWIs. An example is the Electro Granular Bed (EGB), which consists of a packed bed of activated carbon. An electric field is passed through the packed bed; particles entrained in the flue gases are given a negative charge, and the packed bed is given a positive charge. EGB systems function much like an ESP. Particulate matter is collected within the bed; therefore, they will remove dioxins associated with collected particles and

any vapors that adsorb to the particles. Only one facility in the United States currently employs the EGB system, a fluidized bed-RDF MSWI.

Classification Scheme

Based on the array of MSWI technologies described above, a classification system for deriving CDD/CDF emission estimates was developed. As discussed earlier, it is assumed that facilities with common design and operating characteristics have a similar potential for CDD/CDF emissions. The MSWIs operating in 1987 and 1995 were divided according to the eight furnace types and seven APCDs described above. This resulted in 17 design classes in 1987 and 40 design classes in 1995. Because fewer types of APCDs were used in 1987 than in 1995, fewer design classes are needed for estimating emissions. This taxonomy is summarized in Figures 3-7 and 3-8.

3.1.2. Characterization of MSWI Facilities in Reference Years 1995 and 1987

Table 3-1 lists by design/APCD type, the number of facilities and activity level (kg MSW incinerated per year) for MSWIs in the reference year 1995. A similar inventory is provided for reference year 1987 in Table 3-2. This information was derived from four reports: U.S. EPA (1987b), Sytems Applications International (1995), Taylor and Zannes (1996), and Solid Waste Technologies (1994). In general, these studies collected the information via telephone interviews with the plant operators.

Using Tables 3-1 and 3-2, a number of comparisons can be made between the two reference years:

- The number of facilities stayed about the same (113 in 1987 and 130 in 1995), but the amount of MSW incinerated more than doubled (13.8-billion kg in 1987 and 28.8-billion kg in 1995).
- The dominant furnace technology shifted from modular in 1987 (57 units and 1.4-billion kg) to mass burn waterwall facilities in 1995 (57 units and 17-billion kg).
- The dominant APCD technology shifted from hot-sided ESPs in 1987 (54 units and 11-billion kg) to fabric filters in 1995 (55 units and 16-billion kg).
- The use of hot-sided ESPs dropped from 54 facilities in 1987 (11-billion kg) to 16 facilities in 1995 (2.2-billion kg).
- The number of uncontrolled facilities dropped from 38 in 1987 (0.6-billion kg) to 10 facilities in 1995 (0.2-billion kg).

3.1.3. Estimation of CDD/CDF Emissions from MSWIs

Compared to other CDD/CDF source categories, MSWIs have been more extensively evaluated for CDD/CDF emissions. Within the context of this report, adequate emission testing for CDD/CDFs were available for 11 of the 113 facilities in the 1987 inventory and 27 of the 130 facilities in the 1995 inventory. Nationwide CDD/CDF air emissions from MSWIs were estimated using a three-step process as described below.

Step 1. Estimation of emissions from all stack tested facilities. The EPA stack testing method (EPA Method 23) produces a measurement of CDD/CDF in units of mass concentration of CDD/CDF (i.e., nanograms per dry standard cubic meter of combustion gas [ng/dscm]) at standard temperature and pressure (20°C and one atmosphere), and adjusted to a measurement of 7 percent oxygen in the flue gas (U.S. EPA, 1995b). This concentration is assumed to represent conditions at the point of release from the stack into the air. Equation 3-1 below was used to derive annual emission estimates for each tested facility:

$$E_{TEQ} = \frac{C \; x \; V \; x \; CF \; x \; H}{10^9 \; ng/g} \qquad \text{(Eqn. 3-1)}$$

Where:

E_{TEQ}	=	Annual TEQ emission (g /yr)
C	=	Combustion flue gas TEQ concentration (ng/dscm) (20°C, 1 atm; adjusted to 7% O_2)
V	=	Volumetric flow rate of combustion flue gas (dscm/hour) (20°C, 1 atm; adjusted to 7% O_2)
CF	=	Capacity factor, fraction of time that the MSWI operates (i.e., 0.85)
H	=	Total hours in a year (8,760 hr/yr)

After calculating annual emissions for each tested facility, the emissions were summed across all tested facilities for each reference year. [Note: many of the emission tests do not correspond exactly to these 2 years. In these cases, the equipment conditions present at the time of the test were compared to those during the reference year to determine their applicability.]

Step 2. Estimation of emissions from all non-tested facilities. This step involves multiplying the emission factor and annual activity level for each MSWI design class and

then summing across classes. The activity levels for reference years 1995 and 1987 are summarized in Tables 3-1 and 3-2, respectively. The emission factors were derived by averaging the emission factors across each tested facility in a design class. The emission factor for each facility was calculated using the following equation:

$$EF_{mswi} = \frac{C \ x \ F_v}{I_w} \qquad \text{(Eqn. 3-2)}$$

Where:

EF_{mswi}	=	Emission factor, average ng TEQ per kg of waste burned
C	=	TEQ or CDD/CDF concentration in flue gases (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2)
F_v	=	Volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2)
I_w	=	Average waste incineration rate (kg/hr)

Example: A mass burn waterwall MSWI equipped with cold-sided ESP.

Given:

C	=	10 ng TEQ/dscm (20°C, 1 atm; adjusted to 7% O_2)
F_v	=	40,000 dscm/hr (20°C, 1 atm; adjusted to 7% O_2)
I_w	=	10,000 kg MSW/hr

$$EF_{MBWW} = \frac{10 \ ng}{dscm} \ x \ \frac{40{,}000 \ dscm}{hr} \ x \ \frac{hr}{10{,}000 \ kg}$$

$$EF_{MBWW} = \frac{40 \ ng \ \ TEQ}{kg \ \ MSW \ \ burned}$$

EPA was not able to obtain engineering test reports of CDD/CDF emissions for a number of design classes. In these cases, the above procedure could not be used to derive emission factors. Instead, the emission factors of the tested design class that was judged most similar in terms of dioxin control was assumed to apply to the untested class. The following logic was used to make this decision:

1. The tested APCDs for the furnace type of the untested class were reviewed to see if any operated at a similar temperature.

2. If any operated at similar temperatures, the one with most similar technology was assumed to apply.

3. If none operated at a similar temperature, then the most similar furnace type with same control device was assumed to apply.

Table 3-3 lists all design categories with no tested facilities and shows the class with tested facilities that was judged most similar.

It should be understood that the emission factors for each design class are the same for both reference years. This is because the emission factor is determined only by the design and operating conditions and is independent of the year of the test.

Step 3. Sum emissions from tested and untested facilities. This step simply involves summing emissions from all tested and untested facilities. This process is shown in Tables 3-4 and 3-5 for the reference years 1995 and 1987, respectively. The tables are organized by design class and show separately the emission estimates for the tested and untested facilities. The calculation of emissions from untested facilities is broken out to show the activity level and emission factor for each design class.

3.1.4. Summary of CDD/CDF (TEQ) Emissions from MSWIs for 1995 and 1987

The activity level estimates (i.e., the amount of MSW that is annually combusted by the various MSWI technologies) are given a "high" confidence rating for both 1987 and 1995. For both years, comprehensive surveys of activity levels were conducted by independent sources on virtually all facilities (U.S. EPA, 1987b; Systems Application International, 1995; Taylor and Zannes, 1996; Solid Waste Technologies, 1994).

The emission factor estimates are given a "medium" confidence rating for both 1987 and 1995. A moderate fraction of the facilities were tested in both years: 11 of 113 facilities in 1987 (10 percent), and 27 of 130 facilities (21 percent) in 1995. Moreover, the tested facilities represent 21 and 27 percent of the total activity level of operating MSWIs in 1987 and 1995, respectively. These tests represent most of the design categories

identified in this report. The emission factors were developed from emission tests that followed standard EPA protocols, used strict QA/QC procedures, and were well documented in engineering reports. Because all tests were conducted under normal operating conditions, some uncertainty exists about the magnitude of emissions that may occur during other times (i.e., upset conditions, start-up and shut-down).

These confidence ratings produce an overall "medium" confidence rating. Using the procedures established for this report for a "medium" confidence rating, the best estimate of the annual emissions is assumed to be the geometric average of a range that varies by a factor of five between the low and high ends. For 1987, the central estimate of the annual emissions is 7,915-g TEQ/yr, and the range is calculated to be 3,540- to 17,698-g TEQ/yr. For 1995, the central estimate of annual emissions is 1,100-g TEQ/yr, and the range is calculated to be 492- to 2,460-g TEQ/yr.

3.1.5 Congener Profiles of MSWI Facilities

The TEQ air emissions from MSWIs are actually a mixture of CDD and CDF congeners. These mixtures can be translated into what are termed 'congener profiles,' which represent the distribution of total CDDs and CDFs present in the mixture. A congener profile may serve as a signature of the types of CDDs and CDFs associated with particular MSWI technology and APCD. Figure 3-9 is a congener profile of a mass-burn waterwall MSWI equipped with a dry scrubber and fabric filter (i.e., the most common type of MSWI and APCD design in use today). In general, the congener profile suggests that OCDD dominates total CDD/CDF emissions. In addition, every toxic CDD/CDF congener is detected in the emissions.

3.1.6 Estimated CDD/CDFs in MSWI Ash

Ash from MSWIs is required to be disposed in permitted landfills. Based on protocols of this report, ash from MSWIs are, therefore, not considered environmental releases of CDD/CDFs and are not included in the inventory. For background purposes, however, some information is presented below about the quantities of CDD/CDFs in ash from MSWIs.

An estimated 7-million metric tons of total ash (bottom ash plus fly ash) were generated by MSWIs in 1992 (telephone conversation between J. Loundsberry, U.S. EPA Office of Solid Waste, and L. Brown, Versar Inc., on February 24, 1993). U.S. EPA

(1991b) indicated that 2- to 5-million metric tons of total ash were produced annually in the late 1980s from MSWIs, with fly ash comprising 5 to 15 percent of the total. U.S. EPA (1990c) reported the results of analyses of MSWI ash samples for CDDs and CDFs. Ashes from five state-of-the-art facilities located in different regions of the United States were analyzed for all 2,3,7,8-substituted CDDs and CDFs. The TEQ levels in the ash (fly ash mixed with bottom ash) ranged from 106 to 466 ng/kg, with a mean value of 258 ng/kg. CDD/CDF levels in fly ash are generally much higher than in bottom ash. For example, Fiedler and Hutzinger (1992) reported levels of 13,000-ng TEQ/kg in fly ash. Multiplying the mean TEQ total ash concentration by the estimated amount of MSWI ash generated annually (approximately 7-million metric tons in 1995 and 5-million metric tons in 1987) yields an estimated annual TEQ in MSWI ash of 1,800-g TEQ/yr in 1995 and 1,300-g TEQ/yr in 1987.

Each of the five facilities sampled in U.S. EPA (1990c) had companion ash disposal facilities equipped with leachate collection systems or some means of collecting leachate samples. Leachate samples were collected and analyzed for each of these systems. Detectable levels were only found in the leachate at one facility (TEQ = 3 ng/L); the only detectable congeners were HpCDDs, OCDD, and HpCDFs.

3.1.7 Current EPA Regulatory and Monitoring Activities

On December 19, 1995, EPA promulgated CDD/CDF emission standards for all existing and new MSWI units with aggregate capacities to combust greater than 35 metric tons per day (Federal Register, 1995e). The specific emission standards (expressed as ng/dscm of total CDD/CDF - based on standard dry gas corrected to 7 percent oxygen) are a function of the size, APCD configuration, and age of the facility as listed below:

1995 Emission standard (ng total CDD/CDF/dscm)	Facility age, size, and APCD
60	• Existing; >225 metric tons/day; ESP-based APCD
30	• Existing; >225 metric tons/day; non-ESP-based APCD
125	• Existing; >35 to ≤225 metric tons/day
13	• New; >35 metric tons/day

States have up to 3 years from promulgation of the Federal standards to submit revised State Implementation Plans to EPA for approval. Once approved, States have the primary responsibility to implement the new standards. This could occur as early as the year 2000. As this date approaches, EPA's Office of air Quality Planning and Standards (OAQPS) estimates that the current estimate of national emissions of CDD/CDFs from existing MSWIs will decline from current levels. OAQPS estimates full compliance by all MSWIs with the 1995 standards will result in an annual emission of about 24-g TEQ/yr (U.S. EPA, 1996d).

3.2. HAZARDOUS WASTE INCINERATION

Hazardous waste incineration (HWI) is the controlled pyrolysis and/or oxidation of potentially dangerous liquid, gaseous and solid waste. HWI is one technology used to manage hazardous waste under RCRA and CERCLA (Superfund) programs. As described below, hazardous wastes are burned in a variety of situations and are covered in a number of different sections in this report.

- Much of the hazardous waste is burned in facilities dedicated to burning waste. Most of these dedicated facilities are located "onsite" at chemical manufacturing facilities and only burn waste associated with their on-site industrial operations. Hazardous waste is also burned at dedicated facilities located "offsite" from manufacturing facilities and accept waste from multiple sources. These fixed location facilities dedicated to burning hazardous waste at both on- and off-site locations are addressed in Sections 3.2.1 to 3.2.4.

- Hazardous waste is also burned in industrial boilers and furnaces that are permitted to burn the waste as supplemental fuel. These facilities have significantly different furnace designs and operations than dedicated HWIs; therefore, they are discussed in Section 3.2.5.

- A number of cement kilns are also permitted to burn hazardous waste as auxiliary fuel; these are discussed separately in Section 5.1.

- Mobile HWIs are typically used for site cleanup at Superfund sites and operate for a limited duration at any given location. These units are 'mobile' in the sense that they can be transported from one location to another. Due to the transitory nature of these facilities, they are not included in this inventory.

The following subsections review the types of HWI technologies commonly in use in the United States, and present the derivation of emissions estimates of CDD/CDFs from all facilities operating in 1995 and 1987.

3.2.1. Furnace Designs for Dedicated Hazardous Waste Incinerators

The four principal furnace designs employed for the combustion of hazardous waste in the United States are: liquid injection, rotary kiln, fixed hearth, and fluidized-bed incinerators (Dempsey and Oppelt, 1993). The majority of commercial operations are of the rotary kiln incinerator type. On-site (noncommercial) HWI technologies are an equal mix of rotary kiln and liquid injection facilities, with a few additional fixed hearths and fluidized bed operations (U.S. EPA, 1996h). Each of these MWI technologies is discussed below:

Rotary Kiln HWI: Rotary kiln incinerators consist of a rotating kiln, coupled with a high temperature afterburner. Because these are excess air units designed to combust hazardous waste in any physical form (i.e., liquid, semi-solid, or solid), rotary kilns are the most common type of hazardous waste incinerator used by commercial "off-site" operators. The rotary kiln is a horizontal cylinder lined with refractory material. Rotation of the cylinder on a slight slope provides for gravitational transport of the hazardous waste through the kiln (Buonicore, 1992a). The tumbling action of the rotating kiln causes mixing and exposure of the waste to the heat of combustion, thereby enhancing burnout. Solid and semi-solid wastes are loaded into the top of the kiln by an auger or rotating screw. Fluid and pumpable sludges and wastes are typically introduced into the kiln through a water-cooled tube. Liquid hazardous waste is fed directly into the kiln through a burner nozzle. Auxiliary fuel (natural gas or oil) is burned in the kiln chamber at start-up to reach elevated temperatures. The typical heating value of hazardous waste (i.e., 8,000 Btu/kg) is sufficient to sustain combustion without auxiliary fuel (U.S. EPA, 1996h). The combustion gases emanating from the kiln are passed through a high temperature afterburner chamber to more completely destroy organic pollutants entrained in the flue gases. Rotary kilns can be designed to operate at temperatures as high as 2,580°C, but more commonly operate at about 1,100°C.

Liquid Injection HWI: Liquid injection incinerators (LIIs) are designed to burn liquid hazardous waste. These wastes must be sufficiently fluid to pass through an atomizer for

injection as droplets into the combustion chamber. The LIIs consist of a refractory-lined steel cylinder mounted either in a horizontal or vertical alignment. The combustion chamber is equipped with one or more waste burners. Because of the rather large surface area of the atomized droplets of liquid hazardous waste, the droplets quickly vaporize. The moisture evaporates, leaving a highly combustible mix of waste fumes and combustion air (U.S. EPA, 1996h). Secondary air is added to the combustion chamber to complete the oxidation of the fume/air mixture.

Fixed Hearth HWI: Fixed hearths, the third principal hazardous waste incineration technology, are starved air or pyrolytic incinerators, which are two-stage combustion units. Waste is ram-fed into the primary chamber and incinerated below stoichiometric requirements (i.e., at about 50 to 80 percent of stoichiometric air requirements). The resulting smoke and pyrolytic combustion products are then passed though a secondary combustion chamber where relatively high temperatures are maintained by the combustion of auxiliary fuel. Oxygen is introduced into the secondary chamber to promote complete thermal oxidation of the organic molecules entrained in the gases.

Fluidized-bed HWI: The fourth hazardous waste incineration technology is the fluidized-bed incinerator, which is similar in design to that used in MSW incineration. (See Section 3.1.) In this configuration, a layer of sand is placed on the bottom of the combustion chamber. The bed is preheated by underfire auxiliary fuel at startup. During combustion of auxiliary fuel at start-up, the hot gases are channeled through the sand at relatively high velocity, and the turbulent mixing of combustion gases and combustion air causes the sand to become suspended (Buonicore, 1992a). This takes on the appearance of a fluid medium, hence the incinerator is termed a 'fluidized bed' combustor The incinerator is operated below the melting point temperature of the bed material. Typical temperatures of the fluid medium are within the range of 650 to 940°C. A constraint on the types of waste burned is that the solid waste particles must be capable of being suspended within the furnace. When the liquid or solid waste is combusted in the fluid medium, the exothermic reaction causes heat to be released into the upper portion of the combustion chamber. The upper portion is typically much larger in volume than the lower portion, and temperatures can reach 1,000°C (Buonicore, 1992a). This high temperature is sufficient to combust volatilized pollutants emanating from the combustion bed.

3.2.2. APCDs for Dedicated Hazardous Waste Incinerators

Most HWIs use APCDs to remove undesirable components from the flue gases that evolved during the combustion of the hazardous waste. These unwanted pollutants include suspended ash particles ("particulate matter" or PM), acid gases, metal, and organic pollutants. The APCD controls or collects these pollutants and reduces their discharge from the incinerator stack to the atmosphere. Levels and kinds of these combustion byproducts are highly site-specific, depending on factors such as waste composition and incinerator system design and operating parameters (e.g., temperature and exhaust gas velocity). The APCD is typically comprised of a series of different devices that work together to clean the exhaust combustion flue gas. Unit operations usually include exhaust gas cooling, followed by particulate matter and acid gas control.

Exhaust gas cooling may be achieved using a waste heat boiler or heat exchanger, mixing with cool ambient air, or injection of a water spray into the exhaust gas. A variety of different types of APCDs are employed for the removal of particulate matter and acid gases. Such devices include: wet scrubbers (such as venturi, packed bed, and ionizing systems), electrostatic precipitators, and fabric filters (sometimes used in combination with dry acid gas scrubbing). In general, the control systems can be grouped into the following three categories: "wet," "dry," and "hybrid wet/dry" systems. The controls for acid gases (either dry or wet systems) cause temperatures to be reduced preceding the control device. This impedes the extent of formation of CDDs and CDFs in the post-combustion area of the typical HWI. It is not unusual for stack concentrations of CDD/CDFs at a particular HWI to be in the range of 1- to 100-ng CDD/CDF/dscm (Helble, 1993), which is low in comparison to other waste incineration systems. The range of total CDD/CDF flue gas concentrations measured in the stack emissions of HWIs during trial burns across the class of HWI facilities, however, has spanned four orders of magnitude (ranging from 0.1 to 1,600 ng/dscm) (Helble, 1993). The APCD systems are described below:

- Wet Systems: A wet scrubber is used for both particulate and acid gas control. Typically, a venturi scrubber and packed-bed scrubber are used in a back-to-back arrangement. Ionizing wet scrubbers, wet electrostatic precipitators, and innovative venturi-type scrubbers may be used for more efficient particulate control. Wet scrubbers generate a wet effluent liquid wastestream (scrubber blowdown), are relatively inefficient at fine particulate control compared to dry control techniques,

and have equipment corrosion concerns. However, wet scrubbers do provide efficient control of acid gases and have lower operating temperatures (compared with dry systems), which may help control the emissions of volatile metals and organic pollutants.

- Dry Systems: In dry systems, a fabric filter or electrostatic precipitator (ESP) is used for particulate control. A fabric filter or ESP is frequently used in combination with dry scrubbing for acid gas control. Dry scrubbing systems, in comparison with wet scrubbing systems, are inefficient in controlling acid gases.
- Hybrid Systems: In hybrid systems, a dry technique (ESP or fabric filter) is used for particulate control, followed by a wet technique (wet scrubber) for acid gas control. Hybrid systems have the advantages of both wet and dry systems (lower operating temperature for capture of volatile metals, efficient collection of fine particulate, efficient capture of acid gases), while avoiding many of the individual disadvantages. In some hybrid systems, known as "zero discharge systems," the wet scrubber liquid is used in the dry scrubbing operation, thus minimizing the amount of liquid byproduct waste.
- Uncontrolled HWIs: Facilities that do not use any air pollution control devices fall under a separate and unique category. These are primarily liquid waste injection facilities, which burn low ash and chlorine content wastes; therefore, they are low emitters of PM and acid gases.

3.2.3. Estimation of CDD/CDF Emission Factors for Dedicated Hazardous Waste Incinerators

For purposes of estimating emission factors, this document considers subdividing the combustors in each source category into design classes judged to have similar potential for CDD/CDF emissions. As explained below, it was decided not to subdivide dedicated HWIs.

Combustion research has identified three mechanisms involved in the emission of CDD/CDFs from combustion systems: (1) CDD/CDFs can be introduced into the combustor with the feed and pass through the system not completely burned/destroyed; (2) CDD/CDFs can be formed by chemical reactions inside the combustion chamber; and (3) CDD/CDFs can be formed by chemical reactions outside the combustion chamber. The total CDD/CDF emissions are likely to be the net result of all three mechanisms; however, the relative

importance of the mechanisms can vary among source categories. In the case of HWIs, the third mechanism (i.e., post-combustion formation) is likely to dominate, because HWIs are typically operated at high temperatures and long residence times, and most have sophsiticated real-time monitoring and controls to manage the combustion process. Therefore, any CDD/CDFs present in the feed or formed during combustion are likely to be destroyed before exiting the combustion chamber. Consequently, for purposes of generating emission factors, it was decided not to subdivide this class on the basis of furnace type.

Emissions resulting from the post-combustion formation in HWIs can be minimized through a variety of technologies:

- Rapid Flue Gas Quenching: The use of wet and dry scrubbing devices to remove acid gases usually results in the rapid reduction of flue gas temperatures at the inlet to the PM APCD. If temperature is reduced below 200°C, the low-temperature catalytic formation of CDD/CDFs is substantially retarded.
- Use of Particulate Matter (Pm) Air Pollution Control Devices: PM control devices can effectively capture condensed and adsorbed CDD/CDFs that are associated with the entrained particulate matter (in particular, that which is adsorbed on unburned carbon containing particulates).
- Use of Activated Carbon: Activated carbon injection is used at some HWIs to collect (sorb) CDD/CDFs from the flue gas. This may be achieved using carbon beds or by injecting carbon and collecting it in a downstream PM APCD.

All of these approaches appear very effective in controlling dioxin emissions at dedicated HWIs, and insufficient emissions data are available to generalize about any minor differences. Consequently, for purposes of generating emission factors, it was decided not to subdivide this class on the basis of APCD type.

EPA compiled a data base summarizing the results of stack testing for CDDs and CDFs at 17 HWIs (U.S. EPA, 1996c). Most facilities were tested between 1993 and 1996. For purposes of this report, CDD/CDF emission factors were estimated based on the results of the emission tests contained in this data base. The breakdown of furnace types of tested HWI facilities is as follows: 10 rotary kiln incinerators, 4 liquid injection incinerators, 1 fluidized-bed incinerator, and 2 fixed-bed.

As stated earlier, EPA/ORD decided not to subclassify the dedicated HWI designs for purposes of deriving an emission factor (EF). Instead, the EF was derived as an average across all 17 tested facilties. First, an average emission factor was calculated for each of 17 HWIs with Equation 3-3.

$$EF_{hwi} = \frac{C \ x \ F_v}{I_w} \qquad \text{(Eqn. 3-3)}$$

Where:

EF_{hwi}	=	Emission factor (average ng TEQ per kg of waste burned).
C	=	TEQ or CDD/CDF concentration in flue gases (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2).
F_v	=	Volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2).
I_w	=	Average waste incineration rate (kg/hr).

After developing average emission factors for each HWI, the overall average congener-specific emission factor was derived for all 17 tested HWIs using Equation 3-4.

$$EF_{avgHWI_{n=1-18}} = \sum \left(EF_{HWI_1} + EF_{HWI_2} + EF_{HWI_3} \ldots\ldots EF_{HWI_{18}} \right) \qquad \text{(Eqn. 3-4)}$$

Where:

EF_{HWI} = Average emission factor of 18 tested MWIs, ng/kg

Table 3-6 presents the average emission factors developed for specific congeners, total CDDs/CDFs, and TEQs for operating HWIs. The average congener emission profiles for the 17 HWIs are presented in Figure 3-10. The average TEQ emission factor for the 17 tested HWIs is 3.8-ng TEQ/kg of waste feed (assuming not detected values are zero).

3.2.4. Emission Estimates for Dedicated Hazardous Waste Incinerators

Although emissions data on a relatively high number of dedicated HWIs were available (i.e., 17 of 162 have been tested), the emission factor estimate is assigned a "medium" confidence rating due to uncertainties resulting from:

- *Extreme heterogeneity of the waste feeds.* The physical and chemical composition of the waste can vary from facility to facility and even within a facility.

Consequently, CDD/CDF emissions measured for one feed may not be representative of other feeds.

- *Trial burns*. Much of the CDD/CDF emissions data were collected during trial burns, which are required as part of the RCRA permitting process and are used to establish Destruction Rated Efficiency of principal hazardous organic constituents in the waste. During trial burns, a prototype waste is burned, which is intended to maximize the difficulty in achieving good combustion. For example, chlorine, metals, and organics may be added to the waste. The HWI may also be operated outside normal operating conditions. The temperature of both the furnace and the APCD may vary by a wide margin (high and low temperatures), and the waste feed system may be increased to maximum design load. Accordingly, it is uncertain how representative the CDD/CDF emissions measured during the trial burn will be of emissions during normal operating conditions.

Dempsey and Oppelt (1993) estimated that up to 1.3-million metric tons of hazardous waste were combusted in dedicated HWIs during 1987. The best estimate of the amount of hazardous waste combusted in 1995 is 1.5-million metric tons (Federal Register, 1996b). The activity level estimate for 1995 is assigned a "high" confidence rating, because it is based on a thorough review of the various studies and surveys conducted in the 1990s to assess the quantity and types of hazardous wastes being managed by various treatment, storage, and disposal facilities. A confidence rating of "medium" is assigned to the activity level estimate for 1987.

The annual TEQ emissions for the reference years 1995 and 1987 were estimated using Equation 3-5.

$$E_{HWI} = EF_{HWI} \times A_{HWI} \qquad \text{(Eqn. 3-5)}$$

Where:

E_{HWI} = Annual emissions from all HWIs, tested and non-tested (g TEQ/yr)
EF_{HWI} = Mean emission factor for HWIs (ng TEQ/kg of waste burned)
A_{HWI} = Annual activity level of all operating HWIs (million metric tons/yr)

Applying the average emission factor for dedicated HWIs (3.8-ng TEQ/kg waste) to these production estimates yields estimated emissions of 5.7-g TEQ in 1995 and 5.0-g TEQ in 1987 for HWIs. The "medium" confidence rating assigned to the emission factor, combined with the high confidence rating for the 1995 activity level and medium

confidence rating for the 1987 activity level, yields an overall medium confidence rating for both years. Accordingly, the estimated range of annual emissions is assumed to vary by a factor of five between the low and high ends of the range. For 1995, the range of TEQ emissions is estimated to be 2.6- to 12.8-g TEQ/yr. For 1987, the range of TEQ emissions is estimated to be 2.2- to 11.2-g TEQ/yr.

EPA/OSW has also developed estimates of the CDD/CDF emissions from dedicated HWIs as part of the development of the Hazardous Waste Incineration Rule (U.S. EPA, 1997d). Like ORD, OSW also decided not to subdivide the dedicated HWIs on the basis of design. Instead of an emission factor approach, OSW used an imputation method to estimate emissions at untested facilites. This procedure involved randomly selecting measured CDD/CDF flue gas concentrations (ng/dscm) from the pool of tested HWI facilities and assigning them to the untested facilites. With this procedure, all non-tested HWIs have an equal chance of being assigned any flue gas concentration from the pool of measured values. The flue gas concentrations were combined with flue gas flow rates for each facility to estimate the emission rate. A key difference in these approaches is that ORD uses waste feed rate directly in the calculation of emissions and the OSW approach is independent of waste feed rate. Both procedures are reasonable ways to deal with the broad range of uncertainties and both yield similar emission estimates. ORD has not identified any inherent advantage of one approach over the other and elected to use the emission factor approach primarily because it is consistent with the methods used in this document to characterize CDD/CDF emissions from all other source categories.

3.2.5. Industrial Boilers and Furnaces Burning Hazardous Waste

In 1991, EPA established rules that allow the combustion of some liquid hazardous waste in industrial boilers and furnaces (Federal Register, 1991c). These facilities typically burn oil or coal for the primary purpose of generating electricity. Liquid hazardous waste can only be burned as supplemental (auxiliary) fuel, and usage is limited by the rule to no more than 5 percent of the primary fuels. These facilities typically use an atomizer to inject the waste as droplets into the combustion chamber and are equipped with particulate and acid gas emission controls. In general, they are sophisticated, well controlled facilities, which achieve good combustion.

The national data base contains congener-specific emission concentrations for two tested boilers burning liquid hazardous waste as supplemental fuel. The average congener

and congener group emission profiles for the industrial boiler data set are presented in Figure 3-11. The average congener and TEQ emission factors are presented in Table 3-6. The limited set of emissions data prevented subdividing this class for the purpose of deriving an emission factor. The equation used to derive the emission factor is the same as Equation 3-4 above. The average TEQ emission factor for the two industrial boilers is 0.64-ng TEQ/kg of waste feed. This emission factor is assigned a "low" confidence rating, because it reflects testing at only 2 of the 136 hazardous waste boilers/furnaces.

Dempsey and Oppelt (1993) estimated that approximately 1.2-billion kg of hazardous waste were combusted in industrial boilers/furnaces in 1987. EPA estimates that in 1995 approximately 0.6-billion kg of hazardous waste were combusted in industrial boilers/furnaces (Federal Register, 1996b). The activity level estimate for 1995 is assigned a "high" confidence rating, because it is based on a thorough review of the various studies and surveys conducted in the 1990s to assess the quantity and types of hazardous wastes being managed by various treatment, storage, and disposal facilities (Federal Register, 1996b). A confidence rating of "medium" is assigned to the estimated activity level for 1987. The 1987 estimate was largely based on a review of State permits (Dempsey and Oppelt,1993).

Equation 3-5, used to calculate annual TEQ emissions for dedicated HWIs. was also used to calculate annual TEQ emissions for industrial boilers/furnaces. Multiplying the average TEQ emission factor of 0.64-ng TEQ/kg of waste feed by the total estimated kg of liquid hazardous waste burned in 1995 and 1987 yields the annual emissions in g TEQ/yr. From this procedure, the emissions from all industrial boilers/furnaces burning hazardous waste as supplemental fuel are estimated as 0.38-g TEQ/yr in 1995 and 0.77-g TEQ/yr in 1987. Because of the low confidence rating for the emission factor, the overall confidence rating is low for both the 1987 and 1995 emission estimates. Accordingly, it is assumed that the uncertainty range around the best estimate varies by a factor of 10 between the low and high ends of the range. Thus, the uncertainty ranges are 0.12- to 1.2-g TEQ/yr for 1995 and 0.24- to 2.4-g TEQ/yr for 1987.

3.3. MEDICAL WASTE INCINERATION

Medical waste incineration (MWI) is the controlled burning of solid wastes generated primarily by hospitals, veterinary, and medical research facilities. The U.S. EPA defines medical waste as any solid waste generated in the treatment, diagnosis, or immunization of

humans or animals, or research pertaining thereto, or in the production or testing of biologicals (Federal Register, 1997b). The primary purposes of MWI are to reduce the volume and mass of waste in need of land disposal, and to sterilize the infectious materials. The following subsections review the basic types of MWI designs used to incinerate medical waste, review the distribution of APCDs used on MWIs, summarize the derivation of dioxin TEQ emission factors for MWIs, and summarize the national dioxin TEQ emission estimates for reference years 1995 and 1987.

3.3.1. Design Types of MWIs Operating in the United States

For purposes of this document, EPA has classified MWIs into three broad technology categories: modular furnaces using controlled-air, modular furnaces using excess-air, and rotary kilns. Of the MWIs in use today, the vast majority are believed to be modular furnaces using controlled-air. EPA has estimated that 97 percent are modular furnaces using controlled-air, 2 percent are modular furnaces using excess air, and 1 percent are rotary kiln combustors (U.S. EPA, 1997b).

Modular Furnaces Using Controlled-air: Modular furnaces have two separate combustion chambers mounted in series (one on top of the other). The lower chamber is where the primary combustion of the medical waste occurs. Medical waste is ram-fed into the primary chamber, and underfire air is delivered beneath the incinerator hearth to sustain good burning of the waste. The primary combustion chamber is operated at below stoichiometric levels, hence the terms "controlled" or "starved-air." With sub-stoichiometric conditions, combustion occurs at relatively low temperatures (i.e., 760 to 985°C). Under the conditions of low oxygen and low temperatures, partial pyrolysis of the waste occurs, and volatile compounds are released. The combustion gases pass into a second chamber. Auxiliary fuel (such as natural gas) is burned to sustain elevated temperatures (i.e., 985 to 1,095°C) in this secondary chamber. The net effect of exposing the combustion gases to an elevated temperature is more complete destruction the organic contaminants entrained in the combustion gases emanating from the primary combustion chamber. Combustion air at 100 to 300 percent in excess of stoichiometric requirement is usually added to the secondary chamber. Gases exiting the secondary chamber are directed to an incinerator stack (U.S. EPA, 1997b; U.S. EPA, 1991d; Buonicore, 1992b). Figure 3-12 displays a schematic of a typical modular furnace using controlled-air. Because of their low cost and good combustion performance, this design has been the most popular

choice for MWIs and has accounted for more than 95 percent of systems installed over the past two decades (U.S. EPA, 1990d; U.S. EPA, 1991d; Buonicore, 1992b).

Modular Furnaces Using Excess-air: These systems use the same modular furnace configuration as described above for the controlled air systems. The difference is that the primary combustion chamber is operated at air levels of 100 percent to 300 percent in excess of stoichiometric requirements. Hence the name "excess-air." A secondary chamber is located on top of the primary unit. Auxiliary fuel is added to sustain high temperatures in an excess-air environment. Excess-air MWIs are typically smaller in capacity than controlled-air units and are usually batch-fed operations. This means that the medical waste is ram-fed into the unit and allowed to burn completely before another batch of medical waste is added to the primary combustion chamber.

Rotary Kiln MWI: This technology is similar in terms of design and operational features to the rotary kiln technology employed in both municipal and hazardous waste incineration. (See description in Section 3.1.) Because of their relatively high capital and operating costs, few rotary kiln incinerators are in operation for medical waste treatment (U.S. EPA, 1990d; U.S. EPA, 1991d; Buonicore, 1992b).

MWIs can be operated in three modes: batch, intermittent, and continuous. Batch incinerators burn a single load of waste, typically only once per day. Waste is loaded, and ashes are removed manually. Intermittent incinerators, loaded continuously and frequently with small waste batches, operate less than 24 hours per day, usually on a shift-type basis. Either manual or automated charging systems can be used, but the incinerator must be shut down for ash removal. Continuous incinerators are operated 24 hours per day and use automatic charging systems to charge waste into the unit in small, frequent batches. All continuous incinerators operate using a mechanism to automatically remove the ash from the incinerator (U.S. EPA, 1990d; U.S. EPA, 1991d).

3.3.2. Characterization of MWIs for Reference Years 1995 and 1987

MWI remains a poorly characterized industry in the United States in terms of knowing the exact number of facilities operational over time, the types of APCDs installed on these units, and the aggregate volume and weight of medical waste that is combusted in any given year (U.S. EPA, 1997b). The primary reason for this is that permits were not generally required for the control of pollutant stack emissions from MWIs until the early 1990s when State regulatory agencies began setting limits on emissions of particulate

matter and other contaminants (Federal Register, 1997b). Prior to that timeframe, only opacity was controlled.

The information available to characterize MWIs comes from national telephone surveys, stack emission permits, and data gathered by EPA during public hearings (Federal Register, 1997b). This information suggests the following:

- The number of MWIs in operation was approximately 5,000 in 1987 (U.S. EPA, 1987) and 2,375 in 1995 (Federal Register, 1997b).
- The amount of medical waste combusted annually in the United States was approximately 1.43-billion kg in 1987 (U.S. EPA, 1987d) and 0.77-billion kg in 1995 (Federal Register, 1997b).

These estimates indicate that, between 1987 and 1995, the total number of operating MWIs and the total amount of waste combusted decreased by more than 50 percent. Certain activities caused this to occur, including more stringent air pollution control requirements by State regulatory agencies and the development of less expensive medical waste treatment technologies, such as autoclaving (Federal Register, 1997b). Because many MWIs have small waste charging capacity (i.e., about 50 metric tons per day), the installation of even elementary APCDs proved not to be cost effective. Thus, a large number of facilities elected to close rather than retrofit.

The actual controls used on MWIs on a facility-by-facility basis in 1987 are unknown, and EPA generally assumes that MWIs were mostly uncontrolled (U.S. EPA,1987d). However, the modular design does cause some destruction of organic pollutants within the secondary combustion chamber. Residence time within the secondary chamber is key to inducing the thermal destruction of the organic compounds. Residence time is the time that the organic compounds entrained within the flue gases are exposed to elevated temperatures in the secondary chamber. EPA has demonstrated with full-scale MWIs that increasing residence time from 1/4 second to 2 seconds in the secondary chamber can reduce organic pollutant emissions, including CDD/CDFs, by up to 90 percent (Federal Register, 1997b). In this regard, residence time can be viewed as a method of air pollution control.

EPA estimates that about two-thirds of medical waste burned in MWIs in 1995 went to facilities equipped with some method of air pollution control (Federal Register, 1997b). The types of APCDs installed and the methods used on MWIs include: dry sorbent injection,

fabric filters, electrostatic precipitators (ESPs), wet scrubbers, and fabric filters combined with packed-bed scrubbers (composed of granular activated carbon). Some organic constituents in the flue gases can be adsorbed by the packed bed. Within the uncontrolled class of MWIs, about 12 percent of the waste were combusted in facilities with design capacities of <200 lbs/hr, with the majority of waste burned facilities >200 lb/hr. The estimated breakdown of controlled facilities is: 70 percent of the aggregate activity level are associated with facilities equipped with either wet scrubbers, fabric filters, or ESPs; 29.9 percent are associated with facilities utilizing dry sorbent injection, combined with fabric filters, and less than 1 percent is associated with facilities having the fabric filter/packed-bed APCD (AHA, 1995; Federal Register, 1997b).

3.3.3. Estimation of CDD/CDF Emissions From MWIs

Only 1 percent of existing facilities (i.e., 24 MWIs) has been stack sampled for CDD/CDFs. Consequently, most facilities have unmeasured emission levels of dioxin-like compounds. Because so few have been evaluated, the estimation of annual air emissions of CDD/CDFs from MWIs is quite dependent on extrapolations, engineering judgement, and the use of assumptions. In addition, the information about the activity levels of these facilities is also quite limited. With these data limitations, two approaches have been used in the past to estimate CDD/CDF emissions from MWIs, and a third is proposed here. These three approaches are as follows:

1. EPA/OAQPS Approach: EPA's Office of Air Quality Planning and Standards used this approach in support of the promulgation of final air emission standards for hospital/medical/infectious waste incinerators (Federal Register, 1997b).

2. AHA Approach: The American Hospital Association proposed an approach in its comments on drafts of this document and on the proposed MWI emissions regulations (AHA, 1995).

3. EPA/ORD Approach: In preparation of this document, EPA's Office of Research and Development (ORD) has developed a third approach.

Given the limitations with existing information, both the EPA/OAQPS and AHA approaches are reasonable methods for calculating annual releases of CDD/CDFs from MWIs. Both methods relied heavily on a series of assumptions to account for missing information. In developing a third approach, EPA/ORD built upon the other two approaches by utilizing the

most logical features of each. Because of the uncertainties with existing data, it is currently not known which approach gives the most accurate estimate of CDD/CDF air emissions from all MWIs, nationwide. The three approaches yield different air emission estimates, but the estimates all agree within a factor of four. As discussed below, the EPA/ORD approach used the strengths of the other two approaches, and represents some improvement in estimating CDD/CDF emissions.

3.3.4. EPA/OAQPS Approach for Estimating CDD/CDF Emissions from MWIs

On September 15, 1997, EPA promulgated final standards of performance for new and existing MWIs under the Clean Air Act Amendments (Federal Register, 1997b). CDD/CDF stack emission limits for existing MWIs were established as follows: 125 ng/dscm of total CDD/CDF (at 7 percent O_2, 1 atm), equivalent to 2.3 ng/dscm TEQ. In order to evaluate emissions reductions that will be achieved by the standard, OAQPS estimated, as a baseline for comparison, nationwide annual CDD/CDF emissions from all MWIs operating in 1995.

3.3.4.1. *EPA/OAQPS Approach for Estimating Activity Level*

As a starting point for deriving the national estimates, OAQPS constructed an inventory of the numbers and types of MWIs believed to be operating in 1995. The inventory was based on an inventory of 2,233 MWIs prepared by the American Hospital Association (AHA, 1995), supplemented with additional information compiled by EPA. This created a listing of 2,375 MWIs in the United States. Next a series of assumptions were used to derive activity level estimates, as follows:

1. The analysis divided MWIs into three design types based on the mode of daily operation: batch, intermittent, and continuous. This was done using the information from the inventory on design-rated annual incineration capacity of each facility. The smaller capacity units were assumed to be batch operations, and the others were classified as either intermittent or continuous, assuming a ratio of three to one.

2. The activity level of each facility was estimated by multiplying the design-rated annual incineration capacity of the MWI (kg/hr) by the hours of operation (hr/yr). The annual hours of operation were determined by assuming a capacity factor (defined as the fraction of time that a unit operates over the year) for each design type of MWI (Randall, 1995). Table

3-7 is a summary of the OAQPS estimated annual operating hours per MWI design type.

3.3.4.2. *EPA/OAQPS Approach for Estimating CDD/CDF Emission Factors*

Based on information obtained from AHA and State regulatory agencies, one-third of the population of MWIs operating in 1995 was etimated to have had no APCDs (i.e., were uncontrolled), and two-thirds had some type of APCD. CDD/CDF TEQ emission factors were then developed for uncontrolled and controlled MWIs. The procedure was as follows:

Estimating TEQ Emission Factors for Uncontrolled Facilities: The uncontrolled category of facilities was subdivided by residence time of the secondary combustion chamber. Based on tests at three MWIs, OAQPS concluded that stack emissions of CDD/CDFs from uncontrolled facilities were dependent on the residence time (i.e., the duration of time the compounds are exposed to elevated temperatures within the secondary combustion chamber) (Strong, 1996). The tests demonstrated that when the residence time in the secondary chamber was short (i.e., < 1 sec), the stack emissions of CDDC/CDFs would increase; conversely, the longer the residence time (i.e., > 1 sec), the CDD/CDF emissions decrease. The emissions testing at these MWIs provided the basis for the derivation of CDD/CDF TEQ emission factors for residence times of 1/4-sec, 1-sec and 2-sec. Table 3-8 is a summary of the emission factors developed for each MWI type as a function of residence time.

The OAQPS inventory of MWIs in 1995 did not provide residence times for each facility. OAQPS overcame this data gap by assuming that residence time in the secondary combustion chamber approximately corresponds with the particulate matter (PM) stack emission limits established in State air permits. This approach assumed that the more stringent PM emission limits would require longer residence times in the secondary chamber in order to further oxidize carbonaceous soot particles and reduce PM emissions. Table 3-8 lists the assumed residence times in the secondary chamber corresponding to various State PM emission limits. State Implementation Plans (SIPs) were reviewed to determine the PM emission limits for incinerators, and from this review, both a residence time and a TEQ emission factor were assigned to each uncontrolled MWI on the inventory.

Estimating TEQ Emission Factors for Controlled MWIs: Two-thirds of the MWI population were assumed to have some form of APCD. As previously discussed, APCDs typically used by MWIs consist of one or more of the following: wet scrubber, dry scrubber,

and fabric filter combined with a packed bed. The EPA/OAQPS approach also included the addition of activated carbon to the flue gases as a means of emissions control (i.e., dry scrubbers combined with carbon injection). TEQ emission factors were developed for these control systems based on incinerator emissions testing data gathered in support of the regulations (U.S. EPA, 1997b). Because the inventory did not list the APCDs for all MWIs, State requirements for PM control were used to make assumptions about the type of APCD installed on each facility in the inventory. These assumptions are summarized in Table 3-9.

3.3.4.3. *EPA/OAQPS Approach for Estimating Nationwide CDD/CDF TEQ Air Emissions*

Annual TEQ emissions for each MWI facility were calculated as a function of the design capacity of the incinerator, the annual waste charging hours, the capacity factor, and the TEQ emission factor as shown in Equation 3-6.

$$Em_{mwi} = (C \times H \times C_1) \times F_{TEQ} \qquad \text{(Eqn. 3-6)}$$

Where:

Em_{mwi}	=	Annual MWI CDD/F TEQ stack emissions (g/yr)
C	=	MWI design capacity (kg/hr)
H	=	Annual medical waste charging hours (hr/yr)
C_1	=	Capacity factor (unitless)
F_{TEQ}	=	CDD/CDF TEQ emission factor (g TEQ/kg)

The annual TEQ air emission of all MWIs operating in 1995 is the sum of the annual emissions of each of the individual MWIs. The following equation is applied to estimate annual TEQ emissions from all MWIs.

$$Em_{mwi}(nationwide) = \sum (Em_{mwi_1}) + (Em_{mwi_2}) + \ldots\ldots (Em_{mwi_{2375}}) \qquad \text{(Eqn. 3-7)}$$

Where:

Em_{mwi}(nationwide) = Nationwide MWI TEQ emissions (g/yr)

Table 3-9 is a summary of annual CDD/CDF TEQ emissions for 1995 estimated using the EPA/OAQPS Approach.

3.3.5. AHA Approach for Estimating CDD/CDF Emissions from MWIs

In 1995, the American Hospital Association (AHA) submitted written comments to EPA in response to EPA's request for public comment of the 1994 draft public release of this document (AHA, 1995). As part of these comments, the AHA attached an analysis of CDD/CDF emissions from MWIs prepared by Doucet (1995) for the AHA. Doucet (1995) estimated the total number of MWIs operating in 1995, the distribution of APCDs, CDD/CDF TEQ emission factors, and the nationwide TEQ emissions. The following is a brief discussion of the AHA inventory and the Doucet (1995) analysis.

From a national telephone survey of member hospitals conducted between September and November 1994, the AHA developed what is generally considered as the first attempt to systematically inventory MWIs in the United States. Approximately 6 percent of the hospitals with MWIs were contacted (AHA,1997). The AHA survey showed that, as of December, 1994, 2,233 facilities were in operation. Doucet (1995) subdivided the AHA MWI inventory into two uncontrolled categories on the basis of combustor design-rated capacity and two controlled categories on the basis of APCD equipment. Doucet (1995) then developed CDD/CDF emission factors for each category of MWIs. Test reports of 19 MWIs were collected and evaluated. Average CDD/CDF TEQ flue gas concentrations (i.e., ng/dscm @7 percent O_2) were derived by combining tests from several MWIs in each capacity range category and APCD. The average TEQ flue gas concentrations were then converted to average TEQ emission factors, which were in units of lb TEQ/10^6 lbs of medical waste incinerated (equation for conversion not given). Table 3-10 is a summary of TEQ emission factors calculated by Doucet (1995) for each level of assumed APCDs on MWIs.

Similar to the EPA/OAQPS Approach (Section 3.3.4), the distribution of the APCD categories was derived by assuming that State particulate emission (PM) limits would indicate the APCD on any individual MWI (Doucet, 1995). Table 3-11 displays the AHA assumptions of air pollution control (APC) utilized on MWIs based upon PM emission limits.

With the activity levels, the percent distribution of levels of controls, and the CDD/CDF TEQ emission factors having been calculated with existing data, the final step of the AHA Approach was the estimation of annual TEQ emissions (g/yr) from MWIs,

nationwide. Although no equation is given, it is presumed that the emissions were estimated by multiplying the activity level for each MWI size and APCD category by the associated TEQ emission factor. The sum of these calculations for each designated class yields the estimated annual TEQ emissions for all MWIs, nationwide. Doucet (1995) indicates that these computations are appropriate for TEQ emissions in 1995. Table 3-12 summarizes the nationwide annual TEQ emissions from MWIs using the AHA Approach.

3.3.6. EPA/ORD Approach for Estimating CDD/CDF Emissions from MWIs

Because of limitations in emissions data and on activity levels, the EPA/ORD approach used many of the logical assumptions developed in the EPA/OAQPS and AHA approaches. The discussion below describes the rationale for how these decisions were made, and presents the resulting emission estimates.

3.3.6.1. *EPA/ORD Approach for Classifying MWIs and Estimating Activity Levels*

As with the EPA/OAQPS and AHA approaches, the EPA/ORD approach divided the MWIs into controlled and uncontrolled classes. The decisions about further dividing these two classes are described below:

Uncontrolled MWIs: For purposes of assigning CDD/CDF emission factors and activity levels to the uncontrolled class of MWIs, the EPA/OAQPS approach divided this class on the basis of residence time within the secondary combustion chamber. This approach has theoretical appeal, because it is logical to expect more complete combustion of CDD/CDFs with longer residence times at high temperatures. Unfortunately, the residence times on a facility-by-facility basis are not known, making it difficult to assign emission factors and activity levels on this basis. As discussed earlier, the EPA/OAQPS approach assumed that residence time would strongly correlate with State PM stack emission requirements (i.e., the more stringent the PM requirements, the longer the residence time required to meet the standard). This PM method for estimating residence time resulted in the following distribution of residence times: 6 percent of the waste incinerated at MWIs with 1/4-sec residence time; 26 percent of the waste incinerated at MWIs with 1-sec residence time; and 68 percent of the waste incinerated at MWIs with 2-sec residence time. Thus, about two-thirds of the activity level within the uncontrolled class were assumed in the EPA/OAQPS approach to be associated with facilities with the longest residence time and the lowest CDD/CDF emission factor.

The AHA approach subcategorized the uncontrolled class on the basis of design-rated capacity. There is also theoretical support for this approach. Smaller capacity operations (i.e., <200 lb/hr) are likely to have higher emissions, because they are more likely to be operating in a batch mode. The batch mode results in infrequent operation with more start-up and shut-down cycles. Thus, the batch-operated MWI usually spends more time outside of the ideal range of operating conditions. In support of this approach, the AHA presented limited empirical evidence indicating that CDD/CDF emission factors calculated from emission test reports for the low capacity units were about a factor of two higher than the emission factors for the high capacity units (Doucet, 1995).

Thus, both the EPA/OAQPS and AHA approaches have a sound theoretical basis but lack strong supporting data. In order to decide which of the two approaches to use, ORD first tested the assumption that there is a strong relationship between State PM requirements and residence time. ORD conducted a limited telephone survey of regulatory agencies in four States where a large number of MWI facilities were in operation: Michigan, Massachusetts, New Jersey, and Virginia (O'Rourke, 1996). The results of the limited survey, summarized in Table 3-13, did not verify the existence of a strong dependent relationship between PM emission limits and residence time in the secondary chamber at MWIs.

Next, the available emission testing data for small and high capacity units (i.e., less than and greater than 200 lb/hr) were evaluated to determine if, as posited in the AHA approach, smaller capacity units have greater emission factors than large capacity units. This evaluation indicated a distinct difference in the emission factors between the two capacity categories, although the difference in the set of data evaluated was not as great as the difference observed in the data set evaluated in the AHA approach. The EPA/ORD approach, therefore, adopted the subcategorization scheme used in the AHA approach.

<u>Controlled MWIs</u>: Both the EPA/OAQPS approach and the AHA approach subcategorized the controlled MWIs on the basis of APCD equipment. However, the two approaches differed in the subcategories developed. The AHA approach divided the controlled class into two groups: facilities equipped with wet scrubbers (alone, with an ESP, or with a fabric filter), and facilities equipped with dry sorbent injector and a fabric filter (Doucet, 1995). The EPA/OAQPS approach divided the controlled class into three groups: facilities equipped with wet scrubbers, facilities equipped with dry scrubbers (with or without carbon injection), and facilities equipped with fabric filters and packed bed

scrubbers. This third category is comprised of a few facilities primarily located in the Northeast United States (O'Rourke, 1996). The EPA/ORD approach adopted the two subcategories of the AHA approach and the third subcategory of the EPA/OAQPS approach. For 1995, ORD used the activity levels for each facility as determined by the EPA/OAQPS inventory; the activity levels were then summed across facilities for each APCD subclass.

For 1987, the EPA/ORD approach assumed that every MWI was uncontrolled on the basis of a EPA study of MWI incineration conducted at that time (U.S. EPA, 1987d). This study indicates that MWIs operating in 1987 did not need controls, because they were not subject to State or Federal limits on either PM or organic pollutant emissions. The activity level estimates were derived from additional EPA studies (U.S. EPA, 1987d). This approach resulted in the following activity level assumptions for 1987: (a) 15 percent of the activity level (i.e., 0.2-billion kg medical waste) were incinerated/yr by MWIs with capacities less than or equal to 200 lb/hr, and (b) 85 percent of the activity level (i.e., 1-billion kg/yr) were incinerated by facilities with capacities greater than 200 lb/hr.

3.3.6.2. *EPA/ORD Approach for Estimating CDD/CDF Emission Factors*

EPA/ORD collected the engineering reports of 24 tested MWIs. After reviewing these test reports, 19 met the criteria for acceptability. (See Section 3.1.3 for further details on the criteria.) In some cases, CDD/CDF congener-specific data were not reported, or values were missing. In other cases, the protocols used in the laboratory analysis were not described; therefore, no determination of the adequacy of the laboratory methods could be made.

The EPA stack testing method (EPA Method 23) produces a measurement of CDD/CDFs in units of mass concentration (i.e., nanograms per dry standard cubic meter of combustion gas (ng/dscm)) at standard temperature and pressure and one atmosphere and adjusted to a measurement of 7 percent oxygen in the flue gas (U.S. EPA, 1995b). This concentration is assumed to represent conditions at the point of release from the stack into the air, and to be representative of routine emissions. The emission factors were derived by averaging the emission factors across each tested facility in a design class. The emission factor for each tested MWIs was calculated using the following equation:

$$EF_{mwi} = \frac{C \ x \ F_v}{I_w} \qquad \text{(Eqn. 3-8)}$$

Where:

EF_{mwi}	=	Emission Factor per MWI (average ng TEQ per kg of medical waste burned).
C	=	Average TEQ concentration in flue gases of tested MWIs (ng TEQ/dscm) (20°C, 1 atm; adjusted to 7% O_2).
F_v	=	Average volumetric flue gas flow rate (dscm/hr) (20°C, 1 atm; adjusted to 7% O_2).
I_w	=	Average medical waste incineration rate of the tested MWI (kg/hr).

The emission factor estimate for each design class and the number of stack tests used to derive it are shown in Table 3-14. Figures 3-12 and 3-13 present congener and congener group profiles for air emissions from MWIs lacking APCDs and for MWIs equipped with a wet scrubber/baghouse/fabric filter APCD system, respectively.

3.3.7. Summary of CDD/CDF Emissions From MWIs

Because the stack emissions from so few facilities have been tested (i.e., 19 test reports) relative to the number of facilities in this industry (i.e., 2,375 facilities in 1995 and 5,000 facilities in 1987) and because several tested facilities are no longer in operation or have installed new APCD after testing, the EPA/ORD approach did not calculate nationwide CDD/CDF emissions by calculating emissions from the tested facilities and adding those to calculated emissions for the non-tested facilities. Rather, the EPA/ORD approach (as well as the EPA/OAQPS and AHA approaches) calculated nationwide CDD/CDF emissions by multiplying the emission factor and activity level developed for each design class and then summing the calculated emissions for all classes. Tables 3-14 and 3-15 summarize the resulting national TEQ air emissions for the reference years 1995 and 1987, respectively. In addition, the Tables indicate the activity level and the TEQ emission factor used in estimating annual TEQ emissions.

In estimating annual TEQ emissions in both reference years, a "low" confidence rating was assigned to the estimate of the activity level. The primary reason for the low confidence rating is that very limited information is available on a facility level basis for characterizing MWIs in terms of the frequency and duration of operation, the actual waste

volume handled, and the level of pollution control. The 1987 inventory of facilities was based on very limited information. Although the 1995 EPA/OAQPS inventory was more comprehensive than the 1987 inventory, it was still based on a fairly limited survey of operating facilities (i.e., approximately 6 percent).

The emission factor estimates were given a "low" confidence rating, because only the reports of 19 tested MWI facilities could be used to derive emissions factors representing the 2,375 facilities operating in 1995 (i.e., less than 1 percent of estimated number of operating facilities). Even fewer tested facilities could be used to represent the larger number of facilities operating in 1987 (i.e., 8 tested facilities were used to represent 5,000 facilities). The limited emission tests available do cover all design categories used here to develop emission factors. However, because of the large number of facilities in each of these classes, it is very uncertain whether the few tested facilities in each class capture the true variability in emissions.

- **Reference Year 1995**: Based on the low confidence ratings for both the activity level and the emission factor, the estimated range of potential annual TEQ emissions from MWIs in 1995 is assumed to vary by a factor of 10 (between the low and high ends of the range). From Table 3-14, the central estimate of TEQ emissions in 1995 is estimated to be 477 g/yr, with a range of 151 to 1,510 g TEQ/yr.

- **Reference Year 1987**: Based on the low confidence ratings for both the activity level and the emission factor, the estimated range of potential annual TEQ emissions from MWIs in 1987 is assumed to vary by a factor of 10 (between the low and high ends of the range). From Table 3-15, the central estimate of TEQ emissions in 1987 is estimated to be 2,470 g/yr, with a range of 781- to 7,810-g TEQ/yr.

As explained above, the EPA/ORD approach to estimating national CDD/CDF TEQ emissions is a 'hybridization' of the EPA/OAQPS and AHA approaches. Table 3-16 compares the main features of each of the three approaches. The 1995 TEQ emissions estimated here (477-g TEQ/yr) are about 3.5 times higher than those of OAQPS and AHA (141- and 138-g TEQ/y, respectively). Most of this difference is due to differences in the emission estimates for the uncontrolled facilities (ORD - 436-g TEQ/yr, OAQPS - 136-g

TEQ/yr, AHA - 120-g TEQ/yr). An analysis of the differences in how these groups estimated emissions from the uncontrolled facilities are presented below:

- **Differences between the EPA/ORD and AHA Approaches:** The ORD approach adopted the classification scheme of the AHA approach for the uncontrolled class and assumed similar activity levels. Thus, the difference in emission estimates is primarily due to differences in the emission factors used. Both groups use similar emission factors for facilities with design capacities less than or equal to 200 lbs/h, but the emission factor for MWIs > 200 lbs/hr used in the EPA/ORD approach was higher than that used in the AHA approach by a factor of three. This results from the fact that the two approaches used different sets of emission tests to derive their emission factors.

- **Differences between the EPA/ORD and EPA/OAQPS Approaches:** Because the two approaches subcategorized the uncontrolled facilities into different classes, the activity levels and emission factors cannot be directly compared. Considering the class as a whole, however, both approaches used essentially identical activity levels. The EPA/OAQPS approach assigned 68 percent of the total activity to the class with the lowest emission factor (i.e., those with >2-sec residence time). The emission factor for this class, 74-ng TEQ/kg, is considerably lower than either emission factor used in the EPA/ORD approach (1,700- and 1,860-ng TEQ/kg).

Given the uncertain data base available for making these estimates, it is difficult to know which of these three estimation approaches yields the most accurate annual TEQ estimate. However, despite the differences in methodologies and assumptions used, the three approaches yield annual TEQ estimates that are not fundamentally different; the estimates differ from each other by a factor of four or less. Because the EPA/ORD approach was the last of the three to be developed, it has the benefit of being able to utilize the most logical and supportable features of the previously developed EPA/OAQPS and AHA approaches.

Regardless of the approach taken to estimate what the CDD/CDF emissions from 2,375 MWIs were in 1995, the National Emission Standards promulgated by EPA in September 1997 (Federal Register, 1997b) require substantial reductions of CDD/CDF air

emissions from MWIs. As a result of these standards, MWI emissions will be thoroughly assessed for purposes of compliance with the CDD/CDF standard. Compliance testing will allow the development of a more comprehensive emissions data base and more accurate characterization of this industry.

3.4. CREMATORIA

Bremmer et al. (1994) categorized crematoria into two basic operating types: a "cold" type and a "warm" type. In the "cold" type furnaces, the coffin is placed inside at a temperature of about 300°C. Using a burner, the temperature of the chamber is increased to 800-900°C and kept at that temperature for 2 to 2.5 hours. In the "warm" type furnace, the coffin is placed in a chamber preheated to 800°C or higher for 1.2 to 1.5 hours. The chamber exhausts from both furnace types are incinerated in an after burner at a temperature of about 850°C. Flue gases are then discharged to the atmosphere either: (a) directly without cooling; (b) after mixing with ambient air using an air blast to a temperature of about 200-350°C; or (c) after mixing with ambient air as in "b," followed by further cooling to about 150°C in an air cooler and passage through a fabric filter.

Bremmer et al. (1994) measured CDD/CDF emissions at two crematoria in The Netherlands. The first, a cold-type furnace with direct uncooled emissions, was calculated to yield 2.4-μg TEQ per body. The second furnace, a warm type with cooling of flue gases to 220°C prior to discharge, was calculated to yield 4.9-μg TEQ per body. The higher emission rate for the warm-type furnace was attributed by Bremmer et al. (1994) to the formation of CDD/CDF during the intentional cooling of the flue gases to 220°C.

Jager et al. (1992) (as reported in Bremmer et al., 1994) measured an emission rate of 28-μg TEQ per body for a crematorium in Berlin, Germany. No operating process information was provided by Bremmer et al. (1994) for the facility.

In the United States, CDD/CDF emissions were measured at one crematorium (CARB, 1990c) classified as a warm-type facility using the criteria of Bremmer et al. (1994). The combusted material at this facility was comprised of the body, as well as 4 pounds of cardboard, up to 6 pounds of wood, and an unquantified amount of unspecified plastic wrapping. The three emission tests conducted at this facility yielded an average emission factor of 0.5-μg TEQ/body. Although this emission factor is very similar to the emission factors reported by Bremmer et al. (1994), a "low" confidence rating is assigned to the factor, because it represents testing at only one U.S. facility. Table 3-17 presents

the congener-specific emission factors for this facility. Figure 3-14 presents CDD/CDF congener and congener group emission profiles based on these emission factors.

In 1995, 1,155 crematories were reported in the United States (Springer, 1997). However, there are no readily available data on the number of "cold" versus "warm" crematoria furnaces. In 1995, 21.1 percent of the deceased bodies were cremated (i.e., 488,224 cremations), and 15.2 percent of the deceased were cremated in 1987 (i.e., 323,371 cremations) (Springer, 1997). Cremations are projected to increase to 25 percent in the year 2000 and 37 percent in the year 2010 (Springer, 1997). A high confidence rating is assigned to these activity level estimates, because they are based on recent data provided by the Crematoria Association of North America.

Combining the emission rate of 0.5-μg TEQ/body with the number of cremations in 1995 (488,224) yields an estimated annual release of 0.24-g TEQ per year. Based on the low confidence rating assigned to the emission factor of 0.5-μg TEQ/body, the estimated range of potential emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of annual emissions (0.24-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 0.07- to 0.75-g TEQ/yr. Combining the emission rate of 0.5-μg TEQ/body with the number of cremations in 1987 (323,371) yields an estimated release of 0.16-g (range 0.05- to 0.51-g TEQ/yr).

3.5. SEWAGE SLUDGE INCINERATION

The three principal combustion technologies used to incinerate sewage sludge in the United States are the multiple-hearth incinerator, fluidized-bed incinerator, and the electric furnace (Brunner, 1992; U.S. EPA, 1995b). All of these technologies are "excess-air" processes (i.e., they combust sewage sludge with oxygen in excess of theoretical requirements). Over 80 percent of operating sludge incinerators are multiple-hearth design. About 15 percent are fluidized-bed incinerators, and 3 percent are electric incinerators. Other types of technologies not widely used in the United States are single-hearth cyclones, rotary kilns, and high-pressure wet-air oxidation (U.S. EPA, 1997b).

Multiple-hearth Incinerator: This consists of refractory hearths arranged vertically in series, one on top of the other. Dried sludge cake is fed to the top hearth of the furnace. The sludge is mechanically moved from one hearth to another through the length of the furnace. Moisture is evaporated from the sludge cake in the upper hearths of the furnace. The center hearths are the burning zone, where gas temperatures reach 871°C. The

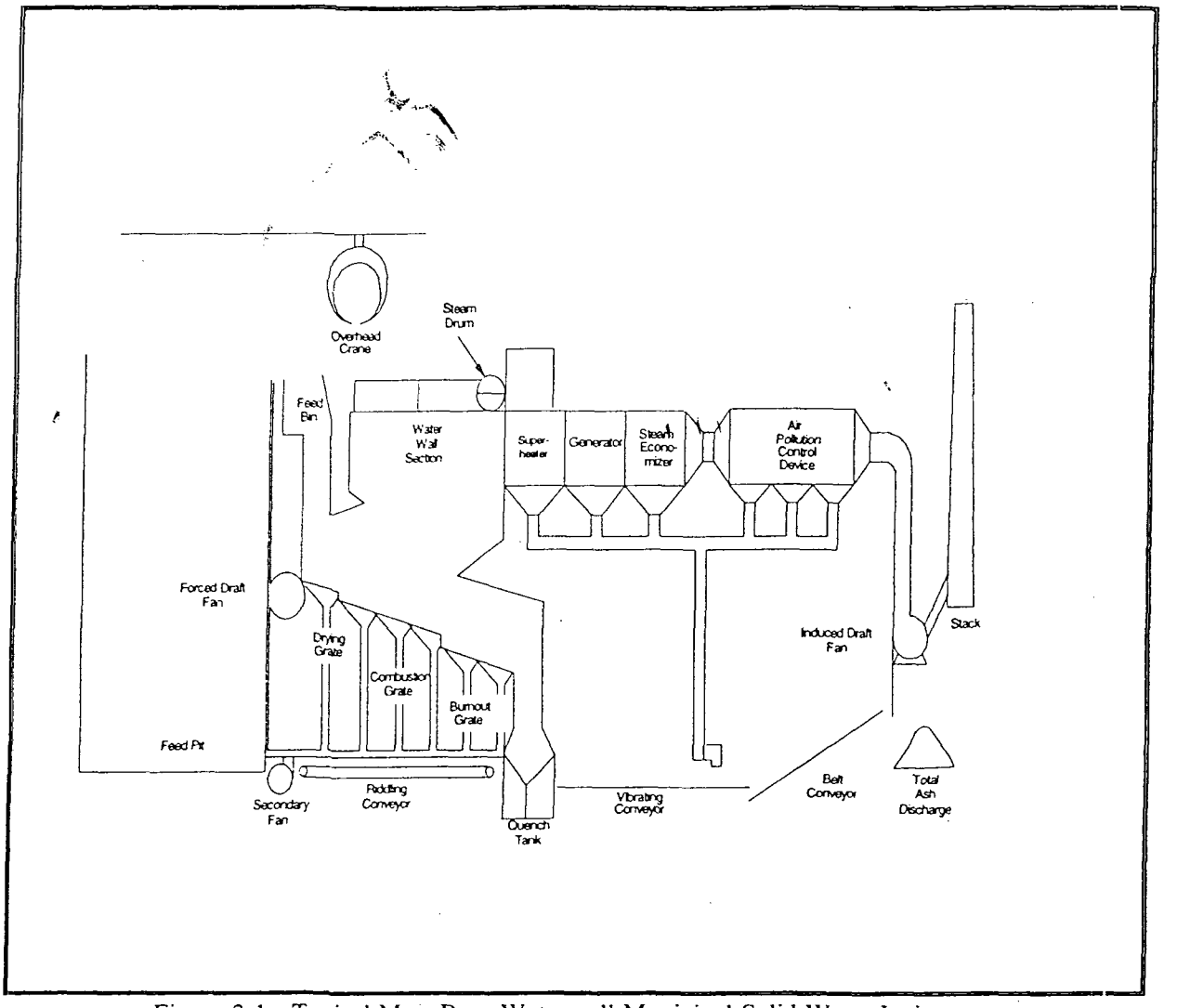


Figure 3-1. Typical Mass Burn Waterwall Municipal Solid Waste Incinerator

Source: U.S. EPA (1997b)

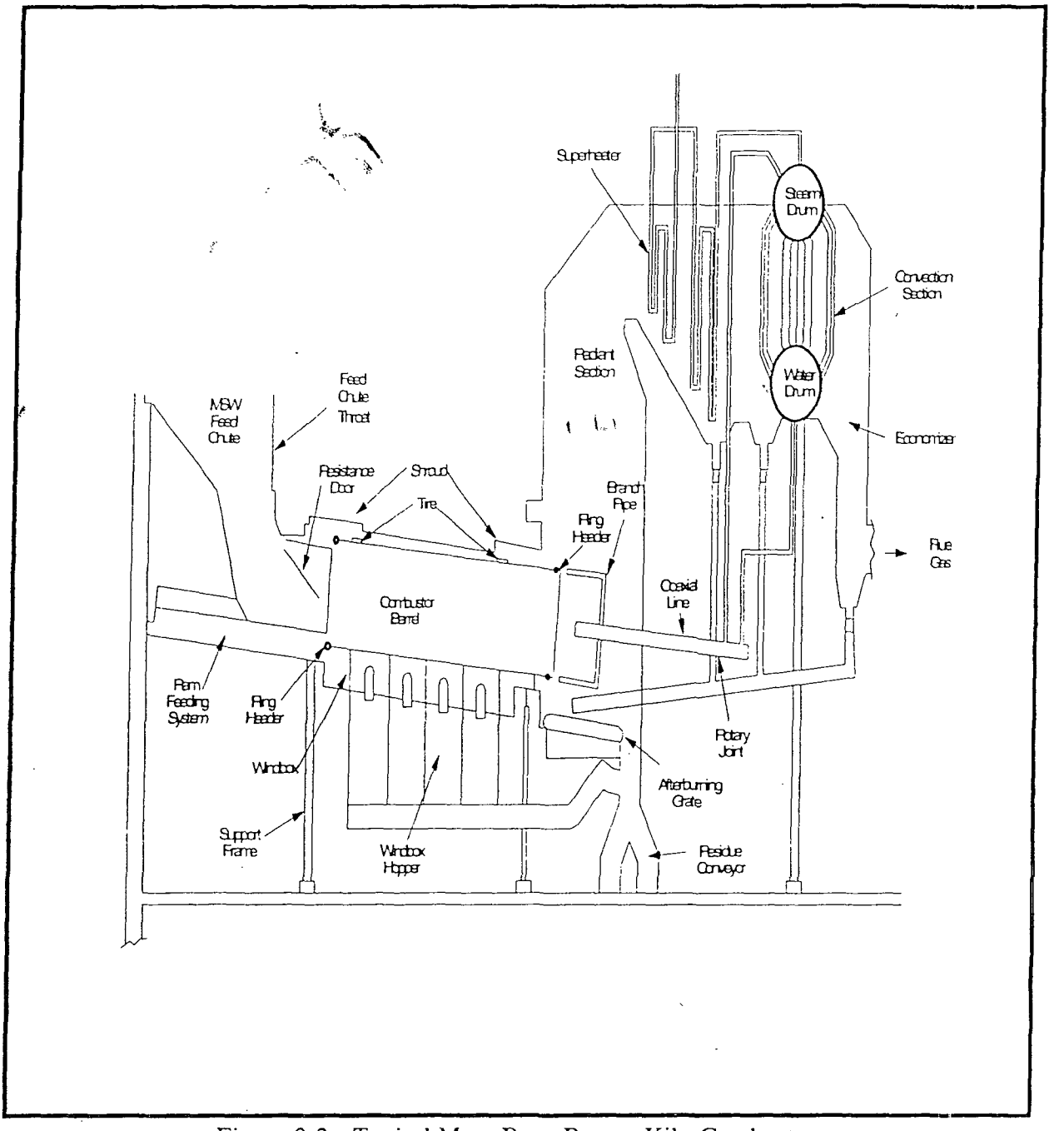


Figure 3-2. Typical Mass Burn Rotary Kiln Combustor

Source: U.S. EPA (1997b)

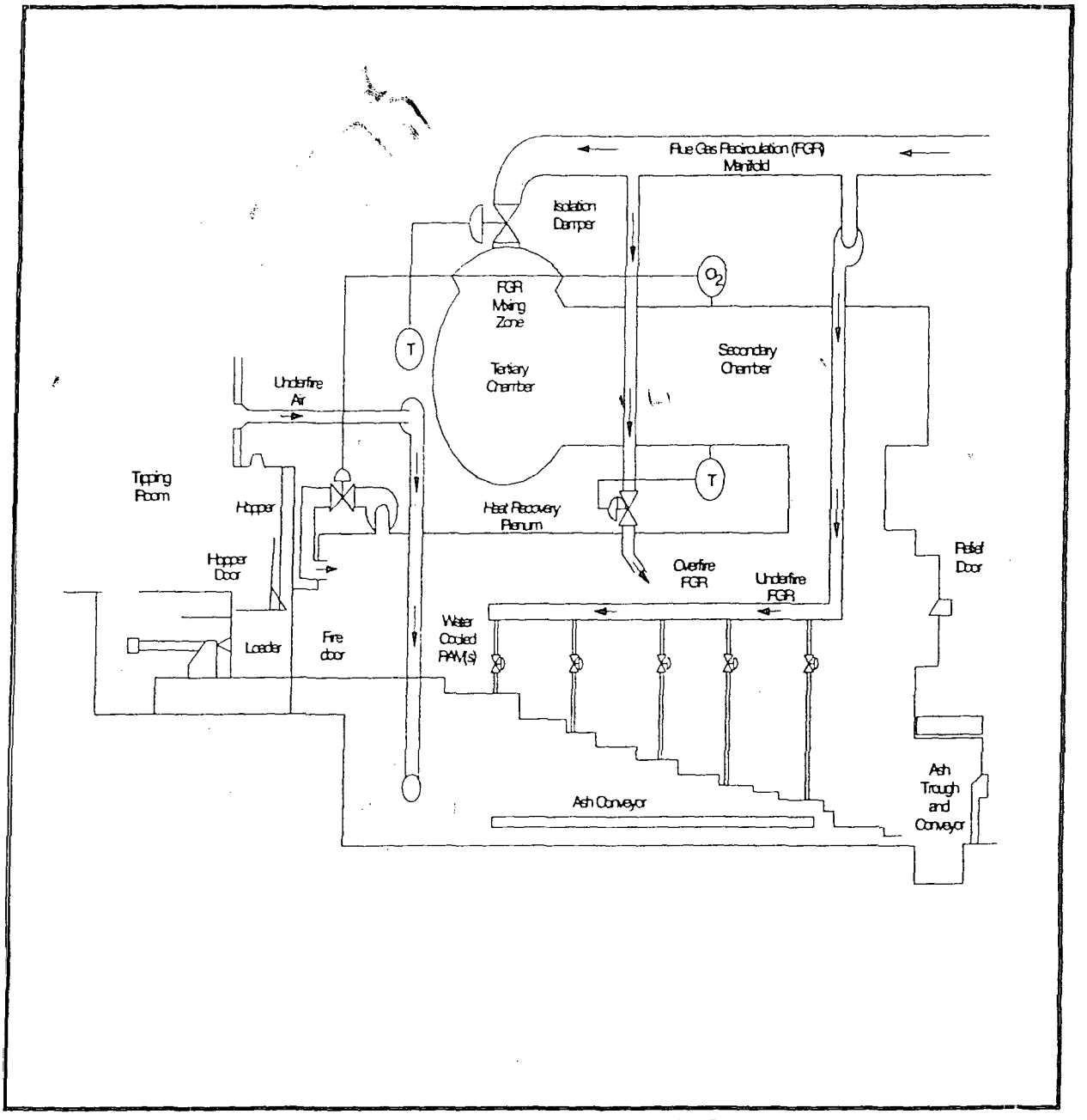


Figure 3-3. Typical Modular Excess-Air Combustor
Source: U.S. EPA (1997b)

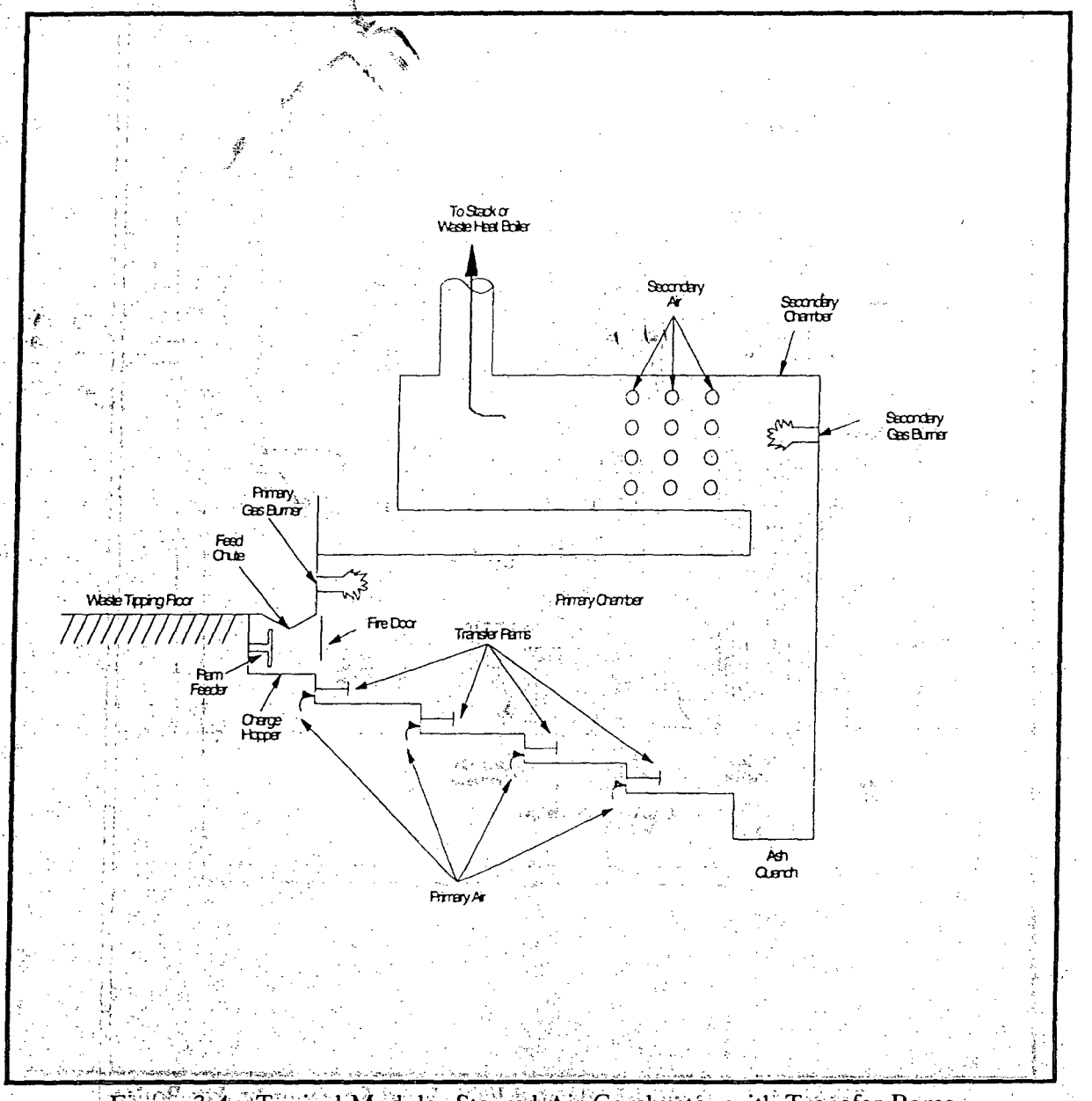


Figure 3-4. Typical Modular Starved-Air Combustor with Transfer Rams
Source: U.S. EPA (1997b)

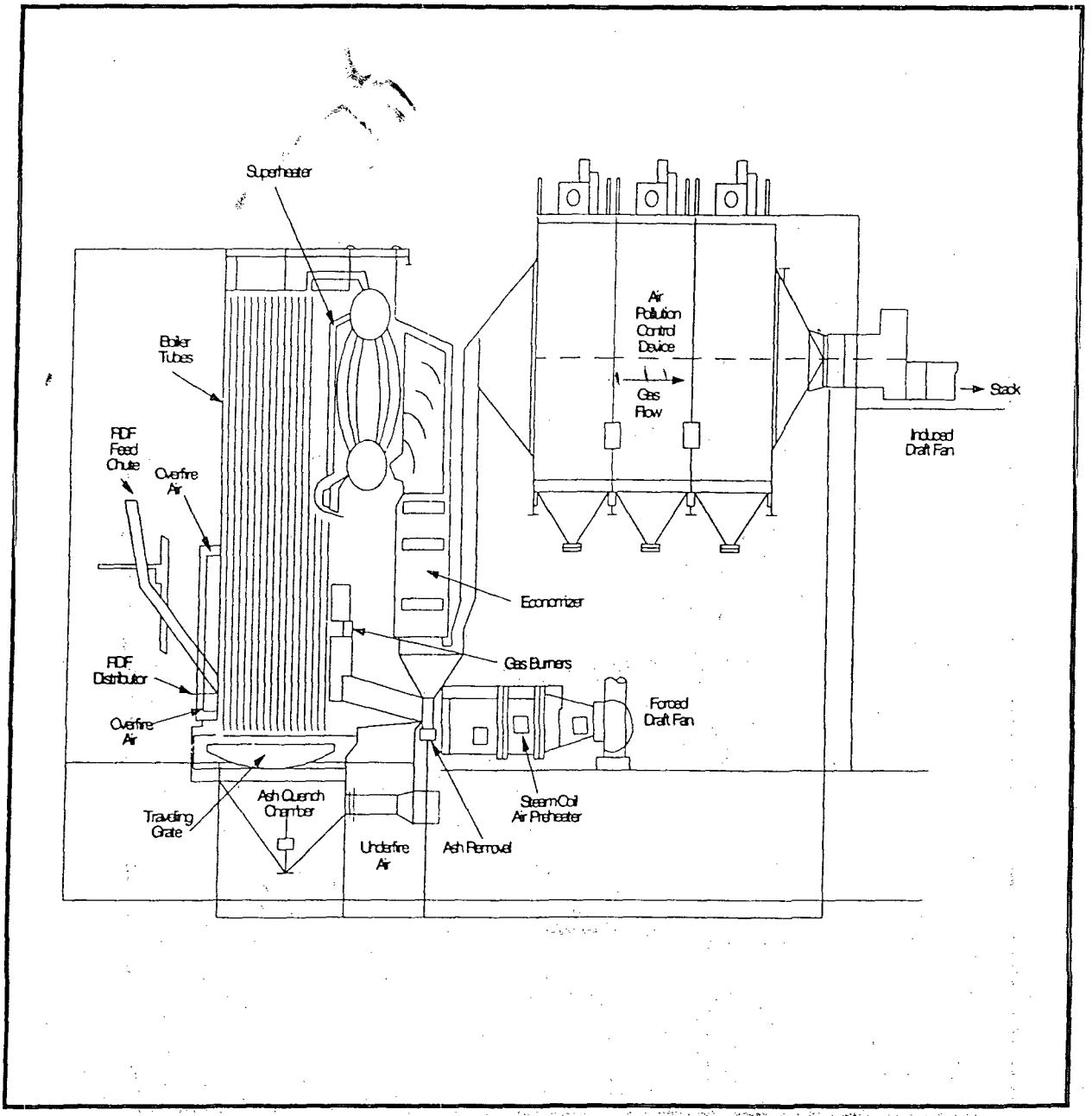


Figure 3-5. Typical Dedicated RDF-Fired Spreader Stoker Boiler
Source: U.S. EPA (1997b)

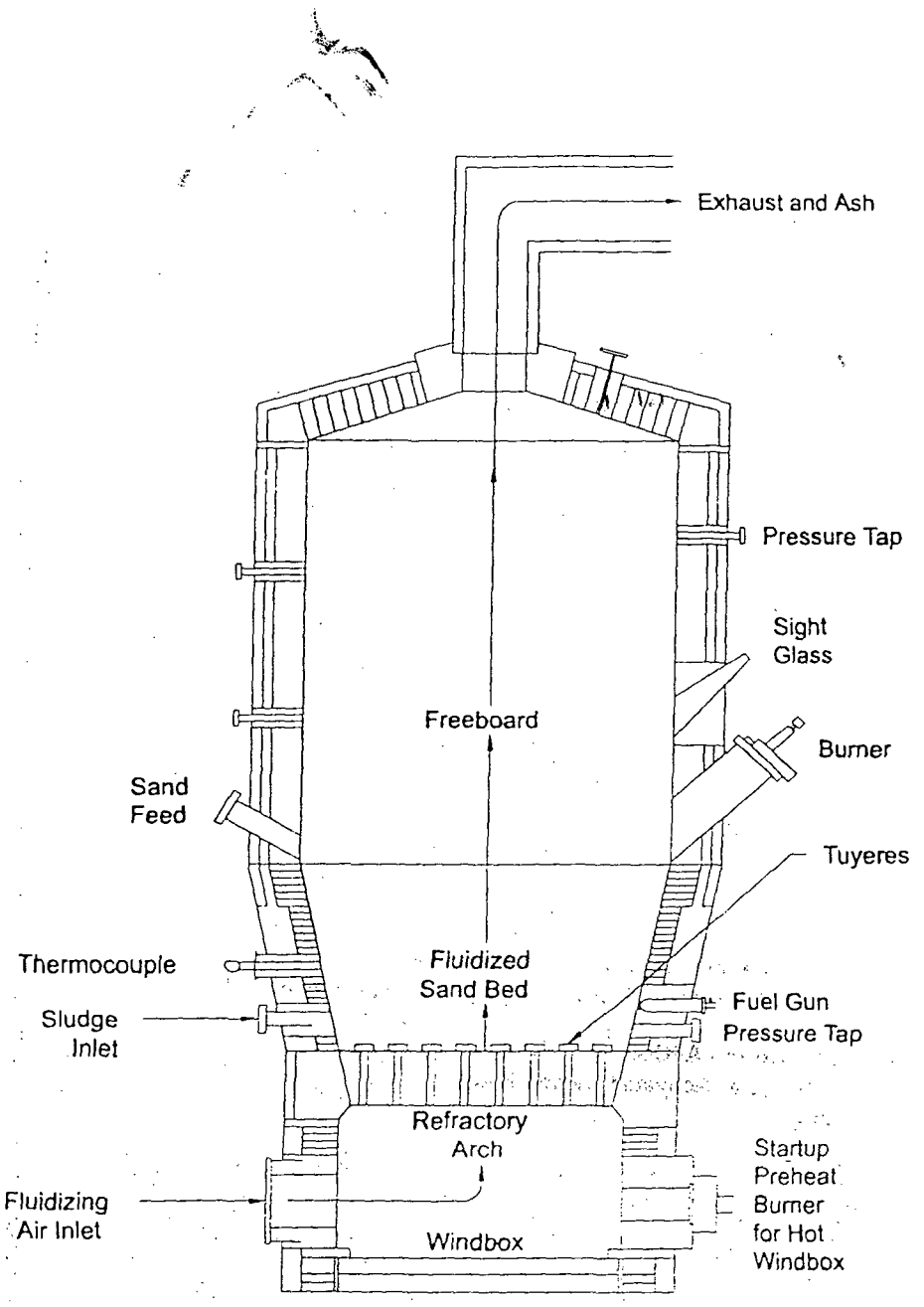
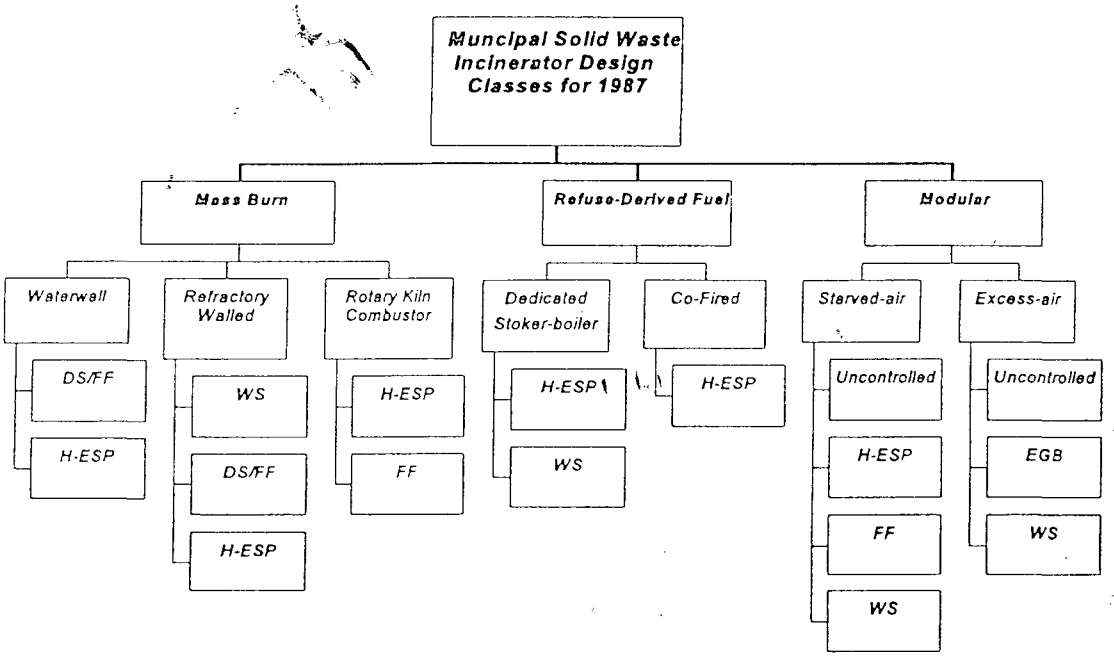
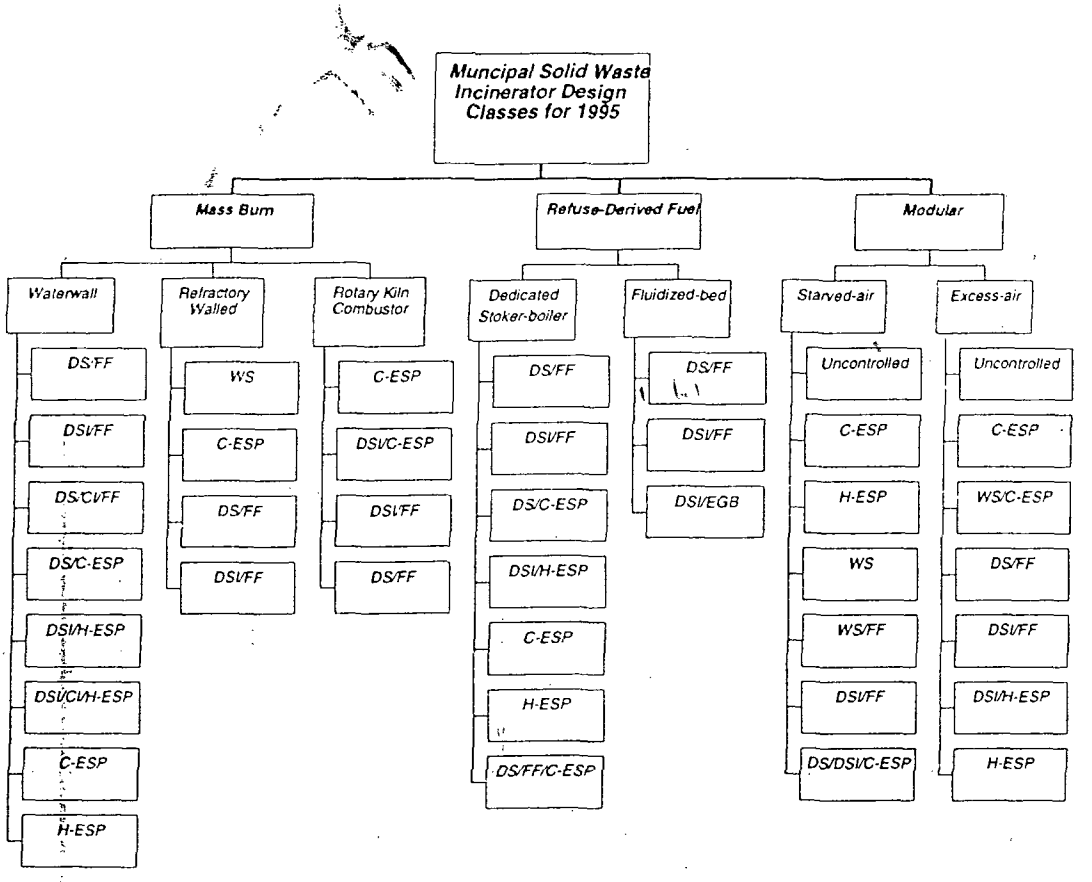


Figure 3-6. Fluidized-Bed RDF Incinerator
Source: U.S. EPA (1997b)



Key: DS/FF = Dry Scrubber combined with a Fabric Filter
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed
FF = Fabric Filter

Figure 3-7. MSWI Design Classes for 1987



Key: DS/FF = Dry Scrubber combined with a Fabric Filter
DSI/FF = Dry Sorbent Injection coupled with a Fabric Filter
DS/CI/FF = Dry Scrubber -Carbon Injection-Fabric Filter
C-ESP = Cold-side Electrostatic Precipitator (Temperature at control device is below ≤230°C)
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed

Figure 3-8. MSWI Design Classes for 1995

Table 3-1. Inventory of MSWIs in 1995 by Technology, APCD, and Activity Level

MSWI		UNC	Hot ESP	Cold ESP	DSI/H-ESP	DS/FF	DS/CI/FF	DS/FF/ C-ESP	WS/FF	WS C-ESP	DS/C-ESP	DS/DSI/ C-ESP	DSI/ CI/ H-ESP	DSI/ C-ESP	DSI/ FF	DSI/ EGB	WS	Total
MB RC	No. Facilities	0	0	2	0	2	0	0	0	0	0	0	0	6	2	0	0	12
	Activity Level, kg/yr	0	0	2.00E+08	0	1.14E+09	0	0	0	0	0	0	0	5.07E+08	2.59E+08	0	0	2.10E+09
MB REF	No Facilities	0	0	1	0	2	0	0	0	0	1	0	0	0	1	0	2	7
	Activity Level, kg/yr	0	0	1.69E+08	0	2.68E+08	0	0	0	0	4.22E+08	0	0	0	1.13E+08	0	2.04E+08	1.18E+09
MB-WW	No. Facilities	0	6	8	1	28	3	0	0	0	8	0	1	0	2	0	0	57
	Activity Level, kg/yr	0	1.04E+09	2.81E+09	4.22E+08	8.57E+09	1.17E+09	0	0	0	2.31E+09	0	2.75E+08	0	1.97E+08	0	0	1.68E+10
FB RDF	No Facilities	0	0	0	0	1	0	0	0	0	0	0	0	0	1	1	0	3
	Activity Level, kg/yr	0	0	0	0	1.69E+08	0	0	0	0	0	0	0	0	8.45E+07	1.13E+08	0	3.66E+08
RDF/Ded	No Facilities	0	1	4	1	7	0	1	0	0	4	0	0	0	1	0	0	19
	Activity Level, kg/yr	0	4.22E+07	1.81E+09	2.00E+08	2.51E+09	0	5.63E+08	0	0	1.75E+09	0	0	0	4.22E+08	0	0	7.30E+09
MOD SA	No Facilities	9	4	4	0	0	0	0	1	0	0	1	0	0	1	0	3	23
	Activity Level, kg/yr	1.87E+08	1.82E+08	1.25E+08	0	0	0	0	2.82E+07	0	0	7.60E+07	0	0	3.24E+07	0	4.90E+07	6.80E+08
MOD-EA	No. Facilities	1	1	3	1	1	0	0	0	1	0	0	0	0	1	0	0	9
	Activity Level, kg/yr	1.41E+07	1.97E+07	8.28E+07	1.41E+07	1.18E+08	0	0	0	6.76E+07	0	0	0	0	1.01E+08	0	0	4.18E+08
Total	No Facilities	10	12	22	3	41	3	1	1	1	13	1	1	6	9	1	5	130
Total	Activity Level, kg/yr	2.01E+08	1.29E+09	5.19E+09	6.37E+08	1.28E+10	1.17E+09	5.63E+08	2.82E+07	6.76E+07	4.49E+09	7.60E+07	2.75E+08	5.07E+08	1.21E+09	1.13E+08	2.53E+08	2.88E+10

Table 3-1. Inventory of MSWIs in 1995 by Technology, APCD, and Activity Level (continued)

MB/RC = Mass Burn Rotary Kiln	UNC = Uncontrolled	DSI/FF = Dry Sorbent Injection with Fabric Filter
MB/REF = Mass Burn Refractory Walled	Hot ESP = Hot side Electrostatic Precipitator	DS/CI/FF = Spray Dryer - Carbon Injection - Fabric Filter
MB/WW = Mass Burn Waterwalled	Cold ESP = Cold side Electrostatic Precipitator	DSI/EGB = Dry Sorbent Injection - Electro Gravel Bed
RDF/Ded = Dedicated Refuse-Derived Fuel	DS/FF = Dry Scrubber with Fabric Filter	
FB/RDF = Fluidized Bed Refuse-Derived Fuel	FF = Fabric Filter	
MOD/SA = Modular Starved Air	EGB = Electro Gravel Bed	
MOD/EA = Modular Excess Air	WS = Wet Scrubber	

Table 3-2. Inventory of MSWIs in 1987 by Technology, APCD, and Annual Activity Level

	MSWI Type	UNC	Hot ESP	DS/FF	FF	EGB	WS	Total
MB/RC	No. of Facilities	0	3	0	1	0	0	4
	Activity Level,kg/yr	0	3.94E+08	0	1.58E+07	0	0	4.10E+08
MB/REF	No. of Facilities	0	12	1	0	0	7	20
	Activity Level,kg/yr	0	2.00E+09	1.41E+07	0	0	9.01E+08	3.04E+09
MB/WW	No. of Facilities	0	19	1	0	0	0	20
	Activity Level,kg/yr	0	5.20E+09	1.55E+08	0	0	0	5.35E+09
RDF/Dedicated	No. of Facilities	0	7	0	0	0	2	9
	Activity Level,kg/yr	0	3.01E+09	0	0	0	3.38E+08	3.35E+09
RDF/cofired	No. of Facilities	0	3	0	0	0	0	3
	Activity Level,kg/yr	0	2.53E+08	0	0	0	0	2.53E+08

Table 3-2. Inventory of MSWIs in 1987 by Technology, APCD, and Annual Activity Level (continued)

	MSWI Type	UNC	Hot ESP	DS/FF	FF	EGB	WS	Total
MOD/SA	No. of Facilities	36	2	0	3	0	4	53
	Activity Level,kg/yr	5.73E+08	1.17E+08	0	1.43E+08	0	5.30E+07	1.15E+09
MOD/EA	No. of Facilities	2	0	0	0	1	1	4
	Activity Level,kg/yr	4.17E+07	0	0	0	6.76E+07	1.27E+08	2.36E+08
	Total No. of Facilities	38	54	2	4	1	14	113
	Total Activity Level,kg/yr	6.15E+08	1.12E+10	2.96E+08	1.59E+08	6.76E+07	1.42E+09	1.38E+10

MB/RC = Mass Burn Rotary Kiln
MB/REF = Mass Burn Refractory Walled
MB/WW = Mass Burn Waterwalled
RDF/Ded = Dedicated Refuse-Derived Fuel
RDF/cofired = RDF cofired with coal
MOD/SA = Modular Starved Air
MOD/EA = Modular Excess Air

UNC = Uncontrolled
Hot ESP = Hot side Electrostatic Precipitator
DS/FF = Dry Scrubber with Fabric Filter
FF = Fabric Filter
EGB = Electro Gravel Bed
WS = Wet Scrubber
kg/y = kilogram per year

Table 3-3 Dioxin TEQ Emission Factors (ng TEQ per kg waste) for Municipal Solid Waste Incineration

Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Average TEQ Emission Factor (ng/kg)	Basis and Rationale
Mass Burn Waterwall	C-ESP	6.1	Based on MB-WW; DS/C-ESP, same furnace and most similar APCD temperature
	DS/C-ESP	6.1	Based on direct tests
	DS/CI/FF	1.5	Based on direct tests
	DS/FF	0.63	Based on direct tests
	DSI/CI/H-ESP	7.74	Based on direct tests
	DSI/FF	1.91	Based on direct tests
	DSI/H-ESP	7.74	Based on MB-WW; DSI/CI/H-ESP, same furnace and most similar APCD temperature
	H-ESP	473	Based on direct tests
Mass Burn Refractory	C-ESP	236	Based on direct tests
	DS/C-ESP	51.1	Based on direct tests
	DS/FF	0.63	Based on MB-WW; DS/FF, most similar furnace and same APCD
	DSI/FF	1.91	Based on MB-WW; DSI/FF, most similar furnace and same APCD
	H-ESP	473	Based on MB-WW; H-ESP, most similar furnace and same APCD
	WS	236	Based on MB-Ref;C-ESP, same furnace and similar APCD temperature
Mass Burn Rotary Kiln	C-ESP	47	Based on MB-RK; DSI/FF, same furnace and similar emission control
	DS/FF	0.646	Based on direct tests
	DSI/C-ESP	47	Based on MB-RK; DSI/FF, same furnace and similar emission control
	DSI/FF	47	Based on direct tests
	FF	47	Based on MB-RK; DSI/FF, same furnace and similar emission control
	H-ESP	285	Based on direct tests
RDF Dedicated	C-ESP	231	Based on direct tests
	DS/C-ESP	0.527	Based on direct tests
	DS/FF	0.24	Based on direct tests
	DS/FF/C-ESP	0.24	Based on RDF-Ded; DS/FF, same furnace and similar APCD
	DSI/FF	231	Based on RDF-Ded; C-ESP, same furnace and similar emission control
	DSI/H-ESP	231	Based on RDF-Ded; C-ESP, same furnace and similar emission control
	H-ESP	1490	Based on direct tests
	WS	231	Based on RDF-Ded; C-ESP, same furnace and similar APCD temperature

Table 3-3 Dioxin TEQ Emission Factors (ng TEQ per kg waste) for Municipal Solid Waste Incineration (continued)

Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Average TEQ Emission Factor (ng/kg)	Basis and Rationale
Modular Starved-air	C-ESP	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and same APCD
	DS/DSI/C-ESP	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar emission control
	DSI/FF	0.0247	Based on direct tests
	FF	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar emission control
	H-ESP	79	Based on direct tests
	UNC	0.0247	Based on Mod-SA; DSI/FF, same furnace and most similar expected emissions
	WS	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar APCD temperature
	WS/FF	16	Based on Mod-EA; C-ESP, similar furnace (modular design) and similar APCD temperature
Modular Excess-air	C-ESP	16	Based on direct tests
	DS/FF	16	Based on Mos-EA; C-ESP, same furnace and similar temperature in APCD - may over-estimate emissions
	DSI/FF	0.0247	Based on Mod-SA; DSI/FF, similar (modular design) furnace and same APCD
	DSI/H-ESP	118	Based on Mod-EA; H-ESP, same furnace and similar emissions
	EGB	0.0247	Based on Mod-SA; DSI/FF, same furnace and most similar expected emissions
	H-ESP	118	Based on direct tests
	UNC	0.0247	Based on Mod-SA; DSI/FF, same furnace and most similar expected emissions
	WS	16	Based on Mod-EA; C-ESP, same furnace and similar APCD temperature
	WS/C-ESP	16	Based on Mod-EA; C-ESP; same furnace and similar APCD
Fluidized-bed RDF	DS/FF	0.63	Based on MB-WW; DS/FF, similar furnace and same APCD
	DSI/EGB	0.63	Based on MB-WW; DS/FF, similar furnace - may under-estimate emissions
	DSI/FF	0.63	Based on MB-WW; DS/FF, similar furnace - may under-estimate emissions

Key:
- ng/kg = Nanograms TEQ per kilograms waste
- DS/FF = Dry scrubber combined with a fabric filter
- DSI/FF = Dry sorbent injection coupled with a fabric filter
- DS/CI/FF = Dry scrubber coupled with carbon injection and a fabric filter
- C-ESP = Cold-sided electrostatic precipitator (temperature at control device is below 220°C
- H-ESP = Hot-sided electrostatic precipitator (temperature at control device is above 220°C
- WS = Wet scrubber
- UNC = Uncontrolled (no APCD)
- EGB = Electro-granular activated carbon bed

Table 3-4 Annual TEQ Emissions (g/yr) From MSWIs Operating in 1995

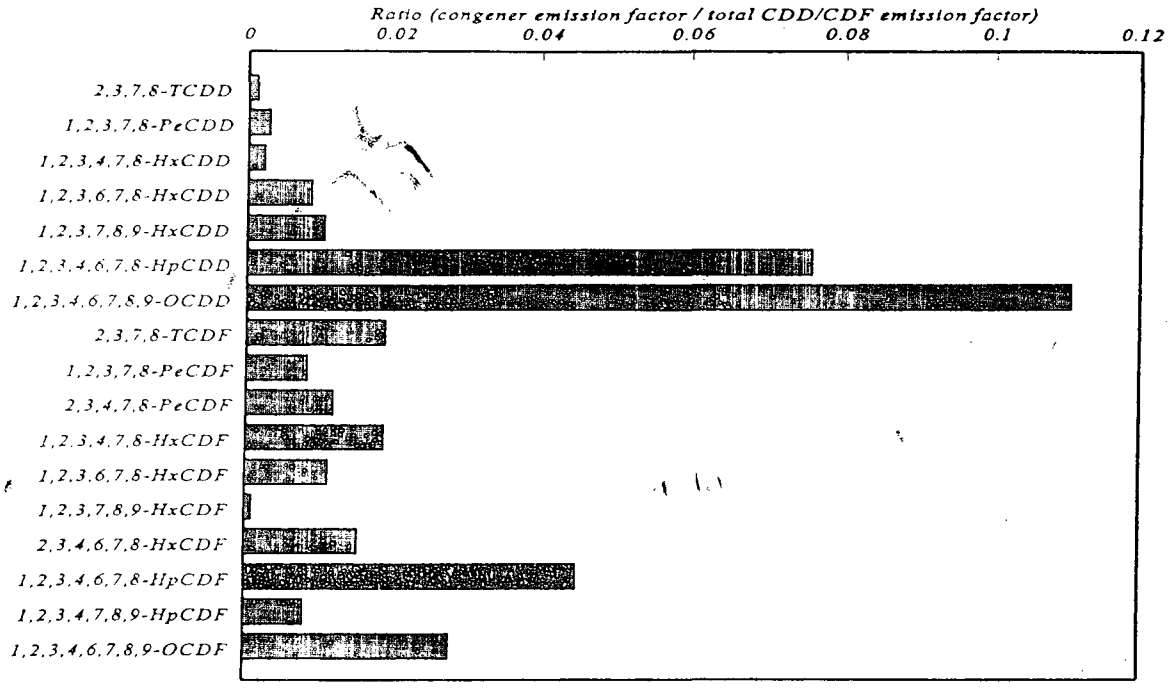
Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Emissions From Tested Facilities (g TEQ/yr)	Average TEQ Emission Factor (ng/kg)	Activity Level Non-Tested Facilities (kg/yr)	Emissions From Non-Tested Facilities (g TEQ/yr)	Total Emissions From All Facilities (g TEQ/yr)
Mass Burn Waterwall	C-ESP	0	6.1	2.81e+09	17.1	17.1
	DS/C-ESP	2.09	6.1	1.88e+09	11.4	13.5
	DS/CI/FF	0.635	1.5	7.44e+08	1.12	1.75
	DS/FF	2.01	0.63	5.98e+09	3.77	5.77
	DSI/CI/H-ESP	2.12	-	0	0	2.12
	DSI/FF	0.279	-	0	0	0.279
	DSI/H-ESP	0	7.74	4.22e+08	3.27	3.27
	H-ESP	163	473	1.79e+08	84.5	247
	Subtotal	170			121	291
Mass Burn Refractory	C-ESP	39.8	-	0	0	39.8
	DS/C-ESP	21.6	-	0	0	21.6
	DS/FF	0	0.63	2.68e+08	0.168	0.168
	DSI/FF	0	1.91	1.13e+08	0.216	0.216
	WS	0	236	2.04e+08	48.1	48.1
	Subtotal	61.4			48.5	110
Mass Burn Rotary Kiln	C-ESP	0	47	2.00e+08	9.4	9.4
	DS/FF	0.245	0.646	7.57e+08	0.489	0.734
	DSI/C-ESP	0	47	5.07e+08	23.8	23.8
	DSI/FF	5.29	47	1.46e+08	6.85	12.1
	Subtotal	5.54			40.6	46.1
RDF Dedicated	C-ESP	32.5	231	1.67e+09	385	418
	DS/C-ESP	0.321	0.527	1.14e+09	0.603	0.924
	DS/FF	0.0975	0.24	1.58e+09	0.379	0.477
	DSI/FF	0	231	4.22e+08	97.6	97.6
	DSI/H-ESP	0	231	2.00e+08	46.2	46.2
	H-ESP	0	1490	4.22e+07	63	63
	DS/FF/C-ESP	0	0.24	5.63e+08	0.135	0.135
	Subtotal	33			593	626
Modular Starved-air	C-ESP	0	16	1.25e+08	2	2
	DSI/FF	0.000801	-	0	0	0.000801
	H-ESP	8.01	79	8.03e+07	6.34	14.4
	UNC	0	0.0247	1.87e+08	0.00463	0.00463
	WS	0	16	4.90e+07	0.785	0.785
	WS/FF	0	16	2.82e+07	0.451	0.451
	DS/DSI/C-ESP	0	16	7.60e+07	1.22	1.22
	Subtotal	8.01			10.8	18.8
Modular Excess-air	C-ESP	0.0643	16	6.25e+07	1	1.07
	DS/FF	0	16	1.18e+08	1.9	1.9
	DSI/FF	0	0.0247	1.01e+08	0.00251	0.00251
	DSI/H-ESP	0	118	1.41e+07	1.66	1.66
	H-ESP	2.32	-	0	0	2.32
	UNC	0	0.0247	1.41e+07	0.000348	0.000348
	WS/C-ESP	0	16	6.76e+07	1.08	1.08
	Subtotal	2.39			5.64	8.03
Fluidized-bed RDF	DS/FF	0	0.63	1.69e+08	0.106	0.106
	DSI/EGB	0	0.63	1.13e+08	0.0709	0.0709
	DSI/FF	0	0.63	8.45e+07	0.0532	0.0532
	Subtotal	0			0.231	0.231
Total		280			820	1,100

Key: DS/FF = Dry Scrubber combined with a Fabric Filter
DSI/FF = Dry Sorbent Injection coupled with a Fabric Filter
DS/CI/FF = Dry Scrubber -Carbon Injection-Fabric Filter
C-ESP = Cold-side Electrostatic Precipitator (Temperature at control device is below ≤230°C)
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed
ng/kg = nanogram per kilogram
kg/yr = kilograms per year

Table 3-5. Annual TEQ Emissions to the Air From MSWIs Operating in 1987

Municipal Solid Waste Incinerator Design	Air Pollution Control Device	Emissions From Tested Facilities (g TEQ/yr)	Average TEQ Emission Factor (ng/kg)	Activity Level Non-Tested Facilities (kg/yr)	Emissions From Non-Tested Facilities (g TEQ/yr)	Total Emissions From All Facilities (g TEQ/yr)
Mass Burn Waterwall	DS/FF	0.0373	-	0	0	0.0373
	H-ESP	433	473	3.27e+09	1550	1980
	Subtotal	433			1550	1980
Mass Burn Refractory	DS/FF	0	0.63	1.41e+08	0.0887	0.0887
	H-ESP	0	473	2.00e+09	944	944
	WS	0	236	9.01e+08	212	212
	Subtotal	0			1,160	1,160
Mass Burn Rotary Kiln	FF	0	47	1.58e+07	0.741	0.741
	H-ESP	48.2	285	2.25e+08	64.2	112
	Subtotal	48.2			65	113
RDF Dedicated	H-ESP	840	1490	2.45e+09	3660	4500
	WS	0	231	3.38e+08	78.1	78.1
	Subtotal	840			3730	4570
RDF Cofired	H-ESP	0	231	2.53e+08	58.6	58.6
Modular Starved-air	FF	0	16	1.43e+08	2.29	2.29
	H-ESP	0.0643	79	3.61e+08	28.5	28.5
	UNC	0	0.0247	5.73e+08	0.0142	0.0142
	WS	0	16	5.30e+07	0.848	0.848
	Subtotal	0.0643			31.6	31.7
Modular Excess-air	EGB	0	0.0247	6.76e+07	0.00167	0.00167
	UNC	0	0.0247	4.17e+07	0.00103	0.00103
	WS	0	16	1.27e+08	2.03	2.03
	Subtotal	0			2.03	2.03
Totals		1,320			6,590	7,915

Key:
DS/FF = Dry Scrubber combined with a Fabric Filter
DSI/FF = Dry Sorbent Injection coupled with a Fabric Filter
DS/CI/FF = Dry Scrubber -Carbon Injection-Fabric Filter
C-ESP = Cold-side Electrostatic Precipitator (Temperature at control device is below ≤230°C)
H-ESP = Hot-side Electrostatic Precipitator (Temperature at control device is ≥230°C)
WS = Wet Scrubber
UNC = Uncontrolled (no APCD)
EGB = Electro Granular Activated Carbon Bed
ng/kg = nanogram per kilogram
kg/yr = kilograms per year



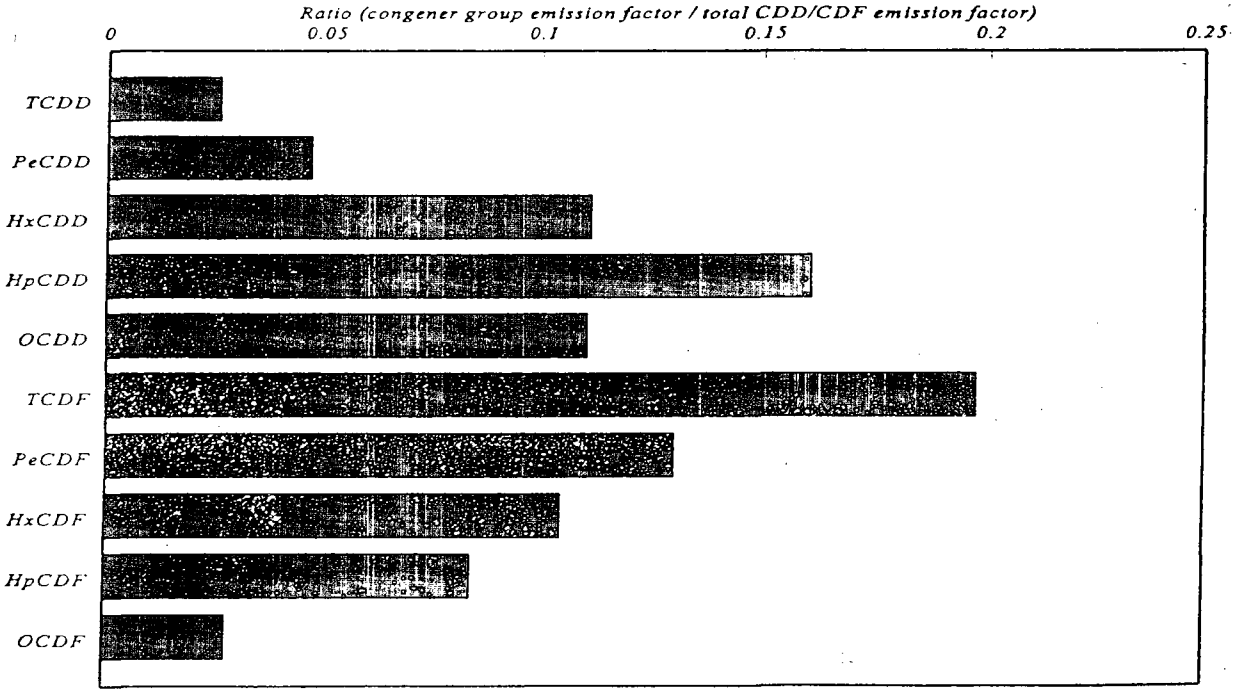


Figure 3-9. Congener and Congener Group Profiles for Air Emissions from a Mass-Burn Waterwall MSWI, Equipped with a Dry Scrubber and Fabric Filter

Table 3-6. CDD/CDF Emission Factors for Hazardous Waste Incinerators and Boilers

Congener/Congener Group	Incinerator Average Mean emission factor (17 facilities) (ng/kg feed)		Hot-Side ESP Boilers Mean emission factor (2 facilities) (ng/kg feed)	
	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero	Nondetects Set to 1/2 Det. Limit	Nondetects Set to Zero
2,3,7,8-TCDD	0.44	0.14	0.10	0.00
1,2,3,7,8-PeCDD	0.18	0.14	0.11	0.04
1,2,3,4,7,8-HxCDD	0.22	0.18	0.15	0.08
1,2,3,6,7,8-HxCDD	0.32	0.28	0.20	0.18
1,2,3,7,8,9-HxCDD	0.49	0.48	0.22	0.20
1,2,3,4,6,7,8-HpCDD	1.77	1.75	1.17	1.17
OCDD	4.13	3.74	5.24	5.24
2,3,7,8-TCDF	2.96	2.69	0.81	0.81
1,2,3,7,8-PeCDF	2.36	2.33	0.38	0.38
2,3,4,7,8-PeCDF	2.56	2.51	0.52	0.52
1,2,3,4,7,8-HxCDF	9.71	9.71	0.83	0.83
1,2,3,6,7,8-HxCDF	3.96	3.95	0.37	0.37
1,2,3,7,8,9-HxCDF	0.31	0.29	0.08	0.02
2,3,4,6,7,8-HxCDF	2.70	2.70	0.56	0.56
1,2,3,4,6,7,8-HpCDF	16.87	16.68	1.04	0.93
1,2,3,4,7,8,9-HpCDF	1.74	1.71	0.18	0.16
OCDF	13.78	13.46	0.70	0.70
Total TEQ (nondetects = 0)		3.83		0.64
Total TEQ (nondetects = 1/2 DL)	4.22		0.78	
Total TCDD			0.77	0.77
Total PeCDD			1.15	0.77
Total HxCDD			1.67	1.62
Total HpCDD			2.34	2.34
Total OCDD			5.24	5.24
Total TCDF			5.47	5.47
Total PeCDF			5.50	5.51
Total HxCDF			4.04	4.04
Total HpCDF			1.94	1.94
Total OCDF			0.70	0.70
Total CDD/CDF (nondetects = 0)		137.36		28.83
Total CDD/CDF (nondetects = 1/2 DL)	137.36		28.83	

ng/kg = nanograms per kilogram

Source: U.S. EPA (1996c).

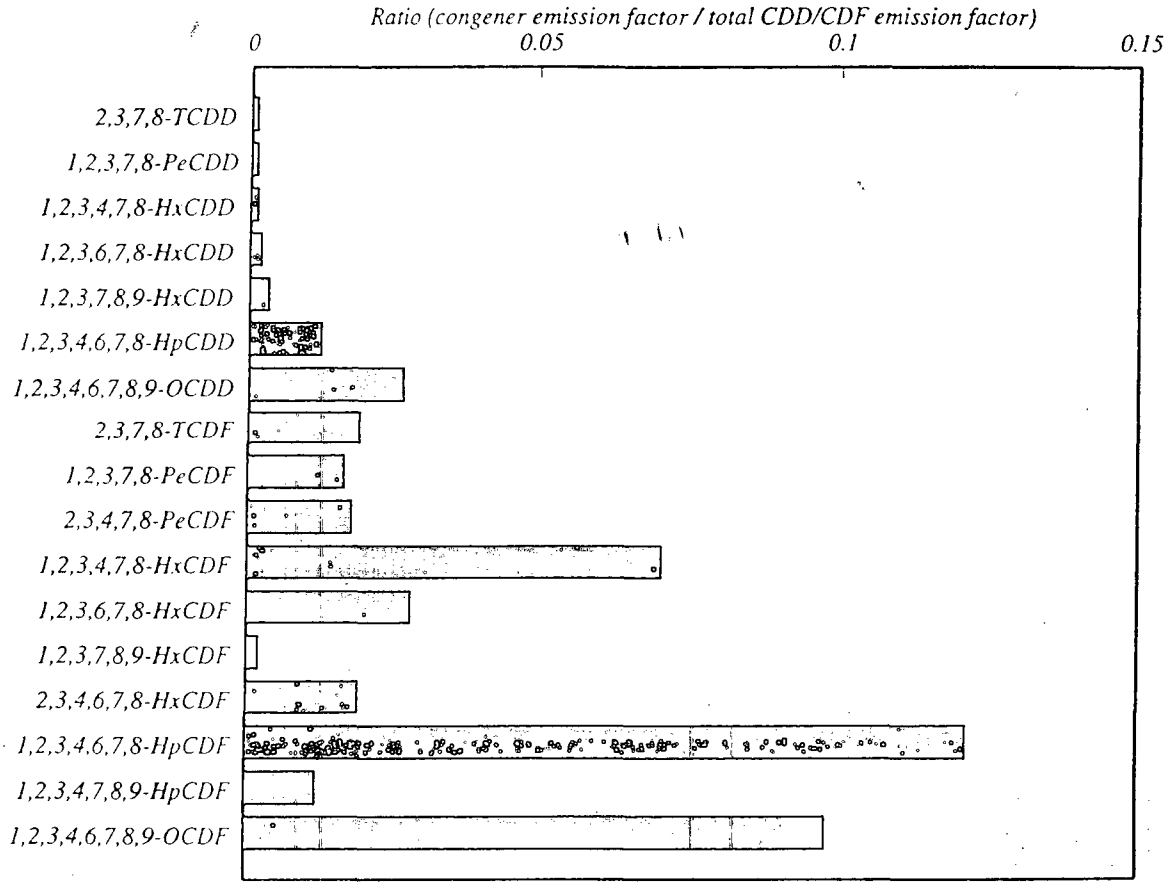
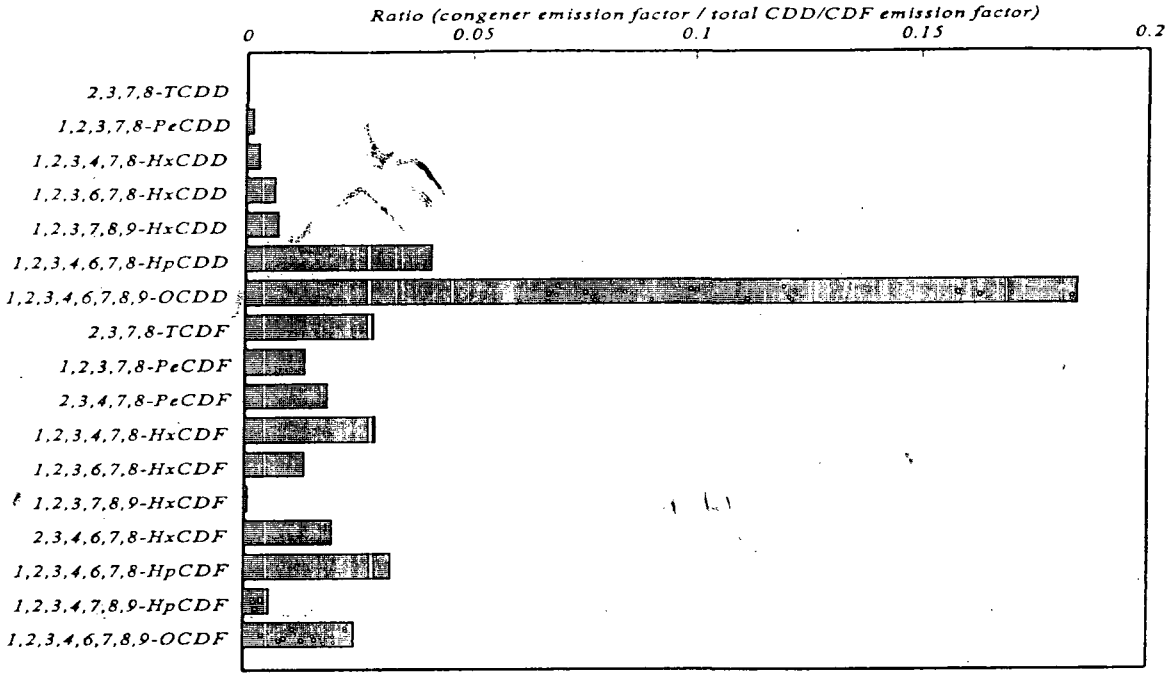


Figure 3-10. Congener Profile for Air Emissions from Hazardous Waste Incinerators



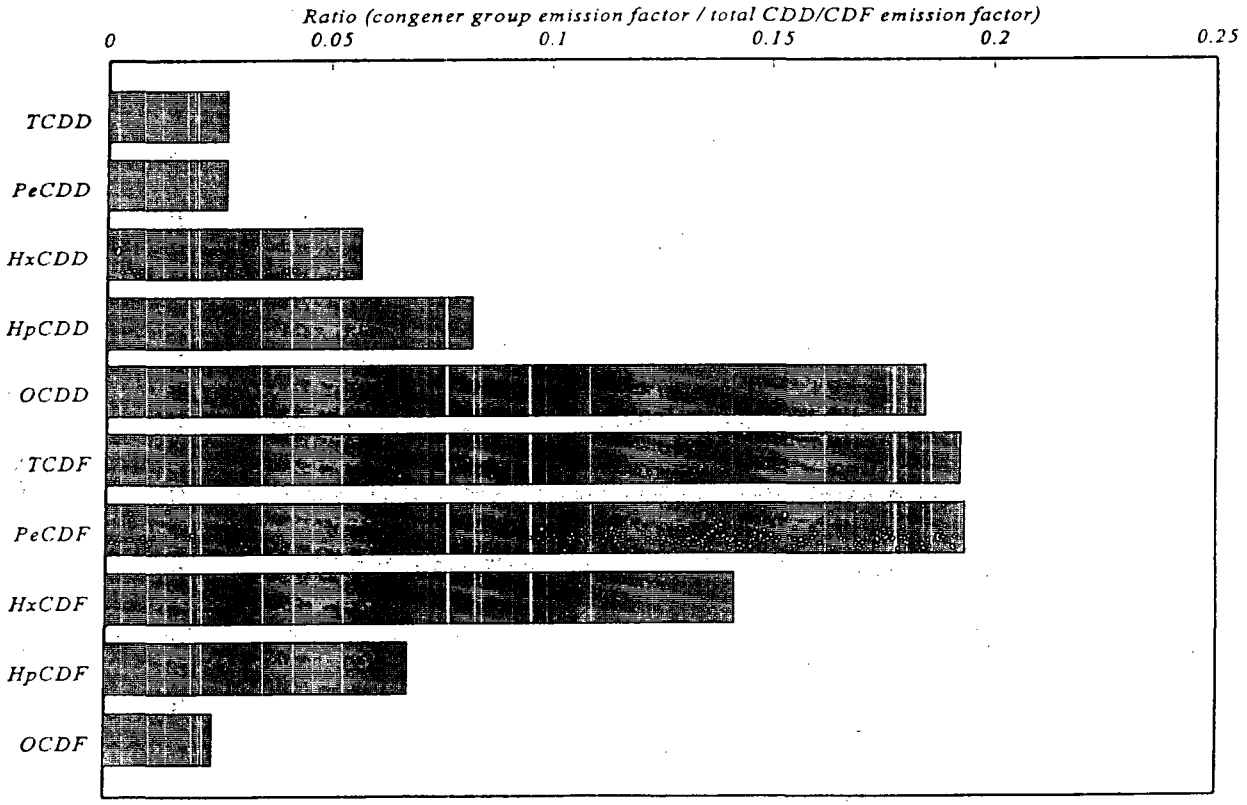


Figure 3-11. Congener and Congener Group Profiles for Air Emissions from Boilers and Industrial Furnaces Burning Hazardous Waste

Table 3-7. Summary of Annual Operating Hours for Each MWI Type

MWI Type	Capacity Ranges (lb/hr)	Annual charging hours (hr/yr)	Maximum annual charging hours (hr/yr)	Capacity Factor
Continuous commercial	>1,000	7,776	8,760	0.89
Continuous onsite	501 - 1,000 >1,000	1,826 2,174	5,475	0.33 0.40
Intermittent	≤ 500	1,250	4,380	0.29
Batch	Case by case	Case by case		Case by case

lb/hr = pounds per hour
hr/yr = hours per year

Table 3-8. OAQPS Approach: PM Emission Limits for MWIs and Corresponding Residence Times in the Secondary Combustion Chamber

MWI Type	PM Emission Limit[a] (gr/dscf)	Residence Time in 2° Chamber (seconds)	TEQ Emission Factor (kg TEQ/kg waste)
Intermittent and Continuous	≥0.3	0.25	3.96 e-9
	0.16 to < 0.30	1.0	9.09 e-10
	0.10 to ≤0.16	2.0	7.44 e-11
Batch	≥0.079	0.25	3.96 e-9
	0.042 to <0.079	1.0	9.09 e-10
	0.026 to <0.042	2.0	7.44 e-11

[a] gr/dscf = grains per dry standard cubic foot at standard temperature and pressure.

Table 3-9. OAQPS Approach: Estimated Nationwide CDD/CDF TEQ Emissions (g/yr) for 1995

MWI Type	Residence Time or APCD	CDD/CDF EF (ng/kg)	TEQ EF (ng/kg)	Activity Level (kg/yr)	CDD/CDF Emissions (g/yr)	TEQ Emissions (g/yr)
Batch	0.25 sec	1.94e+05	3.96e+03	5.95e+06	1.15e+03	2.35e+01
	1.00 sec	4.45e+04	9.09e+02	4.20e+05	1.87e+01	3.82e-01
	2.00 sec	3.65e+03	7.40e+01	2.14e+05	7.82e-01	1.60e-02
Continuous	0.25 sec	1.94e+05	3.96e+03	1.20e+06	2.34e+02	4.77
	1.00 sec	4.45e+04	9.09e+02	5.10e+06	2.27e+02	4.64
	2.00 sec	3.65e+03	7.40e+01	3.01e+07	1.10e+02	2.24
Continuous/ Intermittent	0.25 sec	1.94e+05	3.96e+03	4.54e+06	8.80e+02	1.80e+01
	1.00 sec	4.45e+04	9.09e+02	4.24e+07	1.88e+03	3.85e+01
	2.00 sec	3.65e+03	7.40e+01	9.79e+07	3.57e+02	7.29
Intermittent	0.25 sec	1.94e+05	3.96e+03	4.18e+06	8.11e+02	1.65e+01
	1.00 sec	4.45e+04	9.09e+02	1.83e+07	8.12e+02	1.66e+01
	2.00 sec	3.65e+03	7.40e+01	NA	NA	NA
Subtotal: Uncontrolled				**2.53e+08**	**6.65e+03**	**1.36e+02**
Batch	Wet Scrubber	4.26e+02	10	2.42e+04	1.00e-02	2.00e-04
Continuous	Wet Scrubber	4.26e+02	10	1.88e+08	8.01e+01	1.90
Intermittent	Wet Scrubber	4.26e+02	10	6.04e+07	2.58e+01	6.11e-01
Subtotal: Controlled w/Wet Scrubber				**3.71e+08**	**1.58e+02**	**3.74**
Continuous	Dry Scrubber no carbon	3.65e+02	7	9.94e+07	3.63e+01	7.39e-01
Continuous on-site/ Intermittent	Dry Scrubber with no carbon	3.56e+02	7	7.86e+06	2.87	5.80e-02
Continuous	Dry Scrubber with Carbon	7.00e+01	2	1.43e+07	1.00	2.40e-02
Continuous on-site/ Intermittent	Dry Scrubber with Carbon	7.00e+01	2	3.70e+06	2.61e-01	6.00e-03
Subtotal: Controlled w/Dry Scrubber				**1.46e+08**	**4.80e+01**	**9.82e-01**
Intermittent	Fabric Filter/ Packed Bed	3.34e+04	6.81e+02	6.99e+05	2.34e+01	4.76e-01
Total MWI				**3.71e+08**	**6.88e+03**	**1.41e+02**

NA = Not applicable
ng/kg = nanograms per kilogram
kg/yr = kilograms per year
g/yr = grams per year

Table 3-10. AHA Approach: TEQ Emission Factors Calculated for Air Pollution Control

APC Category	TEQ Emission Factor ($lb/10^6$ lbs waste)	Number of MWI Test Reports Used[a]
Uncontrolled		
MWIs up to 200 lb/hr	1.53e-03	4
MWIs > 200 lb/hr	5.51e-04	13
Wet scrubber/BHF/ESP[b]	4.49e-05	11
Dry sorbent injection/Fabric Filter	6.95e-05	8

a The same MWI may have been used more than once in deriving emission factors.

b Wet scrubbers-bag house filters-electrostatic precipitators. Bag house is also called Fabric Filter.

Source: Doucet (1995).

Table 3-11. AHA Assumptions of the Percent Distribution of Air Pollution Control on MWIs Based on PM Emission Limits

PM Emission Limits[a] (gr/dscf)	Percent MWIs Uncontrolled[b]	Percent MWIs with Wet Scrubbers/ BHFs/ESPs[c]	Percent MWIs DI/FF[d]
≥ 0.10	50%	50%	0%
0.08 to < 0.10	25%	75%	0%
0.03 to < 0.08	0%	98%	2%
< 0.03	0%	30%	70%

a Particulate matter (PM) emission limits at the stack, grains per dry standard cubic foot (gr/dscf).

b *Uncontrolled means there is no air pollution control device installed on the MWI.*

c Scrubbers/BHFs/EDPs means wet scrubbers-bag house filters-electrostatic precipitators.

d DI/FF means dry sorbent injection combined with fabric filters.

Table 3-12. AHA Approach: Estimated Annual Nationwide CDD/CDF TEQ Emissions

APCD[a]	MWI Capacity[b] (lb/hr)	CDD/CDF TEQ Emission Factor[c] (g/kg waste)	MWI Activity Level[d] (kg/yr)	Annual TEQ Emissions (g/yr)
Uncontrolled	≤ 200 > 200	1.54 e-06 5.51 e-07	2.28 e+07 1.54 e+08	3.51e+01 8.48e+01
Subtotal: Uncontrolled			1.77 e+08	1.20e+02
WS/BHF/ESP	> 200	4.49 e-08	3.51 e+08	1.58e+01
DI/FF	> 200	6.95 e-08	2.60 e+07	1.81
Subtotal: Controlled			3.77 e+08	1.76e+01
Total			5.54 e+08	1.38e+02

a APCD = Air Pollution Control Device assumed by AHA. Uncontrolled means there is no air pollution control device installed on the MWI. WS/BHF/ESP = Wet scrubber-bag house filter-electrostatic precipitator. DI/FF = Dry sorbent injection-fabric filter.

b MWI capacity is the design capacity of the primary combustion chamber.

c TEQ Emission Factor derived from tested facilities.

d Activity Level is the annual amount of medical waste incinerated by each APCD class.

lb/hr = pounds per hour
g/kg = grams per kilogram
kg/yr = kilograms per year
g/yr = grams per year

Table 3-13. Comparison Between Predicted Residence Times and Residence Times Confirmed by State Agencies from EPA/ORD Telephone Survey

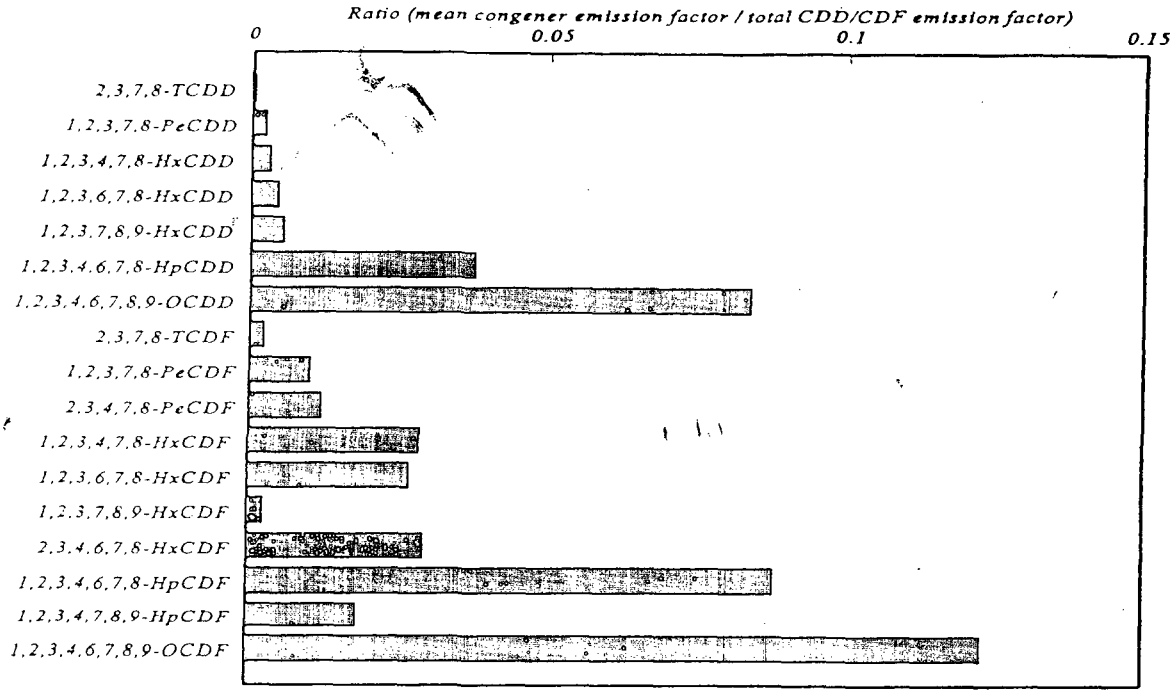
State	Residence Time Categories	Percentage of Uncontrolled MWIs Predicted by PM Method	Percentage of Uncontrolled MWIs Confirmed by State Agency
Michigan	1/4 second 1.0 second 2.0 seconds	2% (6/280 MWIs) 2% (5/280) 96% (269/280)	96% (269/280 MWIs) 3% (9/280) 1% (1/280)
Massachusetts	1/4 second 1.0 second 2.0 seconds	6% (6/94 MWIs) 0% (0/94) 94% (88/94)	Unknown Unknown 4% (2/50)
Virginia	1/4 second 1.0 second 2.0 seconds	11% (6/56) 0 % (0/50) 89% (50/56)	4.5% (1/22) 91% (20/22) 4.5% (1/22)
New Jersey	1/4 second 1.0 second 2.0 seconds	0% (0/53 MWIs) 0% (0/53) 100% (53/53)	Unknown Unknown Unknown

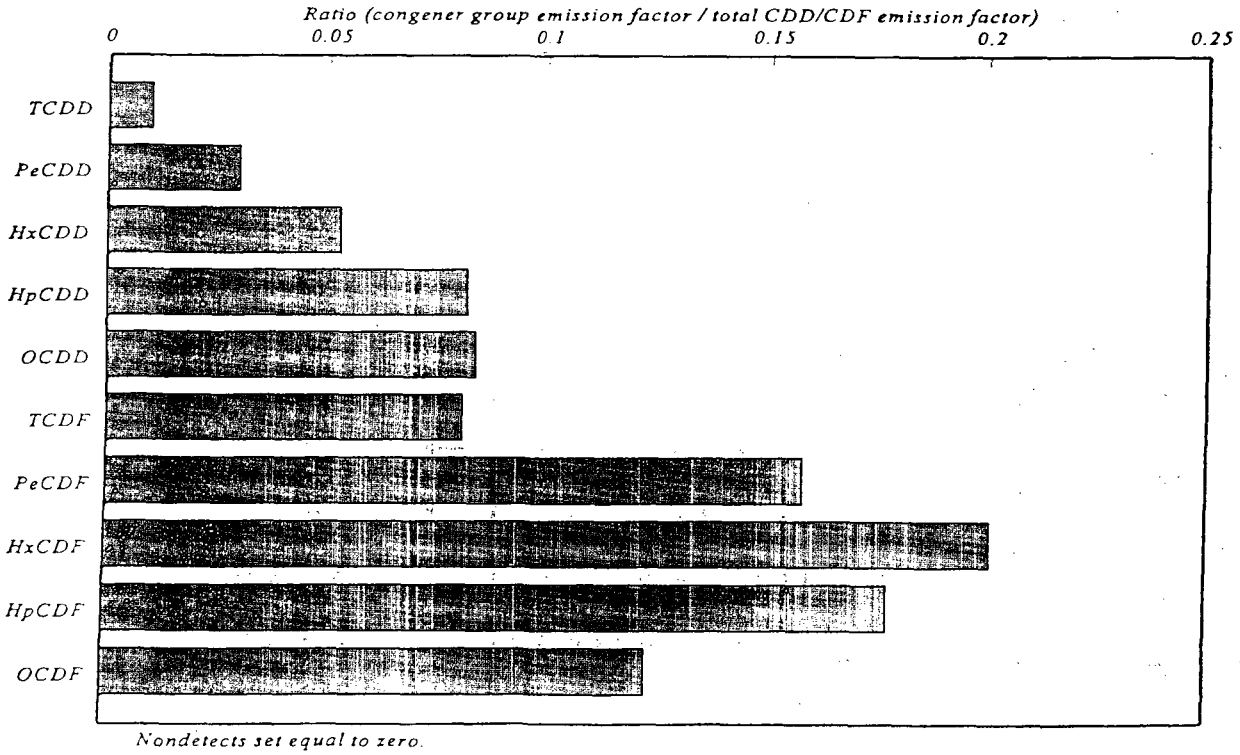
Source: O'Rourke (1996).

Table 3-14. EPA/ORD Approach: Annual TEQ Emissions from Medical Waste Incineration (MWI) for Reference Year 1995

MWI Class (APCD)	MWI Subclass (Capacity or APCD)	No. of Tested Facilities	Emission Factor Total CDD/CDF (ng/kg)	TEQ Emission Factor (ng/kg)	Activity Level (kg/yr)	Annual CDD/F Emissions (g/yr)	Annual TEQ Emissions (g/yr)
Uncontrolled	≤200 lb/hr	3	9.25e+04	1.86e+03	3.06e+07	2.83e+03	5.71e+01
	>200 lb/hr	5	6.02e+04	1.70e+03	2.23e+08	1.34e+04	3.79e+02
Controlled	Wet Scrubber/ Fabric Filter/ ESP	8	4.65e+03	7.2e+01	3.71e+08	1.72e+03	2.68e+01
	Dry Sorbent Injection/ Fabric Filter	2	2.85e+02	7	1.46e+08	4.16e+01	9.90e-01
	Fabric Filter/ Packed Bed Scrubber	1	1.10e+05	1.35e+03	6.99e+05	7.73e+01	9.50e-01
Total					7.71e+08	2.02e+04	4.77e+02

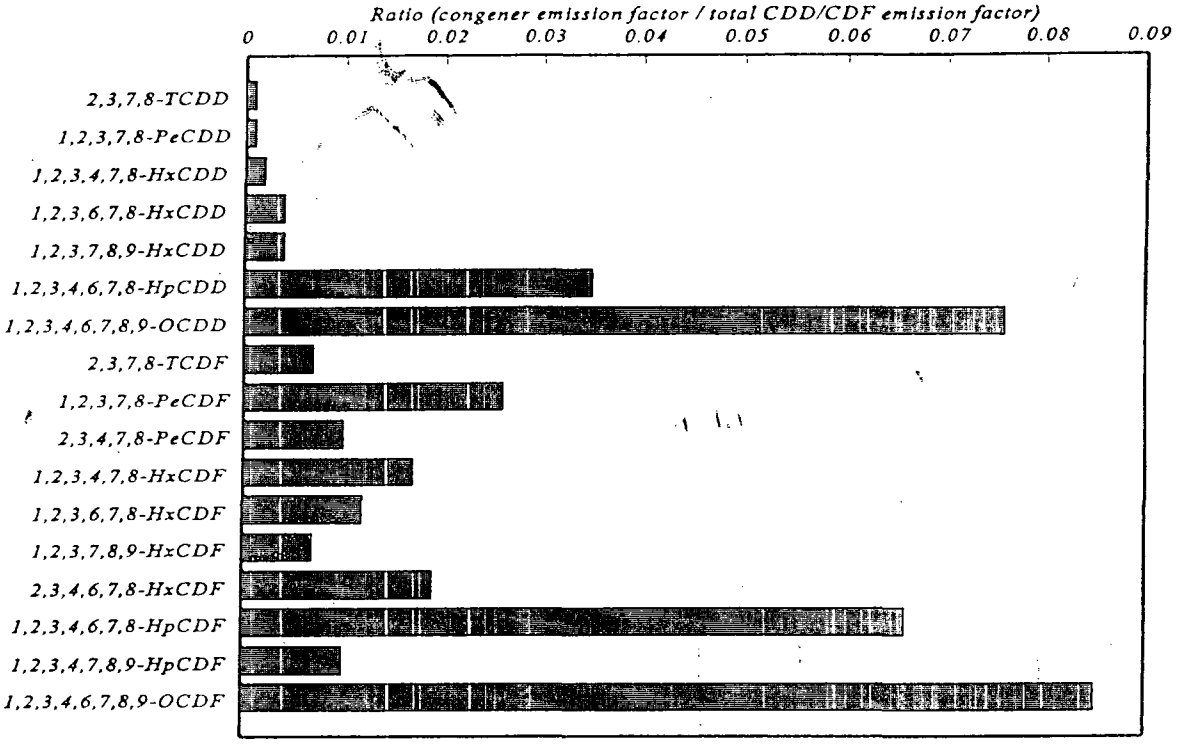
APCD = Air Pollution Control Devices
ng/kg = nanograms per kilogram
kg/yr = kilograms per year
g/yr = grams per year
lb/hr = pounds per hour

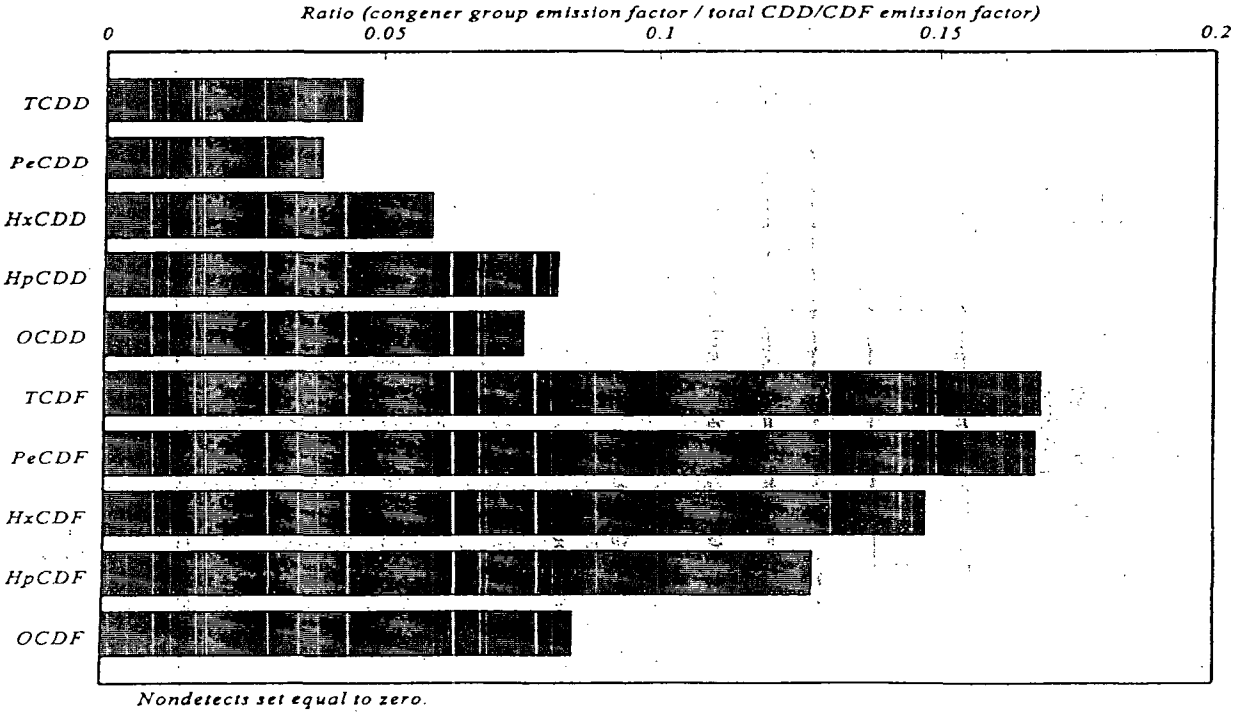




Nondetects set equal to zero.

Figure 3-12. Congener and Congener Group Profiles for Air Emissions from Medical Waste Incinerators without APCD





Nondetects set equal to zero.

Figure 3-13. Congener and Congener Group Profiles for Air Emissions from Medical Waste Incinerators Equipped with a Wet Scrubber, Baghouse, and Fabric Filter

Table 3-15. Summary of Annual TEQ Emissions from Medical Waste Incineration (MWI) for Reference Year 1987

MWI Class[a]	No of Tested Facilities	Activity Level (kg/yr)	Total CDD/F Emission Factor[b] (g/kg)	TEQ Emission Factor (g/kg)	Annual CDD/F Emissions (g/yr)	Annual TEQ Emissions (g/yr)
≤ 200 lb/hr	3	2.19 e+08	9.25 e-05	1.86 e-06	2.02e+04	4.08e+02
> 200 lb/hr	5	1.21 e+09	6.02 e-05	1.70 e-06	7.31e+04	2.08e+03
Total	8	1.43 e+09			9.33e+04	2.47e+03

[a] This uses the categorization scheme of the AHA Approach (Doucet, 1995).

kg/yr = kilograms per year
g/kg = grams per kilogram
g/yr = grams per year
lb/hr = pounds per hour

Table 3-16. Comparisons of Basic Assumptions Used in the EPA/ORD, the EPA/OAQPS, and the AHA Approaches to Estimating Nationwide CDD/CDF TEQ Emissions from MWIs in 1995

Assumptions	EPA/ORD Approach	EPA/OAQPS Approach	AHA Approach
Reference Year	1995	1995	1995
Number of MWIs	2,375	2,375	2,233
Estimated Activity Level	7.71 e+08 kg/yr	7.71 e+08 kg/yr	5.54 e+08 kg/yr
Percent of Activity Level at Uncontrolled MWIs	33%	33%	32%
Percent of Activity Level at Controlled MWIs	67%	67%	68%
Subclassification of Uncontrolled Class	Same as AHA assumption	By residence times (RT) in secondary chamber	By design capacity
Assumed Distribution of Uncontrolled Class	Same as AHA assumption	By RT of 0.25, 1.0 and 2.0 sec by State PM emission limits	By estimated annual hrs of operation of < 200 lb/hr and > 200 lb/hr design capacity
APCDs Assumed for Controlled Class	WS/FF/ESP DI/FF FF/Packed Bed Scrub	WS DS-no Carbon DS-Carbon FF/Packed Bed Scrub	WS/FF/ESP DI/FF
Assumed Distribution of Controls	Yes/ Analogous to AHA method.	Yes/ Analogous to AHA method	Yes/ Based on survey and State PM emission limits
Emission Factor Approach Used	Yes	Yes	Yes
No. of Tested MWIs Used to Develop Emission Factors	Uncontrolled: 8 Controlled: 11	Uncontrolled: 10 Controlled: 23	Uncontrolled: 13 Controlled: 12
Uncontrolled TEQ Emission Factors (ng/kg)	1,865 = ≤200 lb/hr 1,701 = >200 lb/hr	a/ 3,960 = 0.25 s RT b/ 909 = 1.0 s RT c/ 200 lb/hr 74 = 2.0 s RT	d/ 1,540 = ≤200 lb/hr e/ 551 = > 200 lb/hr
Controlled TEQ Emission Factors (ng/kg)	f/ WS/FF/ESP: 72 g/ DSI/FF: 7 h/ FF/PBS: 1,352	i/ WS: 10 j/ DS no carbon: 7 k/ DS with carbon: 2 l/ FF/PBS: 681	m/ WS/FF/ESP: 44.9 n/ DSI/FF: 69.5

WS = Wet Scrubber; FF = Fabric Filter; ESP = Electrostatic Precipitator; DSI = Dry Sorbent Injection; DS = Dry Scrubber; no carbon = without the addition of activated carbon; with carbon = with the addition of activated carbon; PBS = Packed Bed Scrubber.

a 0.25 seconds residence time (RT) in the secondary chamber.
b 1.0 seconds residence time (RT) in the secondary chamber.
c 2.0 seconds residence time (RT) in the secondary chamber.
d design capacities less than or equal to 200 lbs/hr.
e design capacities greater than 200 lbs/hr.

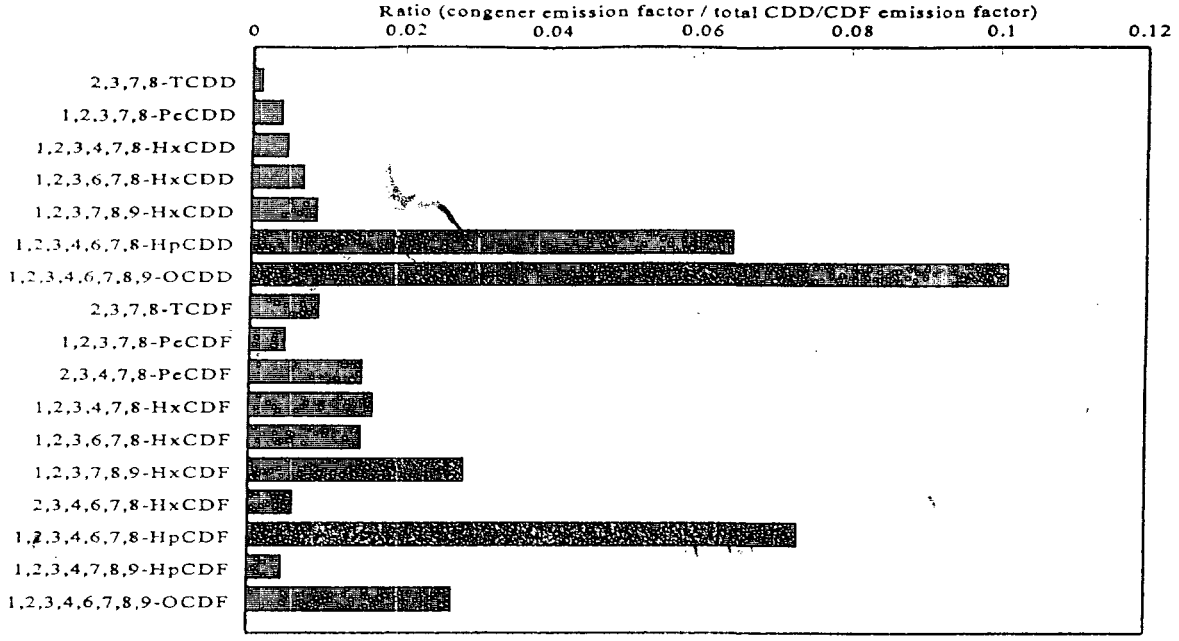
lb/hr = pounds per hour
kg/yr = kilograms per year

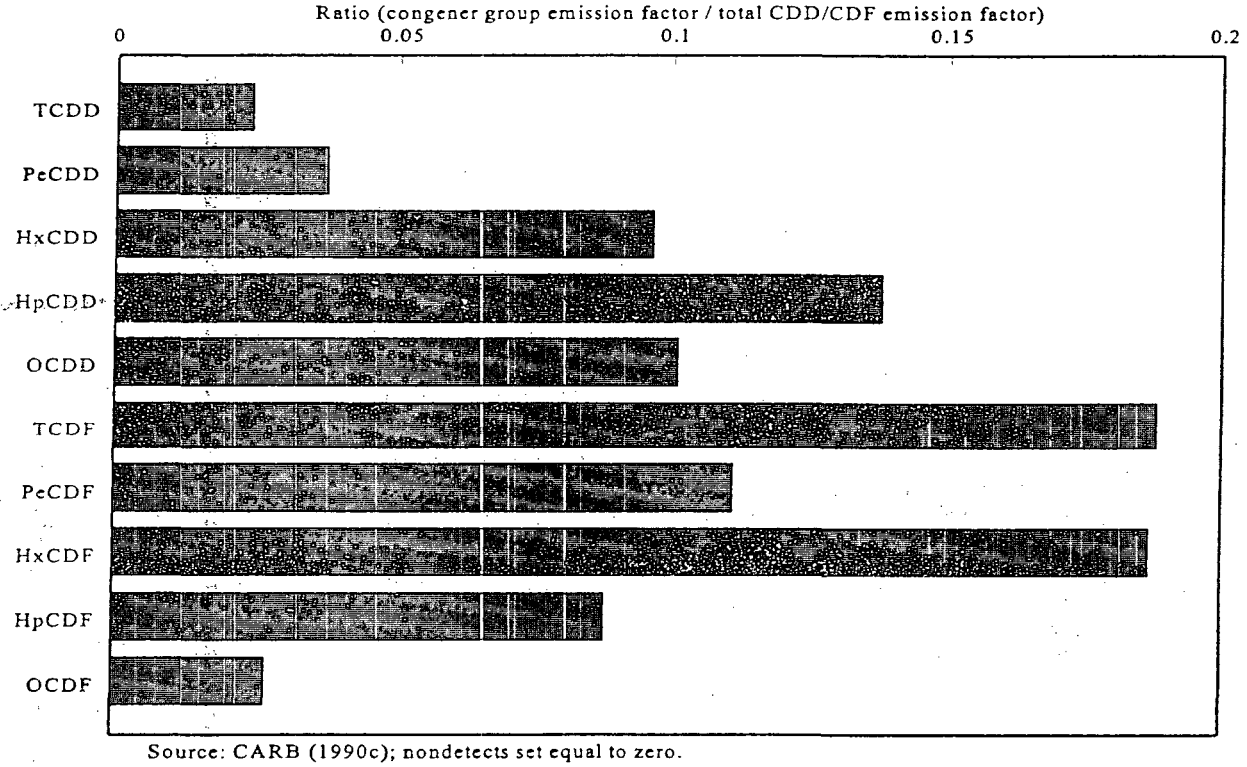
Table 3-17. CDD/CDF Air Emission Factors for a Crematorium

Congener/Congener Group	Mean Facility Emission Factor	
	Assuming ND = zero (ng/body)	Assuming ND = 1/2 det limit (ng/body)
2,3,7,8-TCDD	28.9	28.9
1,2,3,7,8-PeCDD	89.6	89.6
1,2,3,4,7,8-HxCDD	108	108
1,2,3,6,7,8-HxCDD	157	157
1,2,3,7,8,9-HxCDD	197	197
1,2,3,4,6,7,8-HpCDD	1,484	1,484
OCDD	2,331	2,331
2,3,7,8-TCDF	206	206
1,2,3,7,8-PeCDF	108	117
2,3,4,7,8-PeCDF	339	349
1,2,3,4,7,8-HxCDF	374	374
1,2,3,6,7,8-HxCDF	338	338
1,2,3,7,8,9-HxCDF	657	657
2,3,4,6,7,8-HxCDF	135	135
1,2,3,4,6,7,8-HpCDF	1,689	1,813
1,2,3,4,7,8,9-HpCDF	104	112
OCDF	624	624
Total 2,3,7,8-CDD	4,396	4,396
Total 2,3,7,8-CDF	4,574	4,725
Total TEQ	501	508
Total TCDD	554	554
Total PeCDD	860	860
Total HxCDD	2,224	2,224
Total HpCDD	3,180	3,180
Total OCDD	2,331	2,331
Total TCDF	4,335	4,335
Total PeCDF	2,563	2,563
Total HxCDF	4,306	4,306
Total HpCDF	2,030	2,154
Total OCDF	624	624
Total CDD/CDF	23,007	23,131

ng/body = nanograms per body

Source: CARB (1990c)





Source: CARB (1990c); nondetects set equal to zero.

Figure 3-14. Congener and Congener Group Profiles for Air Emissions from a Crematorium

4.3. OIL COMBUSTION

Two major categories of fuel oil are burned by combustion sources: distillate oils and residual oils. These oils are further distinguished by grade numbers, with Nos. 1 and 2 being distillate oils; Nos. 5 and 6 being residual oils; and No. 4 either distillate oil or a mixture of distillate and residual oils. No. 6 fuel oil is sometimes referred to as Bunker C. Distillate oils are more volatile and less viscous than residual oils. They have negligible nitrogen and ash contents and usually contain less than 0.3 percent sulfur (by weight). Distillate oils are used mainly in domestic and small commercial applications. Being more viscous and less volatile than distillate oils, the heavier residual oils (Nos. 5 and 6) must be heated for ease of handling and to facilitate proper atomization. Because residual oils are produced from the residue remaining after the lighter fractions (gasoline, kerosene, and distillate oils) are removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur. Residual oils are used mainly in utility, industrial, and large commercial application (U.S. EPA, 1995b).

4.3.1. Residential/Commercial Oil Combustion

No testing of the CDD/CDF content of air emissions from residential/commercial oil-fired combustion units in the United States could be located. However, U.S. EPA (1997b) has estimated CDD/CDF congener group and TEQ emission factors based on average CDD/CDF concentrations reported for soot samples from 21 distillate fuel oil-fired furnaces used for central heating in Canada, and a particulate emission factor for distillate fuel oil combustors (300 mg/L of oil) obtained from AP-42 (U.S. EPA, 1995b). The TEQ emission factor estimate in U.S. EPA (1997b) was derived using the calculated emission factors for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and the 10 congener groups. These emission factors are presented in Table 4-13, and the congener group profile is presented in Figure 4-6.

Because there are no direct measurements of CDD/CDF emissions in stack gases from U.S. residential oil-fired combustors and because of uncertainties associated with using chimney soot data to estimate stack emissions, no national emission estimates for this category are proposed at this time. However, a preliminary order of magnitude estimate of national TEQ emissions from this source category can be derived using the emission factor presented in Table 4-13 (150 pg TEQ/L of oil combusted). Distillate fuel oil sales to the residential/commercial sector totaled 39.7 billion liters in 1995 (EIA, 1997a).

Application of the TEQ emission factor of 150 pg TEQ/L to this fuel oil sales estimate results in estimated TEQ emissions of 6.0 g TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of the emissions.

4.3.2. Utility Sector and Industrial Oil Combustion

Preliminary CDD/CDF emission factors for oil-fired utility boilers developed from boiler tests conducted over the past several years are reported in U.S. EPA (1995c). The data are a composite of various furnace configurations and APCD systems. Table 4-14 lists the median emission factors presented in U.S. EPA (1995c; 1997b). The congener and congener group profiles based on these data are presented in Figure 4-7. The median TEQ emission factor was reported to be 314 pg/L of oil burned.

In 1993, the Electric Power Research Institute (EPRI) sponsored a project to gather information of consistent quality on power plant emissions. This project, the Field Chemical Emissions Measurement (FCEM) project, included testing of two cold side ESP-equipped oil-fired power plants for CDD/CDF emissions (EPRI, 1994). The averages of the congener and congener group emission factors reported for these two facilities are also presented in Table 4-14. The average TEQ emission factor is 95.5 pg/L of oil burned when nondetected values are treated as zero (170 pg/L when nondetected values are treated as one-half the detection limit).

The TEQ emission factor reported in EPRI (1994) is a factor of three less than the median TEQ emission factor reported in U.S. EPA (1995c; 1997b). For purposes of this assessment, an emission factor of 200 pg/L (i.e., the average of 95.5 and 314 pg/L) is assumed to be current best estimate of the average TEQ emission factor for utility/industrial oil burning. This estimate is assigned a "low" confidence rating.

TEQ emission factors an order of magnitude larger were reported by Bremmer et al. (1994), based on measurements of CDD/CDF emission from three stationary used oil combustion units and from a ferry fired with a blend of used and virgin oil. Flue gases from a garage stove consisting of an atomizer fueled by spent lubricating oil from diesel engines (35 mg Cl/kg) were reported to contain 0.1 ng TEQ/Nm^3 (or 2 ng TEQ/kg of oil burned).

The flue gases from a hot water boiler consisting of a rotary cup burner fueled with the organic phase of rinse water from oil tanks (340 mg Cl^-/kg) contained 0.2 ng TEQ/Nm^3 (or 4.8 ng TEQ/kg of oil burned). The flue gases from a steam boiler consisting of a rotary cup burner fueled by processed spent oil (240 mg Cl^-/kg) contained 0.3 ng TEQ/Nm^3 (or 6.0 ng TEQ/kg of oil burned). The emission rate from the ferry (heavy fuel oil containing 11 ng/kg organic chlorine) was 3.2 to 6.5 ng TEQ/kg of oil burned. From these data, Bremmer et al. (1994) derived an average emission factor for combustion of used oil of 4 ng TEQ/kg of oil burned.

Bremmer et al. (1994) also reported measuring CDD/CDF emissions from a river barge and a container ship fueled with gas oil (less than 2 ng/kg of organic chlorine). The exhaust gases contained from 0.002 to 0.2 ng TEQ/Nm^3. From these data, Bremmer et al. (1994) derived an average emission factor for inland oil-fueled vessels of 1 ng TEQ/kg oil burned.

Residual fuel oil sales totaled 46.6-billion liters in 1995 and 77.3 billion liters in 1987 (EIA, 1992; 1997a). Vessel bunkering was the largest consumer (48 percent of sales) followed by electric utilities and the industrial sector. A "high" confidence rating is assigned to these production estimates. Application of the TEQ emission factor of 200 pg/L to these residual fuel oil sales results in estimated TEQ emissions of 9.3 g TEQ in 1995 and 15.5 g TEQ in 1987. Based on the "low" confidence rating assigned to the emission factors, the estimated range of potential emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the estimate of TEQ emissions in 1995 (i.e., 9.3 g TEQ) is the geometric mean of the range, then the range is calculated to be 2.9 to 29 g TEQ/yr. For the year 1987, the range is calculated to be 4.9 to 49 g TEQ/yr.

4.4. COAL COMBUSTION

During 1995, coal consumption accounted for approximately 22 percent of the energy consumed from all sources in the United States (U.S. DOC, 1997). In 1995, 872-million metric tons of coal were consumed in the United States. Of this total, 88.4 percent (or 771-million metric tons) were consumed by electric utilities, 11.0 percent (or 96-million metric tons) were consumed by the industrial sector (including consumption of 30 million metric tons by coke plants), and 0.6 percent (or 5.3-million metric tons) were consumed by

residential and commercial sources (EIA, 1997b). Comparable figures for 1987 are: total consumption, 759-million metric tons; consumption by electric utilities, 651-million metric tons; consumption by coke plants, 33.5-million metric tons; consumption by other industries, 68.2-million metric tons; and consumption by the residential and commercial sectors, 6.3-million metric tons (EIA, 1995c). These production estimates are assigned a "high" confidence rating because they are based on detailed studies specific to the United States.

The following two subsections discuss the results of relevant emission studies for the utility/industrial and residential sectors and present annual emission estimates.

4.4.1. Utilities and Industrial Boilers

Until recently, few studies had been performed to measure CDD/CDF concentrations in emissions from coal-fired plants, and several of these studies did not have the congener specificity and/or detection limits necessary to fully characterize this potential source (U.S. EPA, 1987a; NATO, 1988; Wienecke et al., 1992). Recently, the results of testing of coal-fired utility and industrial boilers have been reported for facilities in The Netherlands, the United Kingdom, and the United States.

Bremmer et al. (1994) reported the results of emission measurements at two coal-fired facilities in The Netherlands. The emission rate from a pulverized coal electric power plant equipped with an ESP and a wet scrubber for sulfur removal was reported as 0.02 ng TEQ/Nm^3 (at 11 percent O_2) (or 0.35 ng TEQ/kg of coal fired). The emission rate for a grass drying chain grate stoker equipped with a cyclone APCD was reported to be 0.16 ng TEQ/Nm^3 (at 11 percent O_2) (or 1.6 ng TEQ/kg of coal fired). Cains and Dyke (1994) recently reported an emission rate of 102 to 109 ng TEQ/kg of coal at a small-scale facility in the United Kingdom that was equipped with an APCD consisting only of a grit arrestor. Umweltbundesamt (1996) reported that the TEQ content of stack gases from 16 coal-burning facilities in Germany ranged from 0.0001 to 0.04 ng TEQ/m^3; the data provided in this report did not enable emission factors to be calculated.

The U.S. Department of Energy sponsored a project in 1993 to assess emissions of hazardous air pollutants at coal-fired power plants. As part of this project, CDD/CDF stack emissions were measured at seven U.S. coal-fired power plants. The preliminary results of this project (i.e., concentrations in stack emissions) were reported by Riggs et al. (1995)

and are summarized in Table 4-15. The levels reported for individual 2,3,7,8-substituted congeners were typically not detected or very low (i.e., ≤0.033 ng/Nm^3). In general, CDF levels were higher than CDD levels. OCDF and 2,3,7,8-TCDF were the most frequently detected congeners (i.e., at four of the seven plants). Table 4-16 presents characteristics of the fuel used and APCD employed at each plant. Variation in emissions between plants could not be attributed by Riggs et al. (1995) to any specific fuel or operational characteristic.

During the early 1990s, EPRI also sponsored a project to gather information of consistent quality on power plant emissions. This project, the Field Chemical Emissions Measurement (FCEM) project, included testing of four cold-side ESP-equipped coal-fired power plants for CDD/CDF emissions. Two plants burned bituminous coal and two burned subbituminous coal. The final results of the DOE project discussed above were integrated with the results of the EPRI testing and published in 1994 (EPRI, 1994). The average congener and congener group emission factors derived from this 11 facility data set, as reported in EPRI (1994), are presented in Table 4-17. Congener and congener group profiles for the data set are presented in Figure 4-8. The average TEQ emission factor, assuming nondetected values are zero, is 0.087 ng/kg of coal combusted. The average TEQ emission rate, assuming nondetected values are one-half the detection limit, is 0.136 ng/kg of coal combusted. A "medium" confidence rating is assigned to these emission factors because they are based on recent testing at U.S. facilties.

As stated above, consumption of coal by the U.S. utility and industrial sectors (excluding consumption at coke plants) was 837-million metric tons in 1995 and 719-million metric tons in 1987. Applying the TEQ emission factor of 0.087 ng TEQ/kg of coal combusted to these production factors yields estimated annual emissions of 72.8 g TEQ in 1995 and 62.6 g TEQ in 1987.

Based on the "medium" confidence rating assigned to the estimated TEQ emission factor, the estimated range of potential emissions is assumed to vary by a factor of five between the low and high ends of the range. Assuming that the estimated emissions (assuming nondetected values are zero) of 72.8 g TEQ in 1995 and 62.6 g TEQ in 1987 are the geometric means of these ranges for these years, then the ranges are calculated to be 32.6 to 163 g TEQ in 1995 and 28 to 140 g TEQ in 1987.

4.4.2. Residential/Commercial Coal Combustion

Coal is usually combusted in underfeed or hand-stoked furnaces in the residential sector. Other coal-fired heating units include hand-fed room heaters, metal stoves, and metal and masonry fireplaces. Stoker-fed units are the most common design for warm-air furnaces and for boilers used for steam or hot water production. Most coal combusted in these units are either bituminous or anthracite. These units operate at relatively low temperatures and do not efficiently combust the coal. Coal generally contains small quantities of chlorine and CDD/CDF; therefore, the potential for CDD/CDF formation exists. Typically, coal-fired residential furnaces are not equipped with particulate matter or gaseous pollutant control devices that may limit emissions of any CDD/CDFs formed (U.S. EPA, 1997b). No testing of the CDD/CDF content of air emissions from residential/commercial coal-fired combustion units in the United States could be located. However, several relevant studies have been performed in European countries.

Thub et al. (1995) measured flue gas concentrations of CDD/CDF from a household heating system in Germany, fired either with "salt" lignite coal (i.e., total chlorine content of 2,000 ppm) or "normal" lignite coal (i.e., total chlorine content of 300 ppm). CDD/CDFs were detected in the flue gases generated by combustion of both fuel types. (See Table 4-18.) The congener profiles and patterns were similar for both fuel types, with OCDD the dominant congener and TCDF the dominant congener group. However, the emissions were higher for the "salt" coal (0.109 ng TEQ/m^3 or 2.74 ng TEQ/kg of coal) by a factor of eight than for the "normal" coal (0.015 ng TEQ/m^3 or 0.34 ng TEQ/kg of coal).

Eduljee and Dyke (1996) used the results of testing performed by the Coal Research Establishment in the United Kingdom to estimate emission factors for residential coal combustion units as follows:

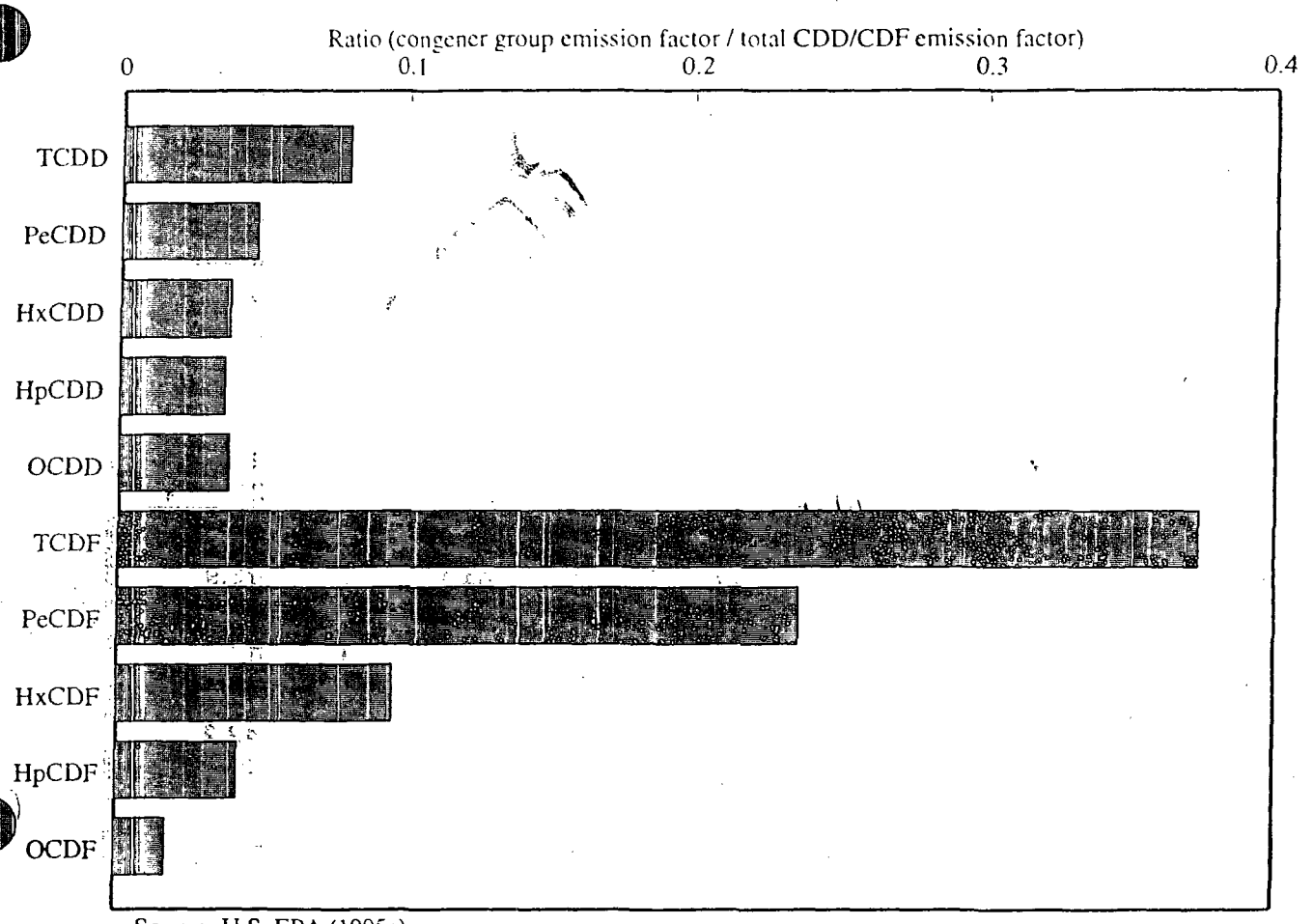
- Anthracite coal: 2.1 ng TEQ/kg of coal; and
- Bituminous coal: 5.7 to 9.3 ng TEQ/kg of coal (midpoint of 7.5 ng TEQ/kg).

CDD/CDF emission factors for coal-fired residential furnaces were estimated in U.S. EPA (1997b) based on average particulate CDD/CDF concentrations from chimney soot samples collected from seven coal ovens, and particulate matter emission factors specific to anthracite and bituminous coal combustion obtained from AP-42 (U.S. EPA, 1995b). The TEQ emission factors estimated in U.S. EPA (1997b) (i.e., 68.0 and 98.5 ng TEQ/kg of anthracite and bituminous coal, respectively) were derived using the calculated emission

factors for 2,3,7,8-TCDD 2,3,7,8-TCDF, and the 10 congener groups. U.S. EPA (1997b) stated that the estimated factors should be considered to represent maximum emission factors, because soot may not be representative of the particulate matter actually emitted to the atmosphere. These emission factors are presented in Table 4-18, and congener group profiles are presented in Figure 4-9.

Although the congener group profiles of the Thub et al. (1995) measurements and the U.S. EPA (1997b) estimates are similar, the TEQ emission factors differ by factors of 175 to 289 between the two studies. The emission factors used by Eduljee and Dyke (1996) to estimate national annual emissions of CDD/CDF TEQs from residential coal combustion in the United Kingdom fall in between those other two sets of estimates but are still about one to two orders of magnitude greater than the estimated emissions factor from industrial/utility coal combustors.

Because there are no direct measurements of CDD/CDF emissions from U.S. residential coal-fired combustors and because of uncertainties regarding the comparability of U.S. and German and British coal and combustion units, no national emission estimate for this category is proposed at this time. However, a preliminary order of magnitude estimate of national TEQ emissions from this source category can be derived using the emission factors of Eduljee and Dyke (1996). As noted above, 5.3-million metric tons of coal were consumed by the residential/commercial sector in 1995 (U.S. DOC, 1997). U.S. EPA (1997b) reports that 72.5 percent of the coal consumed by the residential sector in 1990 were bituminous and 27.5 percent were anthracite. Assuming that these relative proportions reflect the actual usage in 1995, then application of the emission factors from Eduljee and Dyke (1996) (i.e., 2.1 ng TEQ/kg of anthracite coal and 7.5 ng TEQ/kg of bituminous coal) to the consumption value of 5.3-million metric tons results in an estimated TEQ emission of 32.0 g TEQ in 1995, which, when rounded to the nearest order of magnitude to emphasize the uncertainty in this estimate, results in a value of 10 g TEQ/yr. This estimate should be regarded as a preliminary indication of possible emissions from this source category; further testing is needed to confirm the true magnitude of these emissions.



Source: U.S. EPA (1995c)

Figure 4-6. Congener Group Profile for Air Emissions from Residential Oil-fueled Furnaces

Table 4-14. CDD/CDF Emission Factors for Oil-Fired Utility/Industrial Boilers

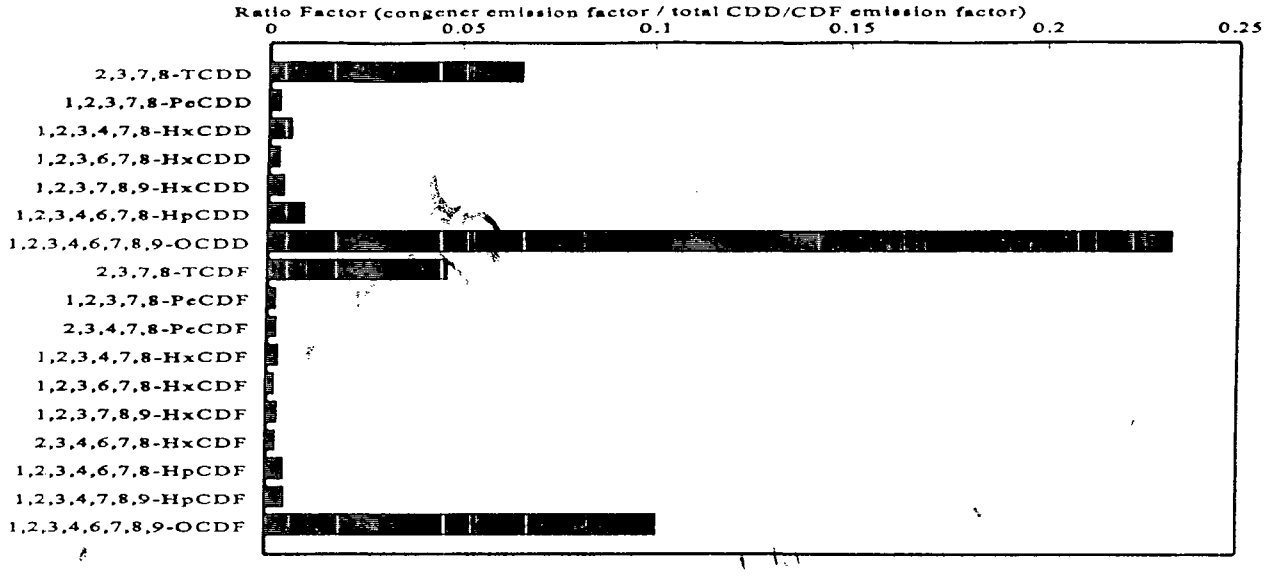
Congener/Congener Group	U.S. EPA (1997b) Median Emission Factor (pg/L oil)	EPRI (1994) Mean Emission Factor	
		ND = zero (pg/L oil)	ND = 1/2 DL (pg/L oil)
2,3,7,8-TCDD	117	0	26.6
1,2,3,7,8-PeCDD	104	24.7	43.1
1,2,3,4,7,8-HxCDD	215	63.3	108
1,2,3,6,7,8-HxCDD	97	65.8	79.3
1,2,3,7,8,9-HxCDD	149	79.7	102
1,2,3,4,6,7,8-HpCDD	359	477	546
OCDD	413	2055	2141
2,3,7,8-TCDF	83	0	35.7
1,2,3,7,8-PeCDF	77	64.1	73.9
2,3,4,7,8-PeCDF	86	49.3	59.6
1,2,3,4,7,8-HxCDF	109	76.5	94.9
1,2,3,6,7,8-HxCDF	68	35.4	45.2
1,2,3,7,8,9-HxCDF	104	0	37.7
2,3,4,6,7,8-HxCDF	86	23.8	42.2
1,2,3,4,6,7,8-HpCDF	169	164	218
1,2,3,4,7,8,9-HpCDF	179	0	137
OCDF	179	0	139
Total 2,3,7,8-CDD	1,453	2,766	3,047
Total 2,3,7,8-CDF	1,141	414	883
Total TEQ	314	95.5	170
Total TCDD	102	NR	NR
Total PeCDD	104	NR	NR
Total HxCDD	145	NR	NR
Total HpCDD	359	NR	NR
Total OCDD	413	NR	NR
Total TCDF	90	NR	NR
Total PeCDF	131	NR	NR
Total HxCDF	172	NR	NR
Total HpCDF	27	NR	NR
Total OCDF	179	NR	NR
Total CDD/CDF	1,722	3,179	3,931

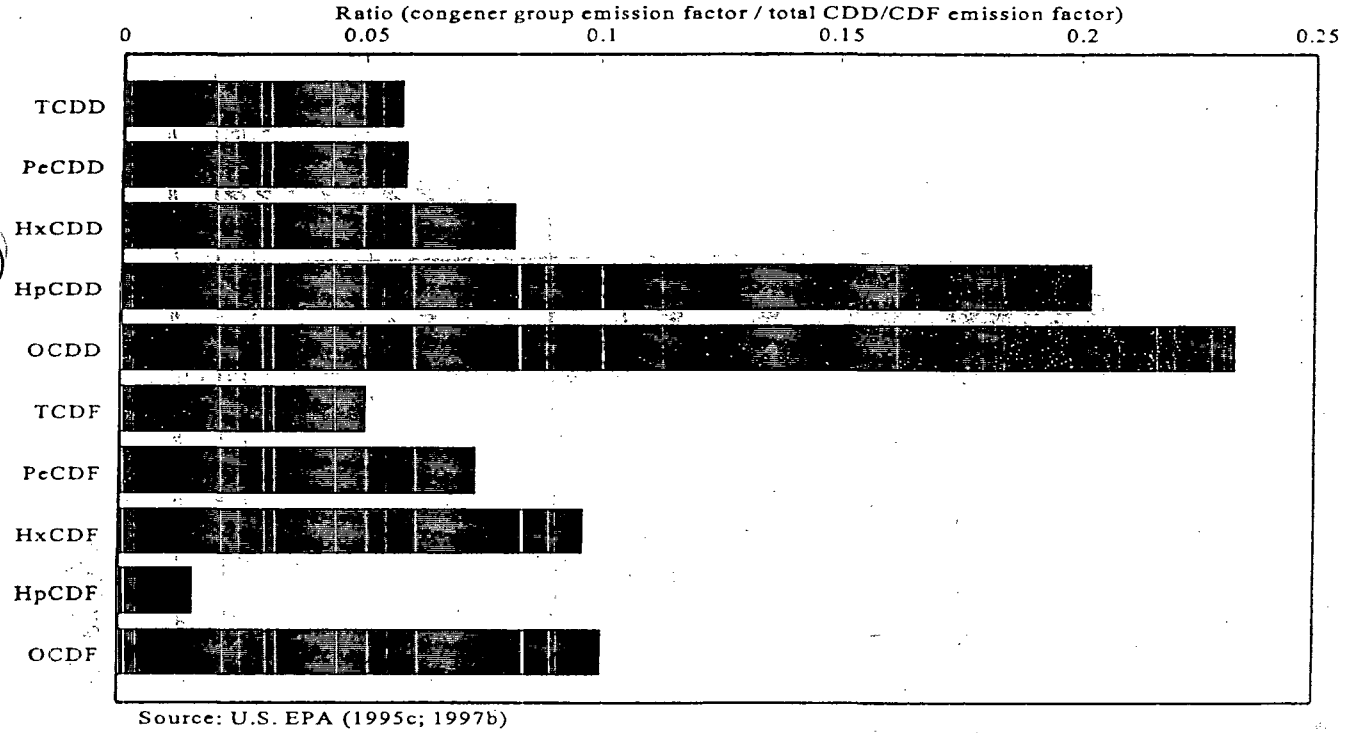
Sources:

U.S. EPA (1997b) - number of facilities not reported.

EPRI (1994) - based on two cold side ESP-equipped power plants.

Note: Assumes a density for residual fuel oil of 0.87 kg/L.





Source: U.S. EPA (1995c; 1997b)

Figure 4-7. Congener and Congener Group Profiles for Air Emissions from Industrial Oil-fueled Boilers

Table 4-15. CDD/CDF Concentrations in Stack Emissions from U.S. Coal-Fired Power Plants

Congener/Congener Group	Plant 1 (pg/Nm^3)	Plant 2 (pg/Nm^3)	Plant 3 (pg/Nm^3)	Plant 4 (pg/Nm^3)	Plant 5 (pg/Nm^3)	Plant 6 (pg/Nm^3)	Plant 7 (pg/Nm^3)
2,3,7,8-TCDD	ND (3.5)	ND (3.5)	1.0	ND (2.0)	ND (3.3)	ND (2.6)	ND (1.7)
1,2,3,7,8-PeCDD	ND (0.56)	ND (4.8)	ND (1.8)	ND (10)	ND (4.7)	ND (3.2)	ND (1.8)
1,2,3,4,7,8-HxCDD	ND (0.56)	ND (5.7)	ND (3.6)	ND (10)	ND (15.4)	ND (2.7)	ND (2.0)
1,2,3,6,7,8-HxCDD	ND (0.44)	5.0	ND (1.8)	ND (10)	ND (9.9)	ND (4.2)	ND (1.4)
1,2,3,7,8,9-HxCDD	ND (0.56)	4.9	ND (1.8)	ND (10)	ND (12.1)	ND (4.3)	ND (1.2)
1,2,3,4,6,7,8-HpCDD	ND (1.7)	29	ND (1.8)	ND (10)	ND (26.4)	4.3	2.4
OCDD	ND (12)	32	ND (14)	ND (20)	ND (131)	20	21.6
2,3,7,8-TCDF	ND (1.7)	8.1	7.8	ND (2.0)	ND (3.3)	13	0.7
1,2,3,7,8-PeCDF	ND (1.0)	ND (5.7)	7.2	ND (10)	ND (3.2)	ND (5.7)	ND (1.1)
2,3,4,7,8-PeCDF	2.4	ND (19)	6.6	ND (10)	ND (3.2)	ND (4.8)	ND (1.4)
1,2,3,4,7,8-HxCDF	3.3	16	8.4	ND (10)	ND (16.4)	ND (5.1)	ND (1.8)
1,2,3,6,7,8-HxCDF	1.1	ND (5.0)	2.9	ND (10)	ND (5.8)	ND (4.0)	ND (1.3)
1,2,3,7,8,9-HxCDF	ND (0.44)	11	ND (1.8)	ND (10)	ND (8.8)	ND (6.9)	ND (1.5)
2,3,4,6,7,8-HxCDF	ND (2.0)	ND (4.2)	3.0	ND (10)	ND (16.4)	ND (2.5)	ND (2.0)
1,2,3,4,6,7,8-HpCDF	2.0	29	6.0	ND (10)	ND (23)	ND (30)	ND (2.2)
1,2,3,4,7,8,9-HpCDF	ND (0.63)	ND (6.1)	ND (3.6)	ND (10)	ND (15.4)	ND (5.0)	ND (2.1)
OCDF	5.6	33	2.4	ND (20)	ND (131)	ND (19)	11.4
Total 2,3,7,8-CDD	0	71	1	0	0	24.3	24
Total 2,3,7,8-CDF	14	97	44.3	0	0	13	12.1
Total TCDD	1.8	12	12	NR	6.7	ND (2.6)	ND (55)
Total PeCDD	ND (1.0)	4.4	6.0	ND (10)	ND (4.7)	ND (3.2)	ND (32)
Total HxCDD	1.3	18	2.7	ND (10)	ND (26.3)	ND (4.0)	ND (24)
Total HpCDD	3.4	45	ND (2.4)	ND (10)	ND (26.4)	ND (14)	ND (8.1)
Total OCDD	ND (12)	32	ND (14)	ND (20)	ND (131)	20	21.6
Total TCDF	ND (5.2)	29	78	ND (2)	ND (3.3)	88	ND (37)
Total PeCDF	5.4	33	61	ND (10)	ND (6.6)	14	3.0
Total HxCDF	7.6	39	29	ND (10)	ND (16.4)	ND (5.0)	ND (27)
Total HpCDF	4.3	34	9.0	ND (10)	ND (29.5)	ND (20)	2.9
Total OCDF	5.6	33	2.4	ND (20)	ND (131)	ND (19)	11.4
Total CDD/CDF	29	279	200.1	0	6.7	122	38.9

ND = Not detected; value in parentheses is the detection limit.
NR = Not reported; suspected contamination problem.
Source: Riggs et al. (1995)

Table 4-16. Characteristics of U.S. Coal-Fired Power Plants Tested by DOE

Plant No.	Coal Type	Coal Chlorine Content (mg/kg)	Temperature (°C) at:			
			Pollution Control Device[a]			Stack
			ESP	Bag	FGD	
1	Bituminous	800	160	--	--	160
2	Bituminous	1,400	130	--	--	130
3	Subbituminous	300	--	150	--	150
4	Subbituminous	390	--	70	130	75
5	Bituminous	1,400	130	--	120	40
6	Lignite	400	170	--	170	110
7	Bituminous	1,000	150	--	--	150

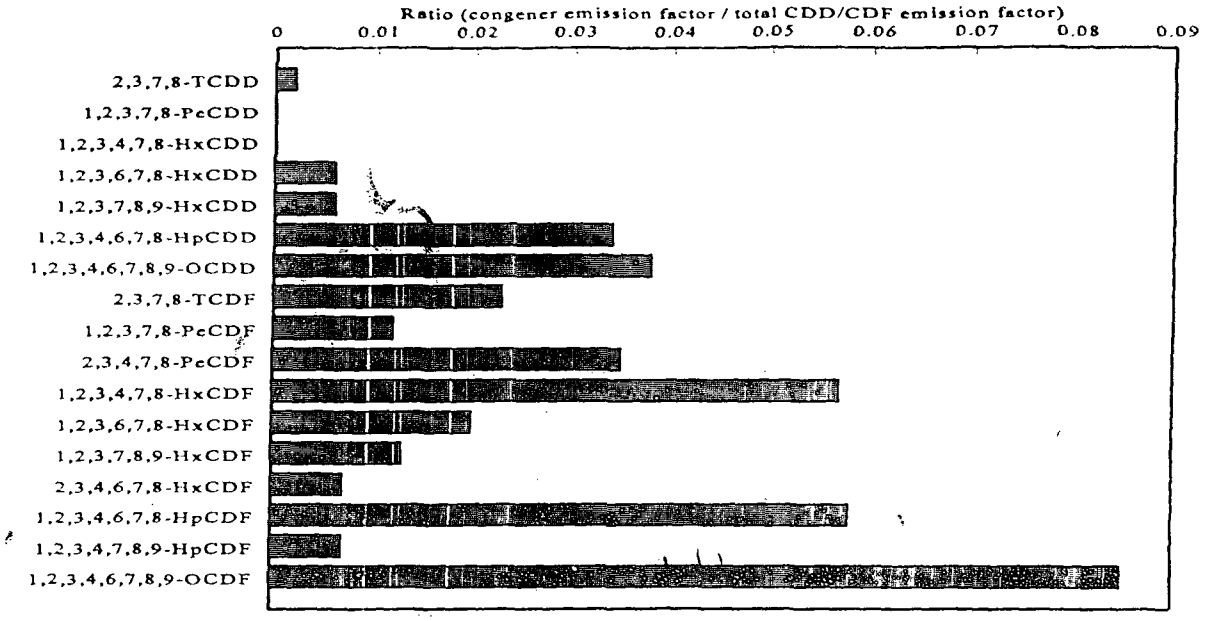
[a] ESP = Electrostatic precipitator, Bag = Baghouse, FGD = Flue gas desulfurization system.

Source: Riggs et al. (1995).

Table 4-17. CDD/CDF Emission Factors for Coal-Fired Utility/Industrial Power Plants

Congener/Congener Group	Mean Emission Factor	
	ND = zero (ng/kg coal)	ND = 1/2 DL (ng/kg coal)
2,3,7,8-TCDD	0.007	0.020
1,2,3,7,8-PeCDD	0	0.018
1,2,3,4,7,8-HxCDD	0	0.038
1,2,3,6,7,8-HxCDD	0.005	0.031
1,2,3,7,8,9-HxCDD	0.005	0.039
1,2,3,4,6,7,8-HpCDD	0.216	0.241
OCDD	0.517	0.648
2,3,7,8-TCDF	0.109	0.117
1,2,3,7,8-PeCDF	0.008	0.025
2,3,4,7,8-PeCDF	0.075	0.085
1,2,3,4,7,8-HxCDF	0.110	0.136
1,2,3,6,7,8-HxCDF	0.016	0.031
1,2,3,7,8,9-HxCDF	0.015	0.043
2,3,4,6,7,8-HxCDF	0.054	0.075
1,2,3,4,6,7,8-HpCDF	0.354	0.385
1,2,3,4,7,8,9-HpCDF	0.097	0.126
OCDF	0.159	0.281
Total 2,3,7,8-CDD	0.750	1.035
Total 2,3,7,8-CDF	0.997	1.304
Total TEQ	0.087	0.136
Total TCDD	0.076	0.078
Total PeCDD	0.027	0.029
Total HxCDD	0.060	0.060
Total HpCDD	0.106	0.120
Total OCDD	0.517	0.648
Total TCDF	0.230	0.250
Total PeCDF	0.347	0.223
Total HxCDF	0.209	0.209
Total HpCDF	0.127	0.133
Total OCDF	0.159	0.281
Total CDD/CDF	1.86	2.03

Source: EPRI (1994) - 11 facility data set.



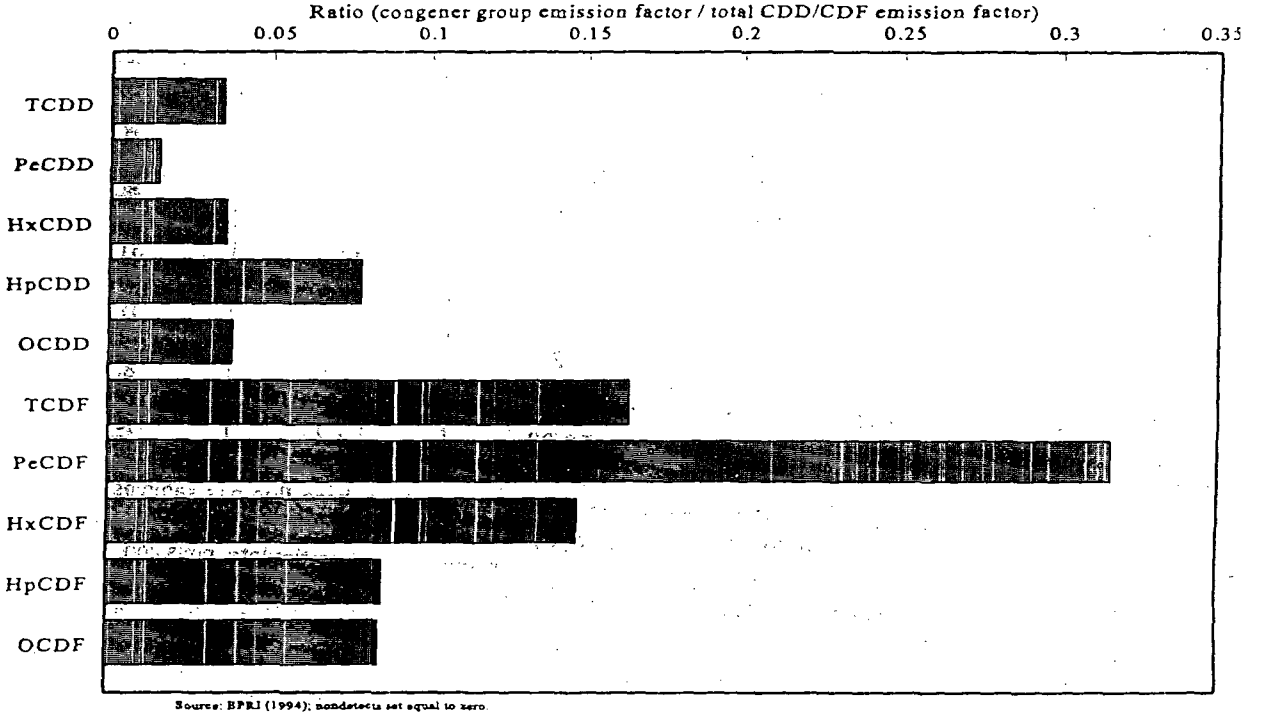


Figure 4-8. Congener and Congener Group Profiles for Air Emissions from Industrial/Utility Coal-fueled Combustors

Table 4-18. CDD/CDF Emission Factors from Residential Coal Combustors

Congener/Congener Group	"Salt" Lignite Ref. A (ng/kg coal)	"Normal" Lignite Ref. A (ng/kg coal)	Anthracite Ref. B (ng/kg coal)	Bituminous Ref. B (ng/kg coal)
2,3,7,8-TCDD	0.58	0.06	1.60	2.40
1,2,3,7,8-PeCDD	0.78	0.08	NR	NR
1,2,3,4,7,8-HxCDD	0.63	0.06	NR	NR
1,2,3,6,7,8-HxCDD	0.60	0.09	NR	NR
1,2,3,7,8,9-HxCDD	0.40	0.06	NR	NR
1,2,3,4,6,7,8-HpCDD	3.24	0.59	NR	NR
OCDD	16.19	2.42	77	120
2,3,7,8-TCDF	2.49	0.50	42.0	63.0
1,2,3,7,8-PeCDF	2.24	0.43	NR	NR
2,3,4,7,8-PeCDF	2.09	0.31	NR	NR
1,2,3,4,7,8-HxCDF	0.38	0.13	NR	NR
1,2,3,6,7,8-HxCDF	1.86	0.36	NR	NR
1,2,3,7,8,9-HxCDF	0.07	0.02	NR	NR
2,3,4,6,7,8-HxCDF	1.01	0.12	NR	NR
1,2,3,4,6,7,8-HpCDF	2.59	0.95	NR	NR
1,2,3,4,7,8,9-HpCDF	0.25	0.06	NR	NR
OCDF	0.63	0.30	4.2	6.3
Total 2,3,7,8-CDD	22.37	3.38	NR	NR
Total 2,3,7,8-CDF	13.60	3.20	NR	NR
Total TEQ	2.74	0.34	60.0	98.5
Total TCDD	14.23	9.00	61.6	92.4
Total PeCDD	14.15	2.22	31	46
Total HxCDD	11.14	1.81	60	90
Total HpCDD	7.06	0.82	57	86
Total OCDD	16.19	2.42	77	120
Total TCDF	80.34	20.33	412	613
Total PeCDF	29.21	8.98	340	550
Total HxCDF	12.72	3.78	130	190
Total HpCDF	3.87	1.27	32	47
Total OCDF	0.63	0.30	4.2	6.3
Total CDD/CDF	189.5	50.93	1,205	1,841

Sources: Ref A: Thub et al. (1995); listed results represent means of three flue gas samples.
Ref B: U.S. EPA (1997b); based on average particulate CDD/CDF concentrations from chimney soot samples collected from seven coal ovens and particulate emission factors for anthracite and bituminous coal combustion.

NR = not reported.

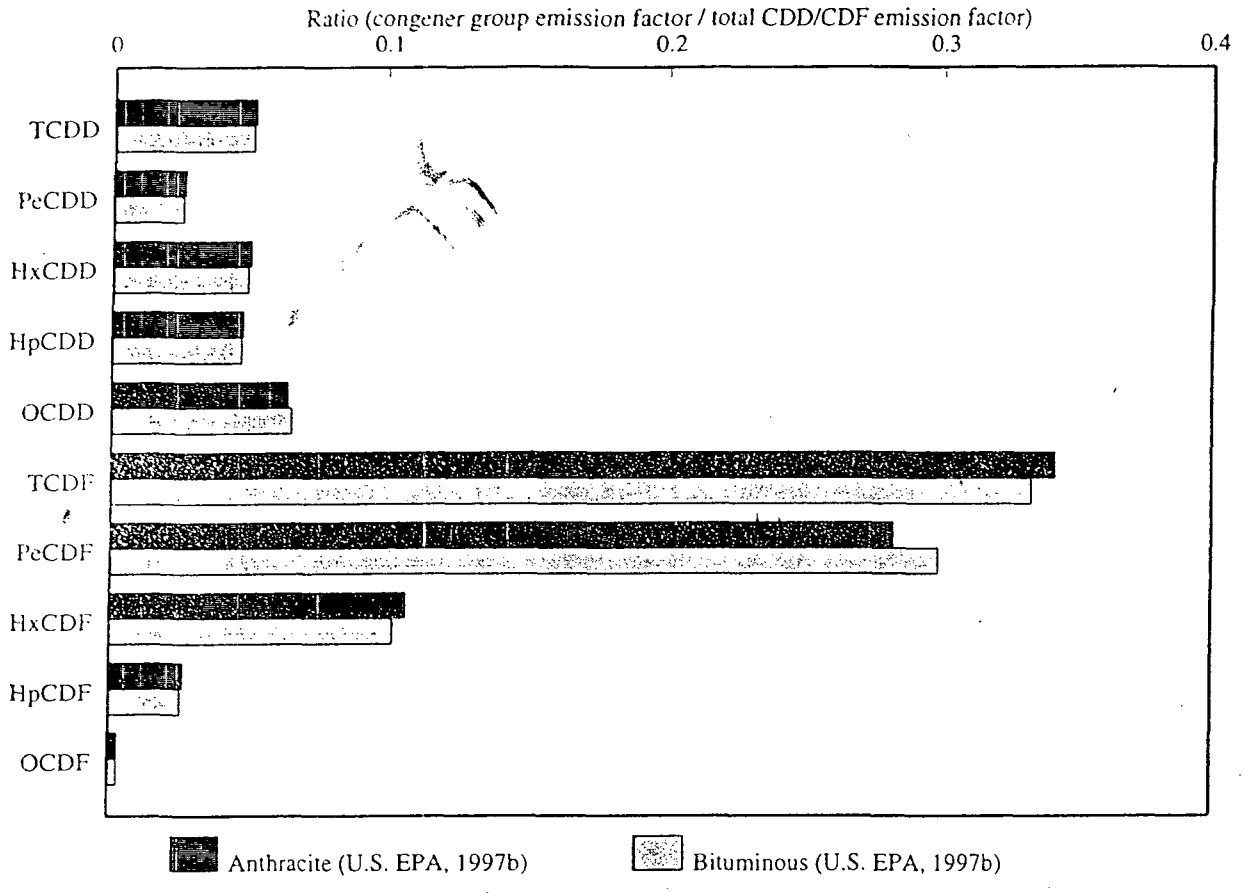


Figure 4-9. Congener Group Profile for Air Emissions from Residential Coal-fueled Combustors

scrap wire recovery facilities. However, a recent inventory of CDD/CDF sources in the San Francisco Bay area noted that two facilities in the Bay area thermally treat electric motors to recover electrical windings (BAAQMD, 1996).

In addition to releases from regulated recovery facilities, CDD/CDF releases from small-scale burning of wire at unregulated facilities and open air sites have occurred; the current magnitude of small-scale, unregulated burning of scrap wire in the United States is not known. For example, Harnly et al. (1995) analyzed soil/ash mixtures from three closed metal recovery facilities and from three closed sites of open burning for copper recovery near a California desert town. The geometric mean of the total CDD/CDF concentrations at the facility sites and the open burning sites was 86,000 and 48,500 ng/kg, respectively. The geometric mean TEQ concentrations were 2,900- and 1,300-ng TEQ/kg, respectively. A significantly higher geometric mean concentration (19,000-ng TEQ/kg) was found in fly ash located at two of the facility sites. The congener-specific and congener group results from this study are presented in Table 7-7. The results show that the five dominant congeners in the soil/ash samples at both the facility and open burning sites were OCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8-HxCDF, and 2,3,7,8-TCDF. A slightly different profile was observed in the fly ash samples with 1,2,3,7,8-PeCDF and 1,2,3,4,7,8,9-HpCDF replacing OCDD, and 2,3,7,8-TCDF as dominant congeners.

Van Wijnen et al. (1992) reported similar results for soil samples collected from unpermitted former scrap wire and car incineration sites in The Netherlands. Total CDD/CDF concentrations in the soil ranged from 60 to 98,000 ng/kg, with 9 of the 15 soil samples having levels above 1,000 ng/kg. Chen et al. (1986) reported finding high levels of CDD/CDFs in residues from open air burning of wire in Taiwan, and Huang et al. (1992) reported elevated levels in soil near wire scrap recovery operations in Japan. Bremmer et al. (1994) estimated an emission rate to air of 500-ng TEQ/kg of scrap for illegal, unregulated burning of cables in The Netherlands.

7.6. DRUM AND BARREL RECLAMATION FURNACES

Hutzinger and Fiedler (1991b) reported detecting CDD/CDFs in stack gas emissions from drum and barrel reclamation facilities at levels ranging from 5 to 27 ng/m^3. EPA measured dioxin-like compounds in the stack gas emissions of a drum and barrel reclamation furnace as part of the National Dioxin Study (U.S. EPA, 1987a).

Drum and barrel reclamation furnaces operate a burning furnace to thermally clean used steel 55-gallon drums of residues and coatings. The drums processed at these facilities come from a variety of sources in the petroleum and chemical industries. The thermally cleaned drums are then repaired, repainted, relined, and sold for reuse. The drum burning process subjects used drums to an elevated temperature in a tunnel furnace for a sufficient time so that the paint, interior linings, and previous contents are burned or disintegrated. The furnace is fired by auxiliary fuel. Used drums are loaded onto a conveyor that moves at a fixed speed. As the drums pass through the preheat and ignition zone of the furnace, additional contents of the drums drain into the furnace ash trough. A drag conveyor moves these sludges and ashes to a collection pit. The drums are air cooled as they exit the furnace. Exhaust gases from the burning furnace are typically drawn through a breeching fan to a high-temperature afterburner.

The afterburner at the facility tested by EPA operated at an average of 827°C during testing and achieved a 95 percent reduction in CDD/CDF emissions (U.S. EPA, 1987a). Emission factors estimated for this facility are presented in Table 7-8. Based on the measured congener and congener group emissions, the average TEQ emission factor was estimated in U.S. EPA (1997b) to be 49.4-ng TEQ per drum. The congener group profile is presented in Figure 7-6.

Approximately 2.8- to 6.4-million 55-gallon drums are incinerated annually in the United States (telephone conversation between P. Rankin, Association of Container Reconditioners, and C. D'Ruiz, Versar, Inc., December 21, 1992). This estimate is based on the following assumptions: (1) 23 to 26 incinerators are currently in operation; (2) each incinerator, on average, handles 500 to 1,000 drums per day; and (3) on average, each incinerator operates 5 days per week, with 14 days downtime per year for maintenance activities. The weight of 55-gallon drums varies considerably; however, on average, a drum weighs 38 lbs (or 17 kg); therefore, an estimated 48- to 109-million kg of drums are estimated to be incinerated annually. Assuming that 4.6-million drums are burned each year (i.e., the midpoint of the range) and applying the mean emission factor developed above (i.e., 49.4-ng TEQ per drum), the estimated annual emission of TEQ is 0.23 grams per year of TEQ. No activity level data are available that would enable annual emission estimates to be made specifically for reference years 1987 and 1995.

A "low" confidence rating is assigned to the activity level estimate because it is based an expert judgement rather than a published reference. A "low" confidence rating is also assigned to the emission factor, because it was developed from stack tests conducted at just one U.S. drum and barrel furnace and, thus, may not represent average emissions from current operations in the United States. Based on these confidence ratings, the estimated range of potential annual emissions is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that the best estimate of annual emissions (0.23-g TEQ/yr) is the geometric mean of this range, then the range is calculated to be 0.07- to 0.73-g TEQ/yr.

Table 7-7. Geometric Mean CDD/CDF Concentrations in Fly Ash and Ash/Soil at Metal Recovery Sites

Congener/Congener Group	Metal Recovery Facilities				Open Burn Sites	
	Fly ash (2 sites)		Ash/Soil (3 sites)		Ash/Soil (3 sites)	
	Geom. mean (µg/kg)	Relative % of Total CDD/CDF	Geom. mean (µg/kg)	Relative % of Total CDD/CDF	Geom. mean (µg/kg)	Relative % of Total CDD/CDF
2,3,7,8-TCDD	*		*		*	
1,2,3,7,8-PeCDD	400	0.1%	0.24	0.3%	0.24	0.5%
1,2,3,4,7,8-HxCDD	1,200	0.2%	0.25	0.3%	0.13	0.3%
1,2,3,6,7,8-HxCDD	2,300	0.5%	0.49	0.6%	0.33	0.7%
1,2,3,7,8,9-HxCDD	1,700	0.3%	1.3	1.5%	0.39	0.8%
1,2,3,4,6,7,8-HpCDD	12,000	2.4%	2.6	3.1%	1.2	2.5%
OCDD	18,000	3.5%	7.2	8.5%	3.4	7.0%
2,3,7,8-TCDF	15,000	2.9%	6.4	7.5%	1.7	3.5%
1,2,3,7,8-PeCDF	35,000	6.9%	2.9	3.4%	0.58	1.2%
2,3,4,7,8-PeCDF	10,000	2.0%	1.4	1.6%	0.66	1.4%
1,2,3,4,7,8-HxCDF	46,000	9.0%	5.9	6.9%	2.7	5.6%
1,2,3,6,7,8-HxCDF	12,000	2.4%	1.8	2.1%	0.76	1.6%
1,2,3,7,8,9-HxCDF	5,000	1.0%	0.92	1.1%	0.66	1.4%
2,3,4,6,7,8-HxCDF	5,000	1.0%	1.6	1.9%	0.49	1.0%
1,2,3,4,6,7,8-HpCDF	71,000	13.9%	12	14.1%	4.3	8.9%
1,2,3,4,7,8,9-HpCDF	25,000	4.9%	3	3.5%	0.71	1.5%
OCDF	100,000	19.6%	14	16.5%	6.6	13.6%
Total TCDD	*	*	*	*	*	*
Total PeCDD	2,000	0.4%	1.4	1.6%	2.8	5.8%
Total HxCDD	4,000	0.8%	2.7	3.2%	0.98	2.0%
Total HpCDD	24,000	4.7%	4.1	4.8%	2.0	4.1%
Total OCDD	18,000	3.5%	7.2	8.5%	3.4	7.0%
Total TCDF	23,000	4.5%	14	16.5%	5.6	11.5%
Total PeCDF	110,000	21.6%	12	14.1%	7.0	14.4%
Total HxCDF	88,000	17.3%	12	14.1%	7.6	15.7%
Total HpCDF	110,000	21.6%	17	20.0%	7.4	15.3%
Total OCDF	100,000	19.6%	14	16.5%	6.6	13.6%
Total TEQ	19,000		2.9		1.3	
Total CDD/CDF	510,000		85		48.5	

* = Analytical method utilized had low sensitivity for TCDDs; results were not reported.

Source: Harnly et al. (1995)

Table 7-8. CDD/CDF Emission Factors for a Drum and Barrel Reclamation Furnace

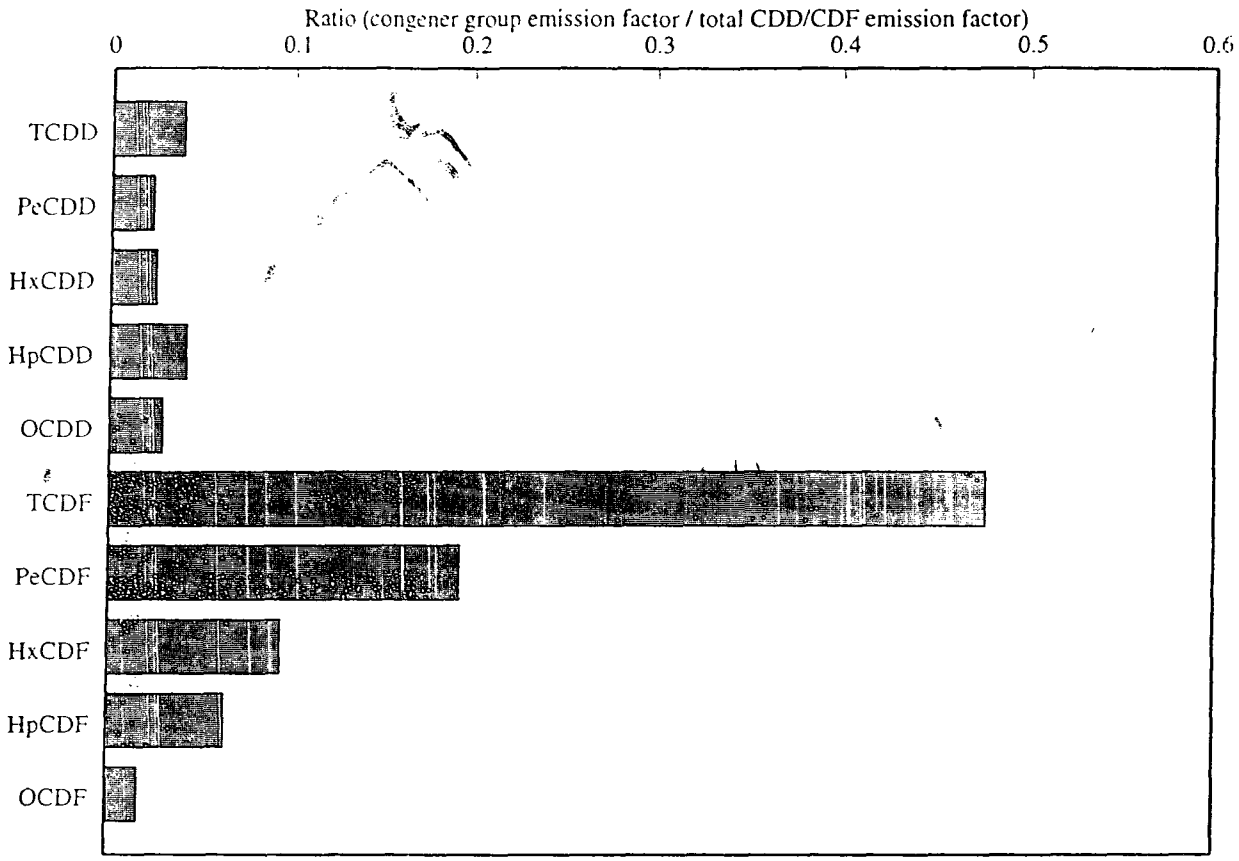
Congener/Congener Group	Mean Facility Emission Factor[a] (ng/drum)
2,3,7,8-TCDD	2.09
1,2,3,7,8-PeCDD	NR
1,2,3,4,7,8-HxCDD	NR
1,2,3,6,7,8-HxCDD	NR
1,2,3,7,8,9-HxCDD	NR
1,2,3,4,6,7,8-HpCDD	NR
OCDD	37.5
2,3,7,8-TCDF	36.5
1,2,3,7,8-PeCDF	NR
2,3,4,7,8-PeCDF	NR
1,2,3,4,7,8-HxCDF	NR
1,2,3,6,7,8-HxCDF	NR
1,2,3,7,8,9-HxCDF	NR
2,3,4,6,7,8-HxCDF	NR
1,2,3,4,6,7,8-HpCDF	NR
1,2,3,4,7,8,9-HpCDF	NR
OCDF	22.4
Total 2,3,7,8-CDD	NR
Total 2,3,7,8-CDF	NR
Total TEQ	49.4[b]
Total TCDD	50.29
Total PeCDD	29.2
Total HxCDD	32.2
Total HpCDD	53.4
Total OCDD	37.5
Total TCDF	623
Total PeCDF	253
Total HxCDF	122
Total HpCDF	82.2
Total OCDF	22.4
Total CDD/CDF	1,303

NR = Not reported.

[a] No nondetected values were reported for 2,3,7,8-TCDD, 2,3,7,8-TCDF, or any congener group in the three test runs.

[b] Estimated in U.S. EPA (1995c) based on the measured congener and congener group emissions.

Source: U.S. EPA (1987a).



Source: U.S. EPA (1987a)

Figure 7-6. Congener Group Profile for Air Emissions from a Drum Incinerator

8. CHEMICAL MANUFACTURING AND PROCESSING SOURCES

8.1. BLEACHED CHEMICAL WOOD PULP AND PAPER MILLS

In March of 1988, EPA and the U.S. pulp and paper industry jointly released the results from a screening study that provided the first comprehensive data on formation and discharge of CDDs and CDFs from pulp and paper mills (U.S. EPA, 1988a). This early screening study of five bleached kraft mills ("Five Mill Study") confirmed that the pulp bleaching process was primarily responsible for the formation of the CDDs and CDFs. The study results showed that 2,3,7,8-TCDD was present in seven of nine bleach pulps, five of five wastewater treatment sludges, and three of five treated wastewater effluents. The study results also indicated that 2,3,7,8-TCDD and 2,3,7,8-TCDF were the principal CDDs and CDFs formed.

To provide EPA with more complete data on the release of these compounds by the U.S. industry, EPA and the U.S. pulp and paper industry jointly conducted a survey during 1988 of 104 pulp and paper mills in the United States to measure levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in effluent, sludge, and pulp (U.S. EPA, 1990a). This study, commonly called the 104-Mill Study, was managed by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) with oversight by EPA, and included all U.S. mills where chemically produced wood pulps were bleached with chlorine or chlorine derivatives. The final study report was released in July 1990 (U.S. EPA, 1990a).

An initial phase of the 104-Mill Study involved the analysis of bleached pulp (10 samples), wastewater sludge (9 samples), and wastewater effluent (9 samples) from eight kraft mills and one sulfite mill for all 2,3,7,8-substituted CDDs and CDFs. These analyses were conducted to test the conclusion drawn in the Five-Mill Study that 2,3,7,8-TCDD and 2,3,7,8-TCDF were the principal CDDs and CDFs found in pulp, wastewater sludge, and wastewater effluent on a toxic equivalents basis. Although at the time of this study there were no reference analytical methods for many of the 2,3,7,8-substituted CDDs/CDFs, the data obtained were considered valid by EPA for the purposes intended based upon the identification and quantification criteria used, duplicate sample results, and limited matrix spike experiments. Table 8-1 presents a summary of the results obtained in terms of the median concentrations and the range of concentrations observed for each matrix (i.e., pulp, sludge, and effluent). Figures 8-1 through 8-3 present congener profiles for each matrix

(normalized to total CDD/CDF and to total TEQ) using the median reported concentrations. Based on examination of the raw, mill-specific data, EPA (1990a) concluded that the congener profiles were fairly consistent across matrices within mills and that 2,3,7,8-TCDD and 2,3,7,8-TCDF account for the majority of TEQ in the samples. Using the median concentrations and treating nondetected values as either zero or the detection limit, EPA (1990a) demonstrated that 2,3,7,8-TCDD and 2,3,7,8-TCDF accounted for 92.8 to 99.0 percent of the total TEQ found in pulp, 92.7 to 95.8 percent of the TEQ in sludge, and 72.7 to 91.7 of the TEQ in effluent.

A similar full-congener analysis study was reported by NCASI for samples collected from eight mills during the mid-1990s (Gillespie, 1997). The results of these analyses are presented in Table 8-2. The frequencies of detection of 2,3,7,8-TCDD and 2,3,7,8-TCDF were significantly lower than in the previous 1988 study. Therefore, deriving meaningful summary statistics concerning the relative importance of 2,3,7,8-TCDD and 2,3,7,8-TCDF to the total TEQ is difficult. Treating all nondetected values as zero indicates that 2,3,7,8-TCDD and 2,3,7,8-TCDF may account for 91 percent of the total effluent TEQ, 46 percent of the total sludge TEQ, and 87 percent of the total pulp TEQ. Because of the high frequency of nondetects, treating all nondetected values as the detection limits indicates that 2,3,7,8-TCDD and 2,3,7,8-TCDF account for only 12 percent of the total effluent TEQ, 14 percent of the total sludge TEQ, and 12 percent of the total pulp TEQ.

In 1992, the pulp and paper industry conducted its own NCASI-coordinated survey of 2,3,7,8-TCDD and 2,3,7,8-TCDF emissions. The collected data were summarized and analyzed in a report entitled *Summary of Data Reflective of the Pulp and Paper Industry Progress in Reducing the TCDD/TCDF Content of Effluents, Pulps, and Wastewater Treatment Sludges* (NCASI, 1993). Ninety-four mills participated in the NCASI study, and NCASI assumed that the remaining 10 (of 104) operated at the same levels as measured in the 1988 104 Mill Study. All nondetected values were counted as half the detection limit. If detection limits were not reported, they were assumed to be 10 ppq for effluent and 1 ppt for sludge or bleached pulp. The data used in the report were provided by individual pulp and paper companies that had been requested by NCASI to generate the data using the same protocols used in the 104-Mill Study. NCASI (1993) reported that the pulp and paper industry had taken numerous steps to reduce CDD/CDF releases since 1988, and that

the 1992 survey results were more reflective of releases at the end of 1992 than the data generated in the 104-Mill Study.

As part of its ongoing efforts to develop revised effluent guidelines and standards for the pulp, paper, and paperboard industry, EPA in 1993 published the Development Document for the guidelines and standards being proposed for this industry (U.S. EPA, 1993d). The Development Document presents estimates of the 2,3,7,8-TCDD and 2,3,7,8-TCDF annual discharges in wastewater from the mills in this industry as of January 1, 1993. EPA used the most recent information about each mill from four data bases (104-Mill Study, EPA short-term monitoring studies at 13 mills, EPA long-term monitoring studies at 8 mills, and industry self-monitoring data submitted to EPA) to estimate these discharges. The 104-Mill Study data were used only for those mills that did not report making any process changes subsequent to the 104-Mill Study and did not submit any more recent effluent monitoring data.

Gillespie (1994; 1995) reported the results of 1993 and 1994 updates, respectively, to the 1992 NCASI survey. As was the case in the 1992 survey, companies were requested to follow the same protocols for generating data used in the 104-Mill Study. Gillespie (1994; 1995) reported that less than 10 percent of mills had 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in effluent above the nominal detection limits of 10 ppq and 100 ppq, respectively. Similar results were obtained in the short- and long-term sampling reported for 18 mills in U.S. EPA (1993d); 2,3,7,8-TCDD was detected at four mills, and 2,3,7,8-TCDF was detected at nine mills. Gillespie (1994) reported that wastewater sludges at most mills (i.e., 90 percent) contained less than 31 ppt of 2,3,7,8-TCDD and less than 100 ppt of 2,3,7,8-TCDF. Gillespie (1995) also reported that 90 percent of the mills reported 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations in sludge of less than 17 ppt and 76 ppt, respectively, in 1994. U.S. EPA (1993d) reported similar results but found detectable levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sludges from 64 percent and 85 percent of the facilities sampled, respectively. Gillespie (1994) reported that nearly 90 percent of the bleached pulps contained less than 2 ppt of 2,3,7,8-TCDD and less than 160 ppt of 2,3,7,8-TCDF. Gillespie (1995) reported that 90 percent of the bleached pulps contained 1.5 ppt or less of 2,3,7,8-TCDD and 5.9 ppt or less of 2,3,7,8-TCDF. The final levels in white paper products would correspond to levels in bleached pulp, so bleached paper products would also be expected to contain less than 2 ppt of 2,3,7,8-TCDD.

Overall, a 92 percent reduction in TEQ generation from 1988 to 1993 was reported by Gillespie (1994), with an additional 2 percent reduction reported in 1994 by Gillespie (1995).

Estimates of National Emissions in 1987 and 1995 - The U.S. annual discharges of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and TEQs due to these two compounds are summarized in Table 8-3 for each of the five surveys discussed above. The release estimates for 1994 from Gillespie (1995) and 1988 from U.S. EPA (1990a) are believed to best represent emissions in the reference years 1995 and 1987, respectively. During the period between the conduct of the 104-Mill Study and the issuance of the U.S. EPA Development Document (U.S. EPA, 1993d), the U.S. pulp and paper industry reduced releases of CDD/CDFs primarily by instituting numerous process changes to reduce the formation of CDD/CDFs during the production of chemically bleached wood pulp. Details on the process changes implemented are provided in U.S. EPA (1993d) and Gillespie (1995). Because most of the reduction between 1988 and 1994 can be attributed to process changes of a pollution prevention nature, it should be expected that the percentage reduction observed in effluent, sludge, and pulp emissions over this time period should be very similar, which is indeed the case. Observed percentage reductions in emissions are 92 percent, 89 percent, and 93 percent for effluent, sludge, and pulp, respectively.

The confidence ratings for these release estimates were judged to be high based on the fact that direct measurements were made at virtually all facilities, indicating a high level of confidence in both the production and emission factor estimates. Based on these high confidence ratings, the estimated ranges of potential annual emissions for effluent, sludge, and pulp are assumed to vary by a factor of 2 between the low and high ends of the ranges. Assuming that the best estimates of annual emissions in 1995 (i.e., the 1994 estimates presented in Table 8-3) are the geometric means of the likely ranges, then the ranges are calculated to be 13.8- to 27.6-g TEQ/yr for effluent, 20.0- to 40.0-g TEQ/yr for sludge, and 17.0- to 34.0-g TEQ/yr for pulp (i.e., TEQs that will enter the environment in the form of paper products). Assuming that the best estimates of annual emissions in 1987 (i.e., the 1988 estimates presented in Table 8-3) are the geometric means of the likely ranges, then the ranges are calculated to be 252- to 504-g TEQ/yr for effluent, 243- to 485-g TEQ/yr for sludge, and 375- to 714-g TEQ/yr for pulp.

In 1990, the majority of the wastewater sludge generated by these facilities was landfilled or placed in surface impoundments (75.5 percent), with the remainder incinerated (20.5 percent), applied to land directly or as compost (4.1 percent), or distributed as a commercial product (less than 1 percent) (U.S. EPA, 1993e). No more recent (i.e., 1995) or earlier (i.e., 1987) data on disposition of wastewater sludges are available. Using these statistics, the best estimate of TEQ applied to land (i.e., not incinerated or landfilled) in 1995 was 1.4 g (i.e., 4.1 percent of 28.4 g), and the range is 1.0- to 2.0-g TEQ/yr. The central estimate and range for 1987 are 14.1-g TEQ (i.e., 4.1 percent of 343 g) and 10- to 20-g TEQ, respectively.

8.2. MANUFACTURE OF CHLORINE, CHLORINE DERIVATIVES, AND METAL CHLORIDES

No testing of CDD/CDF emissions to air, land, or water from U.S. manufacturers of chlorine, chlorine derivatives, and metal chlorides have been reported upon which to base estimates of national emissions. Sampling of graphite electrode sludges from European chlorine manufacturers indicates high levels of CDFs. Limited sampling of chlorine derivatives and metal chlorides in Europe indicates low level contamination in some products.

8.2.1. Manufacture of Chlorine

Chlorine gas is produced by electrolysis of brine electrolytic cells. Until the late 1970s, mercury cells containing graphite electrodes were the primary type of electrolytic process used in the chloralkali industry to produce chlorine. As shown in Table 8-4, high levels of CDFs have been found in several samples of graphite electrode sludge from facilities in Europe. The CDFs dominate the CDDs in these sludges, and the 2,3,7,8-substituted congeners account for a large fraction of the respective congener totals (Rappe et al., 1990b; Rappe et al., 1991; Rappe, 1993; Strandell et al., 1994). During the 1980s, titanium metal anodes were developed to replace graphite electrodes (U.S. EPA, 1982a; Curlin and Bommaraju, 1991). Currently, no U.S. facility is believed to use graphite electrodes in the production of chlorine gas (telephone conversation between L. Phillips, Versar, Inc., and T. Fielding, U.S. EPA, Office of Water, February 1993).

Although the origin of the CDFs in graphite electrode sludge is uncertain, chlorination of the cyclic aromatic hydrocarbons (such as dibenzofuran) present in the coal

gas or in samples of 10 percent sodium hypochlorite, 13 percent sodium hypochlorite, and 31-33 percent hydrochloric acid at a detection limit of 1 μg/kg.

Hutzinger and Fiedler (1991a) reported the results of analyses of samples of $FeCl_2$, $AlCl_3$, $CuCl_2$, CuCl, $SiCl_4$, and $TiCl_4$ for their content of HpCDF, OCDF, HpCDD, and OCDD. The sample of $FeCl_3$ contained HpCDF and OCDF in the low μg/kg range, but no HpCDD or OCDD were detected at a detection limit of 0.02 μg/kg. One of the two samples of $AlCl_3$ analyzed also contained a low μg/kg concentration of OCDF. The samples of $CuCl_2$ and CuCl contained sub μg/kg concentrations of HpCDF, OCDF, and OCDD. The results are presented in Table 8-5.

8.3. MANUFACTURE OF HALOGENATED ORGANIC CHEMICALS

Several chemical production processes generate CDDs and CDFs (Versar, 1985; Hutzinger and Fiedler, 1991a). CDDs and CDFs can be formed during the manufacture of chlorophenols, chlorobenzenes, and chlorobiphenyls (Versar, 1985; Ree et al., 1988). Consequently, disposal of industrial wastes from manufacturing facilities producing these compounds may result in the release of CDDs and CDFs to the environment. Also, the products themselves may contain these compounds, and when used/consumed, may result in additional releases to the environment. CDD and CDF congener distribution patterns indicative of noncombustion sources have been observed in sediments in southwest Germany and The Netherlands. The congener patterns found suggest that wastes from the production of chlorinated organic compounds may be important sources of CDD and CDF contamination in these regions (Ree et al., 1988). The production and use of many of the chlorophenols, chlorophenoxy herbicides, and PCB products are banned or strictly regulated in most countries. However, these products may have been a source of the environmental contamination that occurred prior to the 1970s and may continue to be a source of environmental releases based on limited use and disposal conditions (Rappe, 1992a).

8.3.1. Chlorophenols

Chlorophenols have been widely used for a variety of pesticidal applications. The higher chlorinated phenols (i.e., tetrachlorophenol and pentachlorophenol) and their sodium salts have been primarily used for wood preservation. The lower chlorinated phenols have been used primarily as chemical intermediates in the manufacture of other pesticides. For

example, 2,4-dichlorophenol is used to produce the herbicides 2,4-Dichlorophenoxyacetic acid (2,4-D), 4-(2,4-Dichlorophenoxy)butanoic acid (2,4-DB), 2-(2,4-Dichlorophenoxy)-propanoic acid (2,4-DP), Nitrophen, Genite, and Zytron, while 2,4,5-trichlorophenol was used to produce hexachlorophene, 2,4,5-T, Silvex, Erbon, Ronnel, and Gardona (Gilman et al., 1988; Hutzinger and Fiedler, 1991a). [See Sections 8.3.7 and 8.3.8 for information on EPA actions to control CDD/CDF contamination of pesticides (including pentachlorophenol and its salts) and to obtain additional data on CDD/CDF contamination of pesticides.]

The two major commercial methods used to produce chlorophenols are: (1) electrophilic chlorination of molten phenol by chlorine gas in the presence of catalytic amounts of a metal chloride and organic chlorination promoters and stabilizers; and (2) alkaline hydrolysis of chlorobenzenes under heat and pressure using aqueous methanolic sodium hydroxide. Other manufacturing methods include conversion of diazonium salts of various chlorinated anilines, and chlorination of phenolsulfonic acids and benzenesulphonic acids, followed by the removal of the sulphonic acid group (Gilman et al., 1988; Hutzinger and Fiedler, 1991a).

Because of the manufacturing processes employed, commercial chlorophenol products can contain appreciable amounts of impurities (Gilman et al., 1988). During the direct chlorination of phenol, CDD/CDFs can form either by the condensation of tri-, tetra-, and pentachlorophenols or by the condensation of chlorophenols with hexachlorocyclohexadienone (which forms from excessive chlorination of phenol). During alkaline hydrolysis of chlorobenzenes, CDD/CDFs can form through chlorophenate condensation (Ree et al., 1988; Gilman et al., 1988; Hutzinger and Fiedler, 1991a).

The limited information on CDD/CDF concentrations in chlorophenols published in the 1970s and early 1980s was compiled by Versar (1985) and Hutzinger and Fiedler (1991a). The results of several major studies cited by these reviewers (Firestone et al., 1972; Rappe et al., 1978a and 1978b) are presented in Table 8-6. Typically, CDD/CDFs were not detected in monochlorophenols (MCP) and dichlorophenols (DCP) but were reported in trichlorophenols (TrCP) and tetrachlorophenols (TeCP). More recent results of testing of 2,4-dichlorophenol (2,4-DCP) performed in response to the Toxic Substances Control Act (TSCA) Dioxin/Furan Test Rule showed no detectable concentrations of 2,3,7,8-substituted tetra- through hepta-CDD/CDFs. Other than a study by Hagenmaier (1986) that reported finding 2,3,7,8-TCDD at a concentration of 0.3 μg/kg in a sample of

2,3,4,5-tetrachlorophenol, no more recent data on concentrations of CDDs and CDFs could be found in the literature for the mono- through tetra-chlorophenols. Tables 8-7 and 8-8 present summaries of several studies that reported CDD/CDF concentrations in PCP and in PCP-Na products, respectively. Many of these studies do not report congener-specific concentrations, and many are based on products obtained from non-U.S. sources.

Regulatory Actions - Section 8.3.8 of this report describes regulatory actions taken by EPA to control the manufacture and use of chlorophenol-based pesticides.

In the mid-1980s, EPA's Office of Solid Waste promulgated land disposal restrictions on wastes under RCRA (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorophenols (40 CFR 268). Table 8-9 lists all wastes in which CDDs and CDFs are specifically regulated as hazardous constituents by EPA, including chlorophenol wastes (waste codes F020 and F021). The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely achievable detection limits in the waste extract listed in Table 8-9 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs. Wastes from PCP-wood preserving operations (waste codes K001 and F032) are also regulated as hazardous wastes under RCRA (40 CFR 261).

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated phenols and discharge treated wastewater (40 CFR 414.70). These effluent limitations do not specifically regulate CDDs and CDFs; however, the treatment processes required to control the chlorinated phenols that are regulated (2-chlorophenol and 2,4,-dichlorophenol) are also expected to reduce releases of any CDDs and CDFs that may be present in the untreated wastewater. The effluent limitations for the individual regulated chlorinated phenols are less than or equal to 39 μg/L for facilities that utilize biological end-of-pipe treatment.

DCPs and TrCPs are subject to reporting under the Dioxin/Furan Test Rule, which is discussed in Section 8.3.7 of this report. On the effective date of that rule (i.e., June 5, 1987) and since that date, only the 2,4-DCP isomer has been commercially produced (or imported) in the United States, and as noted in Table 8-6, no CDD/CDFs were detected in the product. Testing is required for the other DCPs and TrCPs, if manufacture or importation resumes. Similarly, TeCPs were subject to reporting under the Dioxin/Furan Pesticide Data Call-In (DCI) (discussed in Section 8.3.8 of this report). Since issuance of

the DCI, the registrants of TeCP-containing pesticide products have elected to no longer support the registration of their products in the United States.

In January 1987, EPA entered into a Settlement Agreement with pentachlorophenol (PCP) manufacturers, which set limits on allowed uses of PCP and its salts and set maximum allowable concentrations of 2,3,7,8-TCDD and HxCDDs effective in February 1989. Section 8.3.8 discusses the 1987 PCP Settlement Agreement and estimates current releases of CDD/CDFs associated with use of PCP in the United States.

Since the late 1980s, U.S. commercial production of chlorophenols has been limited to 2,4-dichlorophenol (2,4-DCP) and PCP. As noted above, disposal of wastes generated during the manufacture of chlorophenols are strictly regulated and thus releases to the environment are expected to be negligible. With regards to releases associated with the use of 2,4-DCP, no CDD/CDFs have been detected in 2,4-DCP. Releases associated with the use of PCP are presented in Sections 8.3.8.

8.3.2. Chlorobenzenes

Chlorobenzenes have been produced in the United States since 1909. U.S. production operations were developed primarily to provide chemical raw materials for the production of phenol, aniline, and various pesticides based on the higher chlorinated benzenes. Due to changes over time in the processes used to manufacture phenol and aniline, and to the phase-out of highly chlorinated pesticides such as DDT and hexachlorobenzene, U.S. production of chlorobenzenes decreased in 1988 to 50 percent of the peak production level in 1969.

Chlorobenzenes can be produced via three methods: (1) electrophilic substitution of benzene (in liquid or vapor phase) with chlorine gas in the presence of a metal salt catalyst; (2) oxidative chlorination of benzene with HCl at 150-300°C in the presence of a metal salt catalyst; and (3) dehydrohalogenation of hexachlorocyclohexane wastes at 200-240°C with a carbon catalyst to produce trichlorobenzene, which can be further chlorinated to produce higher chlorinated benzenes (Ree et al., 1988; Hutzinger and Fiedler, 1991a; Bryant, 1993).

All chlorobenzenes currently manufactured in the United States are produced using the electrophilic substitution process using liquid phase benzene (i.e., temperature is at or below 80°C). Ferric chloride is the most common catalyst employed. Although this method can be used to produce mono- through hexachlorobenzene, the extent of

chlorination is controlled to yield primarily MCBz and DCBz. The finished product is a mixture of chlorobenzenes, and refined products must be obtained by distillation and crystallization (Bryant, 1993).

CDD/CDFs can be inadvertently produced during the manufacture of chlorobenzenes by nucleophilic substitution and pyrolysis mechanisms (Ree et al., 1988). The criteria required for production of CDD/CDFs via nucleophilic substitution are: (1) oxygen as a nuclear substituent (i.e., presence of chlorophenols) and (2) production and/or purification of the substance under alkaline conditions. Formation via pyrolysis requires reaction temperatures above 150°C (Ree et al., 1988; Hutzinger and Fiedler, 1991a). The liquid-phase electrophilic substitution process currently used in the United States does not meet any of these criteria. Although Ree et al. (1988) and Hutzinger and Fiedler (1991a) state that the criteria for formation of CDD/CDFs via nucleophilic substitution may be present in the catalyst neutralization and purification/distillation steps of the manufacturing process, Opatick (1995) states that the chlorobenzene reaction product in U.S. processes remains mildly acidic throughout these steps.

Table 8-10 summarizes the very limited published information on CDD/CDF contamination of chlorobenzene products. The presence of CDD/CDFs has been reported in TCBz, PeCBz, and HCBz. No CDD/CDFs have been reported in monochlorobenzene (MCBz) and DCBz. Conflicting data exist concerning the presence of CDD/CDFs in TCBz. One study (Villanueva et al., 1974) detected no CDD/CDFs in one sample of 1,2,4-TCBz at a detection limit of 0.1 μg/kg. Hutzinger and Fiedler (1991a) reported unpublished results of Dr. Hans Hagenmaier showing CDD/CDF congener group concentrations ranging from 0.02 to 0.074 μg/kg in a sample of mixed TCBz. Because the TCBz examined by Hagenmaier contained about 2 percent hexachlorocyclohexane, it is reasonable to assume that the TCBz was produced by dehydrohalogenation of hexachlorocyclohexane (a manufacturing process not currently used in the United States).

Regulatory Actions - EPA has determined, as part of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Pesticide Data Call-In (discussed in Section 8.3.8), that the 1,4-DCBz manufacturing processes used in the United States are not likely to form CDD/CDFs. MCBz, DCBz, and TCBz are also listed as potential precursor chemicals under the TSCA Dioxin/Furan Test Rule and are subject to reporting. (See Section 8.3.7.) In addition, a Significant New Use Rule (SNUR) was issued by EPA under Section 5(a)(2) of

TSCA on December 1, 1993, with an effective date of January 14, 1994, for PeCBz and 1,2,4,5-TeCBz (Federal Register, 1993c). This rule requires persons to submit a significant new use notice to EPA at least 90 days before manufacturing, importing, or processing either of these compounds in amounts of 10,000 pounds or greater per year per facility for any use. All registrations of pesticide products containing HCBz were cancelled in the mid-1980s (Carpenter et al., 1986).

EPA's Office of Solid Waste promulgated land disposal restrictions on wastes (i.e., wastewaters and nonwastewaters) resulting from the manufacture of chlorobenzenes (40 CFR 268). Table 8-9 lists all solid wastes in which CDDs and CDFs are specifically regulated as hazardous constituents by EPA, including chlorobenzene wastes. The regulations prohibit the land disposal of these wastes until they are treated to a level below the routinely achievable detection limits in the waste extract listed in Table 8-7 for each of the following congener groups: TCDDs, PeCDDs, HxCDDs, TCDFs, PeCDFs, and HxCDFs.

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated benzenes and discharge treated wastewater (40 CFR 414.70). Although these effluent limitations do not specifically address CDDs and CDFs, the treatment processes required to control the chlorinated benzenes that are regulated (chlorobenzene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; and hexachlorobenzene) are expected to reduce releases of any CDDs and CDFs that may be present in the untreated wastewater. The effluent limitations for the individual regulated chlorinated benzenes are less than or equal to 77 μg/L for facilities that utilize biological end-of-pipe treatment and are less than or equal to 196 μg/L for facilities that do not employ biological end-of-pipe treatment.

Since at least 1993, U.S. commercial production of chlorobenzenes has been limited to MCBz, 1,2-dichlorobenzene (1,2-DCBz), 1,4-dichlorobenzene (1,4-DCBz), and, to a much lesser extent, 1,2,4-trichlorobenzene (1,2,4-TCBz). As noted above, CDD/CDF formation is not expected under the normal operating conditions of the processes currently used in the United States to produce these four chemicals. No tetra-, penta-, or hexachlorinated benzenes are now intentionally produced or used in the United States (Bryant, 1993). Thus, releases of CDD/CDFs from manufacture of chlorobenzenes in 1995 were estimated as negligible. Because the available information on CDD/CDF content of MCBz to PeCBz is very limited and is based primarily on unpublished European data and because information

on the chlorobenzene manufacturing processes in place during 1987 is not readily available, no emission estimates can be made for 1987.

8.3.3. Chlorobiphenyls

PCBs are manufactured by the direct batch chlorination of molten biphenyl in the presence of a catalyst followed by separation and purification of the desired chlorinated biphenyl fractions. During the manufacture of PCBs, the inadvertent production of CDFs also occurred. The purpose of this section is to address potential releases of CDD/CDFs associated with leaks and spills of PCBs. CDFs have been shown to form when PCB-containing transformers and capacitors undergo malfunctions or are subjected to fires that result in accidental combustion of the dielectric fluid. This combustion source of PCB-associated CDFs is discussed in Section 6.6. Section 11.2 addresses releases of dioxin-like PCBs.

Production of PCBs is believed to have been confined to 10 countries. The total amount of PCBs produced worldwide since 1929 (i.e., the first year of known production) is estimated to total 1.5-billion kg. Initially, PCBs were primarily used as dielectric fluids in transformers. After World War II, PCBs found steadily increasing use as dielectric fluids in capacitors, as heat-conducting fluids in heat exchangers, and as heat-resistant hydraulic fluids in mining equipment and vacuum pumps. PCBs also were used in a variety of "open" applications (i.e., uses from which PCBs cannot be re-collected) including: plasticizers, carbonless copy paper, lubricants, inks, laminating agents, impregnating agents, paints, adhesives, waxes, additives in cement and plaster, casting agents, dedusting agents, sealing liquids, fire retardants, immersion oils, and pesticides (DeVoogt and Brinkman, 1989).

PCBs were manufactured in the United States from 1929 until 1977. U.S. production peaked in 1970, with a volume of 85-million pounds. Monsanto Corporation, the major U.S. producer, voluntarily restricted the use of PCBs in 1971, and annual production fell to 40-million pounds in 1974. Monsanto ceased PCB manufacture in mid-1977 and shipped the last inventory in October 1977. Regulations issued by EPA beginning in 1977, principally under TSCA (40 CFR 761), strictly limited the production, import, use, and disposal of PCBs. (See Section 4.1 for details on TSCA regulations.) The estimated cumulative production and consumption volumes of PCBs in the United States

environment during the years 1988 through 1993. These TRI data include emissions to the air, discharges to bodies of water, and releases to land. Based on these data, annual emissions of PCBs to air during 1988 and 1993 could have been as high as 2.7 kg and as low as 0 kg, respectively. If it is further assumed that the ratio of TEQ to total PCB in the air emissions was 0.17:1,000,000 (i.e., the average of the TEQ contents for Clophen A-30 and Clophen A-50 [i.e., 170 μg/kg] reported by Hagenmaier (1987) and presented in Table 8-12), then annual emissions of TEQs to air in 1988 and 1993 could have been 0.5 and 0 mg, respectively. Similar assumptions for PCB releases to water of 4.5 kg in 1988 and 0 kg in 1993 yield estimated TEQ emissions during 1988 and 1993 of 0.8 and 0 mg, respectively. For land releases of 341 kg in 1988 and 120 kg in 1993, estimated TEQ emissions during 1988 and 1993 are 58 and 20 mg, respectively. All of these estimated releases are considered to be negligible (i.e., less than 1 gram per year).

8.3.4. Polyvinyl Chloride

Although it is recognized that CDD/CDFs are formed during the manufacture of ethylene dichloride (EDC) and vinyl chloride monomer (VCM), polyvinyl chloride (PVC) manufacturers and environmental public interest groups disagree as to the quantity of CDD/CDFs formed and released to the environment in wastes and possibly PVC products. Insufficient information is available at this time to enable EPA to make definitive release estimates. Although EPA regulates emissions from EDC/VC production facilities under the Clean Water Act (40 CFR 61), the Clean Air Act (40 CFR 414), and RCRA (40 CFR 268 - Waste Codes F024, K019, and K020), CDD/CDFs are not specifically regulated pollutants; as a consequence, monitoring data for CDD/CDFs in emissions are generally lacking. The Interim Phase I Report addressing products and treated wastewater was submitted to EPA in November 1996 (The Vinyl Institute, 1996). The remainder of this section summarizes the available information and presents the release estimates made by various interested parties.

In 1993, Greenpeace International issued a report on dioxin emissions associated with the production of EDC/VCM (Greenpeace, 1993). Greenpeace estimated that 5- to 10-g TEQ are released to the environment (air, water, and ground combined) annually for every 100,000 metric tons of VCM produced. This emission factor was based on data gathered by Greenpeace on four European plants. The Vinyl Institute responded with a

critique of the Greenpeace report (ChemRisk, 1993). Miller (1993) summarized the differing views of the two parties. According to Miller (1993), European PVC manufacturers claim the emission factor is 0.01- to 0.5-g TEQ/100,000 metric tons of VCM. Although Greenpeace (1993) and ChemRisk (1993) used basically the same monitoring information to develop their emission factors, Greenpeace adjusted the emission factor to account for unquantified fugitive emissions and waste products containing unspecified amounts of CDD/CDFs.

In 1995, Greenpeace issued another study reiterating the organization's concern that the generation and emissions of CDD/CDFs may be significant and urging that further work be initiated to quantify and prevent emissions (Stringer et al., 1995). However, this study acknowledged that because EDC/VCM production technologies and waste treatment/disposal practices are very site-specific, the limited information currently available on CDD/CDF generation and emissions makes it difficult to quantify amounts of CDD/CDFs generated and emitted.

Tiernan et al. (1995) reported the results of testing two samples of ethylene dichloride, two samples of vinyl chloride monomer, and two samples from each of two different batches of powdered PVC pipe resin. The PVC resin analyses were performed using an extraction procedure that results in complete dissolution of the PVC resin, followed by liquid-liquid extraction of the dissolved material. With the exception of OCDD, no CDD/CDFs were detected in any of the samples at detection limits ranging from less than 1 ng/kg for the tetra- and hexa- congener groups and 0.5 to 4.6 ng/kg for hexa- through octa-CDDs and CDFs. The OCDD levels detected (6 to 8 ng/kg) were of the same magnitude as the OCDD levels detected in the blank samples implying background contamination.

Stringer et al. (1995) presented the results of analyses of three samples of chlorinated wastes obtained from U.S. EDC/VCM manufacturing facilities. The three wastes were characterized according to EPA hazardous waste classification numbers as follows: (1) an F024 waste (i.e., waste from the production of short chain aliphatics by free radical catalyzed processes); (2) a K019 waste (i.e., heavy ends from the distillation of ethylene from EDC production); and a probable K020 waste (i.e., heavy ends from distillation of VC in VCM manufacture). Table 8-13 presents the analytical results reported by Stringer et al. (1995). The reported CDD/CDF concentrations in the three wastes were

20-μg TEQ/kg, 5,928-μg TEQ/kg, and 3.2-μg TEQ/kg for the F024, K019, and K020 waste, respectively. Stringer et al. (1995) stated that the concentration found in the K020 waste was similar to levels found in comparable waste from a VCM manufacturing facility in the United Kingdom (3.1 to 7.6-μg/kg).

In response to the lack of definitive studies and at the request of EPA, U.S. PVC manufacturers initiated an extensive monitoring program to evaluate the extent of any CDD/CDF releases to air, water, land, as well as product contamination. Emission and product testing are being performed at various facilities representative of various manufacturing and process control technologies. An independent peer review panel has been formed and is reviewing the results of all monitoring studies prior to their public release. The Interim Phase I Report from this study has been submitted to EPA, and the results are summarized in Table 8-14.

The Interim Phase I Report (The Vinyl Institute, 1996) presented results for treated wastewater samples from six sites that manufacture only PVC and from four sites that manufacture EDC/VCM or EDC/VCM/PVC (range: ND - 2.2-pg TEQ/L; mean = 0.60-pg TEQ/L assuming NDs = 0 and 4.5-pg TEQ/L assuming NDs = 1/2 DL). The method detection limit was 10 pg/L for all congeners, except OCDD and OCDF (50 pg/L). Based on these sample data and facility-specific production data, The Vinyl Institute estimated that total TEQ releases to waters from U.S. EDC, VCM, and PVC production facilities are in the range of 0.043 to 0.36 grams/year.

The Vinyl Institute (1996) presented results for 22 samples from 14 of the 24 U.S. facilities manufacturing suspension and mass PVC resins (i.e., pipe, bottle, and packaging resins). CDD/CDFs were detected in only one sample (0.043-ng TEQ/kg), which upon resampling showed nondetect (ND) as well. The method detection limit was 2 ng/kg for all congeners except OCDD and OCDF (6 ng/kg). The Vinyl Institute (1996) also presented results for six samples from four of the seven U.S. facilities manufacturing dispersion PVC resins. The results ranged from ND to 0.008-pg TEQ/g (mean = 0.001-pg TEQ/g assuming NDs = 0, and 0.4-pg TEQ/g assuming NDs = 1/2 DL). The method detection limit was 2 pg/g for all congeners except OCDD and OCDF (4 pg/g). The Vinyl Institute (1996) also presented results for 5 samples from 5 of the 15 U.S. facilities manufacturing EDC. CDD/CDFs were detected in only one sample (0.03-pg TEQ/g). The method detection limit for all congeners was 1 pg/g. Based on 1995 production data and the average TEQ

observed for the samples analyzed, total releases of CDD/CDF TEQs from suspension/mass PVC resins, emulsion PVC resins, and "sales" EDC were estimated by The Vinyl Institute (1996) to be 0.0 to 3.0 grams, 0.004 to 0.1 grams, and 0.008 to 0.29 grams, respectively.

The estimated PVC production in the United States during 1995 was 5.656-million metric tons per year (The Vinyl Institute, 1996). Applying the worldwide emission factors discussed above to the U.S. PVC industry, gives a range of dioxin emissions of 0.56- to 28.3-g TEQ/yr (based on the ChemRisk (1993) emission factors) to 283- to 565-g TEQ/yr (based on the 1993 Greenpeace emission factors). It is anticipated that the Vinyl Institute will be completing and releasing the full report on PVC resin, wastewater treatment solids, waste water, and incinerator stack releases in the spring of 1998. EPA anticipates that this information, along with the information from previously cited sources, should be adequate to make a reasonable emission estimate for this inventory.

8.3.5. Other Aliphatic Chlorine Compounds

Aliphatic chlorine compounds are used as monomers in the production of plastics, as solvents and cleaning agents, and as precursors for chemical synthesis (Hutzinger and Fiedler, 1991a). These compounds are produced in large quantities. In 1992, 14.6-million metric tons of halogenated hydrocarbons were produced (U.S. ITC, 1946-1994). The production of 1,2-dichloroethane and vinyl chloride accounted for 82 percent of this total production. Highly chlorinated CDDs and CDFs (i.e., hexa- to octachlorinated congeners) have been found in nanograde quality samples of 1,2-dichloroethane (55 ng/kg of OCDF in one of five samples), tetrachloroethene (47 ng/kg of OCDD in one of four samples), epichlorohydrin (88 ng/kg of CDDs and 33 ng/kg of CDFs in one of three samples), and hexachlorobutadiene (360 to 425 ng/kg of OCDF in two samples) obtained in Germany from Promochem (Hutzinger and Fiedler, 1991a; Heindl and Hutzinger, 1987). No CDD/CDFs were detected in two samples of ally chloride, three samples of 1,1,1-trichloroethane, and four samples of trichloroethylene (detection limit ranged from 5 to 20 ng/kg) (Heindl and Hutzinger, 1987). Because no more recent or additional data could be found in the literature to confirm these values for products manufactured or used in the United States, no national estimates of CDD/CDF emissions are made for the inventory.

EPA's Office of Water promulgated effluent limitations for facilities that manufacture chlorinated aliphatic chlorine compounds and discharge treated wastewater (40 CFR 414.70). Although these effluent limitations do not specifically address CDDs and CDFs, the treatment processes required to control the chlorinated aliphatic compounds that are regulated (e.g., 68 μg/L for 1,2-dichloroethane and 22 μg/L for tetrachloroethylene) are expected to reduce releases of any CDDs and CDFs that may be present in the untreated wastewater. Similarly, EPA's Office of Solid Waste promulgated restrictions on land disposal of wastes generated during manufacture of many chlorinated aliphatics (40 CFR 268); however, these restrictions do not specifically regulate CDD/CDFs.

8.3.6. Dyes, Pigments, and Printing Inks

Several researchers analyzed various dyes, pigments, and printing inks obtained in Canada and Germany for the presence of CDDs and CDFs (Williams et al., 1992; Hutzinger and Fiedler, 1991a; Santl et al., 1994c). The following paragraphs discuss the findings of these studies.

Dioxazine Dyes and Pigments - Williams et al. (1992) analyzed the CDD/CDF content in dioxazine dyes and pigments available in Canada. As shown in Table 8-15, OCDD and OCDF concentrations in the μg/g range, and HpCDD, HxCDD, and PeCDD concentrations in the ng/g range were found in Direct Blue 106 dye (3 samples), Direct Blue 108 dye (1 sample), and Violet 23 pigments (6 samples) (Williams et al., 1992). These dioxazine pigments are derived from chloranil, which has been found to contain high levels of CDD/CDFs and has been suggested as the source of contamination among these dyes (Christmann et al., 1989a; Williams et al., 1992; U.S. EPA, 1992b). In May 1990, EPA received test results showing that chloranil was heavily contaminated with dioxins; levels as high as 3,065-μg TEQ/kg were measured in samples from four importers (mean value of 1,754-μg TEQ/kg) (U.S. EPA, 1992b; Remmers et al., 1992). (See Section 8.3.7 for analytical results.)

In the early 1990s, EPA learned that dioxin TEQ levels in chloranil could be reduced by more than two orders of magnitude (to less than 20 μg/kg) through manufacturing feedstock and process changes. EPA's Office of Pollution Prevention and Toxics (OPPT) subsequently began efforts to complete an industry-wide switch from the use of contaminated chloranil to low-dioxin chloranil. Although chloranil is not manufactured in

the United States, significant quantities are imported. As of May 1992, EPA had negotiated agreements with all chloranil importers and domestic dye/pigment manufacturers known to EPA that use chloranil in their products to switch to low-dioxin chloranil. In May 1993, when U.S. stocks of chloranil with high levels of CDD/CDFs had been depleted, EPA proposed a significant new use rule (SNUR) under Section 5 of TSCA that requires industry to notify EPA at least 90 days prior to the manufacture, import, or processing, for any use, of chloranil containing total CDD/CDFs at a concentration greater than 20 μg/kg (Federal Register, 1993a; U.S. EPA, 1993c).

In 1983, approximately 36,500 kg of chloranil were imported (U.S. ITC, 1984). The U.S. International Trade Commission (ITC) has not published quantitative import data for chloranil since 1984. If it is assumed that this import volume reflects actual usage of chloranil in the United States during 1987 and the CDD/CDF contamination level was 1,754-μg TEQ/kg, then the maximum release into the environment via processing wastes and finished products was 64.0 g of TEQ. If it is assumed that the import volume in 1995 was also 36,500 kg, but that the imported chloranil contained 10-μg TEQ/kg on average, then the total potential annual CDD/CDF release associated with chloranil in 1995 was 0.36 g of TEQ. Given the low confidence in the estimates of import volumes in 1987 and 1995, the estimated range of potential annual emissions for both years is assumed to vary by a factor of 10 between the low and high ends of the range. Assuming that 64.0-g TEQ/yr was the geometiric mean of this range for 1987, then the range is calculated to be 20- to 200-g TEQ/yr. Assuming that 0.36-g TEQ/yr was the geometric mean of this range in 1995, then the range is calculated to be 0.11- to 1.1-g TEQ/yr.

Phthalocyanine Dyes and Printing Inks - Hutzinger and Fiedler (1991a) found CDD/CDFs (tetra-, penta-, and hexachlorinated congeners) in the μg/kg range in a sample of a Ni-phthalocyanine dye. No CDD/CDFs were detected (detection limit of 0.1 to 0.5 μg/kg) in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye (Hutzinger and Fiedler, 1991a).

Santl et al. (1994c) reported the results of analyses of four printing inks obtained from a supplier in Germany. Two of the inks are used for rotogravure printing, and two are used for offset printing. The results of the analyses are presented in Table 8-16. The TEQ content of the inks ranged from 17.5 to 90.1 ng/kg. Primarily non-2,3,7,8-substituted

congeners were found. The identities of the dyes/pigments in these inks were not reported.

8.3.7. TSCA Dioxin/Furan Test Rule

Based on evidence that halogenated dioxins and furans may be formed as by-products during chemical manufacturing processes (Versar, 1985), EPA issued a rule under Section 4 of TSCA that requires chemical manufacturers and importers to test for the presence of chlorinated and brominated dioxins and furans in certain commercial organic chemicals (Federal Register, 1987c). The rule listed 12 manufactured or imported chemicals that required testing and 20 chemicals not currently manufactured or imported that would require testing if manufacture or importation resumed. These chemicals are listed in Table 8-17. The specific dioxin and furan congeners that require quantitation and the target limits of quantitation (LOQ) are specified in the Rule are listed in Table 8-18. Under Section 8(a) of TSCA, the final rule also required that chemical manufacturers submit data on manufacturing processes and reaction conditions for chemicals produced using any of the 29 precursor chemicals listed in Table 8-19. The rule stated that subsequent to this data gathering effort, testing may be proposed for additional chemicals if any of the manufacturing conditions used favored the production of dioxins and furans.

Sixteen sampling and analytical protocols and test data for 10 of the 12 chemicals that required testing were submitted to EPA (Holderman and Cramer, 1995). Data from 15 submissions were accepted; one submission is under review. Manufacture/import of two substances (tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate) have stopped since the test rule was promulgated. [NOTE: All data and reports in the EPA TSCA Docket are available for public review/inspection at EPA Headquarters in Washington, DC.]

Table 8-20 presents the results of analytical testing for dioxins and furans for the eight chemicals with data available in the TSCA docket. Five of these 10 chemicals contained dioxin/furans. Positive results were obtained for: 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione (chloranil), pentabromodiphenyloxide, octabromodiphenyloxide, decabromodiphenyloxide, and 1,2-Bis(tribromophenoxy)-ethane. Table 8-21 presents the quantitative analytical results for the four submitted chloranil samples, as well as the

results of analysis by EPA of a sample of carbazole violet, which is manufactured from chloranil.

It should be noted that although testing conducted under this test rule for 2,4,6-tribromophenol indicated no halogenated dioxins or furans above the LOQs, Thoma and Hutzinger (1989) reported detecting BDDs and BDFs in a technical grade sample of this substance. Total TBDD, TBDF, and PeBDF were found at 84 μg/kg, 12 μg/kg, and 1 μg/kg, respectively. No hexa-, hepta-, or octa-BDFs were detected. Thoma and Hutzinger (1989) also analyzed analytical grade samples of two other brominated flame retardants, pentabromophenol and tetrabromophthalic anhydride; no BDDs or BDFs were detected (detection limits not reported).

8.3.8. Halogenated Pesticides and FIFRA Pesticides Data Call-In

In the late 1970s and early 1980s, attention began to focus on pesticides as potential sources of CDDs and CDFs in the environment. Up to that time, CDD and CDF levels were not regulated in end-use pesticide products. Certain pesticide active ingredients, particularly chlorinated phenols and their derivatives, were known or suspected, however, to be contaminated with CDDs and CDFs (e.g., pentachlorophenol (PCP), Silvex, and 2,4,5-T). During the 1980s, EPA took several actions to investigate and control CDD/CDF contamination of pesticides.

In 1983, EPA cancelled the sale of Silvex and 2,4,5-T for all uses (Federal Register, 1983). Earlier, in 1979, EPA ordered emergency suspension of the forestry, rights-of-way, and pasture uses of 2,4,5-T; emergency suspensions of the forestry, rights-of-way, pasture, home and garden, commercial/ornamental turf, and aquatic weed control/ditch bank uses of Silvex were also ordered (Federal Register, 1979; Plimmer, 1980). The home and garden, commercial/ornamental turf, and aquatic weed control/ditch bank uses of 2,4,5-T had been suspended in 1970.

EPA entered into a Settlement Agreement in 1987 with PCP manufacturers to allow continued registrations for wood uses (Federal Register, 1987a) under a restricted use basis but which set tolerance levels for HxCDD and 2,3,7,8-TCDD. TCDD levels were not allowed to exceed 1.0 ppb in any product, and after February 2, 1989, (a gradually phased in requirement), any manufacturing-use PCP released for shipment could not contain HxCDD levels that exceeded an average of 2 ppm over a monthly release or a batch level of

4 ppm. On January 21, 1987, EPA issued a Final Determination and Intent to Cancel and Deny Applications for Registrations of Pesticide Products Containing Pentachlorophenol (Including but not limited to its salts and esters) for Nonwood Uses, which prohibited the registration of PCP and its salts for most nonwood uses (Federal Register, 1987b). EPA deferred action on several uses (i.e., uses in pulp/paper mills, oil wells, and cooling towers) pending receipt of additional exposure, use, and ecological effects data. On January 8, 1993, EPA issued a press advisory stating that the EPA Special Review of these deferred nonwood uses was being terminated, because all of these uses either had been voluntarily cancelled by the registrants or had been cancelled by EPA for failure of the registrants to pay the required annual maintenance fees (U.S. EPA, 1993f).

An estimated 8,400 metric tons of PCP were used for wood preservation in the United States in 1994 (Micklewright, 1994); for purposes of this report, it is assumed that an identical amount was used in 1995. An estimated 12,000 metric tons were used in 1987 (WHO, 1991). Historically, PCP has contained about 3-mg TEQ/kg, based on data presented in Table 8-7. Figure 8-4 presents congener and congener group profiles, respectively, for PCP, based on the results of those studies presented in Table 8-7 that provided complete congener and congener group measurements. Combining these two estimates indicates that 25,000 g and 36,000 g of TEQ may have entered the environment in the form of PCP-treated wood products in 1995 and 1987, respectively. These release estimates are assigned a H/H confidence rating, indicating high confidence in both the activity and emission factor estimates. Based on this high confidence rating, the estimated range of potential release in the form of treated wood products is assumed to vary by a factor of 2 between the low and high ends of the range. Assuming that the estimated releases of 25,000 g and 36,000 g of TEQ are the geometric means of these ranges, then the ranges are calculated to be 17,700- to 35,400-g TEQ for 1995 and 25,500 to 51,000 for 1987.

In addition to the pesticide cancellations and product standards, EPA's Office of Pesticide Programs (OPP) issued two Data Call-Ins (DCIs) in 1987. Pesticide manufacturers are required to register their products with EPA in order to market them commercially in the United States. Through the registration process, mandated by FIFRA, EPA can require that the manufacturer of each active ingredient generate a wide variety of scientific data through several mechanisms. The most common process is the five-phase reregistration

effort to which the manufacturers (i.e., registrants) of older pesticide products must comply. In most registration activities, registrants must generate data under a series of strict testing guidelines, 40 CFR 158--Pesticide Assessment Guidelines (U.S.EPA, 1988b). Some pesticide active ingredients may require additional data, outside of the norm, to adequately develop effective regulatory policies for those products. Therefore, EPA can require additional data, where needed, through various mechanisms, including the DCI process.

The purpose of the first DCI (dated June and October 1987), Data Call In Notice for Product Chemistry Relating to Potential Formation of Halogenated Dibenzo-p-dioxin or Dibenzofuran Contaminants in Certain Active Ingredients, was to identify through an analysis of raw materials and process chemistry, those pesticides that may contain halogenated dibenzo-p-dioxin and dibenzofuran contaminants. The list of 93 pesticides (76 pesticide active ingredients) to which this DCI applied, along with their corresponding Shaughnessey and Chemical Abstract code numbers, are presented in Table 8-22. [Note: the Shaughnessey code is an internal EPA tracking system--it is of interest because chemicals with similar code numbers are similar in chemical nature (e.g., salts, esters, and acid forms of 2,4-D).] All registrants supporting registrations for these chemicals were subject to the requirements of this DCI, unless their product qualified for a Generic Data Exemption (i.e., a registrant exclusively used a FIFRA-registered pesticide product(s) as the source(s) of the active ingredient(s) identified in Table 8-22 in formulating their product(s)). Registrants whose products did not meet the Generic Data Exemption were required to submit the types of data listed below to enable EPA to assess the potential for formation of tetra- through hepta-halogenated dibenzo-p-dioxin or dibenzofuran contaminants during manufacture. Registrants, however, had the option to voluntarily cancel their product or "reformulate to remove an active ingredient," described in Table 8-22, to avoid compliance with the DCI.

- Product Identity and Disclosure of Ingredients: EPA required submittal of a Confidential Statement of Formula (CSF), based on the requirements specified in 40 CFR 158.108 and 40 CFR 158.120 - Subdivision D: Product Chemistry. Registrants who had previously submitted still current CSFs were not required to resubmit this information.

- Description of Beginning Materials and Manufacturing Process: Based on the requirements mandated by 40 CFR 158.120 - Subdivision D, EPA required submittal of a manufacturing process description for each step of the manufacturing process, including specification of the range of acceptable conditions of temperature, pressure, or pH at each step.
- Discussion of the Formation of Impurities: Based on the requirements mandated by 40 CFR 158.120 - Subdivision D, EPA required submittal of a detailed discussion/assessment of the possible formation of halogenated dibenzo-p-dioxins and dibenzofurans.

The second DCI (dated June and October 1987), Data Call-In for Analytical Chemistry Data on Polyhalogenated Dibenzo-p-Dioxins/Dibenzofurans (HDDs and HDFs), was issued for 68 pesticides (16 pesticide active ingredients) suspected to be contaminated by CDD/CDFs. (See Table 8-23.) All registrants supporting registrations for these pesticides were subject to the requirements of this DCI, unless the product qualified for various exemptions or waivers. Pesticides covered by the second DCI were strongly suspected by EPA to contain detectable levels of HDD/HDFs.

Under the second DCI, registrants whose products did not qualify for an exemption or waiver were required to generate and submit the following types of data in addition to the data requirements of the first DCI:

- Quantitative Method For Measuring HDDs or HDFs: Registrants were required to develop an analytical method for measuring the HDD/HDF content of their products. The DCI established a regimen for defining the precision of the analytical method (i.e., for internal standard--precision within +/- 20 percent and recovery range of 50 to 150 percent, also a signal to noise ratio of at least 10:1 was required). Target quantification limits were established in the DCI for specific HDD and HDF congeners. (See Table 8-24.)
- Certification of Limits of HDDs or HDFs: Registrants were required to submit a "Certification of Limits" in accordance with 40 CFR 158.110 and 40 CFR 158.120 - Subdivision D. Analytical results were required that met the guidelines described above.

Registrants could select one of two options to comply with the second DCI. The first option was to submit relevant existing data, develop new data, or share the cost to develop new data with other registrants. The second option was to alleviate the DCI requirements through several exemption processes including a Generic Data Exemption, voluntary cancellation, reformulation to remove the active ingredient of concern, an assertion that the data requirements do not apply, or the application/award of a low-volume, minor-use waiver.

The data contained in CSFs, as well as any other data generated under Subdivision D, are typically considered Confidential Business Information (CBI) under the guidelines prescribed in FIFRA, because they usually contain information regarding proprietary manufacturing processes. In general, all analytical results submitted to EPA in response to both DCIs are considered CBI and cannot be released by EPA into the public domain. Summaries based on the trends identified in that data, as well as data made public by EPA, are summarized below.

The two DCIs included 161 pesticides. Of these, 92 are no longer supported by registrants. Based on evaluations of the process chemistry submissions required under the DCIs, OPP determined that formation of CDD/CDFs was not likely during the manufacture of 43 of the remaining 69 pesticides; thus, analysis of samples of these 43 pesticides was not required by OPP. Evaluation of process chemistry data is ongoing at OPP for an additional seven pesticides. Tables 8-22 and 8-23 indicate which pesticides are no longer supported, those for which OPP determined that CDD/CDF formation is unlikely, and those for which process chemistry data or analytical testing results are under review in OPP (U.S. EPA, 1995a).

OPP required that analysis of production samples be performed on the remaining 19 pesticides. (See Table 8-25.) The status of the analytical data generation/evaluation to date is summarized as follows: (1) no detection of CDD/CDFs above the LOQs in registrant submissions for 13 active ingredients; (2) detection of CDD/CDFs above the LOQs for 2,4-D acid (two submissions) and 2,4-D 2-ethyl hexyl acetate (one submission); and (3) ongoing data generation or evaluation for four pesticides.

Table 8-24 presents a summary of results recently obtained by EPA for CDDs and CDFs in eight technical 2,4-D herbicides; these data were extracted from program files in OPP. Because some of these files contained CBI, the data in this table were reviewed by

OPP staff to ensure that no CBI was being disclosed (Funk, 1996). Figure 8-5 presents a congener profile for 2,4-D, based on the average congener concentrations reported in Table 8-24.

Schecter et al. (1997) recently reported the results of analyses of samples of 2,4-D manufactured in Europe, Russia, and the United States. (See Table 8-26.) The total TEQ concentrations measured in the European and Russian samples are similar to those measured in the EPA DCI samples; however, the levels reported by Schecter et al. (1997) for U.S. samples are significantly lower.

An estimated 26,300 metric tons of 2,4-D were consumed in the United States in 1995, making it one of the top 10 pesticides in terms of quantity used (U.S. EPA, 1997a). An estimated 30,400 metric tons were consumed during 1987 (U.S. EPA, 1988c). Based on the average CDD/CDF congener concentrations in 2,4-D presented in Table 8-24 (i.e., not including OCDD and OCDF), the corresponding TEQ concentration is 0.70 μg/kg. Combining this TEQ concentration with the activity level estimates for 1995 and 1987 indicates that 18.4 g and 21.3 g of TEQ may have entered the environment in 1995 and 1987, respectively. These release estimates are assigned a H/H confidence rating indicating high confidence in both the production and emission factor estimates. Based on this high confidence rating, the estimated range of potential release is assumed to vary by a factor of 2 between the low and high ends of the range. Assuming that the estimated releases of 18.4 g and 21.3 g of TEQ are the geometric means of these ranges, then the ranges are calculated to be 13.0- to 26.0-g TEQ in 1995 and 15.1- to 30.2-g TEQ in 1987.

8.4. OTHER CHEMICAL MANUFACTURING AND PROCESSING SOURCES

8.4.1. Municipal Wastewater Treatment Plants

Sources - CDD/CDFs have been measured in nearly all sewage sludges tested, although the concentrations and, to some extent, the congener profiles and patterns differ widely. Potential sources of the CDD/CDFs include microbial formation (discussed in Chapter 9), runoff to sewers from lands or urban surfaces contaminated by product uses or deposition of previous emissions to air, household wastewater, industrial wastewater, chlorination operations within the wastewater treatment facility, or a combination of all the

Table 8-1. CDD/CDF Concentrations in Pulp and Paper Mill Bleached Pulp, Wastewater Sludge, and Effluent (circa 1988)

Congener/Congener Group	Bleached Pulp			Wastewater Sludge			Wastewater Effluent		
	Median (ng/kg)	Range (ng/kg)	No. of Detects (10 samples)	Median (ng/kg)	Range (ng/kg)	No. of Detects (9 samples)	Median (pg/L)	Range (pg/L)	No. of Detects (9 samples)
2,3,7,8-TCDD	6.4	0.4 to 124	10	63	ND (6.3) to 180	8	42	ND (11) to 98	8
1,2,3,7,8-PeCDD	ND (0.3)	ND (0.1) to 1.4	2	ND (2.5)	ND (1.4) to 28	1	ND (9.6)	ND (2.8) to ND (25)	0
1,2,3,4,7,8-HxCDD	ND (0.4)	ND (0.2) to 0.4	1	ND (3.1)	ND (1.5) to 40	1	ND (12)	ND (6.6) to ND (32)	0
1,2,3,6,7,8-HxCDD	ND (0.5)	ND (0.2) to 1.6	2	ND (3.2)	ND (1.7) to 95	1	ND (12)	ND (6.6) to ND (24)	0
1,2,3,7,8,9-HxCDD	ND (0.5)	ND (0.2) to 0.5	1	ND (3.9)	ND (1.7) to 80	1	ND (12)	ND (6.6) to ND (23)	0
1,2,3,4,6,7,8-HpCDD	3.3	2.3 to 8.4	10	37	18 to 490	9	170	77 to 270	9
OCDD	46	28 to 81	10	698	263 to 1,780	9	3,000	1,000 to 4,600	9
2,3,7,8-TCDF	18	1.4 to 716	10	233	13 to 1,150	9	120	12 to 840	9
1,2,3,7,8-PeCDF	ND (0.7)	ND (0.1) to 3.9	4	6.2	ND (1.2) to 22	6	ND (7.2)	ND (2.2) to 36	2
2,3,4,7,8-PeCDF	ND (0.2)	ND (0.1) to 4.7	3	4.7	ND (0.9) to 38	6	ND (6.3)	ND (2.2) to 33	2
1,2,3,4,7,8-HxCDF	ND (0.3)	ND (0.2) to ND (0.6)	0	ND (2.5)	ND (0.9) to 31	2	ND (8.4)	ND (4.8) to ND (15)	0
1,2,3,6,7,8-HxCDF	ND (0.3)	ND (0.1) to ND (0.4)	0	ND (1.4)	ND (0.9) to 33	1	ND (7.1)	ND (4.8) to ND (15)	0
1,2,3,7,8,9-HxCDF	ND (0.3)	ND (0.1) to ND (0.4)	0	ND (1.7)	ND (0.9) to ND (4.0)	0	ND (6.2)	ND (2.5) to ND (15)	0
2,3,4,6,7,8-HxCDF	ND (0.3)	ND (0.2) to ND (0.4)	0	ND (1.7)	ND (0.9) to 34	1	ND (8.2)	ND (4.8) to ND (15)	0
1,2,3,4,6,7,8-HpCDF	ND (0.6)	ND (0.1) to 0.8	3	6.6	ND (3.6) to 70	7	ND (23)	ND (13) to 44	3
1,2,3,4,7,8,9-HpCDF	ND (0.6)	ND (0.1) to ND (2.1)	0	ND (1.6)	ND (1.2) to 10	1	ND (22)	ND (6.4) to ND (41)	0
OCDF	2.2	ND(2.8) to 4.3	8	22	ND (54) to 168	8	190	ND (180) to 230	8
Total 2,3,7,8-CDD[a,b]	55.7			798			3,212		
Total 2,3,7,8-CDF[a,b]	18			272.5			310		
Total TEQ (ND = zero)[b]	8.28			90.1			59		
Total TEQ (ND = DL)[b]	8.83			93.1			73		
Total CDD/CDF[b]	120			1,695			4,013		

ND = not detected; values in parentheses are detection limits (DL).
[a] Calculated assuming nondetected values are zero.
[b] Sum of median values.
ng/kg = nanograms per kilogram
pg/L = picograms per liter
Source: U.S. EPA (1990a).

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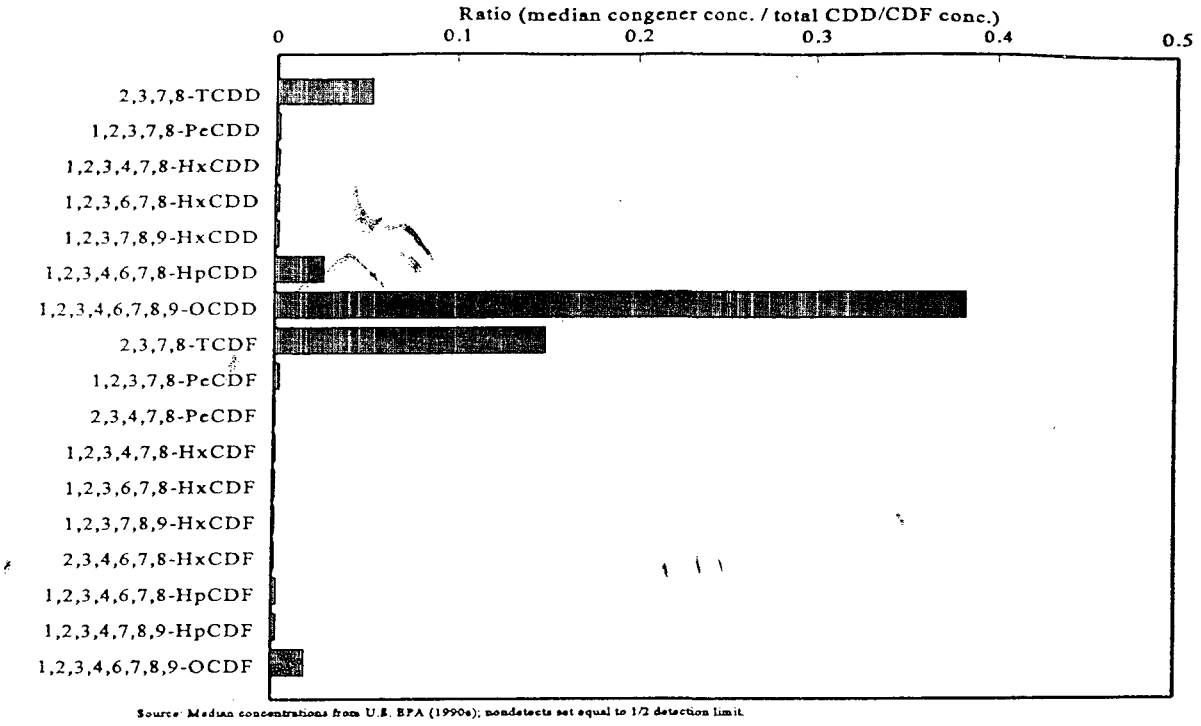
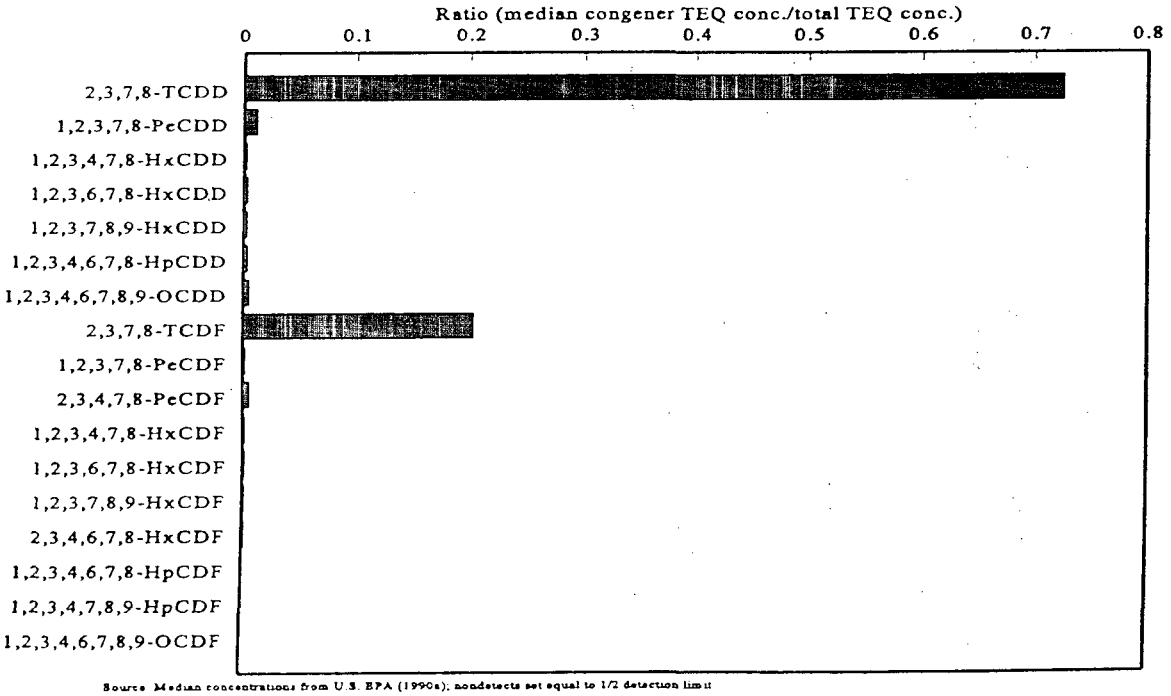
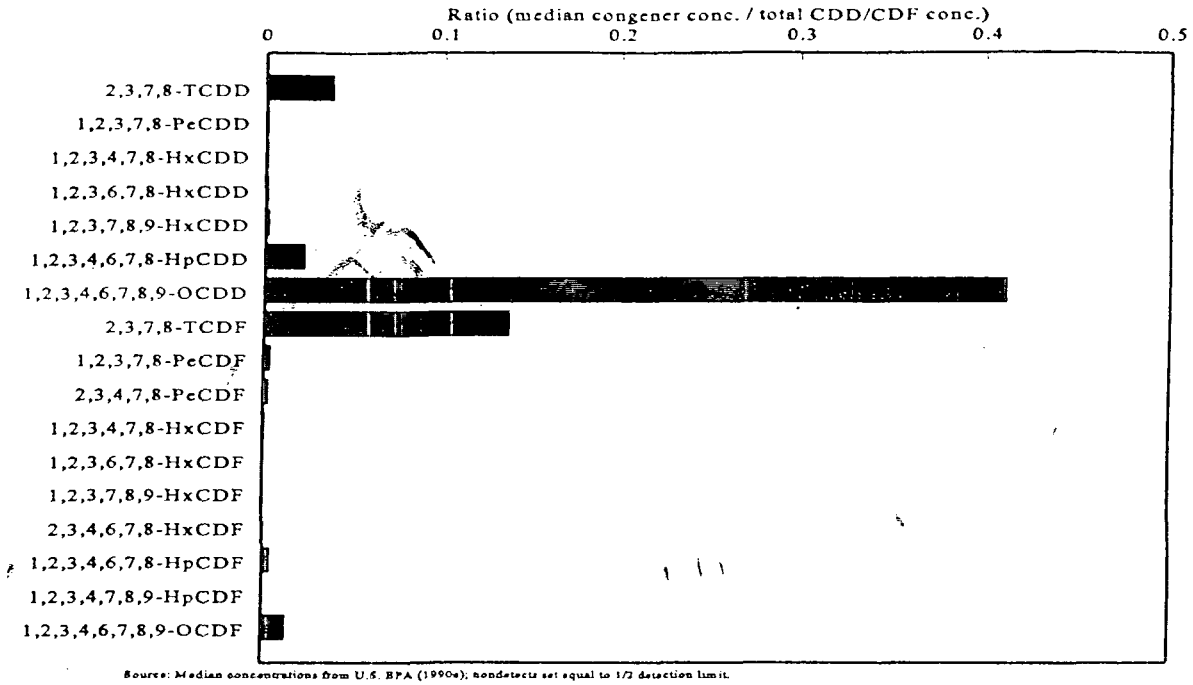


Source: Median concentrations from U.S. EPA (1990s); nondetects set equal to 1/2 detection limit.

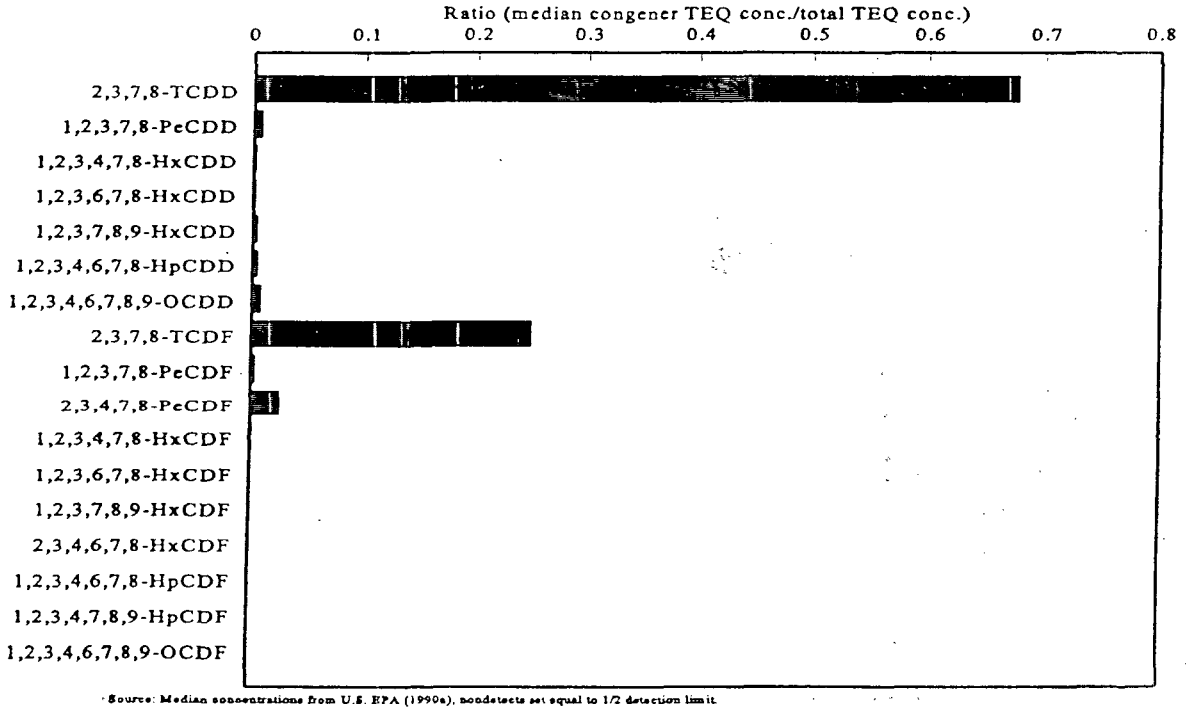


Source: Median concentrations from U.S. EPA (1990s); nondetects set equal to 1/2 detection limit.

Figure 8-1. 104-Mill Study Full Congener Analysis Results for Pulp

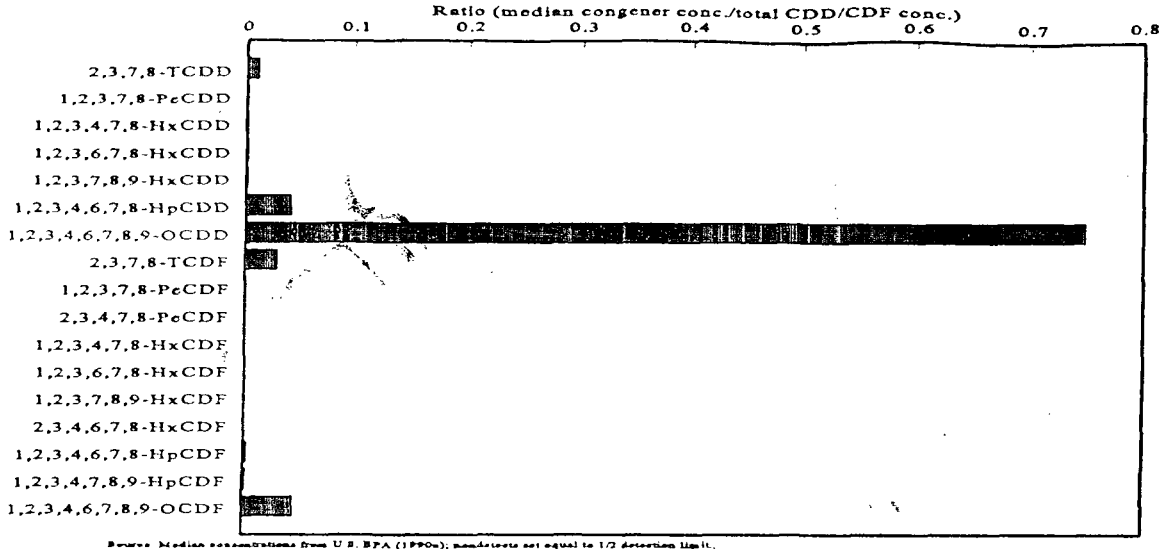


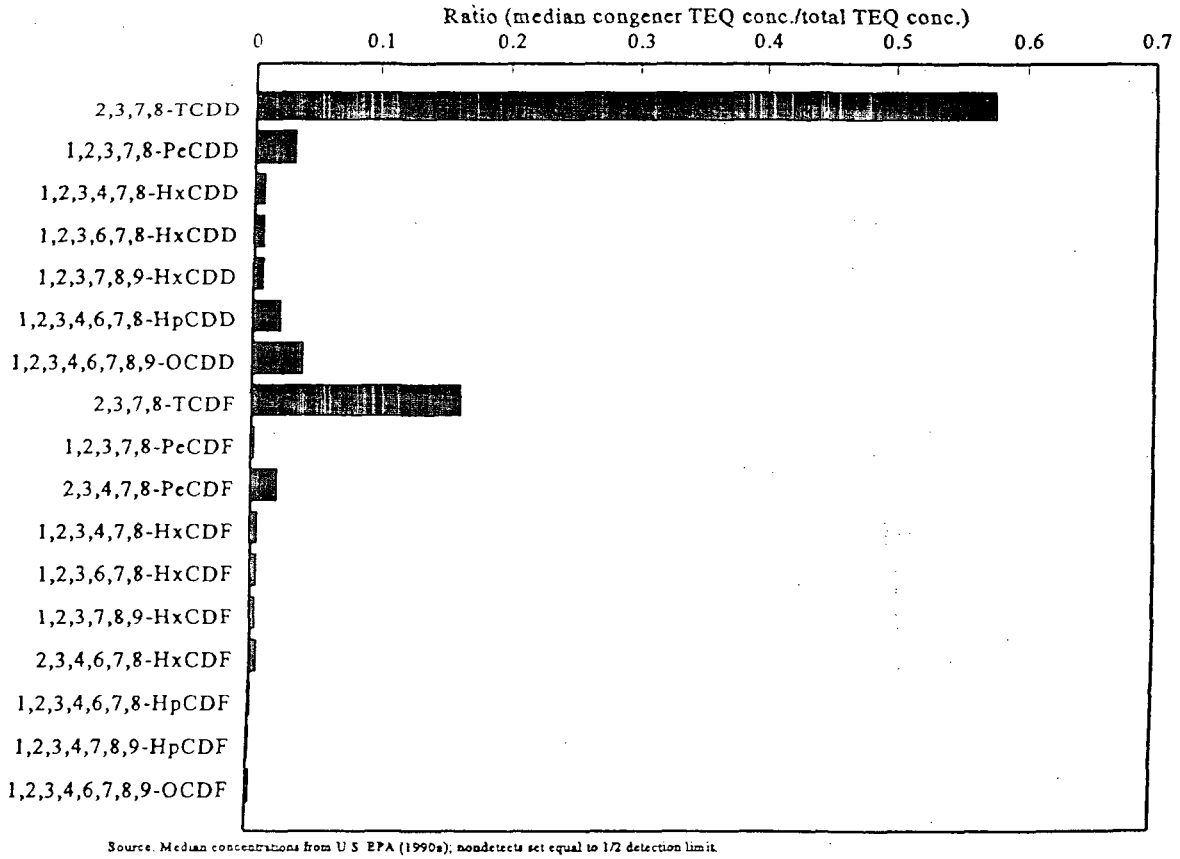
Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.



Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-2. 104-Mill Study Full Congener Analysis Results for Sludge





Source: Median concentrations from U.S. EPA (1990s); nondetects set equal to 1/2 detection limit.

Figure 8-3. 104-Mill Study Full Congener Analysis Results for Effluent

Table 8-2. CDD/CDF Concentrations in Pulp and Paper Mill Bleached Pulp, Wastewater Sludge, and Effluent (circa 1996)

Congener/Congener Group	Bleached Pulp				Wastewater Sludge				Wastewater Effluent			
	Mean ND = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of Detects/ No. of Samples	Mean ND = 0 (ng/kg)	Median (ng/kg)	Range (ng/kg)	No. of Detects/ No. of Samples	Mean ND = 0 (pg/L)	Median (ng/kg)	Range (pg/L)	No. of Detects/ No. of Samples
2,3,7,8-TCDD	0.3	ND(1)	ND(1) to 5	1/18	0.8	ND(1)	ND(1) to 4	4/12	1.2	ND(11)	ND(10) to 21	1/18
1,2,3,7,8-PeCDD	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/12	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8-HxCDD	0	ND(5)	ND(3) to ND(7)	0/18	0.5	ND(5)	ND(4) to 7	1/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,6,7,8-HxCDD	0	ND(5)	ND(3) to ND(7)	0/18	2.3	ND(5)	ND(4) to 18	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,7,8,9-HxCDD	0	ND(5)	ND(3) to ND(7)	0/18	1.6	ND(5)	ND(4) to 14	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,6,7,8-HpCDD	0	ND(5)	ND(3) to ND(7)	0/18	41.4	7	ND(4) to 330	9/13	3.2	ND(53)	ND(50) to 58	1/18
OCDD	2.4	ND(10)	ND(10) to 15	3/18	445	150	21 to 2,900	10/10	99.0	ND(110)	ND(100) to 370	6/14
2,3,7,8-TCDF	10.3	ND(1)	ND(1) to 170	7/18	6.2	3	ND(1) to 31	9/12	2.3	ND(11)	ND(10) to 23	2/18
1,2,3,7,8-PeCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
2,3,4,7,8-PeCDF	0.4	ND(5)	ND(3) to 7	1/18	0.5	ND(5)	ND(4) to 7	1/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,6,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,7,8,9-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
2,3,4,6,7,8-HxCDF	0	ND(5)	ND(3) to ND(7)	0/18	0.5	ND(5)	ND(4) to 6	1/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,6,7,8-HpCDF	0	ND(5)	ND(3) to ND(7)	0/18	1.2	ND(5)	ND(4) to 10	2/13	0	ND(53)	ND(50) to ND(55)	0/18
1,2,3,4,7,8,9-HpCDF	0	ND(5)	ND(3) to ND(7)	0/18	0	ND(5)	ND(4) to ND(52)	0/13	0	ND(53)	ND(50) to ND(55)	0/18
OCDF	0	ND(10)	ND(6) to ND(14)	0/18	0	ND(10)	ND(9) to ND(100)	0/13	0	ND(106)	ND(104) to ND(110)	0/18
Total 2,3,7,8-CDD[a]	2.7				492				103			
Total 2,3,7,8-CDF[a]	10.7				8.4				2.3			
Total TEQ (ND = zero)[a]	1.5				3.0				1.5			
Total TEQ (ND = DL)[a]	11.3				22.9				105			

ND = not detected; values in parentheses are detection limits (DL).

[a] Sum of mean values.

ng/kg = nanograms per kilogram
pg/L = picograms per liter

Source: Gillespie (1997).

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Table 8-3. Summary of Bleached Chemical Pulp and Paper Mill Discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF

Matrix	Congener	1988 Discharge[a] (g/year)	1992 Discharge[b] (g/year)	1992 Discharge[c] (g/year)	1993 Discharge[b] (g/year)	1994 Discharge[b] (g/year)
Effluent	2,3,7,8-TCDD	201	22	71	19	14.6
	2,3,7,8-TCDF	1,550	99	341	76	49.0
	TEQ	356	32	105	27	19.5
Sludge[d]	2,3,7,8-TCDD	210	33	NR	24	18.9
	2,3,7,8-TCDF	1,320	118	NR	114	95.2
	TEQ	343	45	100	35	28.4
Pulp	2,3,7,8-TCDD	262	24	NR	22	16.2
	2,3,7,8-TCDF	2,430	124	NR	106	78.8
	TEQ	505	36	150	33	24.1

NR = Not reported.

[a] 104-Mill Study (U.S. EPA, 1990a): Total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration) summed across all 104 mills.

[b] NCASI 1992 Survey (NCASI, 1993), 1993 Update (Gillespie, 1994), and 1994 Update (Gillespie, 1995): Total discharge rate of congener or TEQ (based only on 2,3,7,8-TCDD and 2,3,7,8-TCDF concentration) summed across all 104 mills. The daily discharge rates reported in NCASI (1993), Gillespie (1994), and Gillespie (1995) were multiplied by a factor of 350 days/yr to obtain estimates of annual discharge rates.

[c] The discharge in effluent was estimated in U.S. EPA (1993d) for January 1, 1993. The TEQ discharges in sludge and pulp were estimated by multiplying the 1988 discharge estimates for each by the ratio of the 1993 and 1988 effluent discharge estimates (i.e., the estimate of the reduction in 1988 discharges achieved by pollution prevention measures taken by the industry between 1988 and 1993).

[d] Approximately 20.5 percent of the sludge generated in 1990 were incinerated. The remaining 79.5 percent were predominantly landfilled (56.5 percent) or placed in surface impoundments (18.1 percent); 4.1 percent were land-applied directly or as compost, and 0.3 percent were distributed/marketed (U.S. EPA, 1993e).

g/year = grams per year

Sources: Gillespie (1995); Gillespie (1994); NCASI (1993); U.S. EPA (1993d); U.S. EPA (1993e).

Table 8-4. CDD/CDF Concentrations in Graphite Electrode Sludge from Chlorine Production

Congener/Congener Group	Sludge 1 (μg/kg)	Sludge 2 (μg/kg)	Sludge 3 (μg/kg)	Sludge 4 (μg/kg)
2,3,7,8-TCDD	ND (0.006)	ND (0.009)	ND (0.009)	ND
1,2,3,7,8-PeCDD	ND (0.007)	ND (0.009)	ND (0.009)	ND (0.033)
1,2,3,4,7,8-HxCDD	ND (0.018)	ND (0.026)	ND (0.029)	ND (0.49)
1,2,3,6,7,8-HxCDD	ND (0.012)	ND (0.016)	ND (0.019)	ND (0.053)
1,2,3,7,8,9-HxCDD	ND (0.016)	ND (0.022)	ND (0.025)	ND (1.2)
1,2,3,4,6,7,8-HpCDD	0.095	0.21	0.25	0.055
OCDD	0.92	2.0	2.2	0.65
2,3,7,8-TCDF	26	56	57	52
1,2,3,7,8-PeCDF	25	55	56	55
2,3,4,7,8-PeCDF	12	25	24	27
1,2,3,4,7,8-HxCDF	32	71	73	44
1,2,3,6,7,8-HxCDF	7	16	15	12
1,2,3,7,8,9-HxCDF	1.3	2.8	2.6	1.7
2,3,4,6,7,8-HxCDF	0.87	1.9	2.0	1.3
1,2,3,4,6,7,8-HpCDF	9.1	19	19	15
1,2,3,4,7,8,9-HpCDF	8.1	19	20	14
OCDF	31	76	71	81
Total 2,3,7,8-CDD*	1.015	2.21	2.45	0.705
Total 2,3,7,8-CDF*	152.37	341.7	339.6	303
Total TEQ*	13.5	30.2	30.2	27.7
Total TCDD	ND (0.006)	ND (0.009)	ND (0.009)	NR
Total PeCDD	ND (0.070)	ND (0.009)	ND (0.009)	NR
Total HxCDD	ND (0.046)	ND (0.064)	ND (0.074)	NR
Total HpCDD	0.22	0.48	0.56	NR
Total OCDD	0.92	2	2.2	0.65
Total TCDF	64	150	140	NR
Total PeCDF	75	240	240	NR
Total HxCDF	68	140	140	NR
Total HpCDF	24	53	54	NR
Total OCDF	31	76	71	81
Total CDD/CDF*	263.14	661.48	647.76	NR

ND = Nondetected (values in parentheses are the reported detection limits)
NR = Not reported
* = Calculated assuming not detected values were zero.
μg/kg = micrograms per kilogram

Sources: Rappe et al. (1991); Rappe (1993)

Table 8-5. CDD/CDF Concentrations in Metal Chlorides

Congener Group	$FeCl_3$ (μg/kg)	$AlCl_3$ (μg/kg)	$AlCl_3$ (μg/kg)	$CuCl_2$ (μg/kg)	CuCl (μg/kg)	$TiCl_4$ (μg/kg)	$SiCl_4$ (μg/kg)
Total TCDD	NR	NR	NR	NR	NR	NR	NR
Total PeCDD	NR	NR	NR	NR	NR	NR	NR
Total HxCDD	NR	NR	NR	NR	NR	NR	NR
Total HpCDD	ND	ND	ND	0.03	ND	ND	ND
Total OCDD	ND	ND	0.1	0.6	0.03	ND	ND
Total TCDF	NR	NR	NR	NR	NR	NR	NR
Total PeCDF	NR	NR	NR	NR	NR	NR	NR
Total HxCDF	NR	NR	NR	NR	NR	NR	NR
Total HpCDF	12	ND	ND	0.1	0.08	ND	ND
Total OCDF	42	ND	34	0.5	0.2	ND	ND

NR = Not reported.
ND = Nondetected (detection limit of 0.02 μg/kg)
μg/kg = micrograms per kilogram

Source: Hutzinger and Fiedler (1991a)

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Table 8-6. CDD/CDF Concentrations in Mono- through Tetra-Chlorophenols

Congener/ Congener Group	2-CP (Ref. A) (mg/kg)	2,4-DCP (Ref. A) (mg/kg)	2,6-DCP (Ref. A) (mg/kg)	2,4,5-TrCP (Na salt) (Ref. A) (mg/kg)	2,4,5-TrCP (Ref. A) (mg/kg)	2,4,6-TrCP (Ref. A) (mg/kg)	2,4,6-TrCP (Na salt) (Ref. B & C) (mg/kg)	2,3,4,6-TeCP (Ref. A) (mg/kg)	2,3,4,6-TeCP (Na salt) (Ref. B & C) (mg/kg)
Total TCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02) - 14	ND (0.02) - 6.5	ND (0.02) - 49	<0.02	ND (0.02)	0.7
Total PeCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02) - 1.5	ND (0.02)	<0.03	ND (0.02)	5.2
Total HxCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	<0.03	ND (0.02) - 15	9.5
Total HpCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	<0.1	ND (0.02) - 5.1	5.6
Total OCDD	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)	<0.1	ND (0.02) - 0.17	0.7
Total TCDF	+	ND	ND	ND	ND	+	1.5	+	0.5
Total PeCDF	ND	ND	ND	ND	ND	+	17.5	+	10
Total HxCDF	ND	ND	ND	ND	ND	+	36	+	70
Total HpCDF	ND	ND	ND	ND	ND	ND	4.8	+	70
Total OCDF	ND	ND	ND	ND	ND	ND	--	+	10
Total CDD/CDF	--	--	--	--	--	--	--	--	--

ND = Not detected; value in parentheses is the detection limit, if reported.
+ = Detected but not quantified.
-- = Not reported.
mg/kg = milligrams per kilogram
Ref. A: Firestone et al. (1972); because of poor recoveries, authors stated that actual CDD/CDF levels may be considerably higher than those reported.
Ref. B: Rappe et al. (1978a); common Scandinavian commercial chlorophenols.
Ref. C: Rappe et al. (1978b); common Scandinavian commercial chlorophenols.

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Table 8-7. Historical CDD/CDF Concentrations in Historical and Current Technical Pentachlorophenol Products

Congener/ Congener Group	PCP (Ref. B) (1973) (µg/kg)	PCP (Ref. C) (1978) (µg/kg)	PCP (Ref. A) (1979) (µg/kg)	PCP (Ref. D) (1984) (µg/kg)	PCP (Ref. I) (1985) (µg/kg)	PCB (Ref. I) (1986) (µg/kg)	PCP (Ref. E) (1987) (µg/kg)	PCP (Ref. F) (1987) (µg/kg)	PCP (Ref. I) (1985-88) (µg/kg)	PCP (Ref. G) (1991) (µg/kg)	PCP (Ref. H) (1987-96) (µg/kg)	PCP (Ref. J) (1987-96) (µg/kg)	PCP (Ref. K) (unknown) (µg/kg)
2,3,7,8-TCDD	--	--	--	ND (10)	ND (0.05)	ND (0.05)	ND (0.03)	ND (0.05)	ND (0.05)	ND	--	ND (0.5)	ND (10)
1,2,3,7,8-PeCDD	--	--	--	ND (10)	ND (1)	ND (1)	1	2	ND (1)	ND	--	--	ND (10)
1,2,3,4,7,8-HxCDD	--	--	--	--	6	8	ND (1)	ND (1)	8	--	--	--	ND (10)
1,2,3,6,7,8-HxCDD	--	--	--	2,200	2,565	1,532	831	1,480	600	--	--	--	860
1,2,3,7,8,9-HxCDD	--	--	--	100	44	28	28	53	13	--	--	--	20
1,2,3,4,6,7,8-HpCDD	--	--	--	100,000	210,000	106,000	78,000	99,900	89,000	--	--	--	36,400
OCDD	--	--	--	610,000	1,475,000	930,000	733,000	790,000	2,723,000	1,100,000	--	--	296,810
2,3,7,8-TCDF	--	--	--	ND (10)	ND (0.5)	ND (0.5)	ND (0.1)	ND (0.1)	ND (0.5)	ND	--	--	ND (10)
1,2,3,7,8-PeCDF	--	--	--	--	ND (1)	ND (1)	0.5	0.2	ND (1)	ND	--	--	ND (10)
2,3,4,7,8-PeCDF	--	--	--	--	ND (1)	ND (1)	1.5	0.9	ND (1)	ND	--	--	ND (10)
1,2,3,4,7,8-HxCDF	--	--	--	--	49	34	125	163	67	--	--	--	200
1,2,3,6,7,8-HxCDF	--	--	--	--	5	4	ND (1)	ND (1)	2	--	--	--	ND (20)
1,2,3,7,8,9-HxCDF	--	--	--	--	5	ND (1)	32	146	ND (1)	--	--	--	ND (20)
2,3,4,6,7,8-HxCDF	--	--	--	--	ND (1)	ND (1)	ND (1)	ND (1)	ND (1)	--	--	--	ND (20)
1,2,3,4,6,7,8-HpCDF	--	--	--	--	34,000	29,000	11,280	19,940	22,000	--	--	--	2,000
1,2,3,4,7,8,9-HpCDF	--	--	--	--	4,100	6,200	637	980	3,400	--	--	--	140
OCDF	--	130,000	--	130,000	222,000	233,000	118,000	137,000	237,000	170,000	--	--	19,940
Total 2,3,7,8-CDD*	--	--	--	712,300	1,687,615	1,037,568	811,860	891,435	2,812,621	--	--	--	334,130
Total 2,3,7,8-CDF*	--	--	--	--	260,159	268,238	130,076	158,230	262,469	--	--	--	22,280
Total TEQ*	--	--	--	1,970	4,445	2,736	1,853	2,321	4,173	>1,270	--	--	811
Total TCDD	ND(20)	--	--	ND (10)	ND	ND	1.9	0.4	ND	ND (10)	ND (1)	ND	--
Total PeCDD	ND(30)	--	--	ND (10)	ND	ND	6.5	15.2	ND	ND (10)	ND (10)	ND	--
Total HxCDD	5,500	--	10,100	4,500	4,694	2,925	1,700	3,300	912	8,900	1,530	1,686	--
Total HpCDD	98,000	--	296,000	135,000	283,000	134,000	154,000	198,000	117,000	130,000	62,900	61,083	--
Total OCDD	220,000	--	1,386,000	610,000	1,475,000	930,000	733,000	790,000	2,723,000	1,100,000	--	231,755	--
Total TCDF	40	900	--	ND (10)	6	ND	0.8	0.4	ND	ND (10)	ND (10)	54	--
Total PeCDF	250	4,000	1,400	--	10	3	141	343	200	ND (10)	ND (10)	509	--
Total HxCDF	22,000	32,000	9,900	--	1,982	1,407	4,300	13,900	1,486	14,000	2,500	15,534	--
Total HpCDF	150,000	120,000	88,000	62,000	125,000	146,000	74,000	127,000	99,000	36,000	38,600	93,377	--
Total OCDF	160,000	130,000	43,000	130,000	222,000	233,000	118,000	137,000	237,000	170,000	--	156,451	--
Total CDD/CDF*	655,800	1,280,000	1,834,400	941,500	2,111,692	1,447,335	1,085,000	1,270,000	3,178,598	1,459,000	--	560,448	--

ND = Not detected; value in parentheses is the detection limit.
-- = Not reported.
* = Calculated assuming not detected values are zero.
µg/kg = micrograms per kilogram

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Table 8-7. Historical CDD/CDF Concentrations in Historical and Current Technical Pentachlorophenol Products (continued)

Sources:

Ref. A: U.S. DHHS (1989); composite of technical grade materials produced in 1979 by Monsanto Industrial Chemical Co. (St. Louis, MO), Reichhold Chemicals, Inc. (White Plains, NY), and Vulcan Materials Co. (Birmingham, AL).
Ref. B: Buser and Bosshardt (1976); mean of 10 samples of "high" CDD/CDF content PCP received from Swiss commercial sources in 1973.
Ref. C: Rappe et al. (1978b); sample of U.S. origin "presumably prepared by alkaline hydrolysis of hexachlorobenzene."
Ref. D: Cull et al. (1984); mean of four "recent" production batches from each of two manufacturers of technical PCP using three different analytical methods; ANOVA showed no statistically significant difference in CDD/CDF concentrations between the eight samples (samples obtained in the United Kingdom).
Ref. E: Hagenmaier and Brunner (1987); sample of Witophen P (Dynamit Nobel - Lot no. 7777) (obtained in Germany).
Ref. F: Hagenmaier and Brunner (1987); sample of PCP produced by Rhone Poulenc (obtained in Germany).
Ref. G: Harrad et al. (1991); PCP-based herbicide formulation from NY State Dept. Environm. Conservation.
Ref. H: Pentachlorophenol Task Force (1997); average of monthly batch samples for the period Jan. 1987 to Aug. 1996.
Ref. I: Pentachlorophenol Task Force (1997); samples of "penta" manufactured in 1985, 1986, and 1988.
Ref. J: KMG-Bermuth, Inc. (1997); average of monthly batch samples for the period Feb. 1987 to Dec. 1996 (excluding the following months for which data were not available: Feb. 1993, Jan. 1992, Dec. 1991, Sept. 1991, Dec. 1988, and Sept. 1988).
Ref. K: Schecter et al. (1997); sample found stored in a barn in Vermont.

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Table 8-8. Historical CDD/CDF Concentrations in Pentachlorophenol-Na

Congener/Congener Group	PCP-Na (Ref. A) (1969) (μg/kg)	PCP-Na (Ref. B) (1973) (μg/kg)	PCP-Na (Ref. C) (1973) (μg/kg)	PCP-Na (Ref. D) (1987) (μg/kg)	PCP-Na (Ref. E) (1987) (μg/kg)	PCP-Na (Ref. F) (1992) (μg/kg)	PCP-Na (Ref. G) (1980s) (μg/kg)
2,3,7,8-TCDD	--	--	--	0.23	0.51	0.076	ND (1.4)
1,2,3,7,8-PeCDD	--	--	--	18.2	3.2	18.7	28.3
1,2,3,4,7,8-HxCDD	--	--	--	28.3	13.3	96	ND (6.1)
1,2,3,6,7,8-HxCDD	--	--	--	2,034	53.0	4,410	4,050
1,2,3,7,8,9-HxCDD	--	--	--	282	19.0	328	ND (1.4)
1,2,3,4,6,7,8-HpCDD	--	--	--	9,100	3,800	175,400	33,800
OCDD	3,600	--	--	41,600	32,400	879,000	81,000
2,3,7,8-TCDF	--	--	--	1.8	0.79	ND (1.0)	149
1,2,3,7,8-PeCDF	--	--	--	8.2	1.9	ND (4.0)	319
2,3,4,7,8-PeCDF	--	--	--	6.6	1.1	ND (4.0)	324
1,2,3,4,7,8-HxCDF	--	--	--	48	4.6	27.6	ND (2.8)
1,2,3,6,7,8-HxCDF	--	--	--	69	1.3	21.9	225
1,2,3,7,8,9-HxCDF	--	--	--	ND (1)	1.3	9.8	480
2,3,4,6,7,8-HxCDF	--	--	--	87	4.6	103	ND (385)
1,2,3,4,6,7,8-HpCDF	--	--	--	699	197	9,650	6,190
1,2,3,4,7,8,9-HpCDF	--	--	--	675	36	2,080	154
OCDF	--	--	--	37,200	4,250	114,600	36,000
Total 2,3,7,8-CDD*	--	--	--	53,063	35,289	1,059,253	118,878
Total 2,3,7,8-CDF*	--	--	--	38,795	4,499	126,492	43,841
Total TEQ*	--	--	--	452	79.5	3,374	1,201
Total TCDD	--	140	50	27	52	3.6	1.9
Total PeCDD	--	40	ND (30)	213	31	142.7	140
Total HxCDD	17,000	140	3,400	3,900	230	9,694	14,000
Total HpCDD	9,600	1,600	38,000	18,500	5,800	260,200	100,000
Total OCDD	3,600	4,000	110,000	41,600	32,400	879,000	81,000
Total TCDF	--	ND (20)	ND (20)	82	12	10.1	1200
Total PeCDF	--	60	40	137	27	88.4	6400
Total HxCDF	--	1,400	11,000	3,000	90	9,082.3	49,000
Total HpCDF	--	4,300	47,000	13,200	860	75,930	91,000
Total OCDF	--	4,300	26,500	37,200	4,250	114,600	36,000
Total CDD/CDF*	--	15,980	235,990	117,859	43,752	1,348,751	378,742

ND = Not detected; value in parentheses is the detection limit.
-- = Not reported.
* = Calculated assuming not detected values are zero.
μg/kg = micrograms per kilogram.

Sources:
Ref. A: Firestone et al. (1972); mean of two samples of PCP-Na obtained in the United States between 1967 and 1969.
Ref. B: Buser and Bosshardt (1976); mean of five samples of "low" CDD/CDF content PCP-Na received from Swiss commercial sources.
Ref. C: Buser and Bosshardt (1976); sample of "high" CDD/CDF content PCP-Na received from a Swiss commercial source.
Ref. D: Hagenmaier and Brunner (1987); sample of Dowicide-G purchased from Fluka; sample obtained in Germany.
Ref. E: Hagenmaier and Brunner (1987); sample of Preventol PN (Bayer AG); sample obtained in Germany.
Ref. F: Santl et al. (1994c); 1992 sample of PCP-Na from Prolabo, France.
Ref. G: Palmer et al. (1988); sample of a PCP-Na formulation collected from a closed sawmill in California in the late 1980s.

Table 8-9. Summary of Specific Dioxin-Containing Wastes That Must Comply with Land Disposal Retrictions

EPA Hazardous Waste Number	Waste Description	Land Disposal Restriction Effective Date	Regulated Waste Constitutent	Treatment Standard[a] (ppb)	
				Wastewaters (μg/L)	Nonwastewaters (μg/kg)
F020	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- or tetrachlorophenol, or of intermediates used to produce their pesticide derivatives. (This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.)	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
F021	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol, or of intermediates used to produce its derivatives.	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
F022	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions.	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
F023	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol.)	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
F026	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
F027	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.)	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1

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Table 8-9. Summary of Specific Dioxin-Containing Wastes That Must Comply with Land Disposal Retrictions (continued)

EPA Hazardous Waste Number	Waste Description	Land Disposal Restriction Effective Date	Regulated Waste Constitutent	Treatment Standard[a] (ppb)	
				Wastewaters (µg/L)	Nonwastewaters (µg/kg)
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Waste Nos. F020-F023, F026, and F027	November 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
F039	Leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous under subpart D of 40 CFR 268. (Leachate resulting from the disposal of one or more of the following EPA Hazardous Wastes and no other Hazardous Wastes retains its EPA Hazardous Waste Number(s): F020, F021, F022, F026, F027, and/or F028.)	August 8, 1990 (wastewater) May 8, 1992 (non-wastewater)	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
K043	2,6-dichlorophenol waste from the production of 2,4-D.	June 8, 1989	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1
K099	Untreated wastewater from the production of 2,4-D.	August 8, 1988	TCDDs	0.063	1
			PeCDDs	0.063	1
			HxCDDs	0.063	1
			TCDFs	0.063	1
			PeCDFs	0.035	1
			HxCDFs	0.063	1

[a] Treatment standards (i.e., maximum allowable concentration in waste extraact) are based on incineration to 99.9999 percent destruction and removal efficiency.
µg/L = micrograms per liter
µg/kg = micrograms per kilogram
Source: 40 CFR 268

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Table 8-10. CDD/CDF Concentrations in Chlorobenzenes

Congener/ Congener Group	MCBz (Ref. A) (μg/kg)	1,2-DCBz (for synthesis) (Ref. A) (μg/kg)	1,2,4-TrCBz ("pure") (Ref. B) (μg/kg)	Mixed TrCBz (47%) (Ref. A) (μg/kg)	1,2,4,5-TeCBz (99%) (Ref. A) (μg/kg)	PeCBz (98%) (Ref. A) (μg/kg)	HCBz (97%) (Ref. A) (μg/kg)	HCBz (Ref. B) (μg/kg)
Total TCDD	ND (0.02)	0.3	ND (0.1)	0.027	ND (0.02)	ND (0.02)	ND (20)	--
Total PeCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.140	0.2	ND (0.02)	ND (20)	--
Total HxCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.259	0.5	0.02	ND (20)	--
Total HpCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.253	0.8	0.02	470	--
Total OCDD	ND (0.02)	ND (0.02)	ND (0.1)	0.081	0.4	0.05	6,700	50 - 212,000
Total TCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.736	0.03	0.02	ND (20)	--
Total PeCDF	ND (0.02)	0.5	ND (0.1)	0.272	0.2	ND (0.02)	ND (20)	--
Total HxCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.091	0.8	ND (0.02)	ND (20)	--
Total HpCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.030	1.5	0.1	455	--
Total OCDF	ND (0.02)	ND (0.02)	ND (0.1)	0.016	2.1	0.1	2,830	350 - 58,300
Total CDD/CDF	--	--	--	1.904	--	--	--	--

ND = Nondetected; value in parentheses is the detection limit, if reported.
-- = Not reported.
μg/kg = micrograms per kilogram.

Ref. A: Hutzinger and Fiedler (1991a); unpublished results of tests performed at the Univ. of Bayreuth, Germany and by Dr. H. Hagenmaier.
Ref. B: Villanueva et al. (1974); range of three samples of commercially available HCBz.

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Table 8-11. Concentrations of CDD/CDF Congener Groups in Unused Commercial PCB Mixtures

PCB Mixture	Year of Manufacture	CDF Congener Group Concentrations (mg/kg)						CDD Congener Group Concentrations (mg/kg)						Reference Number
		TCDF	PeCDF	HxCDF	HpCDF	OCDF	Total CDF	TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total CDD	
Aroclor 1016	1972	ND	ND	ND	--	--	ND	--	--	--	--	--	--	a
Aroclor 1242	--	0.07	0.03	0.003	--	--	0.15	--	--	--	--	--	--	b, c
Aroclor 1242	--	2.3	2.2	ND	--	--	4.5	--	--	--	--	--	--	b, c
Aroclor 1242	--	0.25	0.7	0.81	--	--	1.9	--	--	--	--	--	--	b
Clophen A-30	--	6.377	2.402	0.805	0.108	0.016	9.708	0.0007	ND	0.001	0.006	0.031	0.039	e
Clophen A-30	--	0.713	0.137	0.005	0.001	ND	0.855	ND	ND	ND	0.005	0.025	0.030	d
Aroclor 1248	1969	0.5	1.2	0.3	--	--	2.0	--	--	--	--	--	--	b
Clophen A-40	--	1.289	0.771	0.144	0.020	0.011	2.235	ND	ND	ND	0.012	0.030	0.042	d
Kanechlor 400	--	--	--	--	--	--	20.0	--	--	--	--	--	--	b, c
Aroclor 1254	1969	0.1	0.2	1.4	--	--	1.7	--	--	--	--	--	--	a
Aroclor 1254	1970	0.2	0.4	0.9	--	--	1.5	--	--	--	--	--	--	a
Aroclor 1254	--	0.02	0.2	0.6	--	--	0.8	--	--	--	--	--	--	b, c
Aroclor 1254	--	0.05	0.1	0.02	--	--	0.2	--	--	--	--	--	--	b
Clophen A-50	--	5.402	2.154	2.214	0.479	0.069	10.318	ND	ND	ND	0.011	0.027	0.038	d
Aroclor 1260	--	0.3	1.0	1.10	1.35	--	3.8	--	--	--	--	--	--	b, c
Aroclor 1260	1969	0.1	0.4	0.5	--	--	1.0	--	--	--	--	--	--	a
Aroclor 1260	--	0.8	0.9	0.5	--	--	2.2	--	--	--	--	--	--	b, c
Aroclor 1260	--	0.2	0.3	0.3	--	--	0.8	--	--	--	--	--	--	a
Clophen A-60	--	15.786	11.655	4.456	1.517	0.639	34.052	0.0004	0.002	0.002	0.003	0.015	0.022	e
Clophen A-60	--	16.340	21.164	7.630	2.522	1.024	48.681	ND	ND	ND	0.014	0.032	0.046	d
Clophen A-60	--	1.4	5.0	2.2	--	--	8.6	--	--	--	--	--	--	a
Phenoclor DP-6	--	0.7	10.0	2.9	--	--	13.6	--	--	--	--	--	--	a
Clophen T-64	--	0.3	1.73	2.45	0.82	--	5.4	--	--	--	--	--	--	b
Prodelec 3010	--	1.08	0.35	0.07	--	--	2.0	--	--	--	--	--	--	b

ND = Nondetected
-- = Not reported
mg/kg = milligram per kilogram

References
a: Bowes et al. (1975a)
b: Erickson (1986)
c: ATSDR (1993)
d: Hagenmaier (1987)
e: Malisch (1994)

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Table 8-12. 2,3,7,8-Substituted Congener Concentrations in Unused PCB Mixtures

Congener	Congener Concentrations in Clophens (μg/kg)						Congener Concentrations in Aroclors (μg/kg)									
	A-30 (Ref. A)	A-30 (Ref. B)	A-40 (Ref. B)	A-50 (Ref. B)	A-60 (Ref. A)	A-60 (Ref. B)	1016 (Ref. C)	1242 (Ref. C)	1248 (Ref. D)	1254 (Ref. C)	1254 (Ref. C)	1254 (Ref. C)	1254 (Ref. D)	1260 (Ref. C)	1260 (Ref. C)	1260 (Ref. C)
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8-PeCDD	ND	ND	ND	ND	0.1	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,4,7,8-HxCDD	ND	ND	ND	ND	0.2	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDD	0.8	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8,9-HxCDD	ND	ND	ND	ND	ND	ND	--	--	--	--	--	--	--	--	--	--
1,2,3,4,6,7,8-HpCDD	5.6	2.4	4.4	5.3	2.5	6.8	--	--	--	--	--	--	--	--	--	--
OCDD	31.1	24.7	30.3	26.9	14.9	32.3	--	--	--	--	--	--	--	--	--	--
2,3,7,8-TCDF	1032.6	36.9	250.2	1005.7	2287.7	3077.2	0.10	40.1	330	28.0	20.9	55.8	110	63.5	6.88	29.0
1,2,3,7,8-PeCDF	135.8	14.9	52.7	155.2	465.2	1750.8	--	--	--	--	--	--	--	--	--	--
2,3,4,7,8-PeCDF	509.2	13.1	171.3	407.5	1921.9	2917	1.75	40.8	830	110	179	105	120	135	58.2	112
1,2,3,4,7,8-HxCDF	301.4	1.9	48.4	647.5	1604.2	2324.1	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDF	65.3	0.8	19.6	227.5	157.6	351.3	--	--	--	--	--	--	--	--	--	--
1,2,3,7,8,9-HxCDF	ND	ND	0.7	8.3	42.8	19	0.08	0.26	--	28.8	28.7	19.4	--	5.1	9.7	10.7
2,3,4,6,7,8-HxCDF	50.6	0.1	6.8	62.5	369.5	408.3	--	--	--	--	--	--	--	--	--	--
1,2,3,4,6,7,8-HpCDF	43.7	0.6	7	205.5	480.6	1126.1	--	--	--	--	--	--	--	--	--	--
1,2,3,4,7,8,9-HpCDF	22.5	ND	2.8	72.2	321.7	304	--	--	--	--	--	--	--	--	--	--
OCDF	15.7	ND	11.4	69.2	639.2	1024.3	--	--	--	--	--	--	--	--	--	--
Total TCDD	0.7	ND	ND	ND	0.4	ND	--	--	--	--	--	--	--	--	--	--
Total PeCDD	ND	ND	ND	ND	2.0	ND	--	--	--	--	--	--	--	--	--	--
Total HxCDD	1.2	ND	ND	ND	1.8	ND	--	--	--	--	--	--	--	--	--	--
Total HpCDD	5.6	5.4	11.6	11.0	3.0	13.5	--	--	--	--	--	--	--	--	--	--
Total OCDD	31.1	24.7	30.3	26.9	14.9	32.3	--	--	--	--	--	--	--	--	--	--
Total TCDF	6376.6	713	1289.4	5402.3	15785.7	16340	--	--	--	--	--	--	--	--	--	--
Total PeCDF	2402.4	136.5	770.8	2153.7	11654.6	21164	--	--	--	--	--	--	--	--	--	--
Total HxCDF	804.8	5.1	143.6	2213.8	4455.8	7630.2	--	--	--	--	--	--	--	--	--	--
Total HpCDF	108.3	0.8	19.5	478.8	1517.0	2522.3	--	--	--	--	--	--	--	--	--	--
Total OCDF	15.7	ND	11.4	69.2	639.2	1024.3	--	--	--	--	--	--	--	--	--	--
Total CDD/CDF*	9746.4	885.5	2276.6	10355.7	34074.4	48726.5	--	--	--	--	--	--	--	--	--	--
Total I-TEQ*	407.2	14.70	71.71	327.11	1439.2	1444.2	--	--	--	--	--	--	--	--	--	--

ND = Nondetected.
-- = Not reported.
* = Calculated asumming not detected values are zero.
μg/kg = micrograms per kilogram.

References:
A = Malisch (1994)
B = Hagenmaier (1987)
C = Brown et al. (1988)
D = Bowes (1975b)

Table 8-13. Reported CDD/CDF Concentrations in Wastes from PVC Manufacture

Congener/Congener Group	F024 Waste (μg/kg)	K019 Waste (μg/kg)	K020 Waste (μg/kg)
2,3,7,8-TCDD	0.37	260	0.06
1,2,3,7,8-PeCDD	0.14	890	0.05
1,2,3,4,7,8-HxCDD	0.30	260	0.08
1,2,3,6,7,8-HxCDD	0.14	330	0.06
1,2,3,7,8,9-HxCDD	0.11	620	0.07
1,2,3,4,6,7,8-HpCDD	4.20	920	0.89
OCDD	15.00	1,060	3.00
2,3,7,8-TCDF	0.91	680	0.44
1,2,3,7,8-PeCDF	9.5	975	1.80
2,3,4,7,8-PeCDF	1.6	1,050	0.58
1,2,3,4,7,8-HxCDF78	110	10,100	11.0
	24.0	9,760	2.4
1,2,3,6,7,8-HxCDF	9.5	21,800	1.3
1,2,3,7,8,9-HxCDF	3.1	930	0.89
2,3,4,6,7,8-HxCDF	250	13,400	38.0
1,2,3,4,6,7,8-HpCDF	51.0	1,340	6.0
1,2,3,4,7,8,9-HpCDF	390	43,500	650
OCDF			
Total 2,3,7,8-CDD	20.3	4,340	4.21
Total 2,3,7,8-CDF	849.6	103,535	712.4
Total TEQ	19.98	5,928	3.19
Total TCDD	3.1	1,230	1.9
Total PeCDD	3.6	3,540	1.7
Total HxCDD	1.3	3,950	NR
Total HpCDD	5.0	1,270	1.7
Total OCDD	15.0	1,060	3.0
Total TCDF	15.0	20,600	6.0
Total PeCDF	65.0	45,300	11.0
Total HxCDF	300	63,700	27.0
Total HpCDF	450	16,600	58.0
Total OCDF	390	43,500	650
Total CDD/CDF	1,248	200,750	760.3

NR = Congener group concentration reported in source is not consistent with reported congener concentrations.

μg/kg = micrograms per kilogram

Source: Stringer et al. (1995)

Table 8-14. CDD/CDF Measurements in Products and Treated Wastewater from U.S. PEDC/VCM/PVC Manufacturers

Congener and Congener Groups	Suspension and Mass PVC Resins			Dispersion PVC Resins			Ethylene Dichloride (EDC)			Treated Wastewater		
	No. Detects/ No. Samples	Range of Detected Conc. (ng/kg)		No. Detects/ No. Samples	Range of Detected Conc. (ng/kg)		No. Detects/ No. Samples	Range of Detected Conc. (ng/kg)		No. Detects/ No. Samples	Range of Detected Conc. (pg/L)	
		Min.	Max.		Min.	Max.		Min.	Max.		Min.	Max
2,3,7,8-TCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,7,8-PeCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,4,7,8-HxCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,6,7,8-HxCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,7,8,9-HxCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,4,6,7,8-HpCDD	1/22	nd	0.64	1/6	nd	0.8	0/5	nd	nd	3/10	nd	26
OCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	2/10	nd	260
2,3,7,8-TCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,7,8-PeCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
2,3,4,7,8-PeCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
1,2,3,4,7,8-HxCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	1/10	nd	5.8
1,2,3,6,7,8-HxCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	1/10	nd	3.8
1,2,3,7,8,9-HxCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
2,3,4,6,7,8-HxCDF	1/22	nd	0.37	0/6	nd	nd	0/5	nd	nd	2/10	nd	6.5
1,2,3,4,6,7,8-HpCDF	0/22	nd	nd	0/6	nd	nd	1/5	nd	1.1	4/10	nd	78
1,2,3,4,7,8,9-HpCDF	0/22	nd	nd	0/6	nd	nd	1/5	nd	0.40	3/10	nd	20
OCDF	0/22	nd	nd	2/6	nd	0.38	1/5	nd	11	0/10	nd	3.2
Mean TEQ (ND = zero)		0.002			0.001			0.0005			0.60	
Mean TEQ (ND = 1/2 DL)			0.65			0.35			0.21			4.5
Total TCDD	0/22	nd	nd	1/6	nd	0.24	0/5	nd	nd	0/10	nd	nd
Total PeCDD	0/22	nd	nd	1/6	nd	0.32	0/5	nd	nd	0/10	nd	nd
Total HxCDD	0/22	nd	nd	5/6	nd	0.97	0/5	nd	nd	0/10	nd	nd
Total HpCDD	1/22	nd	0.64	1/6	nd	1.3	0/5	nd	nd	3/10	nd	48
Total OCDD	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	2/10	nd	260
Total TCDF	0/22	nd	nd	0/6	nd	nd	0/5	nd	nd	0/10	nd	nd
Total PeCDF	0/22	nd	nd	1/6	nd	0.3	0/5	nd	nd	0/10	nd	nd
Total HxCDF	1/22	nd	0.37	0/6	nd	nd	0/5	nd	nd	2/10	nd	30
Total HpCDF	0/22	nd	nd	0/6	nd	nd	1/5	nd	2.02	3/10	nd	140
Total OCDF	0/22	nd	nd	2/6	nd	0.38	1/5	nd	11	5/10	nd	900

nd = not detected.
ng/kg = nanograms per kilogram
pg/L = picograms per liter
Source: The Vinyl Institute (1996)

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Table 8-15. CDD/CDF Concentrations in Dioxazine Dyes and Pigments (Canada)

Congener/Congener Group	Blue 106 (μg/kg)			Blue 108 (μg/kg)	Violet 23 (μg/kg)					
2,3,7,8-TCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8-PeCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,7,8-HxCDD	--	--	--	--	--	--	--	--	--	--
1,2,3,6,7,8-HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8,9-HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,6,7,8-HpCDD	31	6	9	ND (0.3)	9	1	16	10	2	4
OCDD	41,953	28,523	18,066	23	7,180	806	11,022	7,929	1,627	1,420
2,3,7,8-TCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,7,8-PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.5	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
2,3,4,7,8-PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,7,8-HxCDF	12	2	2	ND (0.3)	76	4	39	31	9	7
1,2,3,6,7,8-HxCDF	*	*	*	*	*	*	*	*	*	*
1,2,3,7,8,9-HxCDF	--	--	--	--	--	--	--	--	--	--
2,3,4,6,7,8-HxCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
1,2,3,4,6,7,8-HpCDF	50	10	14	9	13	10	11	4	1	12
1,2,3,4,7,8,9-HpCDF	--	--	--	--	--	--	--	--	--	--
OCDF	12,463	1,447	1,006	11	941	125	3,749	1,556	147	425
Total 2,3,7,8-CDD	41,984	28,529	18,075	23	7,189	807	11,038	7,939	1,629	1,424
Total 2,3,7,8-CDF	12,525	1,459	1,022	20	1,031	139	3,799	1,591	157	444
Total TEQ **	56.4	30.2	19.5	0.1	16.0	1.4	18.9	12.7	2.7	2.7
Total TCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total PeCDD	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total HxCDD	ND (0.3)	ND (0.3)	ND (0.3)	1	21	2	7	ND (0.3)	ND (0.3)	1
Total HpCDD	34	8	12	ND (0.3)	30	5	36	11	2	6
Total OCDD	41,953	28,523	18,066	23	7,180	806	11,022	7,929	1,627	1,420
Total TCDF	ND (0.3)	0.3	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.4	ND (0.3)
Total PeCDF	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	0.5	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)	ND (0.3)
Total HxCDF	12	2	2	ND (0.3)	76	5	39	31	9	7
Total HpCDF	71	32	26	12	26	14	29	13	2	21
Total OCDF	12,463	1,447	1,006	11	941	125	3,749	1,556	147	425
Total CDD/CDF**	54,533	30,012	19,112	47	8,275	957	14,882	9,540	1,787	1,880

ND = Nondetected; value in parenthesis is the detection limit.
-- = Not reported.
* = Results listed for 1,2,3,4,7,8-HxCDF include concentrations for 1,2,3,6,7,8-HxCDF.
** = Nondetected values were assumed to be zero for calculation of Total TEQs and Total CDD/CDF.
μg/kg = micrograms per kilogram
Source: Williams et al. (1992)

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Table 8-16. CDD/CDF Concentrations in Printing Inks (Germany)

Congener/Congener Group	Rotogravure (2-color) (ng/kg)	Rotogravure (4-color) (ng/kg)	Offset (4-color) (ng/kg)	Offset (4-color) (ng/kg)
2,3,7,8-TCDD	ND (1)	ND (1.5)	ND (2)	ND (2)
1,2,3,7,8-PeCDD	8	ND (4)	15	6
1,2,3,4,7,8-HxCDD	19	ND (5)	16	11
1,2,3,6,7,8-HxCDD	325	310	82	21
1,2,3,7,8,9-HxCDD	155	105	42	14
1,2,3,4,6,7,8-HpCDD	2,770	1,630	540	240
OCDD	5,810	2,350	890	230
2,3,7,8-TCDF	2.5	14	7	7
1,2,3,7,8-PeCDF	ND (2)	ND (4)	ND (4)	ND (3)
2,3,4,7,8-PeCDF	ND (2)	ND (4)	ND (4)	ND (3)
1,2,3,4,7,8-HxCDF	4	7	27	35
1,2,3,6,7,8-HxCDF	ND (3)	ND (5)	ND (5)	ND (5)
1,2,3,7,8,9-HxCDF	ND (3)	ND (5)	ND (5)	ND (5)
2,3,4,6,7,8-HxCDF	ND (3)	ND (5)	ND (5)	ND (5)
1,2,3,4,6,7,8-HpCDF	40	14	315	42
1,2,3,4,7,8,9-HpCDF	ND (4)	ND (7)	11	ND (6)
OCDF	129	ND (10)	960	165
Total 2,3,7,8-CDD	9,087	4,395	1,585	522
Total 2,3,7,8-CDF	175.5	35	1320	249
Total TEQ *	90.1	66.2	38.2	17.5
Total TCDD	4	ND (2)	77	38
Total PeCDD	58	145	35	25
Total HxCDD	2,679	2,485	660	246
Total HpCDD	5,630	3,460	1,100	445
Total OCDD	5,810	2,350	890	230
Total TCDF	5.5	28	90	35
Total PeCDF	13	ND (4)	340	110
Total HxCDF	29	45	95	94
Total HpCDF	64	14	566	63
Total OCDF	129	ND (10)	960	165
Total CDD/CDF	14,422	8,527	4,813	1,451

ND = Nondetected; value in parenthesis is the detection limit.
-- = Not reported.
* = Calculation of TEQ values assumes nondetected congeners are present at half of their detection limits.
ng/kg = nanograms per kilogram.

Source: Santl et al. (1994c).

Table 8-17. Chemicals Requiring TSCA Section 4 Testing Under the Dioxin/Furan Rule

Currently Manufactured or Imported as of June 5, 1987[a]	
CAS No.	Chemical Name
79-94-7	Tetrabromobisphenol-A
118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione
118-79-6	2,4,6-Tribromophenol
120-83-2	2,4-Dichlorophenol
1163-19-5	Decabromodiphenyloxide
4162-45-2	Tetrabromobisphenol-A-bisethoxylate
21850-44-2	[a]Tetrabromobisphenol-A-bis-2,3-dibromopropylether
25327-89-3	Allyl ether of tetrabromobisphenol-A
32534-81-9	Pentabromodiphenyloxide
32536-52-0	Octabromodiphenyloxide
37853-59-1	1,2-Bis(tribromophenoxy)-ethane
55205-38-4	[a]Tetrabromobisphenol-A-diacrylate
Not Currently Manufactured or Imported as of June 5, 1987[b]	
CAS No.	Chemical Name
79-95-8	Tetrachlorobisphenol-A
87-10-5	3,4',5-Tribromosalicylanide
87-65-0	2,6-Dichlorophenol
95-77-2	3,4-Dichlorophenol
95-95-4	2,4,5-Trichlorophenol
99-28-5	2,6-Dibromo-4-nitrophenol
120-36-5	2[2,4-(Dichlorophenoxy)]-propanoic acid
320-72-9	3,5-Dichlorosalicyclic acid
488-47-1	Tetrabromocatechol
576-24-9	2,3-Dichlorophenol
583-78-8	2,5-Dichlorophenol
608-71-9	Pentabromophenol
615-58-7	2,4-Dibromophenol
933-75-5	2,3,6-Trichlorophenol
1940-42-7	4-Bromo-2,5-dichlorophenol
2577-72-2	3,5-Dibromosalicylanide
3772-94-9	Pentachlorophenyl laurate
37853-61-5	Bismethylether of tetrabromobisphenol-A
-	Alkylamine tetrachlorophenate
-	Tetrabromobisphenol-B

a Tetrabromobisphenol-A-bis-2,3-dibromopropylether and tetrabromobisphenol-A-diacrylate are no longer manufactured in or imported into the United States (Cash, 1993).

b As of August 5, 1995, neither manufacture nor importation of any of these chemicals had resumed in the United States (Holderman, 1995).

Table 8-18. Congeners and Limits of Quantitation (LOQ) for Which Quantitation is Required Under the Dioxin/Furan Test Rule and Pesticide Data Call-In

Chlorinated Dioxins and Furans	Brominated Dioxins and Furans	LOQ (μg/kg)
2,3,7,8-TCDD	2,3,7,8-TBDD	0.1
1,2,3,7,8-PeCDD	1,2,3,7,8-PeBDD	0.5
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxBDD	2.5
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxBDD	2.5
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxBDD	2.5
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpBDD	100
2,3,7,8-TCDF	2,3,7,8-TBDF	1
1,2,3,7,8-PeCDF	1,2,3,7,8-PeBDF	5
2,3,4,7,8-PeCDF	2,3,4,7,8-PeBDF	5
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxBDF	25
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxBDF	25
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxBDF	25
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxBDF	25
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpBDF	1,000
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpBDF	1,000

μg/kg = microgram per kilogram.

Table 8-19. Precursor Chemicals Subject to Reporting Requirements Under TSCA Section 8(a)

CAS No.	Chemical Name
85-22-3	Pentabromoethylbenzene
87-61-6	1,2,3-Trichlorobenzene
87-84-3	1,2,3,4,5-Pentabromo-6-chlorocyclohexane
89-61-2	1,4-Dichloro-2-nitrobenzene
89-64-5	4-Chloro-2-nitrophenol
89-69-0	2,4,5-Trichloronitrobenzene
92-04-6	2-Chloro-4-phenylphenol
97-74-6	4-Chloro-o-toloxy acetic acid
94-81-5	4-(2-Methyl-4-chlorophenoxy) butyric acid
95-50-1	o-Dichlorobenzene
95-56-7	o-Bromophenol
95-57-8	o-Chlorophenol
95-88-5	4-Chlororesorcinol
95-94-3	1,2,4,5-Tetrachlorobenzene
95-50-7	5-Chloro-2,4-dimethoxyaniline
99-30-9	2,6-Dichloro-4-nitroaniline
99-54-7	1,2-Dichloro-4-nitrobenzene
106-37-6	Dibromobenzene
106-46-7	p-Dichlorobenzene
108-70-3	1,3,5-Trichlorobenzene
108-86-1	Bromobenzene
108-90-7	Chlorobenzene
117-18-0	1,2,4,5-Tetrachloro-3-nitrobenzene
120-82-1	1,2,4-Trichlorobenzene
348-51-6	o-Chlorofluorobenzene
350-30-1	3-Chloro-4-fluoronitrobenzene
615-67-8	Chlorohydroquinone
626-39-1	1,3,5-Tribromobenzene
827-94-1	2,6-Dibromo-4-nitroaniline

Table 8-20. Results of Analytical Testing for Dioxins and Furans in the Chemicals Tested To-Date Under Section 4 of the Dioxin/Furan Test Rule

CAS Number	Chemical Name	No. of Chemical Companies That Submitted Data	No. of Positive Studies	Congeners Detected (detection range: μg/kg)
79-94-7	Tetrabromobisphenol-A	3	0	ND[a]
118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione (chloranil)	4	4	See Table 8-21
118-79-6	2,4,6-Tribromophenol	1	0	ND[a]
120-83-2	2,4-Dichlorophenol	1	0	ND[a]
1163-19-5	Decabromodiphenyl oxide	3	3	2,3,7,8-PeBDD (ND-0.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND-0.5) 1,2,3,7,8,9-HxBDD (ND-0.76) 1,2,3,7,8-PeBDF (ND-0.7) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-0.8) 1,2,3,4,6,7,8-HpBDF (17-186)
25327-89-3	Allyl ether of tetrabromobisphenol-A	1	0	ND[a]
32536-52-0	Octabromodiphenyl oxide	3	3	2,3,7,8-TBDD (ND-0.71) 1,2,3,7,8-PeBDD (ND-0.1) 2,3,7,8-TBDF (ND-12.6) 1,2,3,7,8-PeBDF (ND-6.3) 2,3,4,7,8-PeBDF (ND-83.1) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-67.8) 1,2,3,7,8,9-HxBDF (ND-56.0) 1,2,3,4,6,7,8-HpBDF (ND-330)
378-53-59-1	1,2-Bis(tribromo-phenoxy)-ethane	1	1	2,3,7,8-TBDF (ND-0.04) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (ND-0.03) 1,2,3,4,6,7,8-HpBDF (ND-0.33)
32534-81-9	Pentabromodiphenyl oxide	2	2	1,2,3,7,8-PeBDD (ND-5.9) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND-6.8) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD (ND-6.8) 1,2,3,7,8,9-HxBDD (ND-0.02) 2,3,7,8-TBDF(ND-3.1) 1,2,3,7,8-PeBDF (0.7-10.2) 2,3,4,7,8-PeBDF (0.1-2.9) 1,2,3,4,7,8/1,2,3,6,7,8-HxBDF (15.6-61.2) 1,2,3,4,6,7,8-HpBDF (0.7-3.0)
4162-45-2	Tetrabromobisphenol-A-bisethoxylate	1	0	ND[a]

[a] No 2,3,7,8-substituted dioxins and furans detected above the Test Rule target limits of quantitation (LOQ). (See Table 8-18.)
[b] Third study is currently undergoing EPA review.
[c] Study is currently undergoing EPA review.
μg/kg = micrograms per kilogram
Source: Holderman and Cramer (1995).

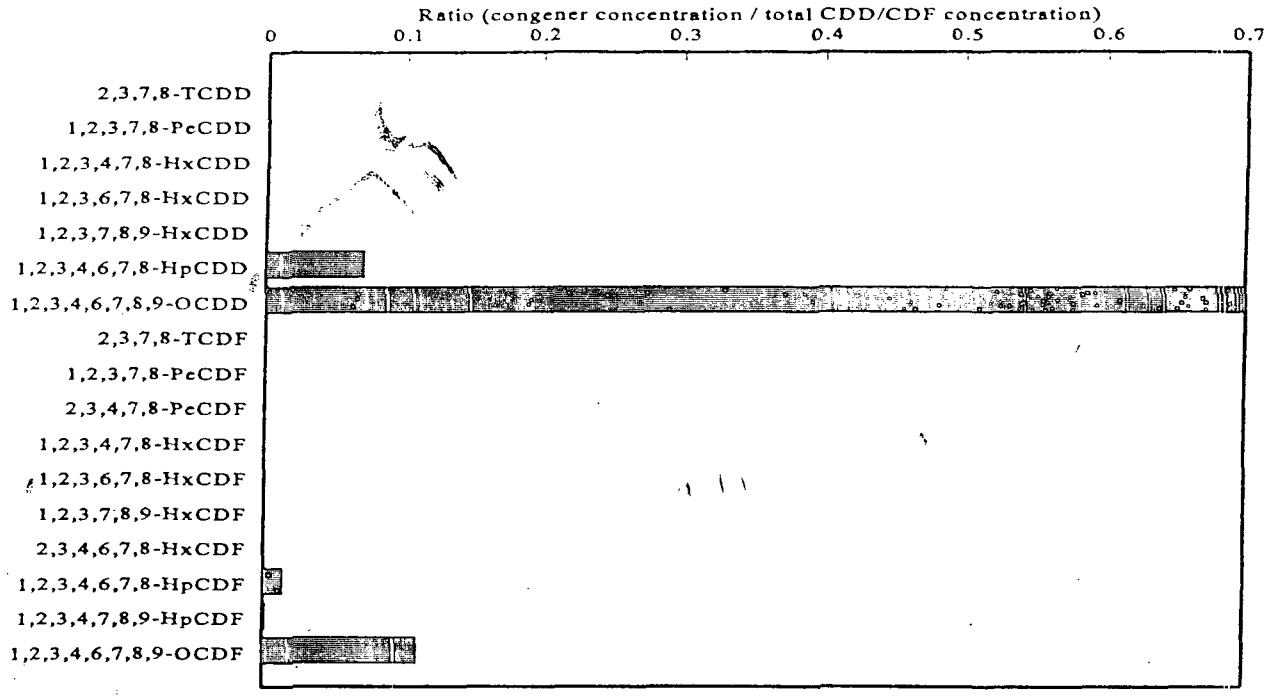
Table 8-21. CDDs and CDFs in Chloranil and Carbazole Violet Samples Analyzed Pursuant to the EPA Dioxin/Furan Test Rule

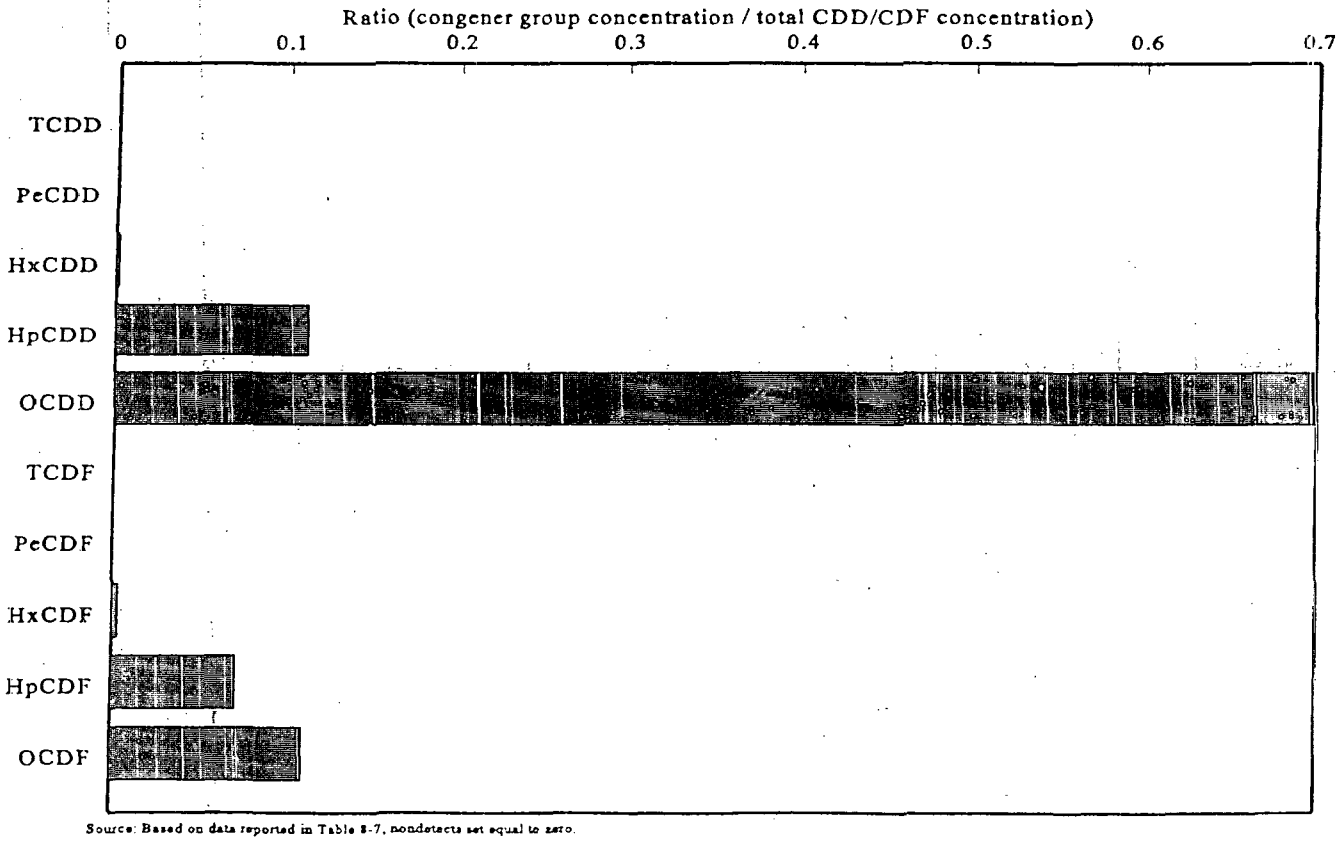
Congener	Concentration (μg/kg) in Chloranil				Concentration (μg/kg) in Carbazole Violet
	Importer 1	Importer 2	Importer 3	Importer 4	
2,3,7,8-TCDD	nd (1)	nd (1)	nd (2)	nd (2)	nd (0.8)
1,2,3,7,8-PeCDD	nd (2)	nd (2)	nd (5)	nd (6)	nd (0.5)
1,2,3,4,7,8-HxCDD	nd (3)	nd (10)	nd (5)	nd (3)	nd (1.2)
1,2,3,6,7,8-HxCDD	nd (3)	75	nd (5)	6	nd (1.2)
1,2,3,7,8,9-HxCDD	nd (1)	48	nd (5)	9	nd (1.2)
1,2,3,4,6,7,8-HpCDD	110	8,200	390	2,300	28
OCDD	240,000	180,000	760,000	71,000	1,600
2,3,7,8-TCDF	nd (1)	nd (2)	nd (1)	nd (2)	nd (1.6)
1,2,3,7,8-PeCDF	nd (1)	nd (1)	nd (3)	nd (5)	nd (0.9)
2,3,4,7,8-PeCDF	nd (1)	nd (1)	nd (3)	nd (5)	nd (0.9)
1,2,3,4,7,8-HxCDF	35	nd (860)	nd (4)	5,600	nd (20)
1,2,3,6,7,8-HxCDF	nd (5)	nd (860)	nd (4)	nd (600)	nd (20)
1,2,3,7,8,9-HxCDF	6	nd (680)	nd (4)	nd (600)	nd (20)
2,3,4,6,7,8-HxCDF	nd (5)	nd (680)	nd (4)	nd (600)	nd (20)
1,2,3,4,6,7,8-HpCDF	33	240,000	36	230,000	15,000
1,2,3,4,7,8,9-HpCDF	nd (15)	nd (100)	nd (15)	nd (400)	nd (20)
OCDF	18,000	200,000	50,000	110,000	59,000
TOTAL TEQ*	263	2,874	814	3,065	211

Source: Remmers et al. (1992).

nd = nondetected; minimum limit of detection shown in parenthesis.
μg/kg = micrograms per kilogram.

* = Calculated assuming not detected values are zero.





Source: Based on data reported in Table 8-7, nondetects set equal to zero.

Figure 8-4. Congener and Congener Group Profiles for Technical PCP

Table 8-22. Status of First Pesticide Data-Call-In: Pesticides Suspected of Having the Potential to Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
000014	Dichlorodifluoromethane	75-71-8	Yes	--
008706	O-(4-Bromo-2,5-dichlorophenyl) O,O-dimethyl phosphorothioate	2104-96-3	Yes	--
009105	Dimethylamine 2,3,5-triiodobenzoate	17601-49-9	Yes	--
012001	Neburon	555-37-3	Yes	--
012101	Crufomate	299-86-5	Yes	--
019201	MCPB, 4-butyric acid [4-(2-Methyl-4-chlorophenoxy)butyric acid]	94-81-5	No	Yes
019202	MCPB, Na salt [Sodium 4-(2-methyl-4-chlorophenoxy)butyrate]	6062-26-6	No	No
019401	4-Chlorophenoxyacetic acid	122-88-3	No	Yes
025501	Chloroxuron	1982-47-4	Yes	--
027401	Dichlobenil	1194-65-6	No	Yes
028201	Propanil [3',4'-Dichloropropionanilide]	709-98-8	No	No
028601	Dichlofenthion [O-(2,4-Dichlorophenyl) O,O-diethyl phosphorothioate)]	97-17-6	Yes	--
029201	DDT [Dichloro diphenyl trichloroethane]	50-29-3	Yes	--
029601	Dichlone [2,3-dichloro-1,4-naphthoquinone]	117-80-6	Yes	--
029902	Ammonium chloramben [3-amino-2,5-dichlorobenzoic acid]	1076-46-6	Yes	--
029906	Sodium chloramben [3-amino-2,5-dichlorobenzoic acid]	1954-81-0	Yes	--
030602	Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate	136-78-7	Yes	--
031301	DCNA [2,6-Dichloro-4-nitroaniline]	99-30-9	No	Yes
031503	Potassium 2-(2-methyl-4-chlorophenoxy)propionate	1929-86-8	Yes	--
031516	MCCP, DEA Salt [Diethanolamine 2-(2-methyl-4-chlorophenoxy)propionate]	1432-14-0	Yes	--
031563	MCPP, IOE [Isooctyl 2-(2-methyl-4-chlorophenoxy)propionate]	28473-03-2	No	No
034502	Dicapthon [O-(2-chloro-4-nitrophenyl) O,O-dimethyl phosphorothioate]	2463-84-5	Yes	--
035502	Monuron trichloroacetate [3-(4-chlorophenyl)-1,1-dimethylurea trichloroacetate]	140-41-0	Yes	--
035505	Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]	330-54-1	No	No

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Table 8-22. Status of First Pesticide Data-Call-In: Pesticides Suspected of Having the Potential to Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation (continued)

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
035506	Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea]	330-55-2	No	No
035901	Metobromuron [3-(p-bromophenyl)-1-methoxy-1-methylurea]	3060-89-7	Yes	--
053501	Methyl parathion [O,O-Dimethyl O-p-nitrophenyl phosphorothioate]	298-00-0	No	No
055001	Dichlorophene [Sodium 2,2'-methylenebis(4-chlorophenate)]	97-23-4	Yes	--
055005	Dichlorophene, sodium salt [Sodium 2,2'-methylenebis(4-chlorophenate)]	10254-48-5	Yes	--
055201	1,2,4,5-Tetrachloro-3-nitrobenzene	117-18-0	Yes	
057501	Ethyl Parathion [O,O-diethyl O-p-nitrophenyl phosphorothioate]	56-38-2	No	No
058102	Carbophenothion [S-(((p-chlorophenyl)thio)methyl) O,O-diethyl phosphorodithioate]	786-19-6	Yes	--
058301	Ronnel [O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate]	229-84-3	Yes	--
058802	Mitin FF [Sodium 5-chloro-2-(4-chloro-2-(3-(3,4-dichlorophenyl)ureido)phenoxy) benzenesulfonate]	3567-25-7	No	No
059401	Orthodichlorobenzene	95-50-1	Yes	--
061501	Paradichlorobenzene	106-46-7	No	No
062201	Chlorophene [2-Benzyl-4-chlorophenol]	120-32-1	No	No
062202	Potassium 2-benzyl-4-chlorophenate	35471-49-9	No	In review
062203	Sodium 2-benzyl-4-chlorophenate	3184-65-4	No	In review
062204	2-Chlorophenol	95-57-8	Yes	--
062206	2-Chloro-4-phenylphenol	92-04-6	Yes	--
062207	Potassium 2-chloro-4-phenylphenate	18128-16-0	Yes	--
062208	4-Chloro-2-phenylphenol	not available	Yes	--
062209	4-Chloro-2-phenylphenol, potassium salt	53404-21-0	Yes	--
062210	6-Chloro-2-phenylphenol	85-97-2	Yes	--
062211	6-Chloro-2-phenylphenol, potassium salt	18128-17-1	Yes	--
062212	4-Chloro-2-phenylphenol, sodium salt	10605-10-4	Yes	--
062213	6-Chloro-2-phenylphenol, sodium salt	10605-11-5	Yes	--

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Table 8-22. Status of First Pesticide Data-Call-In: Pesticides Suspected of Having the Potential to Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation (continued)

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
062214	4 and 6-Chloro-2-phenylphenol, diethanolamine salt	53537-63-6	Yes	--
062215	2-Chloro-4-phenylphenol, sodium salt	31366-97-9	Yes	--
064202	4-Chloro-2-cyclopentylphenol	13347-42-7	Yes	--
064208	Fentichlor [2,2'-Thiobis(4-chloro-6-methylphenol)]	4418-66-0	Yes	--
064209	Fentichlor [2,2'-Thiobis(4-chlorophenol)]	97-24-5	Yes	--
064214	4-Chloro-2-cyclopentylphenol, potassium salt of	35471-38-6	Yes	--
064218	4-Chloro-2-cyclopentylphenol, sodium salt	53404-20-9	Yes	-
067707	Chlorophacinone	3691-35-8	No	No
069105	ADBAC [Alkyl* dimethyl benzyl ammonium chloride *(50% C14, 40% C12, 10% C16)]	68424-85-1	No	No
069144	ADBAC [Alkyl* dimethyl 3,4-dichlorobenzyl ammonium chloride *(61% C12, 23% C14, 11% C16, 5% C18)]	not available	No	No
077401	Niclosamide [2-Aminoethanol salt of 2',5-dichloro-4'-nitrosalicylanilide]	1420-04-8	No	No
077406	5-Chlorosalicylanilide	4638-48-6	Yes	--
078780	2-Methyl-4-isothiazolin-3-one	not available	Yes	--
079202	Tetradifon [4-chlorophenyl 2,4,5-trichlorophenyl sulfone]	116-29-0	Yes	--
079301	Chloranil [tetrachloro-p-benzoquinone]	118-75-2	Yes	--
080403	6-Chlorothymol	89-68-9	Yes	--
080811	Anilazine [2,4-Dichloro-6-(o-chloroanilino)-s-triazine]	101-05-3	Yes	--
081901	Chlorothalonil [tetrachloroisophthalonitrile]	1897-45-6	No	Yes
082602	Sodium 2,3,6-Trichlorophenylacetate	2439-00-1	Yes	--
084101	Chlorfenvinphos	470-90-6	Yes	--
084901	O-(2-Chloro-1-(2,5-dichlorophenyl)vinyl) O,O-diethyl phosphorothioate	1757-18-2	Yes	--
086801	PCMX [4-Chloro-3,5-xylenol]	88-04-0	No	No
097003	Piperalin [3-(2-Methylpiperidino)propyl 3,4-dichlorobenzoate]	3478-94-2	No	No

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Table 8-22. Status of First Pesticide Data-Call-In: Pesticides Suspected of Having the Potential to Become Contaminated with Dioxins if Synthesized under Conditions Favoring Dioxin Formation (continued)

Shaughnessey Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
100601	Fenamiphos	not available	No	No
101001	p-Chlorophenyl diiodomethyl sulfone	20018-12-6	Yes	--
101101	Metribuzin	21087-64-9	No	No
104301	Bifenox [methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate]	42576-02-3	Yes	--
106001	Methazole [2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione]	20354-26-1	Yes	--
108201	Diflubenzuron [N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide]	35367-38-5	No	Yes
109001	Oxadiazon [2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)- delta 2 -1,3,4- oxadiazoline-5-one]	19666-30-9	No	Yes
109301	Fenvalerate	51630-58-1	No	In review
109302	Fluvalinate [N-2-Chloro-4-trifluoromethyl)phenyl-DL-valine (+-)-cyano(3-phenoxy- phenyl)methyl ester]	69409-94-5	No	No
109801	Iprodione [3-(3,5-Dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide (9CA)]	36734-19-7	No	No
109901	Triadimefon [1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone]	43121-43-3	No	No
110902	Diclofop - methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propanoate]	51338-27-3	No	Yes
111401	Profenofos [O-(4-Bromo-2-chlorophenyl)-O-ethyl S-propyl phosphorothioate]	41198-08-7	No	In review
111601	Oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene]	42874-03-3	No	In review
111901	Imazalil [1-(2-(2,4-Dichlorophenyl)-2-(2-propenyloxy)ethyl)-1H-imidazole]	35554-44-0	No	No
112802	Bromothalin [N-Methyl-2,4-dinitro-n-(2,4,6-tribromophenyl)-6-(trifuloromethyl)benzenamine]	63333-35-7	No	No
113201	Vinclozolin [3-(3,5-Dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione (9CA)]	50471-44-8	No	No
119001	Fenridazon [Potassium 1-(p-chlorophenyl)-1,4-dihydro-6-methyl-4-oxo- pyridazine- 3-carboxylate]	83588-43-6	No	In review
123901	Tridiphane [2-(3,5-Dichlorophenyl)-2-(2,2,2-trichloroethyl) oxirane]	58138-08-2	No	No
125601	Paclobutrazol	76738-62-0	No	No
128838	Linalool	78-70-6	No	In review
206600	Fenarimol [a-(2-chlorophenyl)-a-(4-chlorophenyl)-5-pyrimidinemethanol]	60168-88-9	No	No

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Table 8-23. Status of Second Pesticide Data-Call-In: Pesticides Suspected of Being Contaminated with Dioxins

Shaughnessy Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
029801	Dicamba [3,6-dichloro-o-anisic acid]	1918-00-9	No	Yes
029802	Dicamba dimethylamine [3,6-dichloro-o-anisic acid]	2300-66-5	No	Yes
029803	Diethanolamine dicamba [3,6-dichloro-2-anisic acid]	25059-78-3	Yes	--
030001	2,4-Dichlorophenoxyacetic acid	94-75-7	No	Yes
030002	Lithium 2,4-dichlorophenoxyacetate	3766-27-6	No	No
030003	Potassium 2,4-dichlorophenoxyacetate	14214-89-2	Yes	--
030004	Sodium 2,4-dichlorophenoxyacetate	2702-72-9	No	No
030005	Ammonium 2,4-dichlorophenoxyacetate	2307-55-3	Yes	--
030010	Alkanol* amine 2,4-dichlorophenoxyacetate *(salts of the ethanol and ispropanol series)	not available	Yes	--
030011	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C12)	2212-54-6	Yes	--
030013	Alkyl* amine 2,4-dichlorophenoxyacetate *(100% C14)	28685-18-9	Yes	--
030014	Alkyl* amine 2,4-dichlorophenoxyacetate *(as in fatty acids of tall oil)	not available	Yes	--
030016	Diethanolamine 2,4-dichlorophenoxyacetate	5742-19-8	No	No
030017	Diethylamine 2,4-dichlorophenoxyacetate	20940-37-8	Yes	--
030019	Dimethylamine 2,4-dichlorophenoxyacetate	2008-39-1	No	No
030020	N,N-Dimethyloleylamine 2,4-dichlorophenoxyacetate	53535-36-7	Yes	--
030021	Ethanolamine 2,4-dichlorophenoxyacetate	3599-58-4	Yes	--
030023	Heptylamine 2,4-dichlorophenoxyacetate	37102-63-9	Yes	--
030024	Isopropanolamine 2,4-dichlorophenoxyacetate	6365-72-6	Yes	--
030025	Isopropylamine 2,4-dichlorophenoxyacetate	5742-17-6	No	No
030028	Morpholine 2,4-dichlorophenoxyacetate	6365-73-7	Yes	--
030029	N-Oleyl-1,3-propylenediamine 2,4-dichlorophenoxyacetate	2212-59-1	Yes	--
030030	Octylamine 2,4-dichlorophenoxyacetate	2212-53-5	Yes	--
030033	Triethanolamine 2,4-dichlorophenoxyacetate	2569-01-9	Yes	--
030034	Triethylamine 2,4-dichlorophenoxyacetate	2646-78-8	No	No

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Table 8-23. Status of Second Pesticide Data-Call-In: Pesticides Suspected of Being Contaminated with Dioxins (continued)

Shaughnessy Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
030035	Triisopropanolamine 2,4-dichlorophenoxyacetate	32341-80-3	No	No
030039	N,N-Dimethyl oleyl-linoleyl amine 2,4-dichlorophenoxyacetate	55256-32-1	Yes	--
030052	Butoxyethoxypropyl 2,4-dichlorophenoxyacetate	1928-57-0	Yes	--
030053	Butoxyethyl 2,4-dichlorophenoxyacetate	1929-73-3	No	No
030055	Butoxypropyl 2,4-dichlorophenoxyacetate	1928-45-6	Yes	--
030056	Butyl 2,4-dichlorophenoxyacetate	94-80-4	Yes	--
030062	Isobutyl 2,4-dichlorophenoxyacetate	1713-15-1	Yes	--
030063	Isooctyl(2-ethylhexyl) 2,4-dichlorophenoxyacetate	1928-43-4	No	Yes
030064	Isooctyl(2-ethyl-4-methylpentyl) 2,4-dichlorophenoxyacetate	25168-26-7	Yes	--
030065	Isooctyl(2-octyl) 2,4-dichlorophenoxyacetate	1917-97-1	Yes	--
030066	Isopropyl 2,4-dichlorophenoxyacetate	94-11-1	No	No
030072	Propylene glycol butyl ether 2,4-dichlorophenoxyacetate	1320-18-9	Yes	--
030801	4-(2,4-Dichlorophenoxy)butyric acid	94-82-6	No	Yes
030804	Sodium 4-(2,4-dichlorophenoxy)butyrate	10433-59-7	No	No
030819	Dimethylamine 4-(2,4-dichlorophenoxy)butyrate	2758-42-1	No	No
030853	Butoxyethanol 4-(2,4-dichlorophenoxy)butyrate	32357-46-3	Yes	--
030856	Butyl 4-(2,4-dichlorophenoxy)butyrate	6753-24-8	Yes	--
030863	Isooctyl 4-(2,4-dichlorophenoxy)butyrate	1320-15-6	Yes	--
031401	2-(2,4-Dichlorophenoxy)propionic acid	120-36-5	No	Yes
031419	Dimethylamine 2-(2,4-dichlorophenoxy)propionate	53404-32-3	No	No
031453	Butoxyethyl 2-(2,4-dichlorophenoxy)propionate	53404-31-2	No	No
031463	Isooctyl 2-(2,4-dichlorophenoxy)propionate	28631-35-8	No	No
031501	MCPP acid [2-(2-Methyl-4-chlorophenoxy)propionic acid]	7085-19-0	No	Yes

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Table 8-23. Status of Second Pesticide Data-Call-In: Pesticides Suspected of Being Contaminated with Dioxins (continued)

Shaughnessy Code	Pesticide [Active Ingredient]	CAS Number	Support Withdrawn	Testing Required
031519	MCPP, DMA [Dimethylamine 2-(2-methyl-4-chlorophenoxy)propionate]	32351-70-5	No	No
035301	Bromoxynil [3,5-dibromo-4-hydroxybenzonitrile]	1689-84-5	No	Yes
044901	Hexachlorophene [2,2'-Methylenebis(3,4,6-trichlorophenol)]	70-30-4	Yes	--
044902	Hexachlorophene, Na salt [Monosodium 2,2'-methylenebis(3,4,6-trichlorophenate)]	5736-15-2	Yes	--
044904	Hexachlorophene, K salt [Potassium 2,2'-methylenebis(3,4,6-trichlorophenate)]	67923-62-0	Yes	--
054901	Irgasan [5-Chloro-2-(2,4-dichlorophenoxy)phenol]	3380-34-5	No	Yes
063004	Tetrachlorophenols	25167-83-3	Yes	--
063005	Tetrachlorophenols, sodium salt	25567-55-9	Yes	--
063006	Tetrachlorophenols, alkyl* amine salt*(as in fatty acids of coconut oil)	not available	Yes	--
063007	Tetrachlorophenols, potassium salt	53535-27-6	Yes	--
064203	Bithionolate sodium [Disodium 2,2'-thiobis(4,6-dichlorophenate)]	6385-58-6	Yes	--
064212	Phenachlor [2,4,6-Trichlorophenol]	88-06-2	Yes	--
064219	Potassium 2,4,6-trichlorophenate	2591-21-1	Yes	--
064220	2,4,6-Trichlorophenol, sodium salt	3784-03-0	Yes	--
064501	Phenothiazine	92-84-2	Yes	--
078701	Dacthal-DCPA [Dimethyl tetrachloroterephthalate]	1861-32-1	No	Yes
079401	Endosulfan [hexachlorohexahydromethano-2,4,3-benzodioxathiepin-3-oxide]	115-29-7	No	No
082501	Silvex [2-(2,4,5-trichlorophenoxy)propionic acid]	93-72-1	Yes	--
083701	Tetrachlorvinphos [2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate]	961-11-5	No	Yes
104101	Edolan [Sodium 1,4',5'-trichloro-2'-(2,4,5-trichlorophenoxy) methanesulfonanilide]	69462-14-2	Yes	--

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Table 8-24. Summary of Results for CDDs and CDFs in Technical 2,4-D and 2,4-D Ester Herbicides

Congener	EPA LOQ[a] (µg/kg)	Total Number of Technicals	Number of Technicals Greater Than LOQ	Observed Maximum Concentration (µg/kg)	Average Concentration[b] (µg/kg)
2,3,7,8-TCDD	0.1	8	2	0.13	0.06
1,2,3,7,8-PeCDD	0.5	8	3	2.6	0.78
1,2,3,4,7,8-HxCDD	2.5	8	0	0.81	0.31
1,2,3,6,7,8-HxCDD	2.5	8	0	0.77	0.39
1,2,3,7,8,9-HxCDD	2.5	8	0	0.68	0.24
1,2,3,4,6,7,8-HpCDD	100	8	0	1.5	0.21
OCDD	--	--	--	--	--
2,3,7,8-TCDF	1	8	0	0.27	0.07
1,2,3,7,8-PeCDF	5	8	0	0.62	0.38
2,3,4,7,8-PeCDF	5	7	0	0.73	0.07
1,2,3,4,7,8-HxCDF	25	8	0	1.6	0.36
1,2,3,6,7,8-HxCDF	25	8	0	1.2	0.11
1,2,3,7,8,9-HxCDF	25	8	0	1.4	0.16
2,3,4,6,7,8-HxCDF	25	8	0	1.1	0.14
1,2,3,4,6,7,8-HpCDF	1000	8	0	8.3	2.17
1,2,3,4,7,8,9-HpCDF	1000	8	0	1.2	0.18
OCDF	--	--	--	--	--
				TOTAL[c]	5.60 (0.70 TEQ)

Source: U.S. EPA Office of Pesticide Program file

[a] Limit of quantitation required by EPA in the Data Call-In.

[b] Average of the mean results for multiple analyses of four technical 2,4-D and/or 2,4-D ester products for which detectable CDD/CDF congener concentrations less than the LOQs were quantified; not detected values were assumed to be zero.

[c] Total equals the sum of the individual congener averages.

µg/kg = micrograms per kilogram.

"--" indicates analyses not performed.

Table 8-25. Summary of Analytical Data Submitted to EPA in Response to Pesticide Data Call-Ins

Shaughnessey Code	Pesticide		Number of Positive Submissions[a] To-Date
	Common Name	Chemical Name	
019201	MCPB, 4-butyric acid	4-(2-methyl-4-chlorophenoxy)butyric acid	0
019401	4-CPA	4-Chlorophenoxyacetic acid	0
027401	Dichlobenil	2,6-Dichlorobenzonitrile	0
029801	Dicamba	3,6-Dichloro-o-anisic acid	0
029802	Dicamba, dimethylamine	3,6-Dichloro-o-anisic acid, dimethylamine salt	0
030001	2,4-D	2,4-Dichlorophenoxy acetic acid	2
030063	2,4-D, 2EH	Isooctyl(2-ethylhexyl)2,4-dichlorophenoxyacetate	1
030801	2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid	0
031301	DCNA	2,6-Dichloro-4-nitroaniline	Pending
031401	2,4-DP	2-(2,4-Dichlorophenoxy)propionic acid	0
031501	Mecoprop (MCPP)	2-(2-methyl-4-chlorophenoxy)propionic acid	0
035301	Bromoxynil	3,5-Dibromo-4-hydroxybenzonitrile	0
054901	Irgasan	5-Chloro-2-(2,4-dichlorophenoxy)phenol	0
078701	Dacthal (DCPA)	Dimethyl tetrachloroterephthalate	Pending
081901	Chlorothalonil	Tetrachloroisophthalonitrile	Pending
083701	Tetrachlorvinphos	2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate	0
108201	Diflubenzuron	N-(((4-chlorophenyl)amino)carbonyl)-2,6-difluorobenzamide	0
109001	Oxadiazon	2-Tert-butyl-4(2,4-dichloro-5-isopropoxyphenyl)-delta2-1,3,4-oxadiazoline-5-one	Pending
110902	Dichlofop-methyl	Methyl-2-(4-(2,4-dichlorophenoxy)phenoxy) propanoate	0

Source: U.S. EPA (1995a); personal communication with S. Funk (EPA/OPP/HED) on March 27, 1996.

[a] "Positive" is defined as the detection of any congener at a concentration greater than or exceeding the LOQs listed in Table 8-24

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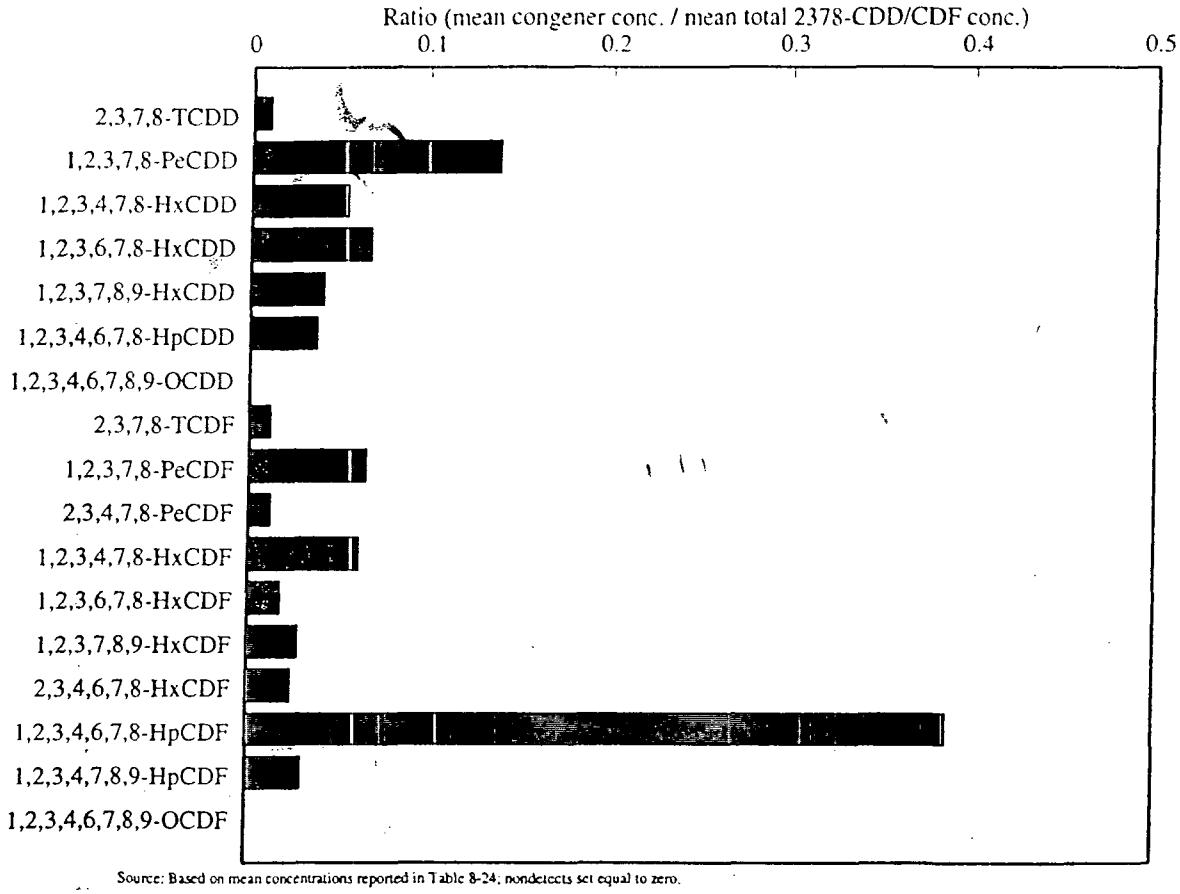

Source: Based on mean concentrations reported in Table 8-24; nondetects set equal to zero.

Figure 8-5. Congener Profile for 2,4-D (salts and esters)

Table 8-26. CDD/CDF Concentrations in Samples of 2,4-D and Pesticide Formulations Containing 2,4-D

Congener/Congener Group	Acbar Super (Gaza City*) (μg/kg)	Amco Super (Gaza City*) (μg/kg)	(Bethlehem)* (μg/kg)	Chimprom (Russia) (μg/kg)	Dragon Lawn Weed Killer (μg/kg)	KGRO (U.S.) (μg/kg)	Pro Care Premium (U.S.) (μg/kg)	Ortho Weed-B-Gone (U.S.) (μg/kg)	Sigma Co. (U.S.) (μg/kg)	American Brand Chemical Co. (U.S.) (μg/kg)
2,3,7,8-TCDD	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.02)	ND (0.001)	--	--	--	--	--
1,2,3,7,8-PeCDD	0.1	ND (0.1)	1.2	0.03	0.0014	--	--	--	--	--
1,2,3,4,7,8-HxCDD	ND (0.1)	ND (0.1)	ND (0.1)	0.02	ND (0.001)	--	--	--	--	--
1,2,3,6,7,8-HxCDD	ND (0.1)	0.2	0.6	0.05	0.0024	--	--	--	--	--
1,2,3,7,8,9-HxCDD	ND (0.1)	ND (0.1)	0.4	ND (0.02)	0.0010	--	--	--	--	--
1,2,3,4,6,7,8-HpCDD	0.1	1.2	0.3	0.23	0.0017	--	--	--	--	--
OCDD	0.1	2.6	0.1	0.85	0.0063	--	--	--	--	--
2,3,7,8-TCDF	0.3	ND (0.1)	ND (0.1)	ND (0.1)	0.0036	--	--	--	--	--
1,2,3,7,8-/1,2,3,4,8-PeCDF	ND (0.1)	0.2	0.7	1.2	0.0010	--	--	--	--	--
2,3,4,7,8-PeCDF	ND (0.1)	ND (0.1)	0.1	0.06	0.0011	--	--	--	--	--
1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF	ND (0.1)	0.1	0.4	0.08	0.0013	--	--	--	--	--
1,2,3,6,7,8-HxCDF	ND (0.1)	ND (0.1)	0.1	0.11	ND (0.001)	--	--	--	--	--
1,2,3,7,8,9-HxCDF	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.02)	ND (0.001)	--	--	--	--	--
2,3,4,6,7,8-HxCDF	ND (0.1)	ND (0.1)	0.1	0.05	0.0011	--	--	--	--	--
1,2,3,4,6,7,8-HpCDF	0.1	0.8	0.1	0.24	0.0016	--	--	--	--	--
1,2,3,4,7,8,9-HpCDF	ND (0.1)	ND (0.1)	ND (0.1)	0.02	ND (0.001)	--	--	--	--	--
OCDF	0.2	3.8	0.4	0.46	0.0039	--	--	--	--	--
Total 2,3,7,8-CDD (ND = 0)	0.3	4	2.6	1.18	0.0128	0.0144	0.0143	0.0091	0.127	0.0278
Total 2,3,7,8-CDF (ND = 0)	0.6	4.9	1.9	2.22	0.0136	0.1628	0.4253	0.1095	3.0507	0.0822
Total TEQ (ND = 0)	0.082	0.066	0.850	0.142	0.0023	0.0009	0.0012	0.0014	0.0013	0.0019
Total TEQ (ND = 1/2 det. limit)	0.195	0.197	0.915	0.159	0.0029	0.0016	0.0018	0.0029	0.0040	0.0046
Total TCDD	--	--	--	--	--	--	--	--	--	--
Total PeCDD	--	--	--	--	--	--	--	--	--	--
Total HxCDD	--	--	--	--	--	--	--	--	--	--
Total HpCDD	--	--	--	--	--	--	--	--	--	--
Total OCDD	--	--	--	--	--	--	--	--	--	--
Total TCDF	--	--	--	--	--	--	--	--	--	--
Total PeCDF	--	--	--	--	--	--	--	--	--	--
Total HxCDF	--	--	--	--	--	--	--	--	--	--
Total HpCDF	--	--	--	--	--	--	--	--	--	--
Total OCDF	--	--	--	--	--	--	--	--	--	--
Total CDD/CDF	--	--	--	--	--	--	--	--	--	--

* 2,4-D manufactured in Europe and packaged in Palestine.
-- = Not reported.
μg/kg = micrograms per kilogram.

Source: Schecter et al. (1997)

Table 8-27. Mean CDD/CDF Measurements in Effluents from Nine U.S. POTWs

Congener/Congener Group	No. Detections/ No. Samples	Range of Detection Limits	Range of Detected Concentrations (POTW mean basis)		Overall Means*	
			Minimum Detected Conc. (pg/L)	Maximum Detected Conc. (pg/L)	Mean Conc. (ND = 0) (pg/L)	Mean Conc. (ND = 1/2DL) (pg/L)
2,3,7,8-TCDD	0/30	0.31 - 8.8	nd	nd	0.00	0.98
1,2,3,7,8-PeCDD	0/30	0.45 - 15	nd	nd	0.00	1.32
1,2,3,4,7,8-HxCDD	0/30	0.43 - 9.8	nd	nd	0.00	1.38
1,2,3,6,7,8-HxCDD	0/30	0.81 - 10	nd	nd	0.00	1.42
1,2,3,7,8,9-HxCDD	0/30	0.42 - 9.7	nd	nd	0.00	1.31
1,2,3,4,6,7,8-HpCDD	3/30	0.75 - 18	nd	5.0	1.06	3.61
OCDD	13/30	6.2 - 57	nd	99.75	29.51	37.95
2,3,7,8-TCDF	1/27	0.74 - 4.4	nd	1.3	0.14	0.98
1,2,3,7,8-PeCDF	1/30	0.64 - 9.4	nd	2.0	0.22	1.58
2,3,4,7,8-PeCDF	1/30	0.61 - 14	nd	2.8	0.31	1.68
1,2,3,4,7,8-HxCDF	1/30	0.25 - 6.8	nd	2.4	0.27	1.22
1,2,3,6,7,8-HxCDF	1/30	0.23 - 6.8	nd	1.5	0.17	0.97
1,2,3,7,8,9-HxCDF	1/30	0.57 - 10	nd	2.0	0.22	1.72
2,3,4,6,7,8-HxCDF	1/30	0.25 - 7.9	nd	nd	0.00	0.93
1,2,3,4,6,7,8-HpCDF	2/30	0.36 - 6.9	nd	4.6	0.68	1.83
1,2,3,4,7,8,9-HpCDF	0/30	0.19 - 11	nd	nd	0.00	1.18
OCDF	1/30	0.86 - 28	nd	3.2	0.36	3.40
Total 2,3,7,8-CDD			nd	99.75	30.57	47.98
Total 2,3,7,8-CDF			nd	16.6	2.37	15.49
Total TEQ			nd	2.32	0.29	3.66
Total TCDD	4/27	1.2 - 8.8	nd	9.7	1.23	2.61
Total PeCDD	0/27	0.62 - 200	nd	nd	0.00	6.27
Total HxCDD	1/30	0.84 - 11	nd	1.7	0.19	1.93
Total HpCDD	3/30	0.75 - 18	nd	8.4	1.83	4.77
Total OCDD	13/30	6.2 - 57	nd	99.75	29.51	37.95
Total TCDF	2/30	0.39 - 6.8	nd	25.0	6.61	7.70
Total PeCDF	1/30	0.64 - 25	nd	20.0	2.22	4.72
Total HxCDF	1/30	0.93 - 17	nd	13.0	1.44	3.43
Total HpCDF	2/30	0.36 - 19	nd	4.6	0.68	2.41
Total OCDF	1/30	0.86 - 28	nd	3.2	0.36	3.40
Total CDD/CDF			nd	99.75	42.00	71.96

nd = not detected.
* = The "overall means" are the means of the individual POTW mean concentrations.
pg/L = picograms per liter.

Source: California Regional Water Quality Control Board (1996).

Table 8-28. CDD/CDF Concentrations Measured in EPA's National Sewage Sludge Survey

Congener	Percent Detected	Maximum Concentration (ng/kg)	Median Concentration (ng/kg)		Mean Concentration (ng/kg)	
			Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit	Nondetects Set to Zero
2,3,7,8-TCDD	16	116	6.86	0	NR	NR
1,2,3,7,8-PeCDD	18	736	9.84	0	NR	NR
1,2,3,4,7,8-HxCDD	25	737	22.5	0	NR	NR
1,2,3,6,7,8-HxCDD	49	737	27.3	0	NR	NR
1,2,3,7,8,9-HxCDD	39	737	28.0	0	NR	NR
1,2,3,4,6,7,8-HpCDD	98	52,500	335	335	NR	NR
OCDD	100	905,000	3,320	3,320	NR	NR
2,3,7,8-TCDF	65	337	17.0	3.90	NR	NR
1,2,3,7,8-PeCDF	22	736	9.60	0	NR	NR
2,3,4,7,8-PeCDF	26	736	10.4	0	NR	NR
1,2,3,4,7,8-HxCDF	43	1,500	28.0	0	NR	NR
1,2,3,6,7,8-HxCDF	35	737	18.0	0	NR	NR
1,2,3,7,8,9-HxCDF	16	1,260	18.0	0	NR	NR
2,3,4,6,7,8-HxCDF	27	737	18.0	0	NR	NR
1,2,3,4,6,7,8-HpCDF	71	7,100	57.0	36.0	NR	NR
1,2,3,4,7,8,9-HpCDF	26	842	23.0	0	NR	NR
OCDF	80	69,500	110	80.0	NR	NR
Total TEQ		1,820	50.4	11.2	86*	50*
Total 2,3,7,8-CDD/CDF		NR	NR	NR	NR	NR

Source: U.S. EPA (1996a); for POTWs with multiple samples, the pollutant concentrations were averaged before the summary statistics presented in the table were calculated. All concentrations are in units of ng/kg dry weight.

NR = Not reported.
* = Values presented by Rubin and White (1992) for 175 rather than 174 POTWs.
ng/kg = nanograms per kilogram.

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Table 8-29. CDD/CDF Concentrations Measured in 99 Sludges Collected from 75 U.S. POTWs During 1994

Congener	Percent Detected	Maximum Concentration Detected (ng/kg)	Median Concentration (ng/kg)		Mean Concentration (ng/kg)	
			Nondetects Set to Det. Limit	Nondetects Set to Zero	Nondetects Set to Det. Limit[1]	Nondetects Set to Zero[1]
2,3,7,8-TCDD	40	12.3	1.95	0	2.72 (2.40)	1.71 (2.86)
1,2,3,7,8-PeCDD	23	37.5	8.23	0	10.9 (7.80)	3.34 (7.43)
1,2,3,4,7,8-HxCDD	34	45.6	5.25	0	11.1 (8.13)	6.03 (10.2)
1,2,3,6,7,8-HxCDD	87	130	25.6	24.7	33.8 (27.6)	32.2 (28.8)
1,2,3,7,8,9-HxCDD	64	88.8	12.3	9.48	20.2 (17.7)	17.0 (19.8)
1,2,3,4,6,7,8-HpCDD	98	5,380	642	642	981 (977)	981 (977)
OCDD	99	65,500	6,630	6,630	11,890 (12,540)	11,890 (12,540)
2,3,7,8-TCDF	76	156	7.53	6.28	12.8 (19.6)	11.1 (20.2)
1,2,3,7,8-PeCDF	21	60.3	7.91	0	10.7 (11.3)	3.53 (9.36)
2,3,4,7,8-PeCDF	42	155	9.70	0	15.7 (19.8)	10.5 (21.6)
1,2,3,4,7,8-HxCDF	48	170	11.5	0	20.4 (25.3)	14.0 (25.9)
1,2,3,6,7,8-HxCDF	17	200	14.0	0	30.4 (53.6)	5.13 (21.9)
1,2,3,7,8,9-HxCDF	4	115	7.53	0	11.1 (13.6)	1.56 (11.7)
2,3,4,6,7,8-HxCDF	35	356	9.85	0	21.8 (40.4)	13.6 (41.0)
1,2,3,4,6,7,8-HpCDF	64	1,460	91.7	31.8	223 (271)	97.5 (207)
1,2,3,4,7,8,9-HpCDF	31	213	11.7	0	27.1 (34.8)	15.0 (33.4)
OCDF	93	11,200	286	281	786 (1,503)	775 (1,506)
Total TEQ (facility basis)[2]		246	49.1	30.0	64.6 (50.6)	47.7 (45.0)
Total 2,3,7,8-CDD/CDF		73,520	7,916	7,881	14,110 (14,390)	13,880 (14,200)

Source: Green et al. (1995); Cramer et al. (1995).

[1] Values in parentheses are standard deviations.
[2] For POTWs with multiple samples, the sample TEQ concentrations were averaged by Green et al. (1995) to POTW averages before calculation of the total TEQ mean and median values presented in the table.

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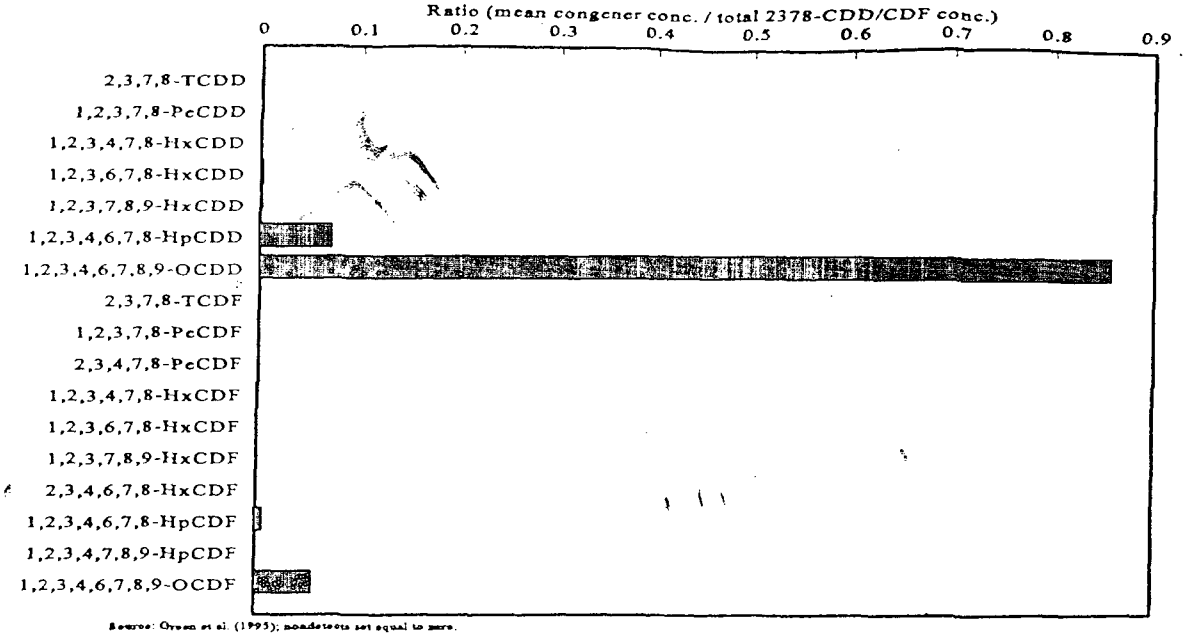
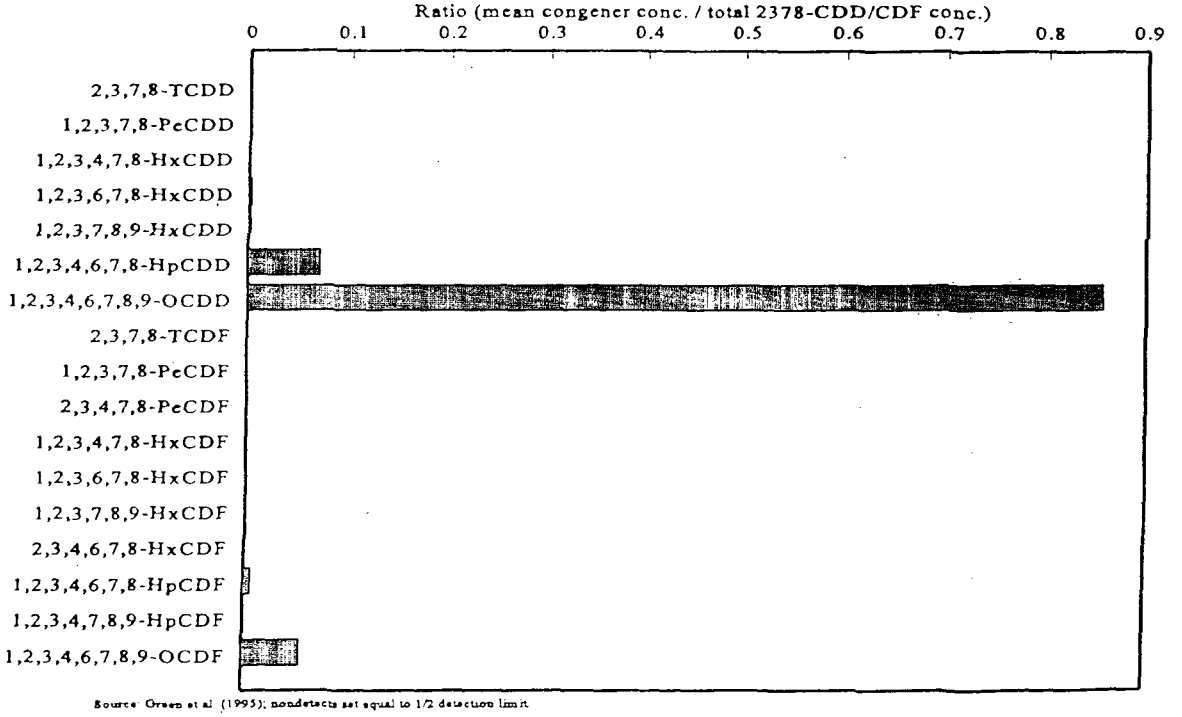


Source: Green et al. (1995); nondetects set equal to zero.



Source: Green et al. (1995); nondetects set equal to 1/2 detection limit.

Figure 8-6. Congener Profiles for Sewage Sludge

Table 8-30. Quantity of Sewage Sludge Disposed Annually by Primary, Secondary, or Advanced Treatment POTWs and Potential Dioxin TEQ Releases

Use/Disposal Practice	Volume Disposed (thousands of dry metric tons/year)	Percent of Total Volume	Potential Dioxin Release[c] (g of TEQ/yr)
Land Application	1,714	32.0[e]	85.7
Distribution and Marketing	71	1.3	3.6
Surface Disposal Site/Other	396	7.4	19.8
Sewage Sludge Landfill	157	2.9	7.8
Co-Disposal Landfills[a]	1,819	33.9	91.0
Sludge Incinerators and Co-Incinerators[b]	865	16.1	(f)
Ocean Disposal	(336)[d]	(6.3)[d]	(0)[d]
TOTAL	5,357	100.0	207.9

a Landfills used for disposal of sewage sludge and solid waste residuals.

b Co-incinerators treat sewage sludge in combination with other combustible waste materials.

c Potential dioxin TEQ release for nonincinerated sludges was estimated by multiplying the sludge volume generated (i.e., column 2) by the average of the median dioxin TEQ concentrations in sludge reported by Rubin and White (1992) (i.e., 50.4-ng/kg dry weight) and Green et al. (1995) and Cramer et al. (1995) (i.e., 49.1-ng TEQ/kg).

d The Ocean Dumping Ban Act of 1988 generally prohibited the dumping of sewage sludge into the ocean after December 31, 1991. Ocean dumping of sewage sludge ended in June 1992 (Federal Register, 1993b). The current method of disposal of the 336,000 metric tons of sewage sludge that were disposed in the oceans in 1988 has not been determined.

e Includes 21.9 percent applied to agricultural land, 2.8 percent applied as compost, 0.6 percent applied to forestry land, 3.1 percent applied to "public contact" land, 1.2 percent applied to reclamation sites, and 2.4 percent applied in undefined settings.

f See Section 3.6.5 for estimates of CDD/CDF releases to air from sewage sludge incinerators.

Sources: Federal Register (1990); Federal Register (1993b); Rubin and White (1992); Green et al. (1995); Cramer et al. (1995).

Table 8-31. CDD/CDF Concentrations in Swedish Liquid Soap, Tall Oil, and Tall Resin

Congener/Congener Group	Liquid Soap (ng/L)	Tall Oil (ng/kg)	Tall Resin (ng/kg)
2,3,7,8-TCDD	ND (0.009)	3.6	ND (1)
1,2,3,7,8-PeCDD	0.400	5.3	3.1
1,2,3,4,7,8-HxCDD	ND (0.020)	ND (2)	ND (4)
1,2,3,6,7,8-HxCDD	0.320	ND (2)	810
1,2,3,7,8,9-HxCDD	0.180	ND (2)	500
1,2,3,4,6,7,8-HpCDD	1.900	ND (1)	5,900
OCDD	1.000	5.3	6,000
2,3,7,8-TCDF	0.620	17	ND (2)
1,2,3,4,8-/1,2,3,7,8-PeCDF	0.290	4.2	ND (0.4)
2,3,4,7,8-PeCDF	0.200	1.9	ND (0.5)
1,2,3,4,7,8/9-HxCDF	0.013	1.4	24
1,2,3,6,7,8-HxCDF	ND (0.004)	0.7	--
1,2,3,7,8,9-HxCDF	ND (0.004)	ND (0.7)	ND (1)
2,3,4,6,7,8-HxCDF	ND (0.004)	ND (0.5)	ND (0.7)
1,2,3,4,6,7,8-HpCDF	ND (0.005)	ND (0.8)	10
1,2,3,4,7,8,9-HpCDF	ND (0.010)	ND (2)	9.0
OCDF	NA	NA	NA
Total 2,3,7,8-CDD	3.8	14.2	13213.1
Total 2,3,7,8-CDF	1.123	25.2	43
Total TEQ	0.447	9.5	200
Total TCDD	0.120	31	ND (1)
Total PeCDD	15.000	380	25
Total HxCDD	3.400	3.3	6,800
Total HpCDD	3.600	ND (1)	11,000
Total OCDD	1.000	5.3	6,000
Total TCDF	1.000	26	ND (2)
Total PeCDF	1.300	41	ND (0.5)
Total HxCDF	0.150	4.9	56
Total HpCDF	ND (0.010)	ND (2)	19
Total OCDF	NA	NA	NA
Total CDD/CDF	25.57	491.5	23,900

Source: Rappe et al. (1990c).

ND = Nondetected; value in parenthesis is the detection limit.
NA = Not analyzed.
-- = Not reported.
ng/kg = nanograms per kilogram.

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Dioxin From Cradle to Grave - Summary of Findings

Written by Joe Thornton
April 1997

The purpose of this report is to show that the lifecycle of polyvinyl chloride plastic, also known as PVC or vinyl, is a major source of dioxin pollution. When PVC is manufactured, disposed of by incineration, burned accidentally, or when products containing PVC (usually as a coating or covering on a metal product) are recycled in combustion-based processes, large quantities of dioxin are formed. In fact, **PVC is a major chlorine donor -- and thus a significant cause of dioxin generation -- in a large percentage of identified dioxin sources.** There are strong grounds for holding PVC responsible for a substantial and growing proportion of global dioxin production and release. Fortunately, cleaner substitutes exist for almost all uses of PVC.

Dioxin is a Global Health Risk

Dioxin and dioxin-like compounds are a family of toxic substances produced accidentally in a host of industrial processes involving chlorine or chlorine-based chemicals. These compounds are extremely long-lived in the environment, and, because they are fat soluble, they concentrate in the tissues of humans and other species high on the food chain. Since the advent of the modern chemical industry, dioxins have gradually accumulated on a truly global basis -- from the local farm to the deep oceans, from the Gulf of Mexico to the North Pole. Every person is now exposed to significant amounts of dioxins, primarily through the food supply. Even larger quantities of dioxin are passed from one generation to the next via mothers' milk and across the placenta.

Evidence gathered in the last decade, much of it presented in the U.S. Environmental Protection Agency's (EPA) "Dioxin Reassessment," indicates that global dioxin contamination poses a long-term threat to the health of the general human population. Of particular concern is the ability of tiny doses of dioxin to interfere with the body's hormones which could lead to a wide variety of effects on reproduction, child development, and the immune system, as well as cancer. Wildlife populations -- fish, birds, and marine mammals -- have already been severely affected by dioxin pollution. In the human population, dioxin exposure may already have played a role in the incidence of cancer, endometriosis, cognitive deficits in developing children, and other conditions and diseases.

We do not know the extent to which dioxin exposure has already affected human health on a global scale, but we know with certainty that universal exposure to these chemicals represents a risk to public health. Any increase in exposure will increase that risk. Because dioxin is so persistent in the environment, continued discharges will add to the global dioxin burden, increasing the threat to public health. We must bring dioxin creation and releases to zero as quickly as possible, with priority given to the largest dioxin sources.

Dioxin Sources

There are two ways to characterize dioxin sources: we can focus on the facilities that release dioxin into the environment, or we can identify the materials that cause industrial and natural processes to produce dioxin in the first place. EPA and others have used the first method to identify the major dioxin sources in the U.S. and other nations. All of these inventories note that incinerators and other combustion sources are the largest sources of dioxin: garbage incinerators, medical waste incinerators, incinerators and cement kilns that burn industrial hazardous waste, metals smelters, and other combustion processes account for over 90 percent of dioxins and furans entering the environment from known sources. Pulp and paper mills that use chlorine-based bleaches and manufacturers of chlorinated organic chemicals are the two most important dioxin sources not related to combustion.

With this approach, EPA has offered a preliminary characterization of dioxin discharge points, but the resulting list of sources is long, diverse, and confusing. The chemical industry has used this list of dioxin sources to argue that a dioxin curtailment strategy would require a byzantine set of regulations addressing virtually every industrial activity and combustion process. Many dioxin sources, however, can be tied together by the chlorine-containing feedstocks they share. The superior approach, thus, emphasizes the materials that cause dioxin formation in diverse processes. It turns out that four products -- PVC plastic, chlorinated solvents, chlorinated pesticides, and chlorine bleached paper -- are the major causes of dioxin releases from almost all of the sources identified by the various inventories.

EPA's current method of identifying dioxin sources does not point to clear strategies to prevent dioxin pollution. Focusing on discharge points leads to an emphasis on better management and control technologies for each dioxin discharger. These technologies are typically very expensive, cannot eliminate all dioxins, and thus perpetuate dioxin contamination of air, water, or land. **In contrast, the materials-based approach focuses on those substances that, when introduced into industrial or other processes, cause dioxin formation. By avoiding the production of these materials, we can prevent virtually all dioxin generation.**

In general, the cause of dioxin formation is the material that supplies chlorine for incorporation into dioxin. Dioxin formation requires only three things: a source of chlorine, a source of organic matter, and a reactive environment in which these materials can combine. The latter two are ubiquitous; synthetic chlorine production is the uniquely preventable factor in dioxin generation. In virtually all dioxin sources, the chlorine donor is a material -- a plastic, solvent, bleach, or pesticide, for instance -- that has been produced by the chemical industry.*

Most studies in laboratory, pilot scale, and full-scale incinerators confirm this view: reducing the input of PVC and other chlorinated organic chemicals to incinerators reduces dioxin formation. While a few studies have found no such relationship, the weight of the evidence from these studies confirms that reducing chlorine input in incineration will decrease dioxin output.

PVC and Dioxin

Dioxins are produced throughout the lifecycle of PVC plastic. PVC manufacture begins when chlorine gas is produced by the energy-intensive electrolysis of brine, a process in which dioxin is formed. Next, chlorine is combined with ethylene to produce ethylene dichloride (EDC). In this process, large quantities of dioxin are formed. Some portion of these dioxins are released in air emissions and wastewater discharges. Samples taken downstream from EDC manufacturers in the U.S. and Europe indicate significant contamination of sediment and the foodchain in the vicinity of these plants. The largest quantities of dioxin are directed into the wastes or tars that result from EDC synthesis, according to European studies. Greenpeace analyses at U.S. chemical facilities indicates that the wastes from this process are among the most dioxin-contaminated wastes known. These chlorine-rich wastes are typically incinerated, producing and releasing dioxins into the environment.

EDC is then converted into vinyl chloride monomer (VCM), which is polymerized, formulated, and formed into a final PVC-containing product. After PVC products are sold, they produce dioxins if they encounter reactive conditions, as they do when a building or vehicle burns in an accidental fire. After their useful lifetime, PVC products that are incinerated or serve as coatings or coverings on metals recycled in smelters create additional dioxins. Incinerators and smelters in which PVC is burned are among the most important dioxin sources yet identified. More than 1 billion pounds of PVC may be burned in U.S. trash and medical waste incinerators and in accidental structural fires each year. The unknown quantities of PVC burned in industrial and warehouse fires, automobile fires, metals smelters, and wood combustion add to this total.

The lifecycle of PVC plastic may thus be the cause of more dioxin formation than that of any other single material. Sources in which PVC is a major chlorine donor account for a significant proportion of the identified dioxin emissions in the EPA's inventory. PVC is a significant, and sometimes predominant, chlorine donor in most of the major dioxin sources, including municipal waste incinerators, medical waste incinerators, smelters for copper and accidental fires and open waste burning. Wastes from PVC production are important chlorine donors in hazardous waste incinerators, and PVC is an important chlorine donor in wood combustion.

Nearly 40% of all the chlorine produced by the chemical industry is used in PVC, so it is not surprising that PVC is a significant chlorine source in so many dioxin producing processes. **PVC is also an unusually fast-growing dioxin source. While production of many other chlorinated compounds is declining and others hold steady, U.S. and worldwide production of PVC and its feedstocks is rapidly growing, both for use in the U.S. and for export, primarily to developing nations.** Finally, a certain percentage of longer lived PVC products (e.g., construction materials) will be reaching the end of their useful lives in the coming years. If burned, these PVC stocks may lead to a new influx of dioxin pollution.

Recommendations

The health risk posed by dioxin calls for immediate action. As a major cause of dioxin pollution and numerous other environmental impacts, PVC must be a priority in any dioxin prevention program. Greenpeace recommends the following elements of a materials-based dioxin prevention strategy for PVC:

1. Prevent PVC-Related Dioxin Pollution

EPA should announce a PVC sunset program, the intent of which is to progressively reduce the production and use of PVC in the U.S. to zero. Priority should be given to those use sectors that cause the most dioxin formation during their lifecycle (e.g., those most likely to be incinerated or involved in fires) or are most easily replaced with safer, chlorine-free substitutes. Specific action should include:

- A moratorium on permits for new production facilities/expansions for EDC, VCM, and PVC and modification of permits at existing plants to require that dioxin releases to all media, including wastes destined for disposal, be brought to zero within 5 years.
- A moratorium on permits for new incinerators and other waste combustion facilities, and modification of existing permits to require that dioxin emissions to all media to be brought to zero within 5 years by eliminating the input of chlorinated wastes and product.
- A phase-out of medical waste and municipal solid waste incineration.
- Rapid phase-outs of:
  - all short-life PVC uses (packaging, toys, IV-bags, etc.);
  - PVC products in areas susceptible to fire (construction materials, PVC coated cables, appliances, and vehicles); and
  - recycling of metals containing PVC residues in combustion-based processes (i.e., electrical cables, automobiles).

2. Acknowledge and Investigate the Role of PVC in Dioxin Formation

First, EPA must acknowledge the important role of PVC in dioxin formation. Since at least 1990, EPA has had information that the incineration and manufacture of PVC produce dioxins. Since 1993, extensive information on these subjects has been submitted to the agency. Nevertheless, EPA has failed to acknowledge or substantively investigate the critical role of PVC as a chlorine donor in major dioxin sources.

EPA has made no attempt to collect or analyze samples of waste, wastewater, or air emissions from the nation's 14 EDC/VCM facilities or the incinerators that burn wastes from these plants. Instead, the EPA is allowing the industry trade organization, the Vinyl Institute, to voluntarily "self-characterize" the industry's dioxin emissions. The industry will collect samples from its own plants, analyze their dioxin content, interpret the data, and submit it to EPA. Although there is a "peer review" committee to examine the methodology and results of the vinyl industry's self-characterization, the industry will ultimately choose where, when, and how samples will be taken and analyzed, and which data are suitable for submission. By the time the agency's reassessment is finalized, the industry is expected to have only submitted data to EPA on dioxin contamination of wastewater and resins -- the two media with the lowest and most difficult to detect concentrations of dioxins -- but no data on dioxins in wastes, tars, sludges; or incinerator

emissions, ashes, or sludges, which, directly or indirectly, are responsible for the vast majority of dioxin emissions.

3. Focus Dioxin Policy on Materials

EPA should reorient its dioxin research and policy towards pollution prevention. This requires a fundamental shift away from the agency's current reliance on pollution control techniques for managing dioxin sources. The agency should establish a goal of zero dioxin discharges to all environmental media and focus on reducing the production and use of materials that cause dioxin generation during their lifecycle. Research on dioxin sources should also be reoriented to emphasize the identification of dioxin-producing materials.

4. Address Environmental Justice Concerns Associated with the PVC Lifecycle

Pollution associated with the lifecycle of PVC has a disproportionate effect on low-income and minority communities. Incinerators where municipal, medical, and hazardous wastes rich in PVC and its by-products are burned tend to be located more predominantly in African-American, Latino, and Native American communities. A similar pattern holds true for the manufacture of PVC, as well. There are 14 U.S. facilities, mostly located in the Gulf Coast of Louisiana and Texas, that produce ethylene dichloride and/or vinyl chloride monomer feedstocks for PVC. The mean percentage of "non-white" residents in these communities is 57 percent higher than the national average, a preliminary analysis of census data indicates.

Pollution caused by PVC production and disposal is thus an environmental justice issue. EPA should apply its environmental justice policy to investigate and initiate action to prevent dioxin formation during the lifecycle of PVC plastic. President Clinton's Executive Order 12898 on Environmental Justice requires that the agency improve "research relating to the health and environment of minority populations" and reduce pollution in these communities.

5. Ensure a Just Transition

Any plan to protect health and the environment from dioxin sources – including a PVC sunset program -- must prevent or compensate for the economic and social dislocation that results. A tax on the production of EDC/VCM would help to drive the transition away from PVC and finance the costs associated with it. The revenues from such a tax could be used for transitional measures to ensure that a PVC phase-out is just, equitable, and orderly. In particular, a transition fund could be used to assist workers and communities affected by the transition, provide for educational opportunities, income protection, and health insurance for those affected by a PVC phase-out, and finance research and development into safer PVC alternatives.

Notes

* Although very small quantities of dioxin can be produced when natural chloride salts are burned in some high-temperature processes, the vast majority of dioxin is associated with burning or processing the products and wastes of industrial chlorine chemistry. Thus, eliminating the feed of PVC and other organically-bound chlorine compounds to incinerators will substantially reduce dioxin formation.

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Dioxin From Cradle to Grave - Introduction

Written by Joe Thornton
April 1997

The purpose of this report is to show that the lifecycle of polyvinyl chloride plastic, also known as PVC or vinyl, is a major source of dioxin pollution. When PVC is manufactured, disposed of by incineration, burned accidentally, or when products containing PVC (usually as a coating or covering on a metal product) are recycled in combustion-based processes, large quantities of dioxin are formed. In fact, **PVC is a major chlorine donor -- and thus a significant cause of dioxin generation -- in a large percentage of identified dioxin sources.** These are strong grounds for holding PVC responsible for a substantial and growing proportion of global dioxin production and release. Fortunately, cleaner substitutes exist for almost all uses of PVC.

TABLE 1: The Many Uses of PVC

Food Wrap	Coatings	Automotive seats	Credit Cards
Flooring	Upholstery	Medical instruments	Bottles
Siding	Garden Hose	Doors	Apparel
Pipe	Shower Curtains	Window Frames	Toys
Wall covering	Wire/Cable insulation	Molding	Appliance housing

Source: Society of the Plastics Industry (SPI), 1995

This report represents the culmination of several years of research on the part of Greenpeace scientists and policy analysts. Greenpeace will continue to conduct literature reviews and primary research to demonstrate and better characterize the links between PVC and other chlorinated compounds and dioxin pollution. It is our hope that this research will convince government agencies and non-governmental organizations throughout the world of the need to address the **materials that lead to dioxin pollution**, the only method that will lead to true pollution prevention for dioxin. The report is divided into the following sections: (1) the health threats posed by dioxin; (2) strategies for dioxin prevention; (3) the PVC-dioxin pollution links, with analysis of the role of PVC in dioxin formation from different sources; (4) strategies for a PVC phase-out; and (5) recommendations.

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Ahead to Dioxin Poses a Global Health Threat

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Dioxin From Cradle to Grave - Chapter 3 - PVC's Role in Dioxin Formation

Written by Joe Thornton
April 1997

The PVC Lifecycle

The lifecycle of PVC represents a large – and possibly the largest – single material source of dioxins. The PVC lifecycle has three stages. In all of them, dioxins are known to be produced.

- **Manufacture.** The first step in PVC's lifecycle is the production of elemental chlorine gas by the energy-intensive electrolysis of salt. Dioxin is produced in this process. This chlorine is then reacted with ethylene to produce ethylene dichloride (EDC), a process in which very large quantities of dioxin are produced. EDC is then converted in another chemical reaction to vinyl chloride monomer (VCM), which is then polymerized to form pure PVC plastic. Pure PVC is then mixed with various additives and used to produce PVC-containing products. Dioxins may be formed in some of these processes, as well. The wastes from the manufacture of PVC and its feedstocks are incinerated in most cases, producing yet more dioxins.
- **Use.** PVC is used in a wide range of consumer, construction, and medical products. In some uses, PVC may encounter reactive conditions, as when a building with PVC cables burns in an accidental fire. When PVC burns, dioxins are produced.
- **Disposal.** After their use, PVC-containing products may be dumped in landfills, burned in incinerators or furnaces, or, in some cases, recycled. When land disposed, PVC products have an essentially infinite lifetime. When burned in incinerators or landfill fires, PVC produces dioxins. When PVC serves as a coating or covering on metals that are recycled in smelters, dioxins are formed.

Indeed, PVC is an important, and sometimes the predominant, chlorine donor in sources responsible for the vast majority of all identified dioxin releases in the EPA's Dioxin Reassessment and in Cohen and Commoner's analysis of dioxin emissions in the Great Lakes [EPA, 1994b, Cohen and Commoner, 1995]. PVC provides a substantial proportion of the organically-bound chlorine in incinerators for trash and medical waste. PVC is also a significant chlorine source in some secondary metals smelters. In accidental fires, wood combustion, and open burning, PVC also contributes substantially to dioxin emissions. Compared to other chlorinated materials, PVC production is on the rise, and thus its contribution to the global dioxin burden is likely to increase substantially.

PVC in Incinerators

Incinerators are responsible for the majority of identified dioxin releases, both in the U.S. and globally. **What are the materials that result in dioxin formation in these combustion sources?** As the Swedish EPA points out, *"In combustion processes in which both chlorine and a carbon source are present, PCDD Fs can be formed* [SEPA, 1996]." Similarly, U.S. EPA's dioxin reassessment notes, *"Dioxin-like compounds can be generated and released to the environment from various combustion processes when chlorine donor compounds are present* [EPA, 1994b]." One recent survey of emissions data from a wide range of combustion facility types indicates a *"clear dependence"* of dioxin and furan emissions on chlorine content of the waste feed [Thomas and Spiro, 1995]. **The material that donates the chlorine is thus the appropriate focus for prevention efforts, be it PVC, chlorinated solvents, etc.**

Although many materials can serve as chlorine-donors in combustion-based processes, one -- PVC plastic -- plays an important role in most of the major dioxin sources. This is not surprising, because PVC is the most abundant product of chlorine chemistry, consuming over 30 percent of all the chlorine produced in the U.S. each year. In

Denmark alone, for instance, some 13,500 tons of PVC is incinerated each year [DTI, 1995]. The quantity that ends up in U.S. incinerators is uncertain, but total PVC production is immense: over 5 million tons per year in the U.S., and 20 million tons per year worldwide [SRI, 1993]. It has been unambiguously shown in the laboratory that burning PVC results in the generation of dioxin [Thiessen, 1991, Christmann, 1991]. Given the large quantities of PVC produced and sold in the U.S. and the fact that the burning of PVC results in the generation of dioxins, it is clear that incineration of PVC will likely result in large dioxin emissions.

Municipal Waste Incinerators

In all inventories, municipal waste incinerators are the number one or two source of dioxin emissions to the environment. In the U.S., there are 211 trash incinerators with combined capacity of 48 million tons of waste each year. EPA's median estimate for dioxin emissions from these facilities is 4800 grams per year (TEQ). Municipal waste incinerators also produce an estimated 7 million metric tons of ash annually, which is disposed in landfills. The more effective the incinerator's emissions control device, the more severely contaminated its ash. Ash from trash incinerators carries about 1800 grams per year of dioxin (TEQ) into the land, based on an average concentration of 258 ppt TEQ [Versar, 1996].

PVC is common in packaging and consumer products. The major chlorinated plastic, PVC contributes a large percentage of the organically-bound chlorine found in municipal waste. PVC accounts for an estimated 0.5 to 0.8 percent of municipal waste. Despite this low percent by weight, PVC can contribute at least 80 percent of organically-bound chlorine and as much as 67 percent of the total chlorine (organochlorines plus inorganic chloride) in the waste stream [Danish EPA, 1993]. Other studies have made similar findings, with PVC comprising 50 percent or more of total chlorine in the waste stream [Kanters and Louw, 1993, Ecocycle, 1994, DTI, 1995, Brahms, 1989]. An estimated 200,000 to 300,000 tons of PVC is incinerated each year in U.S. trash incinerators, based on national incinerator capacity of 48 million tons per year [Versar, 1996], 80 percent capacity utilization, and PVC content ranging from 0.5 to 0.8 percent.

In the Netherlands, where an effective garbage separation system removes most of the organic chlorides in compostable materials, such as food and wood wastes, PVC remains one of the only major source of chlorine and, subsequently, one of the only major dioxin precursors. Dutch incinerator studies indicate that reducing PVC feed causes significant decreases in dioxin emissions [Kanters and Louw, 1993]. Based on these findings, the Dutch Environment Ministry concluded:

> *"These new experiments by the University of Leiden demonstrate clearly a relation between the content of PVC in household waste and dioxin formation in waste incinerators. On the basis of these experiments there is no reason to reconsider present policies regarding PVC applications: the main feature of this policy is that for PVC applications for which no feasible system of recycling and reuse can be established, the use of more environmentally sound alternative materials is to be preferred* [Netherlands Environment Ministry, 1994]."

More recent Dutch research [Kanters, et. al., 1996] confirms these findings. In a laboratory experiment, chlorophenol emissions (an indicator for dioxins) were lowest when the majority of chlorine-containing substances were removed from the wastes. When 20% of the original quantity of compostables was included, emission doubled from this baseline; when 30% of the original quantity of PVC was included, emissions doubled again [Kanters, et. al., 1996].

Medical Waste Incinerators

In U.S. dioxin inventories, medical waste incinerators (MWIs) are the largest or second largest dioxin source. There are about 2400 medical waste incinerators in the U.S., which burn about 848,000 tons of waste per year [Versar, 1996]. EPA's original inventory estimated annual dioxin emissions in the range of 1600 to 16,000 grams of dioxin (TEQ) into the air each year, with a median estimate of 5100 grams, making MWIs the largest dioxin source in the inventory [EPA, 1994b]. Although other analyses have confirmed that MWIs are major dioxin sources, the American Hospital Association has argued that the actual total is much lower [AHA, 1995]. EPA is expected to lower its

quantitative estimate, but there is little doubt that medical waste incinerators will remain a significant dioxin source.

The majority of the available chlorine in waste from hospitals and other health care institutions comes from PVC plastic, which enters these facilities as packaging and in many disposable medical products [Green and Wagner, 1993, Coppinger, 1996]. PVC is the most commonly used polymer in the medical device arena. An estimated 700 million pounds per year of PVC are used in medical devices in the United States, with an annual growth rate of 6.4%. [Chemical Week, 1995]. PVC is used in packaging, gloves, infusion bags, tubing, trays, and numerous other medical applications. Since an estimated 80 percent of U.S. medical waste is incinerated [AWMA, 1994], as much as 280,000 tons of PVC may be burned in medical incinerators each year.

While municipal trash contains about 0.5 percent PVC, an estimated 9.4 to 15 percent of all infectious waste is PVC [Marrack, 1988, Hasselriis, 1993], and as much as 18 percent of non-infectious hospital wastes are PVC [Hasselrris, 1993]. According to one report for the city of New York, PVC gloves and IV-bags alone account for over 90 percent of the organic chlorine and over 80 percent of the total chlorine content of medical waste [Green, 1993]. **All PVC products taken together could likely contribute as much as 90 percent or more of the organically-bound chlorine and 80 percent of the total chlorine fed to medical waste incinerators.** The large quantities of PVC in the medical waste stream is one reason why medical waste incinerators are such a significant dioxin source. The authors concluded that the substitution of PVC plastic is an effective way of reducing the environmental impacts of such incinerators [Green, 1993].

Hazardous Waste Incinerators and Cement Kilns Burning Hazardous Waste

Commercial incinerators and kilns accept complex mixtures of chemical wastes from a wide variety of sources, while many chemical companies operate on-site incinerators, furnaces, and boilers for disposal of their own wastes. EPA estimates that hazardous waste incinerators and kilns release 120 to 1200 grams of dioxin (TEQ) per year, with a median estimate of 409 grams per year [EPA, 1994b]. These estimates are based upon carefully controlled trial burns, so actual emissions during routine operation or upsets may be significantly higher [Costner and Thornton, 1991]. As of 1994, there were 298 permitted incinerators, boilers and furnaces burning 2.3 million tons of hazardous waste per year; 34 cement kilns burned an additional one million tons of hazardous waste each year (including medical waste containing PVC). In addition to dioxin in air emissions, incinerators produce highly contaminated ash which is disposed on land. If pollution control devices are 99 percent effective, ash from these facilities will carry about 100 times more dioxin into the environment than air emissions will. Waste-burning cement kilns produce large quantities of contaminated dust -- an estimated 3 million tons per year with dioxin concentrations averaging 42.2 ppt TEQ [EPA, 1993]. Based on these estimates, kiln dusts would carry 118 grams of dioxin (TEQ) into each year. EPA has found that dusts are released to the environment during storage, transport, and disposal, which often takes place by dumping into quarries or piles [EPA, 1993].

Because hazardous waste destined for incinerators is predominantly organic chemical waste, the organically-bound chlorine content is much higher than in municipal waste, often reaching 10 percent of total waste feed. The major chlorine donors in incinerated hazardous wastes belong to two categories: wastes from the manufacture of organochlorine chemicals and spent chlorinated solvents [Oppelt, 1986, Dempsey, 1993]. Wastes from the manufacture of PVC feedstocks are likely a significant contributor to the first category: EDC/VCM manufacture is the largest use of chlorine in the chemical industry -- accounting for more than half of all chlorine used within the organic chemicals sector [SRI, 1993]; millions of tons of chlorine-rich wastes are generated by these processes that are incinerated in on-site or commercial facilities. Given the large amount of PVC production wastes incinerated each year, it would appear that the PVC lifecycle is an important indirect chlorine donor and dioxin precursor in hazardous waste incinerators, as well.

Metals Recycling

In many cases, products containing PVC (usually as a coating or covering on a metal product) are recycled in combustion-based processes. The result is the formation of significant amounts of dioxin. **Indeed, PVC is an important chlorine donor in the secondary processing facilities that are considered major dioxin sources.** The recycling of PVC itself has not been thoroughly analyzed for the creation of dioxins, and is thus not discussed here.

Secondary copper smelters are major dioxin sources, releasing 74-740 grams of dioxin per year (TEQ), according to EPA. These facilities produce dioxins in large part because they process for recycling large quantities of PVC-coated copper cables, as well as PVC telephone cases and other PVC-laden products at high temperatures [Christmann, 1989a]. A Swedish study described the creation of PCDD/Fs from the recycling of PVC coated wire in a copper smelter [Marklund, et. al., 1986]. In its investigation of a secondary copper smelter, EPA fed a secondary copper smelter a mixture of electronic telephone scrap and other plastic scrap (likely PVC coated), as well as metal scrap, residues, and slag [EPA, 1994a]. The estimated TEQ emission factor for this facility is 779ng/kg of scrap metal smelted [Versar, 1996]. The presence of large amounts of PVC along with copper -- a catalyst that increases the rate of dioxin formation -- makes these major dioxin sources. According to one German study:

> *Considerable amounts of dioxins and furans have been found in the flue gas as well as in soil from the near vicinity of copper reclamation plants. In these facilities, scrap copper containing varying quantities of PVC-coated cables is precleaned by combustion or pyrolysis and then recycled in a copper smelter. In the ambient air near a copper smelter, we could find in imission measurements surprisingly high concentrations of dioxins and furans* [Christmann, et. al., 1989a, b].

Removal of a part of the cable sheathings (typically PVC) before reclamation in a copper smelter resulted in reductions in PCDD/F values of 17%, 48% and 35% (in three different smelters) [Christmann, 1989b]. Other researchers [see Fiedler and Hutzinger, 1990] investigating this same plant found that there is little information on PCDD/F formation in copper recycling. However, after reduction of plastic inputs in this plant (presumed to be PVC, though not specified as such), the researchers noted that stack gas concentrations of PCDD/Fs fell from 200 to 70 ng TEQ/Nm3.

Secondary steel smelters are important dioxin sources in some inventories [Cohen and Commoner, 1995, Thomas and Spiro, 1995], although EPA did not make a quantitative estimate. EPA did note, however, *"The secondary smelters which recover metal from waste products such as scrap automobiles have the potential for dioxin formation due to the plastic (and associated chlorine) in the feed material. Other countries such as Germany have identified this industry as potentially important* [Schaum, 1993]."

These facilities may produce dioxin in part because of the presence of PVC residues in steel scrap, particularly from automobiles, in which PVC may be used for upholstery, interior moldings, underseal, and other parts (EPA, 1994a identifies PVC as one of the chlorinated materials entering these processes). Chlorinated cutting oils provide significant amounts of chlorine for dioxin formation. An analysis [Aittola, 1993] of a metal reclamation facility in Finland with seven different processes for copper, aluminum, and various steels, found that a large part of the emissions of chlorinated aromatic compounds in these processes are formed due to PVC plastic and cables and car components. EPA estimates that between 500 and 850 pounds of auto "fluff" (plastic and other non-metal materials removed from cars destined for reclamation) is generated per car. For 1990 models about 20 pounds is PVC [Carroll, et. al.]. While much of the fluff can be removed by magnetic separation and landfilled or stockpiled, separation techniques are likely not 100 percent effective; at least some PVC is likely to reach the smelting operation. According to one experimental study of a Swedish steel recycler:

> *This pilot study clearly shows that PCDDs and PCDFs are formed during scrap metal melting processes. Combustion of PVC has been reported as one source of PCDDs and PCDFs in different combustion and pyrolytic processes. In this study, PVC is also found to give the highest emissions* [Tysklind, 1989].

Secondary lead smelters also release dioxin. According to a recent report for EPA, *"Historically, the source of CDD/CDFs at secondary lead smelters is the PVC separator used in lead acid batteries. In 1990, about 1 percent of scrap batteries processed at lead smelters contained PVC separators....Less than 0.1 percent of scrap batteries contained PVC separators in 1994 and this trend is continued because no US manufacture of lead-acid automotive batteries currently uses PVC in production* [Versar, 1996]." **This change can be viewed as a model for dioxin prevention: dioxin releases were virtually eliminated by phasing-out PVC from the products that ultimately end up**

in combustion facilities.

Some inventories suggest that primary steel smelters may be major dioxin sources, as well [Lahl, 1993, Lahl, 1994, Brzuzy and Hites, 1996a]. In these facilities, dioxin may be produced due to a few chlorine donors: the use of chlorinated solvents and cutting oils in the production process, paints, and the reintroduction of dusts and slag containing chlorinated materials from recycling of scrap. PVC present as part of the scrap charges to steel mills may contribute to the emissions of chlororganics reported by Oberg and Allhammar, including dioxins [see Johnston, 1993 on Oberg and Allhammar, 1989]. Recycled scrap steel can play an important role in some types of primary steel production. One government study of electrical arc steel manufacture found the potential for the creation of toxic organic micropollutants because of feedstocks that contain organic materials such as oils, emissions, greases, and plastics; chlorinated compounds in these materials may give rise to PCDD/F formation [Air Board, 1995].

Other Combustion Sources

Dioxin formation in the burning of natural wood is negligible. In contrast, industrial and residential wood burning can become an important dioxin source when wood with chemical additives or residues is burned. EPA identifies the industrial and municipal burning of wood as a large dioxin source [EPA, 1994a]. Since much of the wood incinerated is construction debris, and markets for PVC siding, window frames, wallpaper, and flooring are increasing rapidly, this source is likely to increase in the future. The major chlorine donors in this sector appear to be scrap wood with PVC residues, chip board with chloride-containing hardeners, and treated wood preserved with pentachlorophenol [Wilken, 1994, Vikelsoe, 1993, Kolenda, et. al., 1994]. The German Federal Environmental Authority has urged that no chlorine-containing fuels be burned in any furnace, from private fireplaces to industrial plants [Wilken, 1994].

Accidental Fires

PVC is now ubiquitous in modern buildings in flooring, siding, pipes, furniture, wallpaper, and other materials. Construction applications account for more than 60 percent of PVC use [SRI, 1993]. An average house contains 14 to 367 kilograms of PVC, depending on size and date of construction/remodeling [Carroll, 1995]. Industrial and institutional buildings contain even greater quantities. In Denmark alone, it is estimated that 1.2 million tons of PVC are used in existing buildings, which could burn in the case of accidental fires [DTI, 1995]. Combustion conditions associated with an accidental fire -- low oxygen and rapidly cooling temperatures away from the fire -- result in poor combustion conditions and high rates of dioxin formation [SEPA, 1996]. The Danish Technical Institute (1995) summarized:

> *"Rigid PVC does not burn by itself and will not start a fire. If other materials support a fire, PVC will burn under the formation of carbon oxides and hydrochloric acid fumes.... Burning PVC also yields large amounts of soot-containing smoke. The soot will contain several different substances. The presence of chlorine in the material gives the potential for contribution to the formation of polychlorinated dioxins and dibenzofurans during the fire. If formed, it seems that these substances have the highest tendency to be present in the soot. The amount will depend on the fire conditions such as oxygen available, temperature, catalyst available such as copper, and the amount of chlorinated material, eg PVC, involved in the fire....Laboratory tests with different types of PVC product report formation of PCDD/F in the level of microgram per kilo."*

Samples of soot taken from fires in PVC-containing buildings have been found to contain dioxins in concentrations as high as 10,000 nanograms (ng) (TEQ)/per square meter (m2) on surfaces and 45 parts per billion (ppb) TEQ in ash and soot [Fiedler, 1993, UBA, 1992]. Fires in homes, schools and office buildings can produce dioxin concentrations in the 200 ng (TEQ)/sm2 range [DTI, 1995]. Dioxins found in soot, however, represent only a small part of the problem: more than 90 of the dioxins produced in a structural fire are found in the gaseous phase and escape into the atmosphere [Versar, 1996]. **PVC fires may thus make a substantial but yet unquantified contribution to dioxin contamination of the environment.**

According to one industry spokesman, as much as three-quarters of all PVC

manufactured goes into the building and construction market for uses such as piping, siding, window frames, wallpaper, cabling, flooring, and other uses [Reisch, 1994]. As a result, **any fire in a modern building is likely to be a source of dioxin**. The contents of many buildings, including furniture, appliances, computer housings, toys, and other consumer products present in a typical home, are also potential sources of dioxin. Despite the PVC's potential contribution to the U.S. dioxin burden from accidental fires, **EPA, in its draft dioxin reassessment, has failed to adequately account for the contribution of accidental fires to the nation's dioxin burden and in particular the contribution of PVC as a chlorine donor**.

In the U.S. alone, there are 621,000 structural fires per year [Versar, 1996]. As noted in a recent report for the revision of U.S. EPAs dioxin reassessment, *"PVC building materials and furnishings, textiles and paints containing chloroparaffins, and other chlorinated organic compound-containing materials appear to be the primary sources of the chlorine* [Versar, 1996]." Based on the number of fires in Versar, 1996 and the Vinyl Institute's estimate of the amount of PVC in a typical house, Greenpeace estimates that 9,000 to 240,000 tons of PVC may burn in house fires each year.

Large, and potentially unknown, quantities of PVC may burn when accidental fires occur at plastics manufacturing, storage, or recycling sites. For instance, after a single fire at a plastics warehouse in Binghamton, New York, dioxin levels in soil on the site were found to be over 100 times greater than other samples from the same community. Dioxin levels in the soot were as high as 23 ng/m2 TEQ, approximately the same as the state's maximum level for reentry into dioxin-contaminated buildings [Schecter, 1996]. A 1992 fire at Microplast, a PVC recycling company in Lengrich, Germany, resulted in dioxin contamination of residues in the facility and an 88-fold increase in dioxin concentrations in cabbages grown on farms downwind from the facility [UBA, 1992]. A recent study [Meharg, 1996] of three fires involving large quantities (approximately 1000 tonnes) of plastics (PVC and polyethylene) estimated that 50-100 tonnes of aromatic compounds (both chlorinated and non-chlorinated) were produced from each of the three fires investigated.

Substantial dioxin releases from the accidental burning of stockpiled waste containing PVC have also been documented. For example, several fires involving automobile fluff stockpiled at automobile reclamation facilities have occurred. In one fire, between 39,000 and 48,000 pounds of the fluff were burned. Laboratory studies by EPA indicate that burning one kilogram of fluff generates air emissions of approximately 0.0072g of PCDD/PCDFs. The Agency estimates that approximately 2 billion pounds of automobile fluff are generated annually, most of it ultimately disposed of in landfills. If all of this fluff were burned in open fires, more than 31 kg of these PCDD/PCDFs would be released into the air per year [Costner, et. al., 1995 citing Ryan and Lutes, 1993]. This quantity of fluff is so large that it would contribute significantly to the national dioxin burden, even if burned in controlled combustors.

Landfill fires represent a largely unquantified source of dioxins. PVC may comprise between 50 and 75 percent of the total chlorine in landfills [Johnston, 1993]. Other chlorine sources may include organic household wastes, pesticides, and solvents. A large percentage of the PVC used in construction applications will reach the end of its useful life in the coming years, and overall use of PVC is increasing. With a significant portion of this PVC destined for landfills, landfill fires may become an important source of dioxin emissions.

Accidental burning of PVC in automobiles (e.g., dash boards, underseal, upholstery) could represent another important, yet unquantified, dioxin source. According to a report for the U.S. EPA, *"Accidental fires in vehicles are uncontrolled combustion processes that typically result in relative high emissions of incomplete combustion products, including CDD/CDFs, because of poor combustion conditions. PVC vehicle components and other chlorinated organic compound-containing materials appear to be the primary sources of the chlorine. In 1993, approximately 421,000 [vehicle] fires were reported in the US* [Versar, 1996]." Dioxins and furans have been identified in residues from the experimental burning of automobiles (0.044 - 0.052 mg TEQ/car), a subway car (2.6 mg TEQ), and a railway coach (10.3 mg TEQ) [Versar, 1996]. Given the number of automobile fires per year and the amount of dioxin generation per vehicle burnt, vehicle fires could thus represent an important, and still unknown source of dioxin emissions.

Due to the large amounts of dioxin that can be produced in accidental fires, the German Environment Ministry has called for the use of substitutes for PVC in all areas susceptible to fires:

> *"PVC products in the building industry should be substituted for in those areas of use in which considerable dangers to the environment and health occur, and extensive clean-up measures become necessary, as a result of the possible formation of dioxin and hydrogen chloride in fires* [German Environmental Ministers, 1992]."

The German EPA and Ministry of Health have made a similar order:

> *"The use of plastics containing chlorine and bromine should be completely excluded, as far as is possible. UBA and BGA propose a ban on the use of plastics containing chlorine and bromine in apparatus susceptible to fire, in the manufacture of chip-board, as well as the labeling of plastics containing chlorine and if necessary a ban on the use of PVC in packaging* [UBA, 1992]."

Open Burning of Wastes

In dioxin inventories for industrialized nations, open burning is not considered an important dioxin source. In some nations, especially developing nations, the greater prevalence of this practice and the poor combustion conditions encountered may make open burning of chlorine-containing wastes an important dioxin source. Open burning of trash or construction waste that contains PVC may result in significant but unquantified dioxin emissions.

Manufacture of PVC Feedstocks

In addition to the significant dioxin formation associated with PVC during disposal and accidental combustion, dioxin is also generated during the manufacture of the product and its feedstocks. Since at least 1983, the chemical industry has known that dioxin is formed during the manufacture of the PVC feedstocks vinyl chloride (VCM) and 1,2-dichloroethane (EDC) [Beekwilder, 1989, cited in Andersen and Knapp, 1993]. Despite the industry's prior knowledge, it was not until 1989 that a series of sampling programs in Europe brought the problem to the attention on of the scientific community, governments, and the public at large. While only a portion of the dioxin generated during PVC production is released into the environment (some of the dioxins are recycled in internal processes or destroyed during incineration), PVC production represents a potentially large dioxin source.

Dioxin in Wastes

Dioxin formation is particularly significant in the oxychlorination process, in which ethylene is combined with hydrochloric acid and oxygen in the presence of a copper catalyst to produce EDC. Dioxins produced in this process follow one of three paths: the majority remains with the EDC product, and smaller amounts are distributed to the wastewater and offgases from the process [DTI, 1995]. Dioxins contained in the latter two fractions enter pollution control devices and are then released to the environment via air emissions, wastewater discharges, ash residues, and treatment sludges. The EDC product fraction is then purified, and much of the dioxin is partitioned into the "heavy ends," wastes that are non or semi-volatile. These wastes are primarily disposed of by incineration -- a process that produces and releases dioxins and furans from the incineration of the many other chlorinated organic compounds in the wastes [Costner, et. al., 1995]. Some of these wastes, however, may be shipped offsite for treatment or disposal.

The quantities of dioxin formed in wastes appear to be very large.* Laboratory simulations at the University of Amsterdam demonstrated dioxin formation during oxychlorination at a rate equivalent to 419 grams of dioxin (TEQ) per 100,000 tons of EDC produced (4.2ng/g EDC) [Evers, 1989]. A 1994 analysis at a fully modernized EDC/VCM plant in Germany found dioxins in process sludges at concentrations as high as 414 ppb [Lower Saxony, 1994], refuting the claim that only outdated EDC/VCM technologies produce dioxin. An analysis made by ICI Chemicals and Polymers at its vinyl chloride monomer production plant in Runcorn, UK, found that more than 27g TEQ of dioxins are produced in solid and liquid wastes each year (per 200,000 tons) [ICI, 1994, reproduced in Environment Agency, 1997]. If dioxins created during the integrated production of perchlorethylene and trichlorethylene (produced using by-products of the VCM production) are included, this number increases to more than 500g TEQ per year, much of which is currently deposited in off-site salt caverns.**

Admitting the inevitability of producing dioxins in VCM production, ICI notes that, *"It is difficult to see how any of these [process] conditions could be modified so as to prevent PCDD/PCDF formation without seriously impairing the reaction for which the process is designed* [ICI. 1994]."

>In the U.S., dioxins, furans and PCBs have been identified in oxychlorination wastes from the Vulcan Chemical plant in Louisiana at concentrations as high as 6000 ppb TEQ. [Costner, et. al., 1995]. These levels suggest that oxychlorination wastes are among the most dioxin-contaminated wastes ever identified, with concentrations in the same range as wastes from the production of Agent Orange, an notorious herbicide used for defoliation during the Vietnam War.

Production wastes from EDC synthesis also contain PCBs. In 1990, Dow Chemical found that "heavy end" wastes from EDC distillation at its Louisiana facility contained PCBs at concentrations up to 302 parts per million -- well over the legal limit [Dow, 1990]. In fact, EPA had proposed to regulate PCB formation from EDC synthesis as early as 1988, but withdrew its proposal under pressure from the Vinyl Institute and numerous EDC-producing corporations [Costner, 1995].

The fact that dioxins are formed and partitioned into wastes does not mean that they will be released into the environment. Some dioxins are retained in cycling streams in the processes; some may be destroyed in incineration. But at least some portion of the dioxins created will be released to the environment through incomplete combustion or accidental releases; indeed in its sampling of wastes at the Vulcan Chemical plant and other EDC/VCM facilities, Greenpeace investigators found wastes in barrels and other readily accessible storage containers [Costner, et. al., 1995]. In addition, the chlorine-rich wastes created in the EDC/VCM production process contain many other organochlorines, which, when incinerated, can create and release dioxins into the environment as products of incomplete combustion. The quantity of dioxin generated as products of incomplete combustion may, in fact, be far greater than that in the original waste that escapes combustion [Costner, et. al., 1995].

In addition to incinerator air emissions, dioxin-contaminated fly ash and scrubber water from on and off-site incineration facilities must be treated and disposed of. Fly ash and scrubber water may account for up to 88 percent of dioxins created by the incinerator process [Huang and Beuknes, 1995]. Ashes and waste water treatment sludges are typically land-disposed, while effluents are ultimately discharged to waterways. When landfilled, the dioxins in these wastes can threaten groundwater.

Wastes from EDC manufacture is of special concern in developing countries, where incineration technologies are primitive and inadequate landfilling could occur. In the end, the wastes associated with the production of PVC should be considered dioxin-contaminated wastes that pose special threats to air, water, and land.

Releases to Air and Water

Dioxins, furans, PCBs, hexachlorobenzene, and other dioxin-like compounds have been identified in the air emissions and effluent discharges (and wastewater treatment sludges) from several EDC/VCM plants [ICI, 1994, SFT, 1993, Johnston, 1994]. These wastewater dioxin concentrations are of particular interest in relationship to dioxin in sediments. For example, in one study, up to 80 percent of the dioxin in sediment samples from the Rhine River (Netherlands) were attributed to an upstream EDC/VCM facility [Evers, et. al., 1988, Evers, 1989]. In an update to their study [Evers and Olie, 1996], these same researchers linked decreased dioxin levels in sediments to the halting of production of the pesticide 2,4,5-T, an example of a materials policy applied to dioxin; however, they found that *"the congener patterns of PCDD and PCDF in Rhine sediments revealed that the production of vinyl chloride monomer is still an important source of especially OCDF and other higher chlorinated congeners."*

Another research effort identified dioxin concentrations ranging from 433 to 922 ppt TEQ in sediments from a harbor on which an EDC/VCM facility is sited [Evers, et. al., 1989b, Wenning, et. al., 1992]. Studies in the Netherlands, Sweden, and Germany have all found elevated levels of dioxins in sediments, water, and biota downstream from EDC/VCM discharge points [Evers, 1988, Evers, 1993, Cato, 1992, Costner, et. al., 1995, Lower Saxony, 1994, Verhoog, 1988, as cited in Andersen and Knapp, 1994].*** In certain areas of the North Sea and Baltic, EDC/VCM synthesis appears to be a primary source of environmental dioxin contamination. [Evers, 1989, Evers, 1988]. High concentrations of dioxins have been identified in shellfish and sediments in the Venice

lagoon in the vicinity of Enichem's VCM/EDC/PVC production facility [Fabbri. 1996]. Greenpeace found total dioxin concentrations of more than 2.900 parts per trillion (15.4ppt TEQ) in sediments taken slightly downstream from the discharge point of the Geon Corporation in LaPorte. Texas [Costner. et. al.. 1995]. This concentration is approximately four times higher than the average concentration reported for North American sediments in EPAs draft dioxin reassessment.

A National Oceanic and Atmospheric Administration (NOAA) report found high levels of hexachlorobenzene. PCB's. hexachlorobutadiene – all contaminants that tend to be formed as byproducts along with dioxin -- in the sediments and water of estuarial bayous surrounding the PPG and Condea Vista PVC facilities in the Lake Charles. Louisiana area. Fish in these waters are also highly contaminated [NOAA. 1996]. These two firms. along with Conoco. Inc. appeared to make major contributions to the area's contamination burden.

Dioxins in PVC Products

Dioxins have also been found in the PVC product itself. In May 1994. the Swedish Environmental Protection Agency found that PVC plastic contains measurable quantities of dioxins and furans [SEPA. 1994]. Pure PVC suspension from two Swedish PVC producers was found to contain a full range of congeners of dioxins. furans. and PCBs. Total concentrations. including PCBs. ranged from 0.86 to 8.69 ppt (TEQ). In 1995. the UK Ministry of Agriculture. Fisheries. and Food (MAFF) noted the presence of low levels of PCDDs and PCDFs in PVC articles manufactured for use either as food packaging or food processing equipment [Wagenaar. et al. 1996]. In 1992. BF Goodrich (now Geon) submitted information to U.S. EPA indicating that dioxins had been found in concentrations up to 170 parts per trillion (total PCDD/F) in resin and pipes made from "post-chlorinated PVC" (CPVC). an engineering thermoplastic that Goodrich manufactured and sold at the time and has since discontinued [Mattia. 1992. MRI. 1991]. Dioxins were also found in the workplace air in the extrusion of this product [Mattia. 1992]. Since then. the plastics industry in Europe and the U.S. Vinyl Institute have undertaken studies to quantify dioxin levels in PVC resins and products [Wagenaar. et. al.. 1996. Carroll. et. al.. 1996]. Both studies identified trace levels of dioxin contamination (mainly OCDFs) in some samples. The industry suggests that these levels are insignificant and that the results of the Swedish and British government studies are due to contamination. But the evidence clearly warrants a comprehensive. **independent** investigation to characterize the presence of dioxins in PVC resins and products.

Estimates of Total Dioxin Formation

Given the paucity of plant-specific data. it is not possible to estimate with confidence the total quantities of dioxin produced by production processes for PVC feedstocks. As a preliminary estimate. we can extrapolate from the analysis of ICI's Runcorn Plant. which found dioxin production of 27 g TEQ per 200.000 metric tonnes of EDC produced [Environment Agency. 1997]. Based on annual U.S. production of 11 million metric tonnes of EDC [VI. 1996]. U.S. EDC/VCM plants would create an estimated 1485 g TEQ dioxin per year. assuming similar rates of dioxin generation. At least some portion of this dioxin would be released to air. water. and land.

The vinyl industry has argued that European data can not be applied to U.S. plants. The industry has not supplied data on dioxin contamination of wastes from its facilities in this country. however. to fill the gap. In the meantime. there is no reason to suppose that dioxin formation will be substantially different from similar facilities in Europe. Indeed, the U.S. Vinyl Institute has confirmed the presence of low concentrations of dioxin in waste water samples from four U.S. plants that manufacture EDC/VCM [Vinyl Institute, 1996]. As previously noted. samples from U.S. EDC/VCM plants obtained by Greenpeace and analyzed at an independent laboratory contained extremely high levels of dioxin [Costner. et. al.. 1995]. More recent samples of "light end" wastes from Borden's facility in Louisiana contained 310 ppt TEQ. while samples of on-site remediation wastes at the PPG facility in Lake Charles. Louisiana -- from an old area for the dumping of tars -- contained dioxins and furans at the extremely high level of 76.239 ppt [Santillo. 1996]. As a result. there can be no doubt that substantial quantities of dioxins can be produced in PVC production in Europe and in the U.S.

Dioxins in Chlorine Production

Even at the very root of the PVC lifecycle. dioxins can be produced. More than 30

percent of the chlorine produced in the world is directed into PVC [SRI, 1993], so that PVC again is associated with more dioxins produced in the chlor-alkali process than any other product. In this process, chlorine gas is produced by passing a powerful electric current through a solution of salt water. Carbon-containing materials are present in these reactions as trace contaminants, as plastics in plant equipment, or as components of electrodes. During and after the chlor-alkali reaction, chlorine combines with organic material to produce dioxins and other contaminants. Very high concentrations of dioxins (up to 650 ppb total), along with hexachlorobenzene, octachlorostyrene, and hexachloroethane, have been also found in the sludges from spent graphite electrodes used in this process [Rappe, 1991]. These results were found in plants using graphite electrodes.

Although all chlorine plants in North America and many in Europe have replaced graphite electrodes in recent years with titanium substitutes, questions arise as to dioxin formation even at the most modern chlor-alkali plants. Researchers [Strandell, et. al., 1994 as reported in Versar, 1996] have reported that metal electrode sludge from a facility in Sweden contained high levels of PCDFs that might have been formed by the chlorination of polycyclic aromatic hydrocarbons present in the rubber linings of the electrolytic cell. This research raises questions as to the extent to which modern chlorine production processes create dioxins.

Unanswered Questions

An accurate quantification of the total contribution of the PVC lifecycle to the global dioxin burden is not possible at this time due a lack of important information. Data gaps include site-specific emissions to all media and waste streams from EDC/VCM/PVC plants; dioxin releases associated with accidents, near-misses, pressure releases and other production upsets at EDC/VCM/PVC production facilities (which may occur with regularity); amounts of PVC on metals destined for recycling; amounts of PVC involved in accidental fires (structural and transportation); and amounts of PVC otherwise burned in landfills and other combustion processes.

Despite these uncertainties, there is no doubt that PVC is the cause of major dioxin releases from medical waste and municipal waste incineration, and appears to be an important chlorine donor in accidental fires and a number of metals recycling processes. Dioxin generation in many other aspects of the PVC lifecycle appears to be significant, but remains to be quantified. For example, assessment of the total dioxin generation from PVC manufacture complicated by the use of different production technologies and the co-production of chlorinated solvents [Stringer, et. al., 1996]. Important questions remain unanswered concerning the full extent of dioxin generation caused by the PVC lifecycle. Gathering the required objective information is a task that should be pursued aggressively by independent parties, not delegated to the industry itself.

Case Study 2: The PVC Industry's Voluntary Dioxin Study: Science or Public Relations

A 1994 "Crisis Management Plan for the Dioxin Reassessment" prepared for the Vinyl Institute (VI) by a public relations firm precisely forecasts the actions the industry should take -- and has taken -- since the release of EPA's dioxin reassessment. The document instructs the industry how to portray scientific and technical information *"to avoid deselection of PVC by major customers and to prevent punitive regulation of PVC by EPA, Congress, or the state legislatures* [Burnett, 1994]."

According to the document, the Vinyl Institute initiated the strategy just before EPA released its dioxin reassessment, because *"EPA will likely conclude that the incineration of chlorinated compounds is the single largest known contributor of dioxin....We believe that PVC will be specifically mentioned, and potentially slated for further regulation."* The strategy advises industry representatives on how to respond in the media, and it suggests that the industry enter into joint scientific activities with EPA in order to avoid future regulation.

According to the strategy:

> *"The short-term objective of the plan is to mitigate the effects of potential negative press coverage by positioning the vinyl industry as a proactive and cooperative entity, working in tandem with EPA to characterize and minimize sources of dioxin.... The vinyl industry must*

actively and aggressively communicate with the media its commitment to working with EPA to characterize and minimize any dioxin in the PVC lifecycle while at the same time asserting that based on reliable data available to date, the industry believes its contribution is minimal. Cooperative positioning is the key element; solely asserting that PVC is a minor contributor to the problem will only serve to misposition the industry as uncaring and unresponsive in the minds to target audiences.... The most effective message VI can deliver to respond to Greenpeace and leverage its own position in the dioxin debate is the following: The vinyl industry supports EPA's objective of identifying and reducing dioxin emissions and is working with EPA to determine the best means of achieving that goal [Burnett, 1994]."

Soon after the strategy was written, EPA and the Vinyl Institute announced a plan by which the industry would cooperate with EPA's Dioxin Reassessment by "self-characterizing" dioxin emissions from PVC production. This industry program is now the only source of new data on dioxin/PVC links that enters the dioxin reassessment process. The industry collects samples from its own plants, analyzes their dioxin content, interprets the data, and submits it to EPA. While the process and results are overseen by a "peer review" panel, the industry ultimately can choose where, when, and how samples will be taken and analyzed, and which data are suitable for submission. Because information about the samples -- including the facility from which they were taken -- is confidential, there is no way for the review committee, EPA or the public to know whether sampling times or locations accurately represent typical or worst-case dioxin releases or have been specifically selected to provide favorable data. Nor is it possible to otherwise evaluate, confirm, or act on the information.

The VI self-characterization will not look at releases of dioxins throughout the entire PVC lifecycle but will consider only dioxin releases during PVC production. The program only tests certain potential dioxin discharge routes without evaluating the total generation of dioxins at these facilities [Vinyl Institute 1996]. The sampling program will not examine many materials that are potentially important sources of dioxin transfer and release, including recirculating materials in the manufacturing process, products transferred to other facilities in the EDC/VCM/PVC manufacturing chain, and wastes transferred to regulated hazardous waste treatment, storage and disposal facilities. Of particular concern is the failure to evaluate highly-contaminated production wastes; the industry omits these wastes from its program because they do not leave the "system boundary" of the facility, although their incineration, land disposal or accidental release will likely result in their escape across this imaginary boundary. Finally, the program will not address the significant dioxin emissions associated with the disposal of PVC products.

Thus far, the industry has chosen to submit information only on those aspects of the PVC production that are known to contain small amounts of dioxin (wastewater and resins) [Carroll, 1996]. By the time EPA finishes its reassessment, no data are expected to have been submitted on those aspects of production that could cause major dioxin emissions. Data on wastewater treatment sludges and on incinerator stack gases are not expected until mid-1997.**** No data from Phase 2 of the industry's characterization program, including vinyl chloride monomer, spent catalyst, and chlorinated solvent co-products will available for some time to come. Meanwhile, the industry continues to grow rapidly, building new production facilities and expanding sales, exports, and production capacity.

The VI's testing program to date has demonstrated numerous limitations. First, the peer review committee was not brought into the program until it was already in progress, with most of the Phase 1 sampling complete. The committee thus had no meaningful opportunity to evaluate the design of the sampling program or to audit its performance. Still, the committee has noted several limitations in the study including the voluntary participation of VI member companies, possible undocumented differences in field sampling protocols by participating companies, the relatively low number of wastewater treatment systems sampled, lack of documentation on fugitive releases of EDC prior to purification, and the fact that the study has been designed to characterize normal process operations and not upsets or accidents, which occur with regularity [Vinyl Institute, 1996]. Additionally, there is no attempt in the sampling program to conduct single-plant, multi-media studies (total dioxin emissions from a single plant).

It is reasonable for any industry with potential impacts on public health and the environment to be subject to independent evaluation, not "self-characterization." The

vinyl industry in particular has demonstrated a need for oversight. As early as 1949, the industry knew that worker exposure to vinyl chloride monomer, a known human carcinogen, could cause liver damage in humans. Even with information from additional studies in the 1950s and 1960s, the industry failed to take action to protect worker and public health from VCM exposure. Only when studies revealed an association with rare liver cancer deaths in the early 1970s did the industry admit the hazards of vinyl chloride. The U.S. Second Circuit Court noted, *"Indeed, the record shows what can only be described as a course of continued procrastination on the part of the industry to protect the lives of its employees."* When the Occupational Safety and Health Administration (OSHA) proposed a lower occupational health standard for VCM exposure, the industry took OSHA to court, arguing that the new limit would devastate the industry. But when the court upheld OSHA's exposure limit, the industry was able to implement new technologies and reduce exposure levels within 1 year while expanding its operations [Ashford and Caldart, 1991].

Notes

* Researchers have noted that dioxins contained in EDC wastes are generally dominated by the octa-chlorinated dibenzofurans (OCDFs). These octa-chlorinated dioxins and furans receive relatively low weighting in TEQ schemes [Johnston and Troendle, 1993]. Thus, the mass balance of total dioxins in EDC wastes (and emissions from these plants) is much larger.

** The integrated process appears to be used by some facilities in the United States. This integrated process could lead to the generation of wastes with even higher dioxin levels.

*** In some of these studies other production facilities may have existed in the area or production of other chlorinated chemicals may have occurred at the same facilities.

**** While these results may be submitted to EPA before the dioxin reassessment is released, they are not likely to be incorporated into the final document.

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Written by Joe Thornton
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A LITERATURE REVIEW OF FORMATION AND RELEASE OF PCDD/Fs FROM GAS MANUFACTURING: A PREVIOUSLY UNIDENTIFIED SOURCE?

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ABSTRACT

The requirements commonly accepted as requisite for PCDD/F formation in thermal processes of coal and coke (presence of carbon, chlorine, metal catalysts, and adequate temperature) were also found to exist in several places within the gas manufacturing process. The coal and coke used in gas manufacturing typically contained up to about 95% carbon and 0.1% chlorine, which, at the operating temperatures seen in most older, carburetted water gas units, were sufficient for chlorination reactions to occur. Reactor conditions also suggest that PCDD/Fs could be formed during the gas generating process as well as in the waste streams. The gas generating unit has a well-defined temperature profile with maximum temperatures of 1000°C occurring within the bottom of the charge. PCDD/F formation could occur in the upper cooler zone (possibly associated with fly ash) near the gas exit. In addition, PCDD/F formation could occur where residence times are longer such as the fly ash outlet and bottom ash outlets. © 1997 Elsevier Science Ltd

INTRODUCTION

Despite the extensive amount of information published on sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), the U.S. Environmental Protection Agency (EPA) and others have acknowledged that there remain a significant number of unidentified PCDD/F sources (EPA, 1995). Over the past twenty-five years, scientific research has demonstrated that PCDD/Fs are generated during a wide range of activities including pesticide (Cochrane et al., 1982), paint, dye, and pigment production (Remmers et al., 1991; Williams et al., 1992; Christmann et al., 1989; LeBel et al., 1991); petroleum refining (API, 1990); paper pulp bleaching; metallurgical processes (Theisen et al., 1993); combustion processes such as hazardous waste, medical waste, municipal solid waste, and sewage sludge incineration (Heindl and Hutzinger, 1989; Fiedler, 1993); and the incineration of polychlorinated biphenyls (PCBs) (Buser et al., 1978). PCDD/Fs have also been detected in still bottoms from dry cleaners (Towara et al., 1992), automobile exhaust, soot from the chimneys of residential wood stoves, and in commercial detergents (Rappe et al., 1990; Lahl, 1993; Rappe and Andersson, 1992).

Several recent studies have demonstrated that the combustion of coal in utility boilers may be a significant source of PCDD/Fs to the environment (Rotard et al., 1994; Frankenhaeuser et al., 1993, 1994; Ruuskanen et al., 1994; Thub et al., 1995; Cains and Dyke, 1994). Because of similarities in the feedstock and processing, the

production of manufactured gas from coal may also be an important source of PCDD/Fs. For instance, during gas manufacturing, coal is heated and the gases, residues, and ash are cooled through the temperature range that is optimal for PCDD/F formation. Other conditions requisite for PCDD/F formation in coal combustion, including carbon, chlorine and metal catalysts, also exist during the thermal processing step of gas manufacture. The concern that gas production from coal and coke may be a source of PCDD/Fs was first raised by the EPA (Page et al., 1978) in its guideline document for preparation of test plans for coal gasification plants. The document specifically identifies PCDD/Fs as potential contaminants from these facilities, yet no studies have been published that attempt to confirm the presence of these compounds at gas plants or that examine the possible formation of these compounds during gas manufacturing.

For almost 200 years, gas manufacturing provided a cheap source of gas to residential consumers in the United States. Its use has only recently been restricted to supply during peak demand due to the advent of reliable natural gas pipelines. The operations surrounding gas manufacturing were extensive. For example, according to historical records, gas manufacturing occurred along the Passaic River in New Jersey from the late 1800's until the 1970's. Ten plants were required to meet the needs of northern New Jersey communities such as Newark, Jersey City and Paterson. Of these plants, the four largest were each capable of producing 15 million to 40 million cubic feet of gas per day (Public Service Review, 1924).

Although gas manufacturing plants exist throughout the United States, a particularly large amount of data is available regarding the facilities and operations on the Passaic River in northern New Jersey. Consequently, much of the information provided and discussed in this paper is taken from this pool. However, because gas manufacturing processes were similar throughout the country, the conclusions drawn are expected to be applicable to the industry as a whole and not solely to the plants from which the data were obtained.

The specific objectives of this study were to: (1) review the processes by which PCDD/F formation occur in thermal reactions of coal and coke, (2) review the gas manufacturing process with special emphasis on reactor conditions that may be suitable for PCDD/F formation, and (3) compare the conditions under which PCDD/F formation occurs in thermal reactions to those conditions existing in gas manufacturing to assess whether PCDD/F formation could have been a component of gas manufacturing waste streams.

MECHANISMS OF PCDD/F FORMATION IN THERMAL REACTIONS OF COAL AND COKE

The minimal requirements necessary for PCDD/F formation are well-documented and include a source of carbon, a source of chlorine, and thermal conditions exceeding approximately 200°C (EPA, 1980; Addink et al., 1991). Although the precise mechanism by which PCDD/Fs are formed in thermal reactions such as combustion, incineration, and other non-specific thermal events has not been clearly elucidated, (Dickson et al., 1992; Fiedler, 1993) several theories have been postulated (Dickson et al., 1992; Addink et al., 1995; Halonen et al., 1995; Chang and Huang, 1996). The four prevailing PCDD/F formation mechanisms are:

(1) Native PCDD/Fs enter the system and undergo dechlorination/rechlorination;

(II) PCDD/Fs are formed through various ring formations and rearrangements of chlorinated precursors such as PVC, PCBs, and chlorinated benzenes;

(III) PCDD/Fs are formed from appropriate non-chlorinated organic species (i.e., PAHs, lignins, etc.) that partially breakdown and undergo rearrangement and chlorination; and,

(IV) PCDD/Fs are formed via *de novo* synthesis on the surface of particulate carbon.

The primary difference among these mechanisms is the source of the carbon in the final PCDD/F products. Specifically, was the carbon originally organic or inorganic, chlorinated or non-chlorinated? A wide range of chlorinated organic PCDD/F precursors have been described in the scientific literature including chlorophenols, chlorobenzenes, chlorinated aliphatic hydrocarbons, PCBs, polyvinyl chloride, and dioxazine-, phthalocyanine-, and chloranil-based dyes (Williams et al., 1992; Buser et al., 1978; Rappe and Andersson, 1992; Heindl and Hutzinger, 1989). The formation of PCDD/Fs during the combustion of untreated wood suggests that PCDD/Fs are also formed from the breakdown and rearrangement of non-chlorinated organic macromolecules such as lignins (Nestrick et al, 1989). Finally, PCDD/Fs can be formed in the absence of organic precursors, for example, during the chlorination and roasting of siliceous black ore, the smelting of steel and magnesium, and from particulate carbon on the surface of fly ash in the post-combustion chambers of boilers and incinerators (Oehme et al., 1989; Lahl, 1993; Addink et al., 1990; Stieglitz et al., 1993; Schoonenboom et al., 1995).

The relative importance of each of the formation mechanisms is dependent upon the characteristics of the feedstock and the operating conditions of the system. The carbon present in coal and coke (the feedstocks in gas manufacturing) is predominantly in the form of lignins. Lignin-type compounds are degraded to smaller organic molecules such as methane and other volatile organics, polycyclic aromatic hydrocarbons (PAHs), and various heterocyclic compounds including dibenzothiophene and dibenzofuran (ERT, 1984; GRI, 1987). Since these source compounds are non-chlorinated and subjected to severe thermal conditions, only formation mechanisms (III) and (IV) would be expected to be important in gas manufacturing processes. Reaction time, however, may also influence which of the PCDD/F formation mechanisms dominates. For example, Dickson et al. (1992) concluded that the relative importance of precursor-dependent PCDD/F formation (II or III) versus *de novo* synthesis (IV) was primarily governed by residence time. They showed that precursor-dependent formation predominates under the relatively short residence time associated with post-combustion and heat exchange sections of an incinerator, but that in pollution control equipment such as electrostatic precipitators which have longer residence times (1-1000 seconds), *de novo* synthesis may make a significant contribution to PCDD/F emissions.

The carbon content of the feedstock has been shown to affect the amount of PCDD/Fs formed. In a study of PCDD/F formation under *de novo* synthesis, Stieglitz et al. (1989) reported a good correlation between carbon content and PCDD/F concentrations under standard conditions of 300°C, 150 mg/L water vapor, 1% KCl, and 0.4% $CuCl_2$. The amount of PCDD/Fs formed increased with increasing carbon content, until, at the highest carbon concentration evaluated (80%), no further increase in PCDD/Fs was observed. The authors attributed this to the depletion of

available chlorine. Similar relationships between carbon content and amount of PCDD/Fs generated have been observed in studies of municipal solid waste incinerators and mixed waste utility boilers (Wunsch et al., 1994).

Both the form and concentration of chlorine appear to be factors in PCDD/F formation. While it is well-known that Cl_2 is the principal chlorinating agent in many PCDD/F-generating reactions such as PCB and trichlorophenol production (EPA, 1980), Hoffman et al. (1990) concluded that it is probably not the chlorinating agent in *de novo* synthesis. Instead, they argue that HCl reacts with the fly ash surface to form a surface-bound chlorinating agent. Studies of PCDD/F formation during the incineration of municipal solid waste support this view. They indicate that volatile inorganic chlorides (e.g., NaCl and $FeCl_3$) formed during combustion condense on carbon particle surfaces at approximately 440°C and subsequently participate in the formation of chlorinated aromatic compounds such as PCDD/Fs (Fangmark et al., 1994). It has also been suggested that the *de novo* formation of PCDD/Fs formed during the thermal reaction of fly ash results from the degradation of carbon and the formation of volatile halogenated organic compounds (Stieglitz et al., 1993).

The effect of chlorine concentration on PCDD/F formation and distribution has been demonstrated in several studies. Mattila et al. (1992), for example, observed increased PCDD/F formation with increasing chlorine content of mixed fuels (coal, bark, and plastics). Thub et al. (1995) reported similar results for residential combustion of lignite. In this case, the researchers evaluated lignite with chlorine contents of either 300 or 2,000 ppm chlorine. The concentration of total PCDD/Fs generated was approximately 3.5 times greater from the lignite with the higher chlorine content. Specifically, total PCDD/F concentrations were 2,247 pg/m^3 and 7,540 pg/m^3 in the 300 and 2,000 ppm chlorine content briquettes, respectively.

Metals present in the feedstock can serve as catalysts, greatly increasing the rate of PCDD/F formation (Stieglitz et al., 1989; Halonen et al., 1995). According to Stieglitz et al (1989), copper chloride is particularly effective while other divalent metal chlorides such as magnesium, zinc, mercury, cadmium, tin, and lead display only limited catalytic activity. Increasing the copper ion concentration during *de novo* synthesis resulted in a more than proportional rise in PCDD/F formation. Copper is particularly interesting because it has been found to assist in ring condensation reactions from materials such as chlorophenols (Addink et al., 1995; Gullet et al., 1992; Bruce et al., 1991). Addink et al. (1990) demonstrated that $CuCl_2$ catalyzes both ring closure and chlorination of the dibenzofuran and dibenzo-p-dioxin rings. Other studies indicate that catalysis by transition metals eroded from fly ash particles occurs primarily through electrophilic substitution reactions (Hoffman et al., 1990; Schoonenboom et al., 1995), and that the formation of PCDD/Fs likely proceeds via a two-stage mechanism. The first step in this proposed mechanism is the chlorination of the carbon surface and the second is the oxidative decomposition of the chlorinated carbon to yield PCDD/Fs (Schoonenboom et al., 1995).

Temperature is perhaps the most important factor affecting PCDD/F formation. Under optimal combustion conditions (i.e., sufficient oxygen, mixing, and air flow), essentially all organic compounds including PCDD/Fs are destroyed at temperatures exceeding 800°C. Under less optimal conditions such as insufficient oxygen, however, PCDD/Fs may be formed even at elevated temperatures (Gullet et al., 1990). Furthermore, studies of PCDD/F

formation on the surface of fly ash have shown that PCDD/Fs may be formed at temperatures as low as 200°C, and that such *de novo* formation of PCDD/Fs is thermodynamically controlled (Addink et al., 1990). Stieglitz et al. (1989) demonstrated that the optimal temperature for PCDD/F formation on fly ash is 300°C: total PCDDs and total PCDFs formed were 18.6 and 65 ng/g, respectively, at 250°C; 1,060 and 5,337 ng/g at 300°C; and 15.5 and 126 ng/g at 350°C. Low temperature formation of PCDD/Fs has been demonstrated by Fiedler (1993) as well.

THE GAS MANUFACTURING PROCESS

Gas manufacturing from coal or coke essentially involves the thermal conversion of coal to combustible gases. Gasification is achieved by subjecting the coal to a gasifying agent, such as steam, at temperatures above 700°C (Qader, 1985). Tar, sludges, spent oxides, and ash are typical residuals and wastes (ERT, 1984). Depending on the type of coal being processed, and the gas composition product desired, some or all of the following steps are required:

(1) Pretreatment of the coal, involving mild oxidation of the coal (by low temperature heating in the presence of air or oxygen) to destroy the caking characteristics of the coal;

(2) Primary gasification of the coal, via thermal decomposition of the coal, at pressures up to 1,000 psi, with air, oxygen, or steam additions as required to support combustion. The product is usually a low-BTU gas, with other components including tar, oils and phenols, and sometimes a solid char;

(3) Secondary gasification of the carbonaceous residue (char) from the primary gasifier;

(4) Removal of carbon dioxide, hydrogen sulfide, and other gases;

(5) Shift conversion for adjustment of the carbon monoxide/hydrogen mole ratio to the desired ratio. Carbon monoxide and hydrogen produced in the steps above are reacted with steam to produce the ideal 3:1 ratio of carbon monoxide and hydrogen for the production of methane at temperatures no greater than 400°C; and,

(6) Catalytic methanation (hydrogasification) of the carbon monoxide/hydrogen mixture to form methane.

One of the most common means of producing gas, especially from the early 1900s through the 1950s, was the carburetted water gas process. In New Jersey, for example, carburetted water gas was produced at least from 1900 to the mid to late 1940s (Public Service Review, 1924; PSE&G, 1996), and in more limited amounts, through the 1970s. The plants were initially designed to produce "carburetted water gas" of medium thermal content (Public Service Review 1924; Lutz, 1925; PSE&G, 1996).

The basic process flow sheet for this carburetted water gas process is depicted in Figure 1. Fuel, primarily coal and coke, was introduced to the gas generator at a rate of approximately 3 - 4 tons/hr (Lutz, 1925). Note at this time (circa 1920) flow-through or moving-bed gas generators were not yet available, so gas was produced in a batch-type mode where fuel was added as the previous charge was depleted in carbon (Morgan 1931; Speight, 1983; van Heeck, 1981). The use of multiple generating units provided a more or less continual generation of gas from hour to hour. Once in the generator, the fuel was heated by drawing air across the fuel bed and brought up to temperature

with the generator vent in the open position (van Heeck, 1981; Morgan, 1931; Lutz, 1925). When the operating temperature was achieved, steam and air were drawn into the generator fuel and the vent closed.

The water gas created in the generator was drawn to the top of the unit, exiting into the carburettor at a temperature of about 550 to 700°C (van Heeck, 1981; Lutz, 1925). Here, a fine spray of oil was injected into the water gas stream and the mixture drawn into the brick-lined superheater set at a temperature of about 1000°C. Once in the superheater, the oil was "gasified" into gases with much higher thermal content. The ratio of fuel (coal and coke) to oil was approximately 4 kg of fuel to 4 liters of oil (Lutz, 1925). By adding the oil, the thermal content of the resulting gas was increased from about 11 MJ/m^3 to over 20 MJ/m^3. After leaving the superheater, the gas was drawn through a water based "wash box" that served to collect non-gasified oil (which was drained for disposal) and then into a series of condensers and cleaners for removal of impurities (Lutz, 1925). The purified gas was piped to station meters and then to gas storage holders. The approximate composition of gas produced by this system at the Harrison Gas Plant in New Jersey is presented in Table 1 (Philipps, 1947).

Figure 1. Manufacture of Carburetted Water Gas

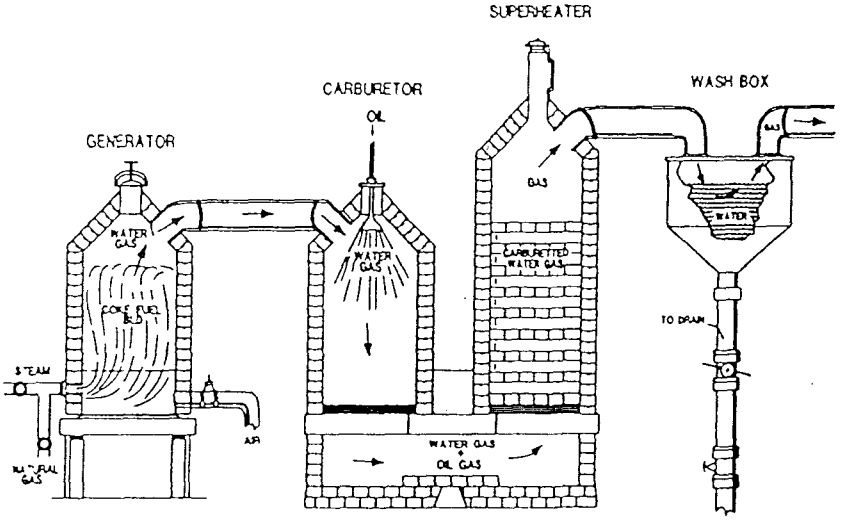


Table 1. Gas Composition in The Carburettion Process the Harrison Gas Plant

Component	%
Carbon monoxide	24.2
Hydrogen	28.8
Methane	16.6
Carbon dioxide	5.1
Nitrogen	16.0
Other	9.3

PCDD/F FORMATION AND RELEASE TO THE ENVIRONMENT DURING GAS MANUFACTURING

Based on the gas manufacturing process outlined above, it is postulated that PCDD/Fs may be formed from appropriate unchlorinated organic species that partially breakdown and undergo rearrangement and chlorination (formation mechanism (III)), and through *de novo* synthesis on the surface of particulate carbon (formation mechanism (IV)). These reactions can take place at various stages of the process and depend upon both the composition of starting materials and the processing parameters used in gas manufacturing.

Composition of Raw Materials

The composition of starting materials for gas manufacture varies widely depending on the source of the coal or coke. The carbon content of coals and cokes from various regions of the world ranges from approximately 35 to 94% by weight (Thub et al., 1995; Frankenhaeuser et al., 1994). In coals mined from Pennsylvania the carbon content ranges from approximately 60 to 80% by weight (DOE, 1982).

Chlorine, an important factor in PCDD/F formation, comprises approximately 0.01 to 0.1% of U.S. coals (DOE, 1982). The Paterson Gas Plant in New Jersey used coke as its primary fuel source and although no specific data are available on its chlorine content, chlorine in coke is known to range from 0.01 to 0.6 percent (Thibaut, 1963). Chlorine in coke and coal exists mostly in the form of salts such as NaCl, KCl, and $MgCl_2$. These salts are known to be the primary sources of chlorine involved in thermal reactions of coal that ultimately result in the formation of PCDD/Fs (Thub et al., 1995). Chlorine is also present in most plant-make-up waters providing an additional, but variable, source.

Coal and coke also contain numerous metals at concentrations sufficient to catalyze the formation of PCDD/Fs (Table 2). The concentrations in Table 2, for example, are comparable to those reported in metal-catalyzed *de novo* synthesis studies of PCDD/Fs (Addink et al., 1990; Stieglitz et al., 1985).

Table 2. Coke and Coal Feedstock Inorganic Chemistry

Trace Element	Reported Concentrations (mg/kg)[1] in Coke	Harrison Gas Plant Coal (mg/kg)[2]
As	0.5 - 3.0	1 - 58
Be	1.0 - 5.0	0.07 -0.9
Cu	5.0 - 100	5.2 - 160
Cd	0.7 - 3.0	0.03 - 3.4
Hg	0.03 - 0.12	0.03 - 0.85
Pb	9 - 69	1.8 - 17
Sb	0.5 - 2	0.2 - 1.4
Se	1.0 - 13.0	1.0 - 7.8
Zn	37 - 90	2.3 - 62
Cl	6 - 1440	66 - 910

[1]Wyatt et al. (1980)
[2]PSE&G, 1996

Gas Manufacturing Operating Conditions and PCDD/F Formation

Within the gas manufacturing process, several locations exhibit conditions suitable for PCDD/F formation. These include:

(1) *The gas generator reactor*: The generator contains burned and unburned coal and off gases.

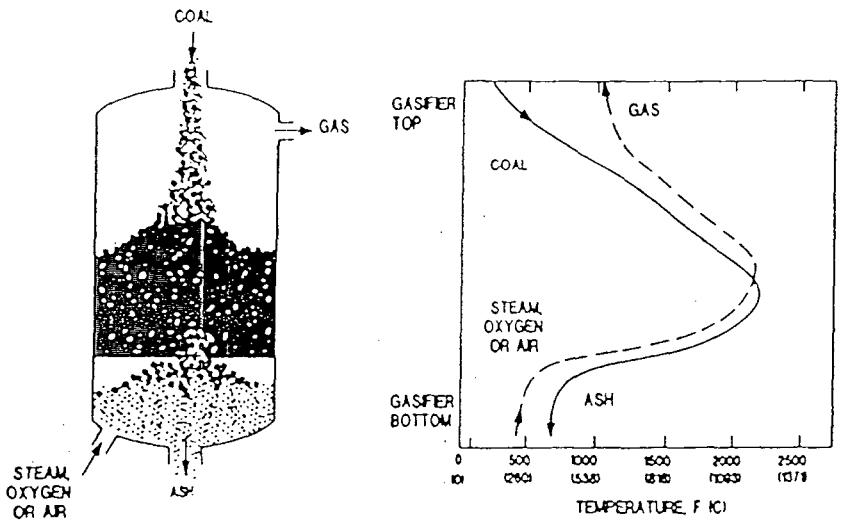
(2) *Stack emissions originating from the reactor vents*: These are gas phase and particulate emissions emanating from the gas generator stack, the superheater units, and the steam generator boilers.

(3) *Ash and spent coke or coal exiting the bottom of the reactor*: These are wastes from the bottom of gas generators and utility boilers that are usually water sluiced from beneath the generator and boiler grates. Residuals include coal and coke dust, spent ash, and clinkers from below the generator grates. Gasifier ash, the residue from the gasification of coal, is similar in composition to fly ash.

(4) *Tar and oil waste enriched in PAHs collected downstream of the reactor*: These wastes consist of condensed gas and coal tar residues collected in water traps and condensers adjacent to product gas exhaust from the superheater.

Figure 2 (Stultz and Kitto, 1992) shows a typical water gas coal gasification reactor and associated temperature profile. In this unit, a column or bed of crushed coal or coke is supported by a grate. At the top of the generator, the coal is heated and dried while the product gas is cooled. The coal is further heated and devolatilized as it descends through the carbonization zone. Below this area, the devolatilized coal is gasified by reaction with steam and carbon dioxide. The profile indicates that in the combustion zone, the maximum temperature for gasification is approximately 1000°C and occurs within the bottom to center of the charge. Spent coal and ash exit the bottom of the reactor at much lower temperatures (usually between 200 and 500°C). As in any stack emission, gases and particulates vented from the top of the generator would also be expected to cool rapidly.

Figure 2. Moving-Bed Gasifier (Dry Ash)



PCDD/F formation within a fixed bed reactor would tend to occur near the bottom ash exit where temperatures rapidly fall below 500°C or near the exit gas vents during heating or replacement of the charge. In both cases, temperature conditions for PCDD/F formation are ideal. Furthermore, there is sufficient chlorine and gas-phase carbon for PCDD/F formation to occur within the reactor. Coal and coke contain salts such as $FeCl_3$, $MgCl_2$, NaCl and KCl as well as catalysts such as $CuCl_2$, CuCl, and $FeCl_3$. If, for example, Na and Mg chlorides control the stability of chlorine in coal (Mohammadi, 1992) then calculations demonstrate that Cl (as HCl) off-gas concentrations could range from 10^{-12} M to 10^{-2} M in the reactor over a temperature range of 400°C to 1000°C. These conditions are consistent with other combustion processes in which the burning of fuel containing carbon and chlorine results in PCDD/F formation (Choudhry and Hutzinger, 1983).

It has also been reported that under less-than-optimal conditions (such as insufficient oxygen), PCDD/Fs may be formed at temperatures that normally would exceed the threshold temperature of 800 °C for PCDD/F formation (Gullet et al., 1990). Insufficient oxygen within the generator reactor frequently leads to the formation of numerous PAH-type compounds, especially during the phase of gas production, where steam injection eliminates air in the generator house. While generator temperatures typically exceed 800°C, PCDD/F formation within the generator may still occur.

The known production of PAHs during the coal gasification process is an important indicator for simultaneous PCDD/F production because the formation of PAHs in coal ash is thought to be similar to the formation of PCDD/Fs (Gohda et al., 1993). Formation of PAHs and possibly PCDD/Fs could result from:

(1) inadequate supply of combustion air, resulting in fuel rich pockets and incomplete oxidation,

(2) low combustion temperatures, resulting in slow and incomplete combustion, and

(3) insufficient turbulence, resulting in inadequate mixing (can cause fuel rich pockets or cool zones).

Compounds, including PAHs and PCDD/Fs, that have formed in the generator are subsequently concentrated with condenser fluids and tars. Mohr and King (1985) report that the condensate water from gasifiers is contaminated with high concentrations of phenols and other organic compounds. PCDD/Fs are thus also likely to accumulate in condensate water.

Venting of stack gases and ash occurred as a normal part of the gasification cycle. For instance, carburetted water gas generators at older plants operated intermittently with alternate periods of blowing and gasification called "blow-or-make" (Schilling et al., 1981). In the first phase, blowing air was used as described earlier to heat the generator by the combustion of coke. In the second phase, the incandescent coke was treated with steam to cause an endothermic reaction that cooled the coke and produced water gas with high contents of carbon monoxide and hydrogen. This gasification was then followed by another period of air blowing to re-heat the generator. During heating, the vents in the generator chambers were always open to allow venting of unwanted gases and particulates.

The role of flue gas particulates and fly ash is likely important in PCDD/F formation in gasifier processes. As noted by Choudhry and Hutzinger (1983), PCDD/Fs are formed from aromatic precursor compounds adsorbed

onto the reactive surface of fly ash entrained in combustion plasmas. Formation occurs in regions where the temperature of the combustion off-gasses has cooled to 200 to 400°C. Chloride ions from inorganic sources such as copper chloride may act as gaseous-phase catalysts to promote surface reactions that convert aromatic precursor compounds to chlorinated dioxins and dibenzofurans. In the case of carburetted water gas production, oil introduced in the superheaters contains numerous trace metals including nickel, vanadium, molybdenum, zinc, lead, chromium, and copper that may also serve to catalyze PCDD/F formation on fly or bottom ash surfaces (Whiticar et al., 1992).

Other possible pathways for PCDD/F formation are associated with the flue gas and bottom ash waste stream and may prove important for gas manufacturing processes. For example, PCDD/Fs have been synthesized through reaction of carbonaceous particulate matter containing Mg- and Al-silicates in the presence of $CuCl_2$ at a temperature of 300°C (Stieglitz et al., 1989). This reaction has also yielded chlorinated benzenes, chlorinated biphenyls, and chlorinated naphthalenes, which are waste stream components common in gas manufacturing.

SUMMARY AND CONCLUSIONS

Based on historical records for gas manufacturing plants located in New Jersey, it has been demonstrated that many of the chemical and physical requirements for PCDD/F formation were present during the production of manufactured gas. These requirements (specifically, the presence of carbon, chlorine, metal catalysts, and adequate temperature) were met in several areas of a typical carburetted water gas plant. These include gas phase and particulate emissions emanating from the gas generator stack, the superheater units, the steam generator boilers; ash and spent coal originated from the bottom of the gas generator and utility boilers; and condensed gas and coal tar residues collected in water traps and condensers adjacent to product gas exhaust from the superheater. The coal and coke used in gas manufacturing typically contained up to about 95% carbon and 0.1% chlorine, which, at the operating temperatures seen in most older, carburetted water gas units, were sufficient for chlorination reactions to occur. Large amounts of metals and metalloids, which have been shown to promote PCDD/F formation in similar situations, have also been found in bottom ash, fly ash, and condenser wastes. Numerous PCDD/F precursor compounds and other organic substrates also existed, particularly in downstream gas clean-up processes. The high amounts of PAHs observed in gasification waste supports the presence of conditions suitable for PCDD/F formation.

Reactor conditions suggest that PCDD/Fs could be formed during the gas generating process as well as in the waste streams. The gas generating unit has a well-defined temperature profile with maximum temperatures of 1000°C occurring within the bottom of the charge. PCDD/F formation could occur in the upper cooler zone (possibly associated with fly ash) near the gas exit. Since PAH compounds escape the superheater, are possibly formed there, and are collected in large quantities within the condenser fluids, PCDD/Fs may form and collect in a similar fashion. In addition, PCDD/F formation could occur where residence times are longer, such as in the fly ash outlet and bottom ash outlets.

Gas manufacturing production has, in general, decreased significantly over the last 20 years. However, based on the numerous process residuals produced from these facilities (PSE&G, 1996), it is not unreasonable to suspect

that these process wastes represent an on-going source of PCDD/Fs to the environment. This seems especially likely in the case of stack emissions which may have impacted a wide area and now circulate in the environment as components of urban runoff.

Because the conditions requisite to formation of PCDD/F formation appear to be present in gas manufacturing, especially the earlier carburetted water gas process, the challenge now lies in determining if PCDD/Fs from this source can be identified within the environment. As noted previously, no studies have been published that attempt to confirm the existence of these compounds at gas plants or examine the possible formation of these compounds during gas manufacturing. Because of the need for large volumes of water for cooling and cycling of waste and process residuals, many former gas manufacturing plants lie along waterways. Sediment and soil located at these facilities sould be examined to confirm the extent to which PCDD/Fs are associated with gas manufacturing facilities.

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THIS DATA CURRENT AS OF THE FEDERAL REGISTER DATED JULY 26, 2002

40 CFR
Protection of Environment
CHAPTER I
ENVIRONMENTAL PROTECTION AGENCY (CONTINUED)

SUBCHAPTER I -- SOLID WASTES (CONTINUED)

PART 261 -- IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

Subpart A -- General

Sec.

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Authority: 42 U.S.C. 6905, 6912(a), 6921, 6922, 6924(y) and 6938.

Source: 45 FR 33119, May 19, 1980, unless otherwise noted.

Subpart A -- General

[TOP]

§261.1 Purpose and scope.

(a) This part identifies those solid wastes which are subject to regulation as hazardous wastes under parts 262 through 265, 268, and parts 270, 271, and 124 of this chapter and which are subject to the notification requirements of section 3010 of RCRA. In this part:

(1) Subpart A defines the terms "solid waste" and "hazardous waste", identifies those wastes which are excluded from regulation under parts 262 through 266, 268 and 270 and establishes special management requirements for hazardous waste produced by conditionally exempt small quantity generators and hazardous waste which is recycled.

(2) Subpart B sets forth the criteria used by EPA to identify characteristics of hazardous waste and to list particular hazardous wastes.

(3) Subpart C identifies characteristics of hazardous waste.

(4) Subpart D lists particular hazardous wastes.

(b)(1) The definition of solid waste contained in this part applies only to wastes that also are hazardous for purposes of the regulations implementing subtitle C of RCRA. For example, it does not apply to materials (such as non-hazardous scrap, paper, textiles, or rubber) that are not otherwise hazardous wastes and that are recycled.

(2) This part identifies only some of the materials which are solid wastes and hazardous wastes under sections 3007, 3013, and 7003 of RCRA. A material which is not defined as a solid waste in this part, or is not a hazardous waste identified or listed in this part, is still a solid waste and a hazardous waste for purposes of these sections if:

(i) In the case of sections 3007 and 3013, EPA has reason to believe that the material may be a solid waste within the meaning of section 1004(27) of RCRA and a hazardous waste within the meaning of

section 1004(5) of RCRA; or

(ii) In the case of section 7003, the statutory elements are established.

(c) For the purposes of §§261.2 and 261.6:

(1) A "spent material" is any material that has been used and as a result of contamination can no longer serve the purpose for which it was produced without processing;

(2) "Sludge" has the same meaning used in §260.10 of this chapter;

(3) A "by-product" is a material that is not one of the primary products of a production process and is not solely or separately produced by the production process. Examples are process residues such as slags or distillation column bottoms. The term does not include a co-product that is produced for the general public's use and is ordinarily used in the form it is produced by the process.

(4) A material is "reclaimed" if it is processed to recover a usable product, or if it is regenerated. Examples are recovery of lead values from spent batteries and regeneration of spent solvents.

(5) A material is "used or reused" if it is either:

(i) Employed as an ingredient (including use as an intermediate) in an industrial process to make a product (for example, distillation bottoms from one process used as feedstock in another process). However, a material will not satisfy this condition if distinct components of the material are recovered as separate end products (as when metals are recovered from metal-containing secondary materials); or

(ii) Employed in a particular function or application as an effective substitute for a commercial product (for example, spent pickle liquor used as phosphorous precipitant and sludge conditioner in wastewater treatment).

(6) "Scrap metal" is bits and pieces of metal parts (*e.g.,*) bars, turnings, rods, sheets, wire) or metal pieces that may be combined together with bolts or soldering (*e.g.,* radiators, scrap automobiles, railroad box cars), which when worn or superfluous can be recycled.

(7) A material is "recycled" if it is used, reused, or reclaimed.

(8) A material is "accumulated speculatively" if it is accumulated before being recycled. A material is not accumulated speculatively, however, if the person accumulating it can show that the material is potentially recyclable and has a feasible means of being recycled; and that -- during the calendar year (commencing on January 1) -- the amount of material that is recycled, or transferred to a different site for recycling, equals at least 75 percent by weight or volume of the amount of that material accumulated at the beginning of the period. In calculating the percentage of turnover, the 75 percent requirement is to be applied to each material of the same type (*e.g.,* slags from a single smelting process) that is recycled in the same way (*i.e.,* from which the same material is recovered or that is used in the same way). Materials accumulating in units that would be exempt from regulation under §261.4(c) are not to be included in making the calculation. (Materials that are already defined as solid wastes also are not to be included in making the calculation.) Materials are no longer in this category once they are removed from accumulation for recycling, however.

(9) "Excluded scrap metal" is processed scrap metal, unprocessed home scrap metal, and unprocessed prompt scrap metal.

(10) "Processed scrap metal" is scrap metal which has been manually or physically altered to either separate it into distinct materials to enhance economic value or to improve the handling of materials. Processed scrap metal includes, but is not limited to scrap metal which has been baled, shredded, sheared, chopped, crushed, flattened, cut, melted, or separated by metal type (i.e., sorted), and, fines, drosses and related materials which have been agglomerated. (Note: shredded circuit boards being sent for recycling are not considered processed scrap metal. They are covered under the exclusion from the definition of solid waste for shredded circuit boards being recycled (§261.4(a)(13)).

(11) "Home scrap metal" is scrap metal as generated by steel mills, foundries, and refineries such as turnings, cuttings, punchings, and borings.

(12) "Prompt scrap metal" is scrap metal as generated by the metal working/fabrication industries and includes such scrap metal as turnings, cuttings, punchings, and borings. Prompt scrap is also known as industrial or new scrap metal.

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[TOP]

§261.2 Definition of solid waste.

(a)(1) A *solid waste* is any discarded material that is not excluded by §261.4(a) or that is not excluded by variance granted under §§260.30 and 260.31.

(2) A *discarded material* is any material which is:

(i) *Abandoned,* as explained in paragraph (b) of this section; or

(ii) *Recycled,* as explained in paragraph (c) of this section; or

(iii) Considered *inherently waste-like,* as explained in paragraph (d) of this section; or

(iv) *A military munition* identified as a solid waste in 40 CFR 266.202.

(b) Materials are solid waste if they are *abandoned* by being:

(1) Disposed of; or

(2) Burned or incinerated; or

(3) Accumulated, stored, or treated (but not recycled) before or in lieu of being abandoned by being disposed of, burned, or incinerated.

(c) Materials are solid wastes if they are *recycled* -- or accumulated, stored, or treated before recycling -- as specified in paragraphs (c)(1) through (4) of this section.

(1) *Used in a manner constituting disposal.* (i) Materials noted with a "*" in Column 1 of Table I are solid wastes when they are:

(A) Applied to or placed on the land in a manner that constitutes disposal; or

(B) Used to produce products that are applied to or placed on the land or are otherwise contained in products that are applied to or placed on the land (in which cases the product itself remains a solid waste).

(ii) However, commercial chemical products listed in §261.33 are not solid wastes if they are applied to the land and that is their ordinary manner of use.

(2) *Burning for energy recovery.* (i) Materials noted with a "*" in column 2 of Table 1 are solid wastes when they are:

(A) Burned to recover energy;

(B) Used to produce a fuel or are otherwise contained in fuels (in which cases the fuel itself remains a solid waste).

(ii) However, commercial chemical products listed in §261.33 are not solid wastes if they are themselves fuels.

(3) *Reclaimed.* Materials noted with a "*" in column 3 of Table 1 are solid wastes when reclaimed (except as provided under §261.4(a)(17)). Materials noted with a " -- "in column 3 of Table 1 are not solid wastes when reclaimed.

(4) *Accumulated speculatively.* Materials noted with a "*" in column 4 of Table 1 are solid wastes when accumulated speculatively.

Table 1

	Use constituting disposal (Sec. 261.2(c)(1))	Energy recovery/ fuel (Sec. 261.2(c)(2))	Reclamation 261.2(c) (except as p in 261.4(a)(mineral pro seconda materia
	1	2	
Spent Materials.....	(*)	(*)	
Sludges (listed in 40 CFR Part 261.31 or 261.32.....	(*)	(*)	
Sludges exhibiting a characteristic of hazardous waste.....	(*)	(*)	
By-products (listed in 40 CFR 261.31 or 261.32).....	(*)	(*)	
By-products exhibiting a characteristic of hazardous waste.....	(*)	(*)	
Commercial chemical products listed in 40 CFR 261.33....	(*)	(*)	
Scrap metal other than excluded scrap metal (see 261.1(c)(9)).....	(*)	(*)	

Note: The terms ``spent materials,'' ``sludges,'' ``by-products,'' and ``scrap metal metal'' are defined in Sec. 261.1.

(d) *Inherently waste-like materials.* The following materials are solid wastes when they are recycled in any manner:

(1) Hazardous Waste Nos. F020, F021 (unless used as an ingredient to make a product at the site of generation), F022, F023, F026, and F028.

(2) Secondary materials fed to a halogen acid furnace that exhibit a characteristic of a hazardous waste or are listed as a hazardous waste as defined in subparts C or D of this part, except for brominated material that meets the following criteria:

(i) The material must contain a bromine concentration of at least 45%; and

(ii) The material must contain less than a total of 1% of toxic organic compounds listed in appendix VIII; and

(iii) The material is processed continually on-site in the halogen acid furnace via direct conveyance (hard piping).

(3) The Administrator will use the following criteria to add wastes to that list:

(i)(A) The materials are ordinarily disposed of, burned, or incinerated; or

(B) The materials contain toxic constituents listed in appendix VIII of part 261 and these constituents are not ordinarily found in raw materials or products for which the materials substitute (or are found in raw materials or products in smaller concentrations) and are not used or reused during the recycling process; and

(ii) The material may pose a substantial hazard to human health and the environment when recycled.

(e) *Materials that are not solid waste when recycled.* (1) Materials are not solid wastes when they can be shown to be recycled by being:

(i) Used or reused as ingredients in an industrial process to make a product, provided the materials are not being reclaimed; or

(ii) Used or reused as effective substitutes for commercial products; or

(iii) Returned to the original process from which they are generated, without first being reclaimed or land disposed. The material must be returned as a substitute for feedstock materials. In cases where the original process to which the material is returned is a secondary process, the materials must be managed such that there is no placement on the land. In cases where the materials are generated and reclaimed within the primary mineral processing industry, the conditions of the exclusion found at §261.4(a)(17) apply rather than this paragraph.

(2) The following materials are solid wastes, even if the recycling involves use, reuse, or return to the original process (described in paragraphs (e)(1) (i) through (iii) of this section):

(i) Materials used in a manner constituting disposal, or used to produce products that are applied to the land; or

(ii) Materials burned for energy recovery, used to produce a fuel, or contained in fuels; or

(iii) Materials accumulated speculatively; or

(iv) Materials listed in paragraphs (d)(1) and (d)(2) of this section.

(f) *Documentation of claims that materials are not solid wastes or are conditionally exempt from regulation.* Respondents in actions to enforce regulations implementing subtitle C of RCRA who raise a claim that a certain material is not a solid waste, or is conditionally exempt from regulation, must demonstrate that there is a known market or disposition for the material, and that they meet the terms of the exclusion or exemption. In doing so, they must provide appropriate documentation (such as contracts showing that a second person uses the material as an ingredient in a production process) to demonstrate that the material is not a waste, or is exempt from regulation. In addition, owners or operators of facilities claiming that they actually are recycling materials must show that they have the necessary equipment to do so.

[50 FR 664, Jan. 4, 1985, as amended at 50 FR 33542, Aug. 20, 1985; 56 FR 7206, Feb. 21, 1991; 56 FR 32688, July 17, 1991; 56 FR 42512, Aug. 27, 1991; 57 FR 38564, Aug. 25, 1992; 59 FR 48042, Sept. 19, 1994; 62 FR 6651, Feb. 12, 1997; 62 FR 26019, May 12, 1997; 63 FR 28636, May 26, 1998; 64 FR 24513, May 11, 1999; 67 FR 11253, Mar. 13, 2002]

[TOP]

§261.3 Definition of hazardous waste.

(a) A solid waste, as defined in §261.2, is a hazardous waste if:

(1) It is not excluded from regulation as a hazardous waste under §261.4(b); and

(2) It meets any of the following criteria:

(i) It exhibits any of the characteristics of hazardous waste identified in subpart C of this part. However, any mixture of a waste from the extraction, beneficiation, and processing of ores and minerals excluded under §261.4(b)(7) and any other solid waste exhibiting a characteristic of hazardous waste under subpart C is a hazardous waste only if it exhibits a characteristic that would not have been exhibited by the excluded waste alone if such mixture had not occurred, or if it continues to exhibit any of the characteristics exhibited by the non-excluded wastes prior to mixture. Further, for the purposes of applying the Toxicity Characteristic to such mixtures, the mixture is also a hazardous waste if it exceeds the maximum concentration for any contaminant listed in table I to §261.24 that would not have been exceeded by the excluded waste alone if the mixture had not occurred or if it continues to exceed the maximum concentration for any contaminant exceeded by the nonexempt waste prior to mixture.

(ii) It is listed in subpart D of this part and has not been excluded from the lists in subpart D of this part under §§260.20 and 260.22 of this chapter.

(iii) [Reserved]

(iv) It is a mixture of solid waste and one or more hazardous wastes listed in subpart D of this part and has not been excluded from paragraph (a)(2) of this section under §§260.20 and 260.22, paragraph (g) of this section, or paragraph (h) of this section; however, the following mixtures of solid wastes and hazardous wastes listed in subpart D of this part are not hazardous wastes (except by application of

paragraph (a)(2)(i) or (ii) of this section) if the generator can demonstrate that the mixture consists of wastewater the discharge of which is subject to regulation under either section 402 or section 307(b) of the Clean Water Act (including wastewater at facilities which have eliminated the discharge of wastewater) and:

(A) One or more of the following solvents listed in §261.31 -- carbon tetrachloride, tetrachloroethylene, trichloroethylene -- *Provided*, That the maximum total weekly usage of these solvents (other than the amounts that can be demonstrated not to be discharged to wastewater) divided by the average weekly flow of wastewater into the headworks of the facility's wastewater treatment or pretreatment system does not exceed 1 part per million; or

(B) One or more of the following spent solvents listed in §261.31 -- methylene chloride, 1,1,1-trichloroethane, chlorobenzene, o-dichlorobenzene, cresols, cresylic acid, nitrobenzene, toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine, spent chlorofluorocarbon solvents -- provided that the maximum total weekly usage of these solvents (other than the amounts that can be demonstrated not to be discharged to wastewater) divided by the average weekly flow of wastewater into the headworks of the facility's wastewater treatment or pretreatment system does not exceed 25 parts per million; or

(C) One of the following wastes listed in §261.32, provided that the wastes are discharged to the refinery oil recovery sewer before primary oil/water/solids separation -- heat exchanger bundle cleaning sludge from the petroleum refining industry (EPA Hazardous Waste No. K050), crude oil storage tank sediment from petroleum refining operations (EPA Hazardous Waste No. K169), clarified slurry oil tank sediment and/or in-line filter/separation solids from petroleum refining operations (EPA Hazardous Waste No. K170), spent hydrotreating catalyst (EPA Hazardous Waste No. K171), and spent hydrorefining catalyst (EPA Hazardous Waste No. K172); or

(D) A discarded commercial chemical product, or chemical intermediate listed in §261.33, arising from *de minimis* losses of these materials from manufacturing operations in which these materials are used as raw materials or are produced in the manufacturing process. For purposes of this paragraph (a)(2)(iv)(D), "de minimis" losses include those from normal material handling operations (e.g., spills from the unloading or transfer of materials from bins or other containers, leaks from pipes, valves or other devices used to transfer materials); minor leaks of process equipment, storage tanks or containers; leaks from well maintained pump packings and seals; sample purgings; relief device discharges; discharges from safety showers and rinsing and cleaning of personal safety equipment; and rinsate from empty containers or from containers that are rendered empty by that rinsing; or

(E) Wastewater resulting from laboratory operations containing toxic (T) wastes listed in subpart D of this part, Provided, That the annualized average flow of laboratory wastewater does not exceed one percent of total wastewater flow into the headworks of the facility's wastewater treatment or pre-treatment system or provided the wastes, combined annualized average concentration does not exceed one part per million in the headworks of the facility's wastewater treatment or pre-treatment facility. Toxic (T) wastes used in laboratories that are demonstrated not to be discharged to wastewater are not to be included in this calculation; or

(F) One or more of the following wastes listed in §261.32 -- wastewaters from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K157) -- Provided that the maximum weekly usage of formaldehyde, methyl chloride, methylene chloride, and triethylamine (including all amounts that can not be demonstrated to be reacted in the process, destroyed through treatment, or is recovered, i.e., what is discharged or volatilized) divided by the average weekly flow of process wastewater prior to any dilutions into the headworks of the facility's wastewater treatment system does

not exceed a total of 5 parts per million by weight; or

(G) Wastewaters derived from the treatment of one or more of the following wastes listed in §261.32 -- organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K156). -- Provided, that the maximum concentration of formaldehyde, methyl chloride, methylene chloride, and triethylamine prior to any dilutions into the headworks of the facility's wastewater treatment system does not exceed a total of 5 milligrams per liter.

(v) *Rebuttable presumption for used oil.* Used oil containing more than 1000 ppm total halogens is presumed to be a hazardous waste because it has been mixed with halogenated hazardous waste listed in subpart D of part 261 of this chapter. Persons may rebut this presumption by demonstrating that the used oil does not contain hazardous waste (for example, by using an analytical method from SW-846, Third Edition, to show that the used oil does not contain significant concentrations of halogenated hazardous constituents listed in appendix VIII of part 261 of this chapter). EPA Publication SW-846, Third Edition, is available for the cost of $110.00 from the Government Printing Office, Superintendent of Documents, PO Box 371954, Pittsburgh, PA 15250-7954. 202-512-1800 (document number 955-001-00000-1).

(A) The rebuttable presumption does not apply to metalworking oils/fluids containing chlorinated paraffins, if they are processed, through a tolling agreement, to reclaim metalworking oils/fluids. The presumption does apply to metalworking oils/fluids if such oils/fluids are recycled in any other manner, or disposed.

(B) The rebuttable presumption does not apply to used oils contaminated with chlorofluorocarbons (CFCs) removed from refrigeration units where the CFCs are destined for reclamation. The rebuttable presumption does apply to used oils contaminated with CFCs that have been mixed with used oil from sources other than refrigeration units.

(b) A solid waste which is not excluded from regulation under paragraph (a)(1) of this section becomes a hazardous waste when any of the following events occur:

(1) In the case of a waste listed in subpart D of this part, when the waste first meets the listing description set forth in subpart D of this part.

(2) In the case of a mixture of solid waste and one or more listed hazardous wastes, when a hazardous waste listed in subpart D is first added to the solid waste.

(3) In the case of any other waste (including a waste mixture), when the waste exhibits any of the characteristics identified in subpart C of this part.

(c) Unless and until it meets the criteria of paragraph (d) of this section:

(1) A hazardous waste will remain a hazardous waste.

(2)(i) Except as otherwise provided in paragraph (c)(2)(ii), (g) or (h) of this section, any solid waste generated from the treatment, storage, or disposal of a hazardous waste, including any sludge, spill residue, ash emission control dust, or leachate (but not including precipitation run-off) is a hazardous waste. (However, materials that are reclaimed from solid wastes and that are used beneficially are not solid wastes and hence are not hazardous wastes under this provision unless the reclaimed material is burned for energy recovery or used in a manner constituting disposal.)

(ii) The following solid wastes are not hazardous even though they are generated from the treatment, storage, or disposal of a hazardous waste, unless they exhibit one or more of the characteristics of hazardous waste:

(A) Waste pickle liquor sludge generated by lime stabilization of spent pickle liquor from the iron and steel industry (SIC Codes 331 and 332).

(B) Waste from burning any of the materials exempted from regulation by §261.6(a)(3)(iii) and (iv).

(C)(*1*) Nonwastewater residues, such as slag, resulting from high temperature metals recovery (HTMR) processing of K061, K062 or F006 waste, in units identified as rotary kilns, flame reactors, electric furnaces, plasma arc furnaces, slag reactors, rotary hearth furnace/electric furnace combinations or industrial furnaces (as defined in paragraphs (6), (7), and (13) of the definition for "Industrial furnace" in 40 CFR 260.10), that are disposed in subtitle D units, provided that these residues meet the generic exclusion levels identified in the tables in this paragraph for all constituents, and exhibit no characteristics of hazardous waste. Testing requirements must be incorporated in a facility's waste analysis plan or a generator's self-implementing waste analysis plan; at a minimum, composite samples of residues must be collected and analyzed quarterly and/or when the process or operation generating the waste changes. Persons claiming this exclusion in an enforcement action will have the burden of proving by clear and convincing evidence that the material meets all of the exclusion requirements.

Constituent	Maximum for any single composite sample--TCLP (mg/l)
Generic exclusion levels for K061 and K062 nonwastewater HTMR residues	
Antimony	0.10
Arsenic	0.50
Barium	7.6
Beryllium	0.010
Cadmium	0.050
Chromium (total)	0.33
Lead	0.15
Mercury	0.009
Nickel	1.0
Selenium	0.16
Silver	0.30
Thallium	0.020
Zinc	70
Generic exclusion levels for F006 nonwastewater HTMR residues	
Antimony	0.10
Arsenic	0.50
Barium	7.6
Beryllium	0.010
Cadmium	0.050
Chromium (total)	0.33
Cyanide (total) (mg/kg)	1.8
Lead	0.15

Mercury	0.009
Nickel	1.0
Selenium	0.16
Silver	0.30
Thallium	0.020
Zinc	70

(2) A one-time notification and certification must be placed in the facility's files and sent to the EPA region or authorized state for K061, K062 or F006 HTMR residues that meet the generic exclusion levels for all constituents and do not exhibit any characteristics that are sent to subtitle D units. The notification and certification that is placed in the generators or treaters files must be updated if the process or operation generating the waste changes and/or if the subtitle D unit receiving the waste changes. However, the generator or treater need only notify the EPA region or an authorized state on an annual basis if such changes occur. Such notification and certification should be sent to the EPA region or authorized state by the end of the calendar year, but no later than December 31. The notification must include the following information: The name and address of the subtitle D unit receiving the waste shipments; the EPA Hazardous Waste Number(s) and treatability group(s) at the initial point of generation; and, the treatment standards applicable to the waste at the initial point of generation. The certification must be signed by an authorized representative and must state as follows: "I certify under penalty of law that the generic exclusion levels for all constituents have been met without impermissible dilution and that no characteristic of hazardous waste is exhibited. I am aware that there are significant penalties for submitting a false certification, including the possibility of fine and imprisonment."

(D) Biological treatment sludge from the treatment of one of the following wastes listed in §261.32 -- organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K156), and wastewaters from the production of carbamates and carbamoyl oximes (EPA Hazardous Waste No. K157).

(E) Catalyst inert support media separated from one of the following wastes listed in §261.32 -- Spent hydrotreating catalyst (EPA Hazardous Waste No. K171), and Spent hydrorefining catalyst (EPA Hazardous Waste No. K172).

(d) Any solid waste described in paragraph (c) of this section is not a hazardous waste if it meets the following criteria:

(1) In the case of any solid waste, it does not exhibit any of the characteristics of hazardous waste identified in subpart C of this part. (However, wastes that exhibit a characteristic at the point of generation may still be subject to the requirements of part 268, even if they no longer exhibit a characteristic at the point of land disposal.)

(2) In the case of a waste which is a listed waste under subpart D of this part, contains a waste listed under subpart D of this part or is derived from a waste listed in subpart D of this part, it also has been excluded from paragraph (c) of this section under §§260.20 and 260.22 of this chapter.

(e) [Reserved]

(f) Notwithstanding paragraphs (a) through (d) of this section and provided the debris as defined in part 268 of this chapter does not exhibit a characteristic identified at subpart C of this part, the following materials are not subject to regulation under 40 CFR parts 260, 261 to 266, 268, or 270:

(1) Hazardous debris as defined in part 268 of this chapter that has been treated using one of the required extraction or destruction technologies specified in Table 1 of §268.45 of this chapter; persons claiming this exclusion in an enforcement action will have the burden of proving by clear and convincing evidence that the material meets all of the exclusion requirements; or

(2) Debris as defined in part 268 of this chapter that the Regional Administrator, considering the extent of contamination, has determined is no longer contaminated with hazardous waste.

(g)(1) A hazardous waste that is listed in subpart D of this part solely because it exhibits one or more characteristics of ignitability as defined under §261.21, corrosivity as defined under §261.22, or reactivity as defined under §261.23 is not a hazardous waste, if the waste no longer exhibits any characteristic of hazardous waste identified in subpart C of this part.

(2) The exclusion described in paragraph (g)(1) of this section also pertains to:

(i) Any mixture of a solid waste and a hazardous waste listed in subpart D of this part solely because it exhibits the characteristics of ignitability, corrosivity, or reactivity as regulated under paragraph (a)(2)(iv) of this section; and

(ii) Any solid waste generated from treating, storing, or disposing of a hazardous waste listed in subpart D of this part solely because it exhibits the characteristics of ignitability, corrosivity, or reactivity as regulated under paragraph (c)(2)(i) of this section.

(3) Wastes excluded under this section are subject to part 268 of this chapter (as applicable), even if they no longer exhibit a characteristic at the point of land disposal.

(4) any mixture of a solid waste excluded from regulation under §261.4(b)(7) and a hazardous waste listed in subpart D of this part solely because it exhibits one or more of the characteristics of ignitability, corrosivity, or reactivity as regulated under paragraph (a)(2)(iv) of this section is not a hazardous waste, if the mixture no longer exhibits any characteristic of hazardous waste identified in subpart C of this part for which the hazardous waste listed in subpart D of this part was listed.

(h)(1) Hazardous waste containing radioactive waste is no longer a hazardous waste when it meets the eligibility criteria and conditions of 40 CFR part 266, Subpart N ("eligible radioactive mixed waste").

(2) The exemption described in paragraph (h)(1) of this section also pertains to:

(i) Any mixture of a solid waste and an eligible radioactive mixed waste; and

(ii) Any solid waste generated from treating, storing, or disposing of an eligible radioactive mixed waste.

(3) Waste exempted under this section must meet the eligibility criteria and specified conditions in 40 CFR 266.225 and 40 CFR 266.230 (for storage and treatment) and in 40 CFR 266.310 and 40 CFR 266.315 (for transportation and disposal). Waste that fails to satisfy these eligibility criteria and conditions is regulated as hazardous waste.

[57 FR 7632, Mar. 3, 1992; 57 FR 23063, June 1, 1992, as amended at 57 FR 37263, Aug. 18, 1992; 57 FR 41611, Sept. 10, 1992; 57 FR 49279, Oct. 30, 1992; 59 FR 38545, July 28, 1994; 60 FR 7848, Feb. 9, 1995; 63 FR 28637, May 26, 1998; 63 FR 42184, Aug. 6, 1998; 66 FR 27297, May 16, 2001; 66 FR 50333, Oct. 3, 2001]

Appendix VII identifies the constituent which caused the Administrator to list the waste as a Toxicity Characteristic Waste (E) or Toxic Waste (T) in §§261.31 and 261.32.

(c) Each hazardous waste listed in this subpart is assigned an EPA Hazardous Waste Number which precedes the name of the waste. This number must be used in complying with the notification requirements of Section 3010 of the Act and certain recordkeeping and reporting requirements under parts 262 through 265, 268, and part 270 of this chapter.

(d) The following hazardous wastes listed in §261.31 or §261.32 are subject to the exclusion limits for acutely hazardous wastes established in §261.5: EPA Hazardous Wastes Nos. FO20, FO21, FO22, FO23, FO26, and FO27.

[45 FR 33119, May 19, 1980, as amended at 48 FR 14294, Apr. 1, 1983; 50 FR 2000, Jan. 14, 1985; 51 FR 40636, Nov. 7, 1986; 55 FR 11863, Mar. 29, 1990]

[TOP]

§261.31 Hazardous wastes from non-specific sources.

(a) The following solid wastes are listed hazardous wastes from non-specific sources unless they are excluded under §§260.20 and 260.22 and listed in appendix IX.

Industry and EPA hazardous waste No.	Hazardous waste	Hazard code
Generic:		
F001	The following spent halogenated solvents used in degreasing: Tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; all spent solvent mixtures/blends used in degreasing containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.	(T)
F002	The following spent halogenated solvents: Tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-	(T)

	trichloro-1,2,2-trifluoroethane, ortho-dichlorobenzene, trichlorofluoromethane, and 1,1,2-trichloroethane; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those listed in F001, F004, or F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.	
F003.....	The following spent non-halogenated solvents: Xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol; all spent solvent mixtures/blends containing, before use, only the above spent non-halogenated solvents; and all spent solvent mixtures/blends containing, before use, one or more of the above non-halogenated solvents, and, a total of ten percent or more (by volume) of one or more of those solvents listed in F001, F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.	(I)*
F004.....	The following spent non-halogenated solvents: Cresols and cresylic acid, and nitrobenzene; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.	(T)
F005.....	The following spent non-halogenated solvents: Toluene, methyl ethyl	(I,T)

	ketone, carbon disulfide, isobutanol, pyridine, benzene, 2-ethoxyethanol, and 2-nitropropane; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, or F004; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.	
F006.....	Wastewater treatment sludges from electroplating operations except from the following processes: (1) Sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum.	(T)
F007.....	Spent cyanide plating bath solutions from electroplating operations.	(R, T)
F008.....	Plating bath residues from the bottom of plating baths from electroplating operations where cyanides are used in the process.	(R, T)
F009.....	Spent stripping and cleaning bath solutions from electroplating operations where cyanides are used in the process.	(R, T)
F010.....	Quenching bath residues from oil baths from metal heat treating operations where cyanides are used in the process.	(R, T)
F011.....	Spent cyanide solutions from salt bath pot cleaning from metal heat treating operations.	(R, T)
F012.....	Quenching waste water	(T)

	treatment sludges from metal heat treating operations where cyanides are used in the process.	
F019.....	Wastewater treatment sludges from the chemical conversion coating of aluminum except from zirconium phosphating in aluminum can washing when such phosphating is an exclusive conversion coating process.	(T)
F020.....	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- or tetrachlorophenol, or of intermediates used to produce their pesticide derivatives. (This listing does not include wastes from the production of Hexachlorophene from highly purified 2,4,5-trichlorophenol.).	(H)
F021.....	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of pentachlorophenol, or of intermediates used to produce its derivatives.	(H)
F022.....	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions.	(H)
F023.....	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the	(H)

	production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of Hexachlorophene from highly purified 2,4,5-trichlorophenol.).	
F024.....	Process wastes, including but not limited to, distillation residues, heavy ends, tars, and reactor clean-out wastes, from the production of certain chlorinated aliphatic hydrocarbons by free radical catalyzed processes. These chlorinated aliphatic hydrocarbons are those having carbon chain lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution. (This listing does not include wastewaters, wastewater treatment sludges, spent catalysts, and wastes listed in Sec. 261.31 or Sec. 261.32.).	(T)
F025.....	Condensed light ends, spent filters and filter aids, and spent desiccant wastes from the production of certain chlorinated aliphatic hydrocarbons, by free radical catalyzed processes. These chlorinated aliphatic hydrocarbons are those having carbon chain lengths ranging from one to and including five, with varying amounts and positions of chlorine substitution.	(T)
F026.....	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials	(H)

	on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	
F027.....	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations containing compounds derived from these chlorophenols. (This listing does not include formulations containing Hexachlorophene sythesized from prepurified 2,4,5-trichlorophenol as the sole component.).	(H)
F028.....	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027.	(T)
F032.....	Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that currently use or have previously used chlorophenolic formulations (except potentially cross-contaminated wastes that have had the F032 waste code deleted in accordance with Sec. 261.35 of this chapter or potentially cross-contaminated wastes that are otherwise currently regulated as hazardous wastes (i.e., F034 or F035), and where the generator does not resume or initiate use of chlorophenolic formulations). This listing does not include K001 bottom sediment sludge from the	(T)

	treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.	
F034.....	Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that use creosote formulations. This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.	(T)
F035.....	Wastewaters (except those that have not come into contact with process contaminants), process residuals, preservative drippage, and spent formulations from wood preserving processes generated at plants that use inorganic preservatives containing arsenic or chromium. This listing does not include K001 bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol.	(T)
F037.....	Petroleum refinery primary oil/water/solids separation sludge--Any sludge generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters and oil cooling wastewaters from petroleum refineries. Such sludges include, but are not limited to, those generated in oil/water/solids separators; tanks and impoundments; ditches and other conveyances; sumps; and stormwater units receiving dry weather	(T)

	flow. Sludge generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges generated in aggressive biological treatment units as defined in Sec. 261.31(b)(2) (including sludges generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and K051 wastes are not included in this listing. This listing does include residuals generated from processing or recycling oil-bearing hazardous secondary materials excluded under Sec. 261.4(a)(12)(i), if those residuals are to be disposed of..	
F038.....	Petroleum refinery secondary (emulsified) oil/water/solids separation sludge--Any sludge and/or float generated from the physical and/or chemical separation of oil/water/solids in process wastewaters and oily cooling wastewaters from petroleum refineries. Such wastes include, but are not limited to, all sludges and floats generated in: induced air flotation (IAF) units, tanks and impoundments, and all sludges generated in DAF units. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges and floats generated in aggressive	(T)

	biological treatment units as defined in Sec. 261.31(b)(2) (including sludges and floats generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and F037, K048, and K051 wastes are not included in this listing.	
F039.....	Leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than one restricted waste classified as hazardous under subpart D of this part. (Leachate resulting from the disposal of one or more of the following EPA Hazardous Wastes and no other Hazardous Wastes retains its EPA Hazardous Waste Number(s): F020, F021, F022, F026, F027, and/or F028.).	(T)

(b) Listing Specific Definitions: (1) For the purposes of the F037 and F038 listings, oil/water/solids is defined as oil and/or water and/or solids.(2) (i) For the purposes of the F037 and F038 listings, aggressive biological treatment units are defined as units which employ one of the following four treatment methods: activated sludge; trickling filter; rotating biological contactor for the continuous accelerated biological oxidation of wastewaters; or high-rate aeration. High-rate aeration is a system of surface impoundments or tanks, in which intense mechanical aeration is used to completely mix the wastes, enhance biological activity, and (A) the units employ a minimum of 6 hp per million gallons of treatment volume; and either (B) the hydraulic retention time of the unit is no longer than 5 days; or (C) the hydraulic retention time is no longer than 30 days and the unit does not generate a sludge that is a hazardous waste by the Toxicity Characteristic.

(ii) Generators and treatment, storage and disposal facilities have the burden of proving that their sludges are exempt from listing as F037 and F038 wastes under this definition. Generators and treatment, storage and disposal facilities must maintain, in their operating or other onsite records, documents and data sufficient to prove that: (A) the unit is an aggressive biological treatment unit as defined in this subsection; and (B) the sludges sought to be exempted from the definitions of F037 and/or F038 were actually generated in the aggressive biological treatment unit.

(3) (i) For the purposes of the F037 listing, sludges are considered to be generated at the moment of deposition in the unit, where deposition is defined as at least a temporary cessation of lateral particle movement.

(ii) For the purposes of the F038 listing,

(A) sludges are considered to be generated at the moment of deposition in the unit, where deposition is defined as at least a temporary cessation of lateral particle movement and

(B) floats are considered to be generated at the moment they are formed in the top of the unit. [46 FR 4617, Jan. 16, 1981]

Editorial Note: For FEDERAL REGISTER citations affecting §261.31, see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

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§261.32 Hazardous wastes from specific sources.

The following solid wastes are listed hazardous wastes from specific sources unless they are excluded under §§260.20 and 260.22 and listed in appendix IX.

Industry and EPA hazardous waste No.	Hazardous waste	Hazard code
Wood preservation: K001	Bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol.	(T)
Inorganic pigments:		
K002	Wastewater treatment sludge from the production of chrome yellow and orange pigments.	(T)
K003	Wastewater treatment sludge from the production of molybdate orange pigments.	(T)
K004	Wastewater treatment sludge from the production of zinc yellow pigments.	(T)
K005	Wastewater treatment sludge from the production of chrome green pigments.	(T)
K006	Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated).	(T)
K007	Wastewater treatment sludge from the production of iron blue pigments.	(T)
K008	Oven residue from the production of chrome oxide green pigments.	(T)
Organic chemicals:		
K009	Distillation bottoms from the production of acetaldehyde from	(T)

	ethylene.	
K010	Distillation side cuts from the production of acetaldehyde from ethylene.	(T)
K011	Bottom stream from the wastewater stripper in the production of acrylonitrile.	(R, T)
K013	Bottom stream from the acetonitrile column in the production of acrylonitrile.	(R, T)
K014	Bottoms from the acetonitrile purification column in the production of acrylonitrile.	(T)
K015	Still bottoms from the distillation of benzyl chloride.	(T)
K016	Heavy ends or distillation residues from the production of carbon tetrachloride.	(T)
K017	Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin.	(T)
K018	Heavy ends from the fractionation column in ethyl chloride production.	(T)
K019	Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production.	(T)
K020	Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production.	(T)
K021	Aqueous spent antimony catalyst waste from fluoromethanes production.	(T)
K022	Distillation bottom tars from the production of phenol/acetone from cumene.	(T)
K023	Distillation light ends from the production of phthalic anhydride from naphthalene.	(T)
K024	Distillation bottoms from the production of phthalic anhydride from naphthalene.	(T)
K025	Distillation bottoms from the production of nitrobenzene by the nitration of benzene.	(T)
K026	Stripping still tails from the production of	(T)

	methy ethyl pyridines.	
K027	Centrifuge and distillation residues from toluene diisocyanate production.	(R, T)
K028	Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane.	(T)
K029	Waste from the product steam stripper in the production of 1,1,1-trichloroethane.	(T)
K030	Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene.	(T)
K083	Distillation bottoms from aniline production.	(T)
K085	Distillation or fractionation column bottoms from the production of chlorobenzenes.	(T)
K093	Distillation light ends from the production of phthalic anhydride from ortho-xylene.	(T)
K094	Distillation bottoms from the production of phthalic anhydride from ortho-xylene.	(T)
K095	Distillation bottoms from the production of 1,1,1-trichloroethane.	(T)
K096	Heavy ends from the heavy ends column from the production of 1,1,1-trichloroethane.	(T)
K103	Process residues from aniline extraction from the production of aniline.	(T)
K104	Combined wastewater streams generated from nitrobenzene/aniline production.	(T)
K105	Separated aqueous stream from the reactor product washing step in the production of chlorobenzenes.	(T)
K107	Column bottoms from product separation from the production of 1,1-dimethyl-hydrazine (UDMH) from carboxylic acid hydrazines.	(C,T)
K108	Condensed column overheads from product separation and condensed reactor vent gases from the production of 1,1-dimethylhydrazine (UDMH)	(I,T)

	bromination of ethene.	
K136.....	Still bottoms from the purification of ethylene dibromide in the production of ethylene dibromide via bromination of ethene.	(T)
K149.....	Distillation bottoms from the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups, (This waste does not include still bottoms from the distillation of benzyl chloride.).	(T)
K150.....	Organic residuals, excluding spent carbon adsorbent, from the spent chlorine gas and hydrochloric acid recovery processes associated with the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups.	(T)
K151.....	Wastewater treatment sludges, excluding neutralization and biological sludges, generated during the treatment of wastewaters from the production of alpha- (or methyl-) chlorinated toluenes, ring-chlorinated toluenes, benzoyl chlorides, and compounds with mixtures of these functional groups.	(T)
K156.....	Organic waste (including heavy ends, still bottoms, light ends, spent solvents, filtrates, and decantates) from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.).	(T)
K157.....	Wastewaters (including scrubber waters,	(T)

	condenser waters, washwaters, and separation waters) from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.).	
K158.....	Bag house dusts and filter/separation solids from the production of carbamates and carbamoyl oximes. (This listing does not apply to wastes generated from the manufacture of 3-iodo-2-propynyl n-butylcarbamate.).	(T)
K159.....	Organics from the treatment of thiocarbamate wastes.	(T)
K161.....	Purification solids (including filtration, evaporation, and centrifugation solids), bag house dust and floor sweepings from the production of dithiocarbamate acids and their salts. (This listing does not include K125 or K126.).	(R,T)
K174.....	Wastewater treatment sludges from the production of ethylene dichloride or vinyl chloride monomer (including sludges that result from commingled ethylene dichloride or vinyl chloride monomer wastewater and other wastewater), unless the sludges meet the following conditions: (i) they are disposed of in a subtitle C or non-hazardous landfill licensed or permitted by the state or federal government; (ii) they are not otherwise placed on the land prior to final disposal; and (iii) the generator maintains documentation demonstrating that the waste was either disposed of in an on-site landfill or consigned to a transporter or disposal	(T)

	facility that provided a written commitment to dispose of the waste in an off-site landfill. Respondents in any action brought to enforce the requirements of subtitle C must, upon a showing by the government that the respondent managed wastewater treatment sludges from the production of vinyl chloride monomer or ethylene dichloride, demonstrate that they meet the terms of the exclusion set forth above. In doing so, they must provide appropriate documentation (e.g., contracts between the generator and the landfill owner/operator, invoices documenting delivery of waste to landfill, etc.) that the terms of the exclusion were met.	
K175.....	Wastewater treatment sludges from the production of vinyl chloride monomer using mercuric chloride catalyst in an acetylene-based process.	(T)
Inorganic chemicals:		
K071.....	Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used.	(T)
K073.....	Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process using graphite anodes in chlorine production.	(T)
K106.....	Wastewater treatment sludge from the mercury cell process in chlorine production.	(T)
K176.....	Baghouse filters from the production of antimony oxide, including filters from the production of intermediates (e.g., antimony metal or crude antimony oxide).	(E)
K177.....	Slag from the production of antimony oxide that is speculatively accumulated or disposed,	(T)

	including slag from the production of intermediates (e.g., antimony metal or crude antimony oxide).	
K178	Residues from manufacturing and manufacturing-site storage of ferric chloride from acids formed during the production of titanium dioxide using the chloride-ilmenite process.	(T)
Pesticides:		
K031	By-product salts generated in the production of MSMA and cacodylic acid.	(T)
K032	Wastewater treatment sludge from the production of chlordane.	(T)
K033	Wastewater and scrub water from the chlorination of cyclopentadiene in the production of chlordane.	(T)
K034	Filter solids from the filtration of hexachlorocyclopentadiene in the production of chlordane.	(T)
K035	Wastewater treatment sludges generated in the production of creosote.	(T)
K036	Still bottoms from toluene reclamation distillation in the production of disulfoton.	(T)
K037	Wastewater treatment sludges from the production of disulfoton.	(T)
K038	Wastewater from the washing and stripping of phorate production.	(T)
K039	Filter cake from the filtration of diethylphosphorodithioic acid in the production of phorate.	(T)
K040	Wastewater treatment sludge from the production of phorate.	(T)
K041	Wastewater treatment sludge from the production of toxaphene.	(T)
K042	Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4,5-T.	(T)
K043	2,6-Dichlorophenol waste from the production of	(T)

	2,4-D.	
K097	Vacuum stripper discharge from the chlordane chlorinator in the production of chlordane.	(T)
K098	Untreated process wastewater from the production of toxaphene.	(T)
K099	Untreated wastewater from the production of 2,4-D.	(T)
K123	Process wastewater (including supernates, filtrates, and washwaters) from the production of ethylenebisdithiocarbamic acid and its salt.	(T)
K124	Reactor vent scrubber water from the production of ethylenebisdithiocarbamic acid and its salts.	(C, T)
K125	Filtration, evaporation, and centrifugation solids from the production of ethylenebisdithiocarbamic acid and its salts.	(T)
K126	Baghouse dust and floor sweepings in milling and packaging operations from the production or formulation of ethylenebisdithiocarbamic acid and its salts.	(T)
K131	Wastewater from the reactor and spent sulfuric acid from the acid dryer from the production of methyl bromide.	(C, T)
K132	Spent absorbent and wastewater separator solids from the production of methyl bromide.	(T)
Explosives:		
K044	Wastewater treatment sludges from the manufacturing and processing of explosives.	(R)
K045	Spent carbon from the treatment of wastewater containing explosives.	(R)
K046	Wastewater treatment sludges from the manufacturing, formulation and loading of lead-based initiating compounds.	(T)
K047	Pink/red water from TNT operations.	(R)
Petroleum refining:		
K048	Dissolved air flotation (DAF) float from the	(T)

	petroleum refining industry.	
K049	Slop oil emulsion solids from the petroleum refining industry.	(T)
K050	Heat exchanger bundle cleaning sludge from the petroleum refining industry.	(T)
K051	API separator sludge from the petroleum refining industry.	(T)
K052	Tank bottoms (leaded) from the petroleum refining industry.	(T)
K169	Crude oil storage tank sediment from petroleum refining operations.	(T)
K170	Clarified slurry oil tank sediment and/or in-line filter/separation solids from petroleum refining operations.	(T)
K171	Spent Hydrotreating catalyst from petroleum refining operations, including guard beds used to desulfurize feeds to other catalytic reactors (this listing does not include inert support media).	(I,T)
K172	Spent Hydrorefining catalyst from petroleum refining operations, including guard beds used to desulfurize feeds to other catalytic reactors (this listing does not include inert support media).	(I,T)
Iron and steel:		
K061	Emission control dust/ sludge from the primary production of steel in electric furnaces.	(T)
K062	Spent pickle liquor generated by steel finishing operations of facilities within the iron and steel industry (SIC Codes 331 and 332).	(C,T)
Primary copper:		
Primary lead:		
Primary zinc:		
Primary aluminum:		
K088	Spent potliners from primary aluminum reduction.	(T)
Ferroalloys:		
Secondary lead:		
K069	Emission control dust/ sludge from secondary lead smelting. (Note: This listing is stayed	(T)

	administratively for sludge generated from secondary acid scrubber systems. The stay will remain in effect until further administrative action is taken. If EPA takes further action effecting this stay, EPA will publish a notice of the action in the Federal Register.	
K100	Waste leaching solution from acid leaching of emission control dust/ sludge from secondary lead smelting.	(T)
Veterinary pharmaceuticals:		
K084	Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.	(T)
K101	Distillation tar residues from the distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.	(T)
K102	Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.	(T)
Ink formulation:		
K086	Solvent washes and sludges, caustic washes and sludges, or water washes and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.	(T)
Coking:		
K060	Ammonia still lime sludge from coking operations.	(T)
K087	Decanter tank tar sludge from coking operations.	(T)
K141	Process residues from the recovery of coal tar, including, but not limited to, collecting sump residues from the production of coke from coal or the recovery of coke by-products	(T)

	produced from coal. This listing does not include K087 (decanter tank tar sludges from coking operations).	
K142	Tar storage tank residues from the production of coke from coal or from the recovery of coke by-products produced from coal.	(T)
K143	Process residues from the recovery of light oil, including, but not limited to, those generated in stills, decanters, and wash oil recovery units from the recovery of coke by-products produced from coal.	(T)
K144	Wastewater sump residues from light oil refining, including, but not limited to, intercepting or contamination sump sludges from the recovery of coke by-products produced from coal.	(T)
K145	Residues from naphthalene collection and recovery operations from the recovery of coke by-products produced from coal.	(T)
K147	Tar storage tank residues from coal tar refining.	(T)
K148	Residues from coal tar distillation, including but not limited to, still bottoms.	(T)

[46 FR 4618, Jan. 16, 1981]

Editorial Note: For FEDERAL REGISTER citations affecting §261.32, see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

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§261.33 Discarded commercial chemical products, off-specification species, container residues, and spill residues thereof.

The following materials or items are hazardous wastes if and when they are discarded or intended to be discarded as described in §261.2(a)(2)(i), when they are mixed with waste oil or used oil or other material and applied to the land for dust suppression or road treatment, when they are otherwise applied to the land in lieu of their original intended use or when they are contained in products that are applied to the land in lieu of their original intended use, or when, in lieu of their original intended use, they are produced for use as (or as a component of) a fuel, distributed for use as a fuel, or burned as a fuel.

Correct Procedure" found in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846, as incorporated by reference in §260.11 of this chapter. Prior to final sampling and analysis method selection, the individual should consult the specific section or method described in SW-846 for additional guidance on which of the approved methods should be employed for a specific sample analysis situation.

[58 FR 46049, Aug. 31, 1993]

Appendix IV to Part 261 [Reserved for Radioactive Waste Test Methods] Appendix V to Part 261 [Reserved for Infectious Waste Treatment Specifications] Appendix VI to Part 261 [Reserved for Etiologic Agents]

Appendix VII to Part 261 -- Basis for Listing Hazardous Waste

EPA hazardous waste No.	Hazardous constituents for which listed
F001	Tetrachloroethylene, methylene chloride trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, chlorinated fluorocarbons.
F002	Tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trichfluoroethane, ortho-dichlorobenzene, trichlorofluoromethane.
F003	N.A.
F004	Cresols and cresylic acid, nitrobenzene.
F005	Toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine, 2-ethoxyethanol, benzene, 2-nitropropane.
F006	Cadmium, hexavalent chromium, nickel, cyanide (complexed).
F007	Cyanide (salts).
F008	Cyanide (salts).
F009	Cyanide (salts).
F010	Cyanide (salts).
F011	Cyanide (salts).
F012	Cyanide (complexed).
F019	Hexavalent chromium, cyanide (complexed).
F020	Tetra- and pentachlorodibenzo-p-dioxins; tetra and pentachlorodi-benzofurans; tri- and tetrachlorophenols and their chlorophenoxy derivative acids, esters, ethers, amine and other salts.
F021	Penta- and hexachlorodibenzo-p-dioxins; penta- and hexachlorodibenzofurans; pentachlorophenol and its derivatives.
F022	Tetra-, penta-, and hexachlorodibenzo-p-dioxins; tetra-, penta-, and hexachlorodibenzofurans.
F023	Tetra-, and pentachlorodibenzo-p-dioxins; tetra- and pentachlorodibenzofurans; tri- and tetrachlorophenols and their chlorophenoxy derivative acids, esters, ethers, amine and other salts.
F024	Chloromethane, dichloromethane, trichloromethane, carbon tetrachloride, chloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, trans-1-2-dichloroethylene, 1,1-dichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, trichloroethylene, 1,1,1,2-tetra-chloroethane, 1,1,2,2-

	tetrachloroethane, tetrachloroethylene, pentachloroethane, hexachloroethane, allyl chloride (3-chloropropene), dichloropropane, dichloropropene, 2-chloro-1,3-butadiene, hexachloro-1,3-butadiene, hexachlorocyclopentadiene, hexachlorocyclohexane, benzene, chlorbenzene, dichlorobenzenes, 1,2,4-trichlorobenzene, tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, toluene, naphthalene.
F025	Chloromethane; Dichloromethane; Trichloromethane; Carbon tetrachloride; Chloroethylene; 1,1-Dichloroethane; 1,2-Dichloroethane; trans-1,2-Dichloroethylene; 1,1-Dichloroethylene; 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; Trichloroethylene; 1,1,1,2-Tetrachloroethane; 1,1,2,2-Tetrachloroethane; Tetrachloroethylene; Pentachloroethane; Hexachloroethane; Allyl chloride (3-Chloropropene); Dichloropropane; Dichloropropene; 2-Chloro-1,3-butadiene; Hexachloro-1,3-butadiene; Hexachlorocyclopentadiene; Benzene; Chlorobenzene; Dichlorobenzene; 1,2,4-Trichlorobenzene; Tetrachlorobenzene; Pentachlorobenzene; Hexachlorobenzene; Toluene; Naphthalene.
F026	Tetra-, penta-, and hexachlorodibenzo-p-dioxins; tetra-, penta-, and hexachlorodibenzofurans.
F027	Tetra-, penta-, and hexachlorodibenzo-p- dioxins; tetra-, penta-, and hexachlorodibenzofurans; tri-, tetra-, and pentachlorophenols and their chlorophenoxy derivative acids, esters, ethers, amine and other salts.
F028	Tetra-, penta-, and hexachlorodibenzo-p- dioxins; tetra-, penta-, and hexachlorodibenzofurans; tri-, tetra-, and pentachlorophenols and their chlorophenoxy derivative acids, esters, ethers, amine and other salts.
F032	Benz(a)anthracene, benzo(a)pyrene, dibenz(a,h)-anthracene, indeno(1,2,3-cd)pyrene, pentachlorophenol, arsenic, chromium, tetra-, penta-, hexa-, heptachlorodibenzo-p-dioxins, tetra-, penta-, hexa-, heptachlorodibenzofurans.
F034	Benz(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, naphthalene, arsenic, chromium.
F035	Arsenic, chromium, lead.
F037	Benzene, benzo(a)pyrene, chrysene, lead, chromium.
F038	Benzene, benzo(a)pyrene chrysene, lead, chromium.
F039	All constituents for which treatment standards are specified for multi-source leachate (wastewaters and nonwastewaters) under 40 CFR 268.43(a), Table CCW.
K001	Pentachlorophenol, phenol, 2-chlorophenol, p-chloro-m-cresol, 2,4-dimethylphenyl, 2,4-dinitrophenol, trichlorophenols, tetrachlorophenols, 2,4-dinitrophenol, cresosote, chrysene, naphthalene, fluoranthene,

	benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benz(a)anthracene, dibenz(a)anthracene, acenaphthalene.
K002	Hexavalent chromium, lead
K003	Hexavalent chromium, lead.
K004	Hexavalent chromium.
K005	Hexavalent chromium, lead.
K006	Hexavalent chromium.
K007	Cyanide (complexed), hexavalent chromium.
K008	Hexavalent chromium.
K009	Chloroform, formaldehyde, methylene chloride, methyl chloride, paraldehyde, formic acid.
K010	Chloroform, formaldehyde, methylene chloride, methyl chloride, paraldehyde, formic acid, chloroacetaldehyde.
K011	Acrylonitrile, acetonitrile, hydrocyanic acid.
K013	Hydrocyanic acid, acrylonitrile, acetonitrile.
K014	Acetonitrile, acrylamide.
K015	Benzyl chloride, chlorobenzene, toluene, benzotrichloride.
K016	Hexachlorobenzene, hexachlorobutadiene, carbon tetrachloride, hexachloroethane, perchloroethylene.
K017	Epichlorohydrin, chloroethers [bis(chloromethyl) ether and bis (2-chloroethyl) ethers], trichloropropane, dichloropropanols.
K018	1,2-dichloroethane, trichloroethylene, hexachlorobutadiene, hexachlorobenzene.
K019	Ethylene dichloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, tetrachloroethanes (1,1,2,2-tetrachloroethane and 1,1,1,2-tetrachloroethane), trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, vinyl chloride, vinylidene chloride.
K020	Ethylene dichloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, tetrachloroethanes (1,1,2,2-tetrachloroethane and 1,1,1,2-tetrachloroethane), trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform, vinyl chloride, vinylidene chloride.
K021	Antimony, carbon tetrachloride, chloroform.
K022	Phenol, tars (polycyclic aromatic hydrocarbons).
K023	Phthalic anhydride, maleic anhydride.
K024	Phthalic anhydride, 1,4-naphthoquinone.
K025	Meta-dinitrobenzene, 2,4-dinitrotoluene.
K026	Paraldehyde, pyridines, 2-picoline.
K027	Toluene diisocyanate, toluene-2, 4-diamine.
K028	1,1,1-trichloroethane, vinyl chloride.
K029	1,2-dichloroethane, 1,1,1-trichloroethane, vinyl chloride, vinylidene chloride, chloroform.
K030	Hexachlorobenzene, hexachlorobutadiene, hexachloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, ethylene dichloride.
K031	Arsenic.
K032	Hexachlorocyclopentadiene.
K033	Hexachlorocyclopentadiene.

K034	Hexachlorocyclopentadiene.
K035	Creosote, chrysene, naphthalene, fluoranthene benzo(b) fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd) pyrene, benzo(a)anthracene, dibenzo(a)anthracene, acenaphthalene.
K036	Toluene, phosphorodithioic and phosphorothioic acid esters.
K037	Toluene, phosphorodithioic and phosphorothioic acid esters.
K038	Phorate, formaldehyde, phosphorodithioic and phosphorothioic acid esters.
K039	Phosphorodithioic and phosphorothioic acid esters.
K040	Phorate, formaldehyde, phosphorodithioic and phosphorothioic acid esters.
K041	Toxaphene.
K042	Hexachlorobenzene, ortho-dichlorobenzene.
K043	2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol.
K044	N.A.
K045	N.A.
K046	Lead.
K047	N.A.
K048	Hexavalent chromium, lead.
K049	Hexavalent chromium, lead.
K050	Hexavalent chromium.
K051	Hexavalent chromium, lead.
K052	Lead.
K060	Cyanide, napthalene, phenolic compounds, arsenic.
K061	Hexavalent chromium, lead, cadmium.
K062	Hexavalent chromium, lead.
K064	Lead, cadmium.
K065	Do.
K066	Do.
K069	Hexavalent chromium, lead, cadmium.
K071	Mercury.
K073	Chloroform, carbon tetrachloride, hexacholroethane, trichloroethane, tetrachloroethylene, dichloroethylene, 1,1,2,2-tetrachloroethane.
K083	Aniline, diphenylamine, nitrobenzene, phenylenediamine.
K084	Arsenic.
K085	Benzene, dichlorobenzenes, trichlorobenzenes, tetrachlorobenzenes, pentachlorobenzene, hexachlorobenzene, benzyl chloride.
K086	Lead, hexavalent chromium.
K087	Phenol, naphthalene.
K088	Cyanide (complexes).
K090	Chromium.
K091	Do.
K093	Phthalic anhydride, maleic anhydride.
K094	Phthalic anhydride.
K095	1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane.
K096	1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane.
K097	Chlordane, heptachlor.
K098	Toxaphene.
K099	2,4-dichlorophenol, 2,4,6-trichlorophenol.
K100	Hexavalent chromium, lead, cadmium.
K101	Arsenic.
K102	Arsenic.
K103	Aniline, nitrobenzene, phenylenediamine.
K104	Aniline, benzene, diphenylamine, nitrobenzene, phenylenediamine.
K105	Benzene, monochlorobenzene,

	dichlorobenzenes, 2,4,6-trichlorophenol.
K106	Mercury.
K107	1,1-Dimethylhydrazine (UDMH).
K108	1,1-Dimethylhydrazine (UDMH).
K109	1,1-Dimethylhydrazine (UDMH).
K110	1,1-Dimethylhydrazine (UDMH).
K111	2,4-Dinitrotoluene.
K112	2,4-Toluenediamine, o-toluidine, p-toluidine, aniline.
K113	2,4-Toluenediamine, o-toluidine, p-toluidine, aniline.
K114	2,4-Toluenediamine, o-toluidine, p-toluidine.
K115	2,4-Toluenediamine.
K116	Carbon tetrachloride, tetrachloroethylene, chloroform, phosgene.
K117	Ethylene dibromide.
K118	Ethylene dibromide.
K123	Ethylene thiourea.
K124	Ethylene thiourea.
K125	Ethylene thiourea.
K126	Ethylene thiourea.
K131	Dimethyl sulfate, methyl bromide.
K132	Methyl bromide.
K136	Ethylene dibromide.
K141	Benzene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene.
K142	Benzene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene.
K143	Benzene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene.
K144	Benzene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene.
K145	Benzene, benz(a)anthracene, benzo(a)pyrene, dibenz(a,h)anthracene, naphthalene.
K147	Benzene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene.
K148	Benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene.
K149	Benzotrichloride, benzyl chloride, chloroform, chloromethane, chlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, pentachlorobenzene, 1,2,4,5-tetrachlorobenzene, toluene.
K150	Carbon tetrachloride, chloroform, chloromethane, 1,4-dichlorobenzene, hexachlorobenzene, pentachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,1,2,2-tetrachloroethane, tetrachloroethylene, 1,2,4-trichlorobenzene.
K151	Benzene, carbon tetrachloride, chloroform, hexachlorobenzene, pentachlorobenzene, toluene, 1,2,4,5-tetrachlorobenzene, tetrachloroethylene.
K156	Benomyl, carbaryl, carbendazim, carbofuran, carbosulfan, formaldehyde, methylene chloride, triethylamine.

K157	Carbon tetrachloride, formaldehyde, methyl chloride, methylene chloride, pyridine, triethylamine.
K158	Benomyl, carbendazim, carbofuran, carbosulfan, chloroform, methylene chloride.
K159	Benzene, butylate, eptc, molinate, pebulate, vernolate.
K161	Antimony, arsenic, metam-sodium, ziram.
K169	Benzene.
K170	Benzo(a)pyrene, dibenz(a,h)anthracene, benzo (a) anthracene, benzo (b)fluoranthene, benzo(k)fluoranthene, 3-methylcholanthrene, 7, 12-dimethylbenz(a)anthracene.
K171	Benzene, arsenic.
K172	Benzene, arsenic.
K174	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD), 1,2,3,4,6,7,8-Heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF), 1,2,3,4,7,8,9-Heptachlorodibenzofuran (1,2,3,6,7,8,9-HpCDF), HxCDDs (All Hexachlorodibenzo-p-dioxins), HxCDFs (All Hexachlorodibenzofurans), PeCDDs (All Pentachlorodibenzo-p-dioxins), OCDD (1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin, OCDF (1,2,3,4,6,7,8,9-Octachlorodibenzofuran), PeCDFs (All Pentachlorodibenzofurans), TCDDs (All tetrachlorodi-benzo-p-dioxins), TCDFs (All tetrachlorodibenzofurans).
K175	Mercury
K176	Arsenic, Lead.
K177	Antimony.
K178	Thallium.

N.A.--Waste is hazardous because it fails the test for the characteristic of ignitability, corrosivity, or reactivity.

[46 FR 4619, Jan. 16, 1981]

Editorial Note: For FEDERAL REGISTER citations affecting Appendix VII, part 261, see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

Appendix VIII to Part 261 -- Hazardous Constituents

Common name	Chemical abstracts name	Chemical abstracts No.	Haz was
A2213	Ethanimidothioic acid, 2-(dimethylamino) -N-hydroxy-2-oxo-, methyl ester.	30558-43-1	
Acetonitrile	Same	75-05-8	
Acetophenone	Ethanone, 1-phenyl-	98-86-2	
2-Acetylaminefluarone	Acetamide, N-9H-fluoren-2-yl-	53-96-3	
Acetyl chloride	Same	75-36-5	
1-Acetyl-2-thiourea	Acetamide, N-(aminothioxomethyl)-	591-08-2	
Acrolein	2-Propenal	107-02-8	
Acrylamide	2-Propenamide	79-06-1	
Acrylonitrile	2-Propenenitrile	107-13-1	
Aflatoxins	Same	1402-68-2	....
Aldicarb	Propanal, 2-methyl-2-(methylthio)-, O-[(methylamino)carbonyl]oxime.	116-06-3	
Aldicarb sulfone	Propanal, 2-methyl-2-(methylsulfonyl) -, O-[(methylamino) carbonyl] oxime.	1646-88-4	
Aldrin	1,4,5,8-Dimethanonaphthalene, 1,2,3,4,10,10-10-hexachloro-1,4,4a,5,8,8a-hexahydro-, (1alpha,4alpha,4abeta,5alpha,8alph	309-00-2	

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40 CFR
Protection of Environment
CHAPTER I
ENVIRONMENTAL PROTECTION AGENCY (CONTINUED)

SUBCHAPTER R -- TOXIC SUBSTANCES CONTROL ACT

PART 766 -- DIBENZO-PARA-DIOXINS/DIBENZOFURANS

Subpart A -- General Provisions

Sec.

766.1 Scope and purpose.
766.2 Applicability and duration of this part.
766.3 Definitions.
766.5 Compliance.
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766.20 Who must test.
766.25 Chemical substances for testing.
766.27 Congeners and LOQs for which quantitation is required.
766 28 Expert review of protocols.
766.32 Exclusions and waivers.
766.35 Reporting requirements.
766.38 Reporting on precursor chemical substances.

Authority: 15 U.S.C. 2603 and 2607.

Source: 52 FR 21437, June 5, 1987, unless otherwise noted.

Subpart A -- General Provisions

[TOP]

§766.1 Scope and purpose.

(a) This part identifies requirements for testing under section 4 of the Toxic Substances Control Act (TSCA), 15 U.S.C. 2603, to ascertain whether certain specified chemical substances may be contaminated with halogenated dibenzodioxins (HDDs)/dibenzofurans (HDFs) as defined in §766.3, and requirements for reporting under section 8 of TSCA, 15 U.S.C. 2607.

(b) Section 766.35(b) requires manufacturers and processors of chemical substances identified in §766.25 to submit to EPA:

(1) Any existing test data showing analysis of the chemical substances for concentrations of HDDs/HDFs, applicable protocols, and the results of the analysis for HDDs/HDFs, (2) allegations of significant adverse reactions to HDDs/HDFs, compiled in accordance with part 717 of this chapter, and (3) health and safety studies on the HDDs/HDFs, in accordance with applicable provisions of part 716 of this chapter.

(c) Section 766.35(a) requires manufacturers and, under certain circumstances, processors of chemical substances identified in §766.25 to submit letters of intent to test and protocols for the analysis of the chemical substances for the presence of HDDs/HDFs. Section 766.20 requires these manufacturers and processors to test their chemical substances for the presence of HDDs/HDFs. Any submissions must be in accordance with the EPA Procedures Governing Testing Consent Agreements and Test Rules contained in part 790 of this chapter and any modifications to such procedures contained in this part.

(d) Section 766.32 specifies conditions under which persons required to test may request an exclusion or waiver from testing.

(e) Deadlines for submission to EPA of protocols, reports, studies, and test results are specified in part 790, subpart C and §766.35.

(f) Sections 766.10, 766.12, 766.14, 766.16, and 766.18 prescribe analytical methods required; §766.27 prescribes target levels of quantitation (LOQ) for each congener for which quantitation is required.

(g) If results of existing tests or tests performed under this part indicate the presence of HDDs/HDFs in the identified chemical substance above the LOQ specified in §766.27, §766.35(c) requires the following additional reporting on the specified chemicals: production, process, use, exposure and disposal data under section 8(a) of TSCA; health and safety studies under section 8(d) of TSCA; and reports of allegations of significant adverse reactions under section 8(c) of TSCA. In some cases, additional reporting may be required of manufacturers reporting no contamination of the identified chemical substances under §766.35(c)(2).

(h) Section 766.38 requires manufacturers of chemical substances produced from chemical substances identified as possible precursors to HDD/HDF formation, to report on chemical substances produced from such precursors.

[TOP]

§766.2 Applicability and duration of this part.

(a) *Chemical substances subject to testing.* (1) This part is applicable to each person who, at any time during the duration of this part, manufactures (and/or imports), or processes, a chemical substance identified under §766.25.

(2) The duration of this part for any testing requirement for any chemical substance is the period commencing with the effective date of this part to the end of the reimbursement period, as defined in §766.3, for each chemical substance. All reporting requirements for any chemical substance listed under §766.25 shall be in effect for the same period as the testing requirement.

(b) *Precursor chemical substances.* (1) This part is applicable to each person who manufactures (and/or imports) a chemical substance from any precursor chemical substance identified in §766.38.

(2) The requirement for precursor reporting under §766.38 shall be in effect until three years after the effective date of this part.

(3) Small manufacturers are exempt from reporting process and reaction condition data on chemical substances made from precursor chemical substances listed under §766.38.

[TOP]

§766.3 Definitions.

The definitions in section 3 of TSCA and the definitions of §§704.3, 716.3, 717.3, and 790.3 of this chapter also apply to this part.

Congener means any one particular member of a class of chemical substances. A specific congener is denoted by unique chemical structure, for example 2,3,7,8-tetrachlorodibenzofuran.

Dibenzofuran means any of a family of compounds which has as a nucleus a triple-ring structure consisting of two benzene rings connected through a pair of bridges between the benzene rings. The bridges are a carbon-carbon bridge and a carbon-oxygen-carbon bridge at both substitution positions.

Dibenzo-p-dioxin or *dioxin* means any of a family of compounds which has as a nucleus a triple-ring structure consisting of two benzene rings connected through a pair of oxygen atoms.

Guidelines means the Midwest Research Institute (MRI) publication *Guidelines for the Determination of Polyhalogenated Dioxins and Dibenzofurans in Commercial Products,* EPA contract No. 68-02-3938; MRI Project No. 8201-A(41), 1985.

HDD or *2,3,7,8-HDD* means any of the dibenzo-p-dioxins totally chlorinated or totally brominated at the following positions on the molecular structure: 2,3,7,8; 1,2,3,7,8; 1,2,3,4,7,8; 1,2,3,6,7,8; 1,2,3,7,8,9; and 1,2,3,4,7,8,9.

HDF or *2,3,7,8-HDF* means any of the dibenzofurans totally chlorinated or totally brominated at the following positions on the molecular structure: 2,3,7,8; 1,2,3,7,8; 2,3,4,7,8; 1,2,3,4,7,8; 1,2,3,6,7,8; 1,2,3,7,8,9; 2,3,4,6,7,8; 1,2,3,4,6,7,8; and 1,2,3,4,7,8,9.

Homolog means a group of isomers that have the same degree of halogenation. For example, the homologous class of tetrachlorodibenzo-p-dioxins consists of all dibenzo-p-dioxins containing four chlorine atoms. When the homologous classes discussed in this part are referred to, the following abbreviations for the prefix denoting the number of halogens are used:

tetra-, T (4 atoms)

penta-, Pe (5 atoms)

hexa-, Hx (6 atoms)

hepta-, Hp (7 atoms)

HRGC means high resolution gas chromatography.

HRMS means high resolution mass spectrometry.

Level of quantitation or *LOQ* means the lowest concentration at which HDDs/HDFs can be reproducibly measured in a specific chemical substance within specified confidence limits, as described in this part.

Polybrominated dibenzofurans refers to any member of a class of dibenzofurans with two to eight bromine substituents.

Polybrominated dibenzo-p-dioxin or *PBDD* means to any member of a class of dibenzo-p-dioxins with two to eight bromine substituents.

Polychlorinated dibenzofuran means any member of a class of dibenzofurans with two to eight chlorine substituents.

Polychlorinated dibenzo-p-dioxin or *PCDD* means any member of a class of dibenzo-p-dioxins with two to eight chlorine substituents.

Polyhalogenated dibenzofuran or *PHDF* means any member of a class of dibenzofurans containing two to eight chlorine, bromine, or a combination of chlorine and bromine substituents.

Polyhalogenated dibenzo-p-dioxin or *PHDD* means any member of a class of dibenzo-p-dioxins containing two to eight chlorine substituents or two to eight bromine substituents.

Positive test result means: (1) Any resolvable gas chromatographic peak for any 2,3,7,8-HDD or HDF which exceeds the LOQ listed under §766.27 for that congener, or (2) exceeds LOQs approved by EPA under §766.28.

Precursor means a chemical substance which is not contaminated due to the process conditions under which it is manufactured, but because of its molecular structure, and under favorable process conditions, it may cause or aid the formation of HDDs/HDFs in other chemicals in which it is used as a feedstock or intermediate.

QA means quality assurance.

QC means quality control.

Reimbursement period means the period that begins when the data from the last test to be completed under this part for a specific chemical substance listed in §766.25 is submitted to EPA, and ends after an amount of time equal to that which had been required to develop that data or 5 years, whichever is later.

TSCA means the Toxic Substances Control Act, 15 U.S.C. 2601 *et seq.*

[TOP]
§766.5 Compliance.

Any person who fails or refuses to comply with any aspect of this part is in violation of section 15 of TSCA. Section 15(1) makes it unlawful for any person to fail or refuse to comply with any rule or order issued under section 4. Section 15(3) makes it unlawful for any person to fail or refuse to submit information required under this part. Section 16 provides that a violation of section 15 renders a person liable to the United States for a civil penalty and possible criminal prosecution. Under section 17 of TSCA, the district courts of the United States have jurisdiction to restrain any violation of section 15.

[TOP]
§766.7 Submission of information.

All information (including letters of intent, protocols, data, forms, studies, and allegations) submitted to EPA under this part must bear the applicable Code of Federal Regulations (CFR) section number (e.g., §766.20) and must be addressed to: Document Control Office, (7407), Information Management Division, Office of Polution Prevention and Toxics, Environmental Protection Agency, 1200 Pennsylvania Ave., NW., Washington, DC 20460, ATTN: Dioxin/Furan Report.

[52 FR 21437, June 5, 1987, as amended at 60 FR 31922, June 19, 1995]

[TOP]
§766.10 Test standards.

Testing required under subpart B of this part must be performed using the protocols submitted to and reviewed by the EPA expert panel established under §766.28. All new data, documentation, records, protocols, specimens, and reports generated as a result of testing under subpart B of this part must be fully developed and retained in accordance with part 792 of this chapter. These items must be made available during an inspection or submitted to EPA upon request by EPA or its authorized representative. Laboratories conducting testing for submission to EPA in response to a test rule promulgated under section 4 of TSCA must adhere to the TSCA Good Laboratory Practices (GLPs) published in part 792 of this chapter. Sponsors must notify the laboratory that the testing is being conducted pursuant to TSCA section 4. Sponsors are also responsible for ensuring that laboratories conducting the testing abide by the TSCA GLP standards. At the time test data are submitted, manufacturers must submit a certification to EPA that the laboratory performing the testing adhered to the TSCA GLPs.

[TOP]
§766.12 Testing guidelines.

Analytical test methods must be developed using methods equivalent to those described or reviewed in *Guidelines for the Determination of Polyhalogenated Dibenzo-p-dioxins and Dibenzofurans in Commercial Products.* Copies are available from the Director, Environmental Assistance Division (7408), Office of Pollution Prevention and Toxics, U.S.Environmental Protection Agency, Room E-543B, 1200 Pennsylvania Ave., NW., Washington, DC 20460, Telephone: (202) 554-1404, TDD: (202) 544-0551. Copies are also located in the public docket for this part (Docket No. OPPTS-83002)

and are available for inspection in the Non-Confidential Information Center (NCIC) (7407), Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Room B-607 NEM, 401 M St., SW., Washington, DC 20460, between the hours of 12 p.m. and 4 p.m. weekdays excluding legal holidays.

[60 FR 34466, July 3, 1995]

[TOP]

§766.14 Contents of protocols.

Protocols should include all parts of the *Quality Assurance Plan for Measurement of Brominated or Chlorinated Dibenzofurans and Dibenzodioxins,* as stated in the Guidelines. For each chemical substance and each process, the manufacturer must submit a statement of how many grades of the chemical substance it produces, a justification for selection of the specific grade of chemical substance for testing, specific plans for collection of samples from the process stream, naming the point of collection, the method of collecting the sample, and an estimate of how well the samples will represent the material to be characterized; a description of how control samples (blanks) and HDD/HDF-reinforced control samples, or isotopically labeled compounds (standards) and duplicate samples will be handled; a description of the chemical extraction and clean up procedures to be used; how extraction efficiency and measurement efficiency will be established; and a description of instrument hardware and operating conditions, including type and source of columns, carrier gas and flow rate, operating temperature range, and ion source temperature.

[TOP]

§766.16 Developing the analytical test method.

Because of the matrix differences of the chemicals listed for testing, no one method for sample selection, preparation, extraction and clean up is prescribed. For analysis, High Resolution Gas Chromatography (HRGC) with High Resolution Mass Spectrometry (HRMS) is the method of choice, but other methods may be used if they can be demonstrated to reach the target LOQs as well as HRGC/HRMS.

(a) *Sample selection.* The chemical product to be tested should be sampled so that the specimens collected for analysis are representative of the whole. Additional guidance for sample selection is provided under §766.12.

(b) *Sample preparation.* The sample must be mechanically homogenized and subsampled as necessary. Subsamples must be spiked or reinforced with surrogate compounds or with standard stock solutions, and the surrogates or standards must be thoroughly incorporated by mechanical agitation. Additional guidance is provided under §766.12.

(c) *Sample extraction and cleanup.* The spiked samples must be treated to separate the HDDs/HDFs from the sample matrix. Methods are reviewed in the Guidelines under §766.12, but the final method or methods are left to the discretion of the analyst, provided the instrumental response of the surrogates meets the criteria listed in the *Quality Assurance Plan for Measurement of Brominated or Chlorinated Dibenzofurans and Dibenzodioxins,* Appendixes B and C of the Guidelines. Cleanup techniques are described in the Guidelines. These are chosen at the discretion of the analyst to meet the requirements of the chemical matrix.

(d) *Analysis.* The method of choice is High Resolution Gas Chromatographic/High Resolution Mass Spectrometric Determination, (HRGC/HRMS) but alternate methods may be used if the manufacturer can demonstrate that the method will reach the target LOQs as well as HRGC/HRMS. Specific operating requirements are found in the Guidelines.

[TOP]

§766.18 Method sensitivity.

The target level of quantitation required under §766.27 for each HDD/HDF congener is the level which must be attempted for each resolved HRGC peak for that congener. For at least one product sample, at least two analyses of the same isotopically labeled HDD/HDF internal calibration standards spiked to a final product concentration equal to the LOQ for that congener must be reproducibly extracted, cleaned up, and quantified to within ±20 percent of each other. For each spiked product sample, the signal to noise ratio for the calibration standard peaks after complete extraction and cleanup must be 10:1 or greater. The recovery of the internal calibration standards in the extracted and cleaned up product samples must be within 50 to 150 percent of the amount spiked, and the results must be corrected for recovery.

Subpart B -- Specific Chemical Testing/Reporting Requirements

[TOP]

§766.20 Who must test.

(a) Any person who manufactures, imports, or processes a chemical substance listed in §766.25 must test that chemical substance and must submit appropriate information to EPA according to the schedules described in §766.35. Chemical substances manufactured, imported or processed between January 1, 1984 and the date of promulgation of this part are subject to testing upon the effective date of this part. All other chemical substances are subject to testing immediately upon manufacture, import or processing. EPA expects that only manufacturers and importers will perform testing, and that the cost of testing will be passed on to processors through the pricing mechanism, thereby enabling them to share in the cost of testing. However, processors will be called upon to sponsor testing should manufacturers and importers fail to do so. A processor may apply for an exemption from testing upon certification to EPA that a manufacturer or importer is testing the chemical substance which that person processes.

(b) If no manufacturer or importer described in §766.20 submits a letter of intent to perform testing within the period described under §766.35(a), or an exemption application under §790.45(a), or a request for an exclusion or waiver under §766.32, EPA will issue a notice in the FEDERAL REGISTER to notify all processors of that chemical substance. The notice will state that EPA has not received any of the documents described in the previous sentence, and that current processors will have 30 days to submit either a letter of intent to perform the test or submit an exemption application.

(c) If no manufacturer, importer or processor submits a letter of intent to perform testing of a specific chemical substance produced by a specific process, EPA will notify all manufacturers, importers, and processors, either by notice in the FEDERAL REGISTER or by letter, that all exemption applications will be denied and that within 30 days all manufacturers, importers, and processors will be in violation of this part until a proposed study plan is submitted for required testing.

(d) Manufacturers, importers, and processors who are subject to this part must comply with the test rule

development and exemption procedures in part 790 of this chapter, except as modified in this part.

[TOP]

§766.25 Chemical substances for testing.

(a) *Listing of chemical substances.* Chemical substances required to be tested for HDDs/HDFs under this rule are listed in this section. The listing is by Chemical Abstracts Service (CAS) Number and common name.

Note: For purposes of guidance only, EPA lists the chemical substances subject to testing under this part in two classes -- those known to be manufactured or imported between January 1, 1984, and promulgation of this part, and those not known to be manufactured or imported at the time of promulgation of this part.

(1) *Chemicals substances known to be manufactured between January 1, 1984 and date of promulgation of this part.*

CAS No.	Chemical name
79-94-7	Tetrabromobisphenol-A.
118-75-2	2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione.
118-79-6	2,4,6-Tribromophenol.
120-83-2	2,4-Dichlorophenol.
1163-19-5	Decabromodiphenyloxide.
4162-45-2	Tetrabromobisphenol-A-bisethoxylate.
21850-44-2	Tetrabromobisphenol-A-bis-2,3-dibromopropyl ether.
25327-89-3	Allyl ether of tetrabromobisphenol-A.
32534-81-9	Pentabromodiphenyloxide.
32536-52-0	Octabromodiphenyloxide.
37853-59-1	1,2-Bis(tribromophenoxy)-ethane.
55205-38-4	Tetrabromobisphenol-A diacrylate.

(2) *Chemicals not known to be manufactured between January 1, 1984 and the date of promulgation of this part.*

CAS No.	Chemical name
79-95-8	Tetrachlorobisphenol-A.
87-10-5	3,4',5-Tribromosalicylanilide.
87-65-0	2,6-Dichlorophenol.
95-77-2	3,4-Dichlorophenol.
95-95-4	2,4,5-Trichlorophenol.
99-28-5	2,6-Dibromo-4-nitrophenol.
120-36-5	2[2,4-(Dichlorophenoxy)]-propionic acid.
320-72-9	3,5-Dichlorosalicyclic acid.
488-47-1	Tetrabromocatechol.
576-24-9	2,3-Dichlorophenol.
583-78-8	2,5-Dichlorophenol.
608-71-9	Pentabromophenol.
615-58-7	2,4-Dibromophenol.
933-75-5	2,3,6-Trichlorophenol.
1940-42-7	4-Bromo-2,5-dichlorophenol.
2577-72-2	3,5-Dibromosalicylanilide.
3772-94-9	Pentachlorophenyl laurate.

37853-61-5	Bismethylether of tetrabromobisphenol-A.
	Alkylamine tetrachlorophenate.
	Tetrabromobisphenol-B.

(b) *Grade to be tested.* If the same process is used to manufacture all grades of the same chemical substance, only one grade need be tested. The grade to be tested must be the grade subject to the most intense heat and alkalinity for the longest duration of time, manufactured under each different process. If the heat, alkalinity and duration of reaction do not differ for various grades, the test substance must be the grade of chemical substance with the highest volume of sales.

[TOP]

§766.27 Congeners and LOQs for which quantitation is required.

Quantitation at the target LOQ shown for each of the following HDDs/HDFs which may be present in the chemical substances is required for the chemical substances listed under §766.25. Analysis must take place for either chlorinated or brominated dibenzodioxins or dibenzofurans, whichever is predominantly expected to occur in the chemical substance to be tested. Only chlorinated and brominated congeners need be quantified; for chemical substances containing predominantly chlorine atoms, only congeners totally chlorinated at the numbered positions need be quantified; for chemical substances containing predominantly bromine atoms, only congeners totally brominated at the numbered positions need be quantified.

Chlorinated dioxins	Brominated dioxins	LOQ
2,3,7,8-TCDD	2,3,7,8-TBDD	0.1 ppb.
1,2,3,7,8-PeCDD	1,2,3,7,8-PeBDD	0.5 ppb.
1,2,3,4,7.8-HxCDD	1,2,3,4,7,8-HxBDD	2.5 ppb.
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxBDD	2.5 ppb.
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxBDD	2.5 ppb.
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpBDD	100 ppb.
2,3,7,8-TCDF	2,3,7,8-TBDF	1 ppb.
1,2,3,7,8-PeCDF	1,2,3,7,8-PeBDF	5 ppb.
2,3,4,7,8-PeCDF	2,3,4,7,8-PeBDF	5 ppb.
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxBDF	25 ppb.
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxBDF	25 ppb.
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxBDF	25 ppb.
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxBDF	25 ppb.
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpBDF	1 ppm.
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpBDF	1 ppm.

[TOP]

§766.28 Expert review of protocols.

EPA will gather a panel of experts in analysis of chemical matrices for HDDs/HDFs to review the protocols for testing submitted to EPA. The panel members will be employees of EPA and/or of other U.S. Government agencies who have had experience in analysis of chemical matrices and/or chemical wastes for HDDs/HDFs. The panel will recommend to the Director, EPA Office of Pollution Prevention and Toxics, whether the protocol submitted is likely to allow analysis down to the target LOQs, or if not, whether the protocol represents a good faith effort on the part of the tester to achieve the lowest

possible LOQs. The final determination to accept or reject the protocol will be made by the Director, Office of Pollution Prevention and Toxics. EPA will review the submitted protocols as rapidly as possible and will complete the review within 90 days after receipt. EPA may require submission of revised protocols. Comments and recommendations will be transmitted to the submitter, and if revisions are required, a final protocol must be submitted to EPA within 90 days after EPA transmits such recommendations.

[TOP]

§766.32 Exclusions and waivers.

(a) *Reasons for exclusions and waivers.* Any person subject to the testing requirements of this part may request an exclusion or waiver from testing for any one of the following reasons:

(1) *Exclusions may be granted if.* (i) Testing of the appropriate grade of the chemical substance has already been carried out, either analytical testing at the lowest LOQ possible, with appropriate QA/QC, or a well-designed bioassay with appropriate QA/QC or;

(ii) Process and reaction conditions of the chemical substance such that no HDDs/HDFs could be produced under those conditions;

(2) *Waivers may be granted if.* (i) A responsible company official certifies that the chemical substance is produced only in quantities of 100 kilograms or less per year, only for research and development purposes; or

(ii) In the judgement of EPA, the cost of testing would drive the chemical substance off the market, or prevent resumption of manufacture or import of the chemical substance, if it is not currently manufactured, and the chemical substance will be produced so that no unreasonable risk will occur due to its manufacture, import, processing, distribution, use, or disposal. (In this case, the manufacturer must submit to EPA all data supporting the determination.)

(iii) Waivers may be appropriately conditioned with respect to such factors as time and conditions of manufacture or use. The grade of decabromodiphenyl oxide produced by Dow Chemical Company (Dow) for the National Toxicology Program (NTP) bioassay on that chemical is excluded from the testing requirement under this part. Provided, however, that this exclusion will not apply if Dow fails to supply to EPA within 60 days of the effective date of this section evidence showing which grade was used for the NTP bioassay.

(b) *Timing.* Exclusion or waiver requests and detailed supporting data must be submitted to EPA within 60 days from the effective date of this part for persons manufacturing, importing or processing a chemical substance as of the date of promulgation, or 60 days prior to the date of resumption of manufacture or import for a chemical substance produced by a specific process if the chemical substance is not manufactured, imported or processed as of the date of promulgation.

(c) *Publication.* Within 10 days of receipt of any exclusion or waiver request, EPA will issue in the FEDERAL REGISTER a notice of such receipt. EPA will also issue a notice of its decision on each exclusion or waiver request within 60 days of receipt.

(d) *Decision.* The EPA Director of the Office of Pollution Prevention and Toxics will make the decision to grant or deny waivers or exclusions.

[TOP]

§766.35 Reporting requirements.

(a) *Letters of intent, exemption applications, and protocols* -- (1) *Letters of Intent.* (i) Persons who have manufactured or imported chemical substances listed under §766.25 between January 1, 1984, and the effective date of this part are required to submit under §790.45 of this chapter a letter of intent to test or an exemption application. These letters must be submitted no later than September 3, 1987.

(ii) Persons who commence manufacture, import or processing of a chemical substance listed under §766.25 that has not been manufactured, imported or processed between January 1, 1984 and the effective date of this part must submit under §790.45 of this chapter, within 60 days after the commencement of manufacture, import, or processing of the chemical substance, a letter of intent to test or an exemption application.

(iii) Persons who commence manufacture, import or processing of a chemical substance listed under §766.25 between the effective date of this part and the end of the reimbursement period for that particular chemical substance produced by a specific process must submit under §790.45 of this chapter, within 60 days after the commencement of manufacture, import or processing of the chemical substance, a letter of intent to test or an exemption application.

(2) *Protocols.* (i) Each person who is manufacturing or processing a chemical substance listed in §766.25 as of the effective date of this part who submits a notice of intent to test under §766.35(a)(1) must submit a protocol for the test as follows:

(A) The protocols for each chlorinated chemical substance produced by each process to be tested must be submitted to EPA no later than 12 months after the effective date of this part.

(B) The protocol for each brominated chemical substance produced by each process to be tested must be submitted to EPA no later than 24 months after the effective date of this part except for the following chemicals.

(*1*) The deadline for submitting the protocols for tetrabromobisphenol-A (CAS No. 79-94-7); 2,4,6 tribromophenol (CAS. No. 118-79-6); decabromodiphenyloxide (CAS No. 1163-19-5); and 1,2-bis(tribromophenoxy)-ethane (CAS No. 37853-59-1) is January 31, 1991.

(*2*) The deadline for submitting protocols for octabromodiphenyloxide (CAS No. 32536-52-0) and allyl ether of tetrabromobisphenol-A (CAS No. 25327-89-3) is January 31, 1991.

(*3*) The deadline for submitting protocols for pentabromodiphenyloxide (CAS No. 32534-81-9) is February 6, 1995. The deadline for submitting tetrabromobisphenol-A-bisethoxylate (CAS No. 4126-45-2) is January 31, 1991.

(*4*) The deadline for submitting protocols for 3,4',5-tribromosalicylanilide (CAS No. 87-10-5) is September 5, 1990.

(ii) For chemical substances produced by a specific process not manufactured or processed as of the effective date of this part, a person who begins manufacture and submits a notice of intent to test must submit protocols for the test as follows:

(A) Except as noted for the submitter and substance specified in the following table, protocols for

testing must be submitted 12 months after manufacture or importation begins for chlorinated chemical substances.

CAS No.	Submitter	Chemical
118-75-2	Rhone-Poulenc.....	2,3,5,6-tetrachloro-2,5-cyclohexaniene 1,4-dione.

(B) Protocols for testing must be submitted 24 months after manufacture begins for brominated chemical substances.

(iii) For persons who have been granted exemptions, waivers or exclusions from testing, protocols must be submitted 12 months after expiration of the exemption, waiver or exclusion for chlorinated chemical substances, and 24 months after expiration of the exemption, waiver or exclusion for brominated chemical substances.

(b) *Information that must be submitted to EPA.* (1) Persons who manufacture or import a chemical substance listed under §766.25 must report no later than October 5, 1987 or 90 days after the person first manufactures or imports the chemical substance, whichever is later, the results of all existing test data which show that chemical substance has been tested for the presence of HDDs/HDFs.

(2) Any manufacturer or importer of a chemical substance listed in §766.25 in possession of unpublished health and safety studies on HDDs/HDFs is required to submit copies of such studies to EPA no later than October 5, 1987 or 90 days after the person first manufactures or imports the chemical substance, whichever is later. The following provisions of part 716 of this chapter apply to submission of these studies: §§716.3, 716.10(a) (1) and (4); 716.20(a) (1), (2), (3), (4), (7), (8) and (10); 716.25; 716.30; 716.35(a) (1), (2), and (4) [if applicable]; 716.35 (b) and (c); 716.40 (a) and (b); 716.50; 716.55; and 716.60(a)(2).

(3) No later than October 5, 1987 or 90 days after the person first manufactures or imports the substance listed in §766.25, any manufacturer or importer of a chemical substance listed in §766.25 must submit records required to be held under part 717 of this chapter on any HDDs/HDFs.

(4) *Test results.* (i) Test results must be submitted to EPA not later than 270 days after EPA's transmission of comments or 180 days after a final protocol is submitted to EPA, whichever is shorter, except as noted for the submitters and substances specified in the following table:

CAS No.	Submitter	Chemical	Due Da
79-94-7	Great Lakes	Tetrabromobisphenol-A	May 26, 1992
1 1 1 1 1 7 9-94-7	Ethyl	Tetrabromobisphenol-A	August 10, 199
79-94-7	Ameribrom	Tetrabromobisphenol-A	April 15, 1994
87-10-5	Pfister	3,4',5-tribromosalicylanilide	45 days after approval

118-75-2	Rhone-Poulenc Inc.	2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione	July 5, 1996
118-79-6	Great Lakes	2,4,6-Tribromophenol	May 26, 1992
1163-19-5	Ameribrom	Decabromodiphenyloxide	April 15, 1994
1163-19-5	Ethyl	Decabromodiphenyloxide	May 26, 1992
1163-19-5	Great Lakes	Decabromodiphenyloxide	May 26, 1992
4162-45-2	Great Lakes	Tetrabromobisphenol-A-bisethoxylate	June 2, 1993
25327-89-3	Great Lakes	Allyl Ether of Tetrabromobisphenol-A	August 10, 199
32534-81-9	Great Lakes	Pentabromodiphenyloxide	March 22, 199
32534-81-9	Akzo Chemicals Inc.	Pentabromodiphenyloxide	February 6, 19
32534-81-9	Ameribrom	Pentabromodiphenyloxide	March 22, 199
32536-52-0	Ameribrom	Octabromodiphenyloxide	January 8, 199
32536-52-0	Ethyl	Octabromodiphenyloxide	May 15, 1994
32536-52-0	Great Lakes	Octabromodiphenyloxide	May 26, 1992
37853-59-1	Great Lakes	1,2-bis(tribromophenoxy)ethane	January 24, 19

(ii) For purposes of reporting test results to EPA, and for further reporting triggered by a positive test result under §766.35(c), a positive test result is defined at §766.3.

(iii) Reporting of test results must follow procedures set out in part 790 of this chapter, except as modified in this part.

(c) *Information required to be submitted to EPA after submission of a positive test result.* (1) Any person who submits a positive test result for a specific chemical substance listed under §766.25 must submit to EPA no later than 90 days after the date of submission of the positive test result the following:

(i) A completed form (EPA 7710-51) for that chemical substance. The form and instructions are available from the Environmental Assistance Division (7408), Office of Pollution Prevention and Toxics, Environmental Protection Agency, 1200 Pennsylvania Ave., NW., Washington, DC 20460. One form must be submitted for each chemical substance for which a positive test result has been submitted.

(ii) Health and safety studies for the chemical substance for which a positive test result has been reported. The following provisions of part 716 of this chapter apply to submission of these studies: §§716.3; 716.10 (a) (1), (2), (3) and (4); 716.20; 716.25; 716.30; 716.35(a) (1), (2), and (4), [if applicable]; 716.35 (b) and (c); 716.40 (a) and (b); 716.50; 716.55; 716.60(a)(2).

(iii) Copies of records on the chemical substances required to be held under part 717 of this chapter.

(2) If a positive test result on a chemical substance is received from one person but not from others, EPA may issue a notice in the FEDERAL REGISTER listing that chemical substance and requiring any person manufacturing, importing or processing that chemical substance who has not submitted a positive test result to submit the information required in Part II of EPA Form 7710-51. Such a notice will be published only if EPA needs additional process data to make a determination of unreasonable risk.

(d)-(e) [Reserved]

(f) *Effective date.* (1) The effective date of this final rule is July 6, 1987, except for paragraphs (a)(2)(i)(B) introductory text, (a)(2)(i)(B)(*1*), (a)(2)(i)(B)(*2*), (a)(2)(i)(B)(*3*), (a)(2)(i)(B)(*4*), the table in paragraph (a)(2)(ii)(A), and the table in paragraph (b)(4)(i) of this section.

(2) The effective date for paragraph (a)(2)(i)(B) introductory text, (a)(2)(i)(B)(*1*), (a)(2)(i)(B)(*2*), and (a)(2)(i)(B)(*4*), is May 21, 1991. The effective date of paragraphs (a)(2)(i)(B)(*3*), and the table in paragraph (a)(2)(ii)(A) is September 29, 1995. The effective date of paragraph (b)(4)(i) introductory text is May 28, 1993, and the effective date of the entries in the table in paragraph (b)(4)(i) is shown in the effective dates column of the table.

(3) The guidelines and other test methods cited in this rule are referenced as they exist on the effective date of the final rule.

[52 FR 21437, June 5, 1987, as amended at 56 FR 23229, May 21, 1991; 57 FR 24960, June 12, 1992; 58 FR 30991, May 28, 1993, 58 FR 34205, June 23, 1993; 59 FR 46356, Sept. 8, 1994; 60 FR 31922, June 19, 1995; 60 FR 50433, Sept. 29, 1995; 60 FR 56955, Nov. 13, 1995; 62 FR 35105, June 30, 1997]

[TOP]

§766.38 Reporting on precursor chemical substances.

(a) *Identification of precursor chemical substances.* Precursor chemical substances are produced under conditions that will not yield HDDs and HDFs, but their molecular structure is conducive to HDD/HDF formation under favorable reaction conditions when they are used to produce other chemicals or products. The following precursor chemical substances are identified by Chemical Abstract Service (CAS) number and name.

CAS No.	Chemical name
85-22-3	Pentabromoethylbenzene.
87-61-6	1,2,3-Trichlorobenzene.
87-84-3	1,2,3,4,5-Pentabromo-6-chloro-cyclohexane.
89-61-2	1,4-Dichloro-2-nitrobenzene.
89-64-5	4-Chloro-2-nitrophenol.
89-69-0	2,4,5-Trichloronitrobenzene.
92-04-6	2-Chloro-4-phenylphenol.
94-74-6	4-Chloro-o-toloxy acetic acid.
94-81-5	4-(2-Methyl-4-chlorophenoxy) butyric acid.
95-50-1	o-Dichlorobenzene.
95-56-7	o-Bromophenol.
95-57-8	o-Chlorophenol.

95-88-5	4-Chlororesorcinol.
95-94-3	1,2,4,5-Tetrachlorobenzene.
97-50-7	5-Chloro-2,4-dimethoxyaniline.
99-30-9	2,6-Dichloro-4-nitroaniline.
99-54-7	1,2-Dichloro-4-nitrobenzene.
106-46-7	p-Dichlorobenzene.
108-70-3	1,3,5-Trichlorobenzene.
108-86-1	Bromobenzene.
108-90-7	Chlorobenzene.
117-18-0	1,2,4,5-Tetrachloro-3-nitrobenzene.
120-82-1	1,2,4-Trichlorobenzene.
348-51-6	o-Chorofluorobenzene.
350-30-1	3-Chloro-4-fluoronitrobenzene.
615-67-8	Chlorohydroquinone.
626-39-1	1,3,5-Tribromobenzene.
827-94-1	2,6-Dibromo-4-nitroaniline.

(b) *Persons required to report.* All persons who manufacture or import a chemical product produced using any of the chemical substances listed in paragraph (a) of this section as feedstocks or intermediates must report no later than September 29, 1987. Small manufacturers and those manufacturers and importers who produce the precursor chemical substances in quantities of 100 kilograms or less per year only for research and development purposes are not required to report under this section

(c) *Data to be reported.* Manufacturers and importers of chemical products made from precursor chemical substances identified in paragraph (a) of this section must report process and reaction condition data on Part II of EPA Form 7710-51 for each chemical product. A separate EPA Form 7710-51 must be submitted for each chemical product reported, and the precursor chemical substance used must be identified. All forms must be submitted to EPA no later than September 29, 1987.

[52 FR 21437, June 5, 1987, as amended at 60 FR 31922, June 19, 1995]