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TASK I

BERRYS CREEK STUDY

VOLUME II

GENERAL LITERATURE SEARCH

October, 1985

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Brentwood, Tennessee Marietta, Georgia

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SUMMARY

Volume II of the Task I report includes a comprehensive review of General Literature under four categories. These categories coincide with the Berrys Creek scope of work and include:

a. Scientific findings regarding the "General Nature of Mercury in the Environment."

b. Remedial Measures Instituted at other Mercury Contaminated Sites.

c. Analytical Methodologies

d. Models Evaluation

The chapters are independent of each other as specific information are addressed in each.

The "General Nature of Mercury in the Environment" is the largest chapter as it attests the volume of information available concerning mercury in the environment. This chapter provides basic information regarding mercury and its transformation and should fill in the gaps of general knowledge needed to understand mercury in the environment.

Chapter b, "Remedial Investigations at Related Sites" discusses other contaminated sites and the activities taken to understand the situation, determine remedial actions and provide long-term monitoring. This chapter is beneficial as it describes the actual remedial measures which have been taken at contaminated sites and how their similarity to Berrys Creek may assist in determining remedial actions at Berrys Creek. Primarily, dredging is the most commonly evaluated alternative at contaminated sites and numerous dredging projects are being considered at present.

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Chapter c. "Analytical Methodologies" is a comprehensive review of acceptable analytical methods for the determination of various forms of mercury in different media. i.e., biota. sediment, water and air. This chapter also presents recommended methods for each media and is supported by a reference document which contains articles describing the sampling and analytical procedures for various mercury species in the above media. This reference document is retained by both ERM-Southeast in Brentwood. Tennessee and Dr. Larry Schmidt in Trenton, New Jersey.

The final Chapter e "Models Evaluation" is a review of models which are applicable to the Berrys Creek Investigation. This evaluation has been conducted by ERM-Southeast with significant input provided by the Vicksburg Corps of Engineers Waterways Experimental Station (WES). Numerous models have been evaluated and details of the effort. purpose and sample parameters for each are discussed. At present, the magnitude and type of modeling is not certain because of the dynamics of the area (an estuary) and the uncertainties with mercury movement. Basic hydraulic and water quality models will be benefitted in determining the general nature of the area. Modeling to predict the fate of mercury in the environment under various remedial measures is not a certain requirement at this time as the high level of sophistication and cost cannot be justified at this time.

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RECOMMENDATIONS

The following items are discussed as required by the Task I scope of work.

1. Field investigative activities including research.
2. Sampling parameters for each field investigation.
3. Recommendations for immediate or long-term field monitoring.

RECOMMENDATIONS 1 AND 2

Since mercury is strongly bound to sediments/soils most of the mercury (mass basis) in the estuary should be in the sediments. Assuming that there are presently no significant discharges of mercury to the estuary the amount of mercury in and the rate of mercury release from the sediments will control the length of time that the existing contamination will pose a threat to public health or the environment. Thus, the following five-part study may be of some use.

Objective

Determine the concentration of mercury in sediment which poses a threat to public health and/or environment.

1. Sample the sediment at numerous locations for total mercury. At a smaller number of these same locations, determine the form of mercury present (inorganic vs. organic or even determine the form or organic mercury: phenyl, methyl). Other parameters of interest could include total organic carbon or percent organic matter in the sediment. The sampling plan for question 3 addresses this in more detail.

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2. Set up some type of in-place mini-ecosystem which can measure the rate of release of mercury within a known area and set of conditions. A number of aquaria could also be used to estimate the rate of release of mercury from the sediments under controlled conditions. Sediment/water systems could be used to estimate the steady-state partition between the sediments and the water (and perhaps release to the atmosphere). Then conditions could be changed to simulate remedial actions. Fish could be added to see if the presence of an organism increases Hg transfer from the sediment and how fast that organism accumulates Hg from the site sediments.

3. Measure the amount of mercury present in the water column (both dissolved and in suspended matter). The mercury concentration will change during the day due to tides. Changes in salinity and dilution from tidal action will change the Hg concentration, thus, diurnal sampling is recommended. Analyses for mercury (various forms of Hg(II) and total) as well as dissolved oxygen, pH, Eh, temperature, salinity and solids (dissolved and suspended) are recommended.

4. Select several types of fish and macroinvertebrates for which bioaccumulation data are available (predator, benthic, forage). Analyze the mercury concentration in fish in the study area (Hg total). Using the average concentration of mercury in the sediment and in these fish, calculate a bioconcentration factor. If it roughly agrees with the literature data, you may then measure bioconcentration factor to calculate the level of Hg in sediment (within 1-2 orders of magnitude) that pose a threat.

5. Try to estimate how long the contaminated sediments will be exposed to the environment before sedimentation isolates the contamination. Since the rate of sedimentation may vary across the area this would probably be of interest in areas with a high Hg content. Utilized sediment dating and determine sedimentation rates.

RECOMMENDATION NO. 3

Immediate or long-term field studies may not be practical until a "safe" level for mercury in sediment can be determined, perhaps by a program similar to that recommended in items 1 and 2. Once this contaminant level has been determined, then:

Short-term: Conduct an extensive survey of Hg in the sediment to quantify contamination with depth and transectionally across Berrys Creek from Moonachie Ave. to the Hackensack River. Sediment is the primary sink for mercury, so it seems like the best strategy would be to find and cleanup the "hot" areas and let time correct the rest. With time, Hg concentrations in fish should decrease if the major sources are removed. If the major sources are of small area compared to the whole site, cleaning up these areas probably won't make any difference.

Long-term: Measure the Hg concentration in fish over time. The concentration should gradually decrease with time (over a period of years).

LITERATURE REVIEW OF MERCURY IN THE ENVIRONMENT

SECTION 1

INTRODUCTION

The environmental release of mercury from agricultural and industrial uses of this metal resulted in several catastrophic outbreaks of heavy metal intoxication. These outbreaks occurred in Sweden, Guatemala, Pakistan, Iraq, the United States, and Japan. Probably the most notorious incident of mercury intoxication occurred in Minamata, Japan. As a result of the consumption of mercury contaminated fish, over one hundred individuals suffered neurologic damage. Symptoms such as loss of sight and hearing, impairment of motor functions, and intellectual deterioration developed among the exposed population (DHEW Study Group, 1971), and the term "Minamata Disease" was coined to described the neurologic disorders since at that time, the causative agent had not been determined. Subsequent investigations revealed that methylmercury was responsible for the disease (Wood, 1971).

Since the Minamata and related incidents, considerable research has been performed on the fate of mercury in the environment. As a result, microorganisms have been found to play an active role in the methylation of mercury as well as arsenic, cadmium, lead, selenium, tin, and tellurium (Summers

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and Silver, 1978). Methylation of heavy metals is significant from an environmental and public health viewpoint because, in general, methylation increases the toxicity of heavy metals.

Mercury is one of the least abundant elements in the earth's crust (0.08 mg/kg) with trace amounts being present in at least thirty ores. Commercial extraction of mercury, however, is conducted primarily from cinnabar (HgS, Krenkel, 1973). Mercury is also present in coal at concentrations ranging from 0.02 to 3000 mg/kg, and in petroleum, natural gas, and oil production brines at 0.02 to 21 mg/kg (D'Itri, 1972).

Mercury is used extensively in industrial processes, agriculture, pharmaceutical products, and as a preservative and antibacterial/fungal agent. Approximately 3.8 million pounds of mercury were used in 1982 (USEPA, 1984). Ultimately, most of the mercury consumed enters the environment either as a manufacturing effluent or waste product, by disposal of the finished product, or by accident. Approximately 72 percent of the mercury utilized in the U. S. subsequently enters the environment (Krenkel, 1973). Chloralkali production, coal combustion, copper smelting, manufacturing of control instrumentation, and paint and battery consumption are major sources for mercury pollution

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(Tierney et al., 1979). Because of the properties of the discharged mercury and the physical characteristics of most discharges, most of the mercury reaches the bottom sediments of lakes, rivers, and the oceans (Jernelov, 1969).

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SECTION 2

PHYSICAL/CHEMICAL PROPERTIES AND REACTIONS

Mercury can exist in either the elemental (Hg^{o}), mercurous (Hg^{+}), or mercuric (Hg^{++}) oxidation states and reaches the environment mainly as metallic (elemental) mercury, inorganic divalent mercury, and phenyl mercury. Mercury tends to form covalent bonds in the divalent state only. As a result, mercuric mercury can form organometallic complexes, such as mono- and dimethylmercury (Schroeder, 1982). Thus, in order to form methylated mercury compounds, divalent mercury must be present. In systems where sulfide is present, the limited solubility of mercuric sulfide can prevent or limit methylation by complexing the available mercuric ions.

Elemental mercury is liquid at room temperatures and has a vapor pressure of 0.246 Pa (1.85×10^{-3} Torr) at $25^{o}C$ (Schroeder, 1982). Additional physical and chemical properties of elemental mercury are presented in Table 1.

Elemental mercury can be oxidized to divalent mercury if the oxidation reduction potential is sufficiently high. The redox potential required to oxidize elemental mercury can be calculated from the following equation (Jernelov. 1972).

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Table 1: Physical-Chemical Properties of Elemental Mercury
(Gordon and Wichers, 1957; Schroeder, 1982)

Atomic Number	80
Atomic Weight	200.61
Boiling Point	356.9°C
Density	13.546g/cm3@20°C
Diffusion of Vapor	0.1124 cm^2/sec
Electrode Potentials:	
Hg(II) + 2e = Hg	0.85v
Hg(II) + 2e = 2Hg	0.79v
2Hg(II) + 2e = $Hg(II)_2$	0.92v
Heat Capacity	0.334 cal/g at 20°C
Heat of Fusion	2.7 cal/g
Ionization Potentials:	
1st electron	10.42v
2nd electron	18.75v
3rd electron	34.3v
4th electron	(72v)
5th electron	(82v)
Melting Point	-38.9°C
Solubility in H_2O	6.4×10^{-5} g/l at 25°C
Vapor Pressure	1.85×10^{-3} Torr at 25°C
Viscosity	0.0155 poise at 20°C

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$$E = 850 + 30 \text{ Log}(Hg(II)/alpha) \quad [1]$$

where:

E = the required redox potential for oxidation, mV

Hg(II) = the concentration of divalent mercury, moles/l

alpha = estimator of the binding strength between the available complexing agents and divalent mercury.

For an organic mud, alpha has a value of approximately 10^{21} (Werner, 1967). Using this alpha value in Equation 1, it has been found that oxidation of elemental mercury to divalent mercury will occur in aquatic systems whenever complexing agents and oxygen are present (Jernelov, 1972).

Mercurous mercury forms metal salts which dissociate in aqueous environments; although, most mercurous metal compounds are only slightly soluble in water. Mercurous mercury forms ionic rather than covalent bonds; therefore, mercurous mercury does not form organometallic compounds (Schroeder, 1982).

Mercuric or divalent mercury can form both inorganic and organic complexes. Inorganic complexes of chloride,

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hydroxide, fluoride, ammonia, cyanide, thiocyanate, sulfate, sulfide, and nitrate can be formed with mercuric ions. Equilibrium constants for the complexation of these ions and divalent mercury are presented in Table 2.

The chloride concentration and pH affect the complexes which mercury forms in aquatic systems. At pH values less than 2, free mercuric ions (Hg^{++}) predominate. Between approximately pH 2 and 4, HgOH is the predominate form, and $Hg(OH)_2$ predominates above pH 4. If the chloride concentration exceeds 10^{-9} M, mercuric chloride complexes can form. $HgCl_2$ forms at chloride concentrations of $10^{-7.5}$ M (1.1 ppb), and $HgCl_3$ and $HgCl_4$ form above 10^{-2} M Cl (350 ppm). Chloride ions can compete with sulfide ions in the formation of Hg(II) complexes, thereby increasing the solubility of Hg(II) (Hahne and Kroontje, 1973). In natural aquatic systems, Hg(II) is most likely to form $HgCl_2$, HgClOH, $Hg(OH)_2$ (Anfalt et al., 1968; Gilmour, 1971). Additional thermodynamic data for the formation of inorganic mercuric complexes can be found in Ahlberg (1962), Ciavatti and Grimaldi (1968), and Benes (1969), among others.

Divalent mercury can also form organic compounds, primarily by binding to carbon and sulfhydryl groups. Amino acids such as cysteine contain free sulhydryl groups to which mercury may bind, and such binding may provide a mechanism for

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Table 2. Equilibrium Constants for Divalent Mercury (Gilmour, 1971)

Equilibrium	log K_n
$Hg^{++} + Cl^- = HgCl+$	7.33, 7.36
$Hg^{++} + 2Cl^- = HgCl_2$	14.15,14.16
$Hg^{++} + 3Cl^- = HgCl_3$	15.15, 15.01
$Hg^{++} + 4Cl^- = HgCl_4$	15.81, 15.72
$Hg^{++} + Cl^- + OH^- = HgClOH$	18.87, 18.25, 18.28
$Hg^{++} + OH^- = HgOH+$	10.53, 10.92
$Hg^{++} + 2OH^- = Hg(OH)_2$	21.89, 22.64
$Hg^{++} + F^- = HgF^+$	1.56
$Hg^{++} + NH_3 = HgNH_3$	8.80
$Hg^{++} + 2NH_3 = Hg(NH_3)_2^{++}$	17.50
$Hg^{++} + 3NH_3 = HG(NH_3)_3+^+$	18.50
$Hg^{++} + 4NH_3 = Hg(NH_3)_4$	19.28
$Hg^{++} + CN^- = HgCN$	18.44
$Hg^{++} + 2CN^- = Hg(CN)_2-$	34.5, 35.36
$Hg^{++} + 3CN^- = Hg(CN)_3=$	38.7, 39.19
$Hg^{++} + 4CN^- = Hg(CN)_4$	41.0, 41.95
$Hg^{++} + CN^- + OH^- = HgCNOH$	29.43
$Hg^{++} + 2SCN^- = Hg(SCN)_2^-$	17.26, 18.37
$Hg^{++} + 3SCN^- = Hg(SCN)_3^=$	19.97
$Hg^{++} + 4SCN^- = Hg(SCN)_4$	21.69
$Hg^{++} + SCN^= + Cl^- = HgClSCN$	16.98
$Hg^{++} + SO_4^- = HgSO_4$	2.60
$Hg^{++} + NO_3^= = HgNO_3$	0.16
$HgS_{(s)} + S = HgS_2^=$	0.48
$HgS_{(s)} + 2HS^- = HgS(HS)_2^=$	-3.60
$HgS_{(s)} + 2H_2S = HgS(H_2S)_2$	-4.31
$HgS_{(s)} + HS + H_2S = Hg(HS)_3^-$	-3.59

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mercury uptake by an organism. In aquatic systems, the redox potential will affect the stability of sulfhydryl-mercury complexes. The bonding of the sulfur to the organic matter increases the stability of the sulfhydryl complex, thereby permitting these complexes to exist at higher redox potentials than for which sulfide sulfur is stable.

Mercury-carbon bonding is the second major group of organomercurials. Mercuric mercury can bond either to one or two carbon atoms. Mercury compounds with one carbon bond, such as phenylmercury or monomethylmercury, act as substituted salts and are reasonably soluble in water. Complexes of mercury with two carbon bonds, such as volatile dimethylmercury, are covalent compounds with a limited water solubility. Although these compounds are thermodynamically unstable, they are not decomposed by water. Apparently, kinetic barriers prevent the decomposition of these compounds (Gavis and Ferguson, 1972).

Mercury complexes involving both sulfur and carbon bonds can also form. For example, in aquatic systems, methylmercury exists primarily as sulfur complexes (e.g., CH_3HgS, $(CH_3Hg)_2S$, CH_3HgSR)). If reduced sulfur species are not present, the primary forms expected would be methylmercuric hydroxide or chloride. The concentration of methylmercuric ion is generally extremely small (Zepp et al., 1974).

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Humic acids can reduce divalent mercury to elemental mercury via a reaction between the mercury and free radicals in the humic acid. This reaction follows first-order kinetics. Although pH affects the amount of mercury reduced, pH does not affect the reaction rate (Alberts et al., 1974). Fulvic acids, on the other hand, chelate divalent mercury (Cheam and Gamble, 1974). A non-equilibrium model for predicting the speciation of mercury in acidic aquatic systems was discussed by Fontaine (1984a,b). An evaluation of this model was not found in the literature.

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SECTION 3

TOXICITY OF MERCURY

Introduction

The toxicity of mercury has been known for many years. Recent catastrophic events such as occurred at Minamata, however, have increased the extent of knowledge on mercury. In this section, the toxicity of mercury to man, microorganisms, and aquatic life is reviewed. The toxicity of mercury to terrestrial life is discussed in limited detail since aquatic organisms should be primarily affected at Berry's Creek. Exposure to man should also occur primarily via consumption of aquatic and not terrestrial organisms. A more extensive analysis of the toxicology of mercury is presented by USEPA (1983). Polson et al. (1983) also discussed the effects of mercury in greater detail.

Toxicity to Man

Mercury is highly toxic to man, and exposure to mercury can result in neurologic and gastrointestinal damage. Both the form of mercury and mode of entry into the body are important to the toxicity of mercury. Ingestion and inhalation are the primary exposure routes, and depending upon the exposure route, inorganic, organic, or both forms of mercury may be of concern.

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Inorganic and organic mercuric compounds can be absorbed from the gastrointestinal tract; thus, ingestion is a primary exposure route for many mercury compounds. If inhalation is the exposure route, both elemental and organic mercuric compounds are of concern, since transfer of these volatile mercury compounds into the bloodstream from the lungs can occur. Once in the bloodstream, the mercury is transferred across the blood-brain barrier and can cause neurologic damage. Alkyl mercury compounds pass the blood brain barrier and the placenta most readily, and can cause neurologic damage (Doi et al., 1984). Chronic mercury exposure and the resulting mercury poisoning usually results from inhalation; although, ingestion of organic mercury, such as occurred at Minamata Bay, Japan can also cause mercury poisoning (Battegelli, 1960a; Falchuk et al., 1977). Chang (1977) reviewed the literature on the effects of mercury on the nervous system and proposed a mechanism for the toxicity of mercury. Exposure to other metals can increase, decrease, or have no effect upon the toxicity of mercury depending upon the relative exposure to each metal (Schubert et al., 1978). The toxicology of the various forms of mercury is briefly discussed below.

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Elemental Mercury

Elemental mercury, in liquid form, can be absorbed into the body by inhalation, injection, ingestion, and skin absorption. If ingested, however, elemental mercury does not enter solution and thus passes through the gastorintestinal tract and is excreted. Direct intravenous injection of elemental mercury has also been reported as not having had a significant effect on at least one person who attempted suicide in this manner. Skin absorption occurs primarily among workers exposed to metallic mercury.

Inhalation is the primary exposure route for elemental mercury. Numerous incidents of occupational exposure to mercury vapors have been documented. Mercurialism, the clinical term for mercury poisoning which is characterized by symptoms such as weight loss, insomnia, tremors, and neurologic damage, has been documented in sodium hydroxide plants, laboratories, and chlorine manufacturing plants (Smith et al., 1970; El-Sadik and El-Dakhahkny, 1970; Williams et al., 1968). Incidents of occupational exposure have also occurred from mercury use in wood preservation, seed treating, animal experiments, felt-hat manufacturing, fur cutting, electrical equipment production, and mercury mining (Lundgren and Swensson, 1949; Battegelli, 1960a,b). High levels of volatile mercury have also been found in

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hospitals and university laboratories (Williams et al., 1968; Goldwater et al., 1956).

Approximately 74% of the metallic mercury inhaled is retained. Once inhaled, the mercury has a half-life in the body of approximately 58 days. The elemental mercury is dissolved in the bloodstream and is transported throughout the body. Significant amounts of mercury are transported to the central nervous system where the elemental mercury is oxidized to the mercuric state. The accumulation of mercury in the central nervous system can lead to dysfunction of the nervous system causing tremors, numbness, and changes in emotional behavior. Other areas of the body can also retain and be adversely affected by mercury, such as the renal system, however, the nervous system is the primary system affected. Exposure to elemental mercury usually leads to increased mercury levels in the blood and urine, and concentrations of mercury in these fluids can be used as an indicator of exposure (Battegelli, 1960b; Wada et al., 1969; Hursh et al., 1976; Falchuk et al., 1977; Nordberg et al., 1978; Langolf et al., 1978; Stopford et al., 1978).

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Inorganic Mercury Salts

Ingestion is the primary exposure route for mercurous and mercuric mercury. Mercurous mercury is not readily absorbed by the gastrointestinal tract, and as a result is not of much toxicological concern. In fact, mercurous mercury is often used as a therapeutic agent. Mercuric mercury, particularly the chloride salt, is very toxic, and at one time was commonly used by persons wishing to commit suicide. Mercuric mercury is primarily deposited in the kidneys resulting in renal failure. The lethal dose for man is estimated to be approximately 20 mg/kg (Polson et al., 1983). In low doses, there may be no pathological effect, except elevated mercury levels in the urine. If exposure to mercury is stopped, excretion of mercury over time will eliminate the toxic effects. Some of the inorganic mercury will also be excreted from the body as volatile mercury from both the lungs and through the skin (Battegelli, 1960a; Clarkson and Rothstein, 1964; Falchuk et al, 1977; Nordberg et al., 1978).

Harbison et al., (1977) developed a polymer (MBP) which selectively binds mercury. In aqueous solutions, a rapid decrease in mercury concentration of the solution occurs, approaching a short-term equilibrium within three to four hours. The polymer can bind 1205 ppm of mercury. When administered to mice in a diet at a dose of 1%, the polymer

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decreased the half-life of mercury in mice from 10 to 4.5 days.

Organic Mercury

Not all organomercurials are highly toxic. Alkylmercury compounds, such as mono- and dimethylmercury, are the most toxic. Arylmercurials (i.e. phenylmercury) are much less toxic than alkylmercurials, while alkoxyalkylmercurials are practically non-toxic. The toxic effects of arylmercurials resemble those of elemental mercury; however, chronic poisoning from arylmercurials is very uncommon (Battegelli, 1960a; Aberg et al., 1969; Falchuk et al., 1977; Parizek, 1978; and Nordberg et al., 1978).

Exposure can occur via all exposure routes, with the central nervous system being the primary system affected. Muscle dysfunction, sight and hearing loss, numbness, and loss of metal capacity are all effects of alkylmercury intoxication. Approximately 100% of the mercury absorbed is retained for at least a short time. The half-life of alkylmercury in the body is approximately 70 days; however, the half-life in the brain is much longer. Selenium, if ingested concurrently with the mercury can reduce the toxic effects of mercury, but there are no known effective treatments to reverse alkylmercury poisoning.

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Some of the early incidents and observed cases of methylmercury poisoning are discussed by Hunter et al. (1940). Decreased food consumption and loss of body weight are early symptoms of methylmercury exposure. Treatment with D-penicillamine during exposure may prevent neurologic damage (Lapin and Carter, 1981). Birke et al. (1971) reported that symptoms of methylmercury poisoning were not apparent in subjects exposed to as much as 0.8 mg of mercury (as methylmercury) per day. Blood levels were correlated to the ingestion intake of methylmercury and also correlated with the methylmercury concentration in hair. The half-life of methylmercury in the blood ranges from 99-120 days. Mercury concentrations in blood have been found to be correlated with the amount of marine food eaten (Hansen et al., 1984; Phelps et al., 1980; Sherlock et al., 1982; Kyle and Ghani, 1982).

Segall and Wood (1974) propose a mechanism for the neurologic damage caused by methylmercury. Spinal ganglia in rats was found to be the primary target of methylmercury poisoning resulting in the degeneration of spinal ganglia. Signs of neurologic damage began to appear after the rats received 28 to 30 mg/kg of body weight by subcutaneous injection (Somjen et al., 1973). Lower brain stem damage may result from methylmercury intoxication (Von Berg & Rustam, 1974), and younger organisms may be more susceptible than older organisms (Hughes et al., 1975). Methylmercury suppresses

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the immune system thereby making an organism more susceptible to disease (Koller, 1979). Chromosomal damage may also result from ingestion of methylmercury (Skerfving et al., 1974). Fiskesjo (1979) found that methylmercury chloride was mutagenic. The levels of methylmercury chloride which were mutagenic were very near the threshold values of toxicity.

Human tissue samples collected as far back as 1913 were analyzed for methyl and total mercury. An increasing trend in the total mercury concentration was not found. Furthermore, methylmercury was either not detected or was present in negligible concentrations (Kevorkian et al., 1973). Diet can affect the rate of methylmercury accumulation and excretion, and by altering diets, it may be possible to more rapidly reduce mercury body burdens (Landry et al., 1979). Excretion of methylmercury is slow and occurs primarily in the feces. In the body, methylmercury distributes preferentially to the liver and kidneys. At non-toxic intake levels, the body burden reaches a steady-state condition in about one year. Neurologic symptoms are believed to appear when the brain methylmercury concentration reaches 8 ppm (Saha, 1972). Kershaw et al. (1980) reported a half-life for methylmercury in the blood of 52 days. After complete tissue distribution, approximately 5.9% of the methylmercury ingested remained in the blood.

Several factors affecting the transfer of methylmercury across the placenta were discussed by Doi et al. (1984) including the lipid solubility of methylmercury, the decreased separation of material and fetal circulation with placental aging, and the difference in hemoglobin concentration between the fetus and the mother.

Selenium decreases the toxicity of and increases the retention of mercury. In higher marine organisms, mercury is generally associated with selenium, thereby protecting the consumer from the toxic effects of mercury. The increased retention of mercury caused by selenium, however, may cause greater biomagnification of mercury in the food chain (Beijer and Jernelov, 1978; Skerfving, 1978).

Stopford and Goldwater (1975) concluded, based upon a literature review, that unless an aquatic environment is contaminated directly with methylmercury, the risk of methylmercury poisoning is slight. According to these researchers, demethylation as opposed to methylation is more likely to occur in aquatic sediments. Furthermore, mercury is rapidly bound by the sediments and thus decreases the potential for uptake by aquatic organisms. The presence of selenium also decreases methylmercury toxicity, and in general, seafood contains an excess of selenium as compared to methylmercury.

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Mercury Standards and Criteria

The U. S. Environmental Protection Agency has developed several criteria and standards for mercury in the environment. The criterion for protecting freshwater aquatic life is 0.00057 ug/l as a 24-hour average, not to exceed 0.0017 ug/l as a 24-hour average and not to exceed 0.0017 ug/l at any time (total recoverable mercury). For marine aquatic life, the total recoverable mercury concentration should not exceed 0.025 ug/l as a 24-hour average and should not exceed 3.7 ug/l at anytime. The ambient water quality criterion for the protection of human health (ingestion of water and consumption of aquatic life) is 0.144 ug/l. The suggested EPA criterion for elemental mercury in the atmosphere is 1 ug/m^3, while NIOSH and OSHA standards for mercury in the workplace atmosphere are 50 and 100 ug/m^3, respectively.

Toxicity to Microorganisms

The presence of one microorganism can decrease the sensitivity of another microorganism to mercury compounds. *Desulfovibrio desulfuricans* was found to decrease the sensitivity of *Pseudomonas aeruginosa* to mercurials. On the other hand, the presence of *P. aeruginosa* had no effect on the sensitivity of *D. desulfuricans* to mercurials. The

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production of hydrogen sulphide by the sulfate reducing microorganisms may be responsible for this protective effect, since hydrogen sulphide will precipitate mercury (Bennett and Bauerle, 1980). These results support those of Booer (1944) who noted an apparent relationship between the sulphur cycle and mercury toxicity.

Escherichia coli was found to increase the resistance of Staphylococcus aureus to mercurials. Several factors accounted for this protective effect including the production of hydrogen sulfide and extracellular glutathione by E. coli which inactivate the inhibitory effect of mercury. In addition, E. coli absorbed more mercury than S. aureus, thereby reducing the concentration of mercury to subinhibitory levels for S. aureus (Stutzenberger and Bennett, 1965).

At concentrations of mercury as low as 3 ug/l, growth of Chlorella phyrenoidosa, an algae, was inhibited. This inhibitory effect can be overcome by this microorganism's ability to bind mercury to inactive sites and to create new inactive sites as needed. The presence micronutrients also reduced the inhibition of this organism to mercury (Kamp-Nielson, 1971). The inhibitory effect of mercury on this algae was confirmed by Agrawal and Kumar (1978). These researchers found that the presence of mercury in an

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industrial effluent was a major reason for the absence of Chlorella and other algae in the effluent channel.

Konetzka (1977) reported that microorganisms carrying the penicilinase plasmid are resistant to mercury as well as cadmium, chromium, lead, arsenate, arsenite, thallium, zinc, and other metals. The ability of the plasmid to convert mercuric compounds to a volatile form was believed to be responsible for the increased resistance of these microorganisms to mercury. These resistance plasmids have been found in may diverse organisms such as E. coli, Aerobacter aerogenes, Serratia marcescens, Pseudomonas aeruginosa, Proteus vulgaris, Providencia, Shigella dysenteriae, and Staphylococcus aereus. A more detailed description of a plasmid conferring resistance to both mercuric ions and sulfonamides is presented by Stanisich et al. (1977).

The inhibitory effect of mercury on Chlorella pyrenoidosa was found to be reduced by the ability of this microorganism to volatilize mercury. The amount of mercury volatilized was found to be dependent upon the concentraion of algae cells, and although the volatile form of mercury was not identified, this mercury compound was believed to be elemental mercury. Uptake of mercury by this microorganism was also found (Ben-Bassat and Mayer, 1975).

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High concentrations of mercury can inhibit dehydrogenase activity, nitrification, and CO_2-production by soil microorganisms. Mercury present in organic forms, i.e. phenylmercury acetate and methylmercury chloride, was found to have a stronger inhibitory effect than mercuric mercury. The inhibitory effects of mercury were more pronounced in sandy soils than in clay soils, as mercury levels of 5 ppm caused strong inhibition in sandy soils; whereas, 100 ppm of mercury were needed in clay soils (van Faassen, 1973). The greater adsorptive capacity of clay soils compared to sandy soils may account for this effect.

Methylmercury was found to significantly inhibit growth of Coelastrum microporum, a green alga. Concentrations of methylmercury as low as 3 ppb substantially reduced growth of this microorganism. In addition, the specific gravity of the cells also appeared to have increased as a result of exposure to methylmercury (Holderness et al., 1975). The addition of mercuric chloride to brackish water can decrease the diversity, and thus also the stability, of the bacterial community. As the diversity decreases, an increase in the population of surviving organisms occurs (Singleton and Guthrie, 1977). Addition of 2.5 ppm of mercuric chloride to Chesapeake Bay water resulted in almost complete inhibition of photosynthesis and nitrification. Nearly complete inhibition of glucose oxidation also occurred in water and

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sediment samples from Chesapeake Bay, with one exception: inhibition was not found in sediments collected from contaminated areas of Chesapeake Bay (Mills and Colwell, 1977).

Mercury concentrations as low as 2 ug/L were found to inhibit the growth of Anabena inaequalis, a freshwater cyanobacterium. At concentrations of 100 ug/L, photosynthesis and acetylene reduction were inhibited (Stratton et al., 1979). Mercury(II) concentrations of 3.4 ug/L resulted in a 16% decrease in reproduction of Daphinia magna (Biesinger and Christensen, 1972). Organic mercury compounds were found by Roderer (1982) to be more toxic to the freshwater alga Poterioochromonas malhamensis than inorganic mercury compounds. Increasing temperature can increase the toxicity of mercury to phytoplankton (Knowles and Zingmark, 1978).

Timoney et al. (1978) reported that in a large proportion of Bacillus strains collected near Long Island, NY, resistance to mercury was related to the formation of elemental mercury. Resistance to mercury resulted from selection pressure due to mercury contamination. Resistance to antibiotics may also be linked to mercury resistance which could be cause for concern if mercury and antibiotic resistance are linked in other microbes, particularly pathogens.

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Toxicity to Aquatic Life

The toxicity of mercury compounds to aquatic life is reviewed in detail by USEPA (1983, Appendix 1). Thus, only a few references not discussed by USEPA (1983) are presented herein.

Estuarine organisms may be more susceptible to mercury toxicity as a result of the fluctuations in environmental conditions in an estuary (Jones, 1973). At concentrations of 3 ug/L, mercury was found to impair the behavior of goldfish (Weir and Hine, 1970). The responses to toxic levels of mercury to fish can be affected by the concentration. At mercury concentrations of 1.15 to 2 mg/L, mummichogs (Fundulus heteroclitus) displayed signs of equilibrium disfunction. At higher concentrations, respiratory stress developed and the fish died within 24 hours of exposure (Klaunig et al., 1975).

Embryonic exposure of *Fundulus heteroclitus* larva to methylmercury and divalent mercury did not increase the tolerance of these organisms to mercury during subsequent exposure (Weis and Weis, 1983). The effects of sublethal concentrations of mercury on fish (*Notopterus notopterus*) were discussed by Verma and Tonk (1983).

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Appendix 1 presents a section from the EPA mercury criteria document which summarizes the toxicity of mercury to aquatic organisms. The discussion also summarizes the rationale for mercury discharge criteria.

Toxicity to Terrestrial Life

If laboratory studies are excluded, relatively little information (compared to aquatic life) is available regarding the accumulation and toxicity of mercury to terrestrial organisms. An extensive body of literature related to exposure of animals (e.g., rodents, dogs, monkeys) to mercury under laboratory conditions does exist, however. The conditions of exposure in a laboratory are often very different from the types of exposure which would occur in the natural environment. Thus, an attempt was made to focus primarily on field studies or on laboratory studies which reflect natural conditions, where such data are available.

Most of the literature which appeared relevant to Berrys Creek discussed the accumulation and resulting effects of mercury exposure upon birds. The ability of birds to bioaccumulate mercury probably first became apparent in the late 1950s and early 1960s. Mercurial fungicides were once extensively used to preserve grain seeds. Consumption of the

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seeds by birds was found to increase mortality (Bor et al., 1969). Once mercury seed dressings were prohibited, the concentration of mercury in birds decreased (Tejning, 1967; Wanntrop et al., 1967).

Only limited toxicity data for birds was found in the literature. An exhaustive search, however, was not conducted. Decreased hatchability of eggs and poor duckling survival resulted from feeding black ducks "a diet containing 3 ppm of mercury." During a two-year study, Finley and Stendell (1978) reported that only 16 ducklings from the mercury-fed group survived one week, as opposed to 73 ducklings surviving one week from the controlled group. Both groups contained 13 pairs of breeders. Fimreite (1979) discussed the toxicity of mercury to birds in detail, including sublethal and behavioral effects. The reader should refer to this discussion for information on mercury toxicity and birds.

Mercury has been found to have both teratogenic and genetic effects on higher animals (e.g., monkeys, dogs, cats, pigs, rodents). Daily doses of 0.5 mg/Kg of mercury (as methylmercury chloride) was found to cause abortions in rhesus monkeys (Dougherty et al., 1974). A daily oral dose of 0.1 mg of methylmercury chloride per kg increased the rate of stillbirths in dogs (Earl et al., 1973). Abortions

occurred in cats at daily, oral doses of 0.25 mg HG/Kg (Khera, 1973). Khera (1979) discussed the teratogenic and genetic effects of mercury in detail.

Other factors besides the dose can affect the toxicity of mercury. Temperature was reported by Yamaguchi et al. (1984) to affect the toxicity of methylmercury to rats. Temperatures higher or lower than room temperature increased both mortality and neurotoxicity. Diet can also affect toxicity as Thomas and Smith (1984) found that sodium selnite when co-administered with methylmercury could affect the distribution of mercury in rats. The sodium selenite increased the mercury concentration in the cerebrum, but reduced the concentration in the kidneys.

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SECTION 4

MERCURY CYCLE AND MOBILITY

Introduction

The mercury cycle in the environment is also fairly well defined, at least in a qualitative sense. Because many mercury compounds are volatile, mercury can be more mobile in the environment than other heavy metals. The mercury cycle is briefly reveiwed in this section, focusing primarily on the fate in aquatic systems. The fate in the atmosphere and soil systems, however, is also briefly reviewed.

Fate in Aquatic Systems

Elemental and mercuric mercury are the primary forms of mercury released to aquatic systems. As discussed in Section 2, elemental mercury can be oxidized to divalent mercury in aerobic aquatic environments. In addition, volatilization will release elemental mercury from the aquatic environment to the atmosphere. These factors, along with the low solubility of elemental mercury and the increased toxicity of some mercuric mercury compounds make mercuric mercury of more importance in an aquatic system. Past outbreaks of methylmercury poisoning have focused considerable attention

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on methylation. Thus, the formation of methylmercury is reviewed in the greatest detail herein.

The dissolved mercury concentration in surface waters generally ranges from less than 0.1 to 17 ug/l, with higher levels found near waste outfalls. In unpolluted waters, the dissolved mercury concentration is generally less than 0.1 ug/l (Wershaw, 1970). Even near mercury deposits, the dissolved mercury concentration is generally low, as a range of 1 to 3 ug/l was reported by Bayev (1968) for streams draining mercury deposits. Groundwaters near mercury deposits were reported to contain approximately 2 ug/l of dissolved mercury by Dall'Aglio (1970). Approximately 30% of the total mercury present in river water may be in the form of methylmercury (Kudo et al., 1982). The mercury concentration in unpolluted waters has been reported to be less than 0.5 ug/g. Higher concentrations in the absence of industrial pollution may represent natural inputs of mercury (Ray et al., 1984).

Seawater is undersaturated with mercury. Kauskopf (1956) investigated several mechanisms which could account for the low mercury concentration and concluded that adsorption and local precipitation of sulfides were primarily responsible for this phenomenon. Fitzgerald and Lyons (1973) analyzed seawater collected near Long Island, NY and found that the

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inorganic and organic mercury concentration were on the same order of magnitude. Total mercury concentration ranged from 0.045 to 0.078 ug/L, within the range of 0.003 to 0.364 ug/L reported in the literature.

Formation of Methylmercury

Three mechanisms for mercury methylation are known to exist, two of which are biologically mediated. Excretion of methylcobalamin by microorganisms is the first mechanism. In this process, the methyl group is transferred from methylcobalamin (or analogs) to Hg(II) to form monomethylmercury. A second methyl group can then be transferred to monomethylmercury to form dimethylmercury. Formation of dimethylmercury, however, is considerably slower than monomethylmercury. The second biological mechanism involves microorganisms incapable of methylcobalamin synthesis, and this process is not as well understood as the first biological process. Finally, abiotic mercury methylation can occur. For example, ultraviolet light has been found to convert mercuric acetate to methylmercury (Hill et al., 1970; Wood, 1974; Summers and Silver, 1978).

Biological methylation or biomethylation refers to the biological attachment of methyl groups to other molecules.

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Methylation of metals and metalloids is known to occur by two general processes. In the first process, transmethylation, an intact methyl group is transferred from a methyl donor to the metal ion. In the second process, a one-carbon molecule from a methyl source is attached to a metal or metalloid and is subsequently reduced to a methyl group (Thayer and Brinckman, 1982). Abiotic or chemical methylation of metals and metalloids can also occur.

Three principal methyl donors are involved in transmethylation: methylcobalamin, S-Adenosylmethionine, and N5-methyltetrahydrofolate. Methylcobalamin is vitamin B-12 with a methyl group attached. Transmethylation by methylcobalamin can occur in three general ways. Type 1 transmethylation refers to the process where the methyl group is transferred as a negatively charged ion, carbonion (CH_3^-). In type 2 methylation, a methyl radical is transferred to the metal or metalloid. The third transfer mechanism associated with methylcobalamin is referred to as redox switch (Ridley et al., 1977).

The methylation mechanism involved with methylcobalamin is dependent upon the oxidation-reduction potential of the metal redox couple. Type 1 methylation reactions generally occur when the redox potential of the couple is greater than 0.805 volts. The more oxidized ion is methylated in type 1

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methylation. At redox potentials below approximately 0.559 volts, type 2 methylation occurs. In type 2, the more reduced ion is methylated. Between approximately 0.559 and 0.805 volts, the redox switch mechanism predominates. (Ridley et al., 1977; Thayer, 1979a, 1981; Thayer and Brickman, 1982).

Two types of methyl transfers involving methylcobalamin can occur. Following cleavage of the methyl group, a water molecule is attached to form acquocobalamin. Mercury can also bind to the 5,6-dimethylbenzimidazole group to form a "base-off" methylcobalamin. Methylmercury is then formed by the dealkylation of the dimethylbenzimidazole group. The maximum rate of methylmercury production by the base-off reaction occurs at approximately pH 5.5.

The "base-on" species, without mercury attached to the cobalt atom, forms methylmercury considerably faster than the "base-off" reaction, by the displacement of the dimethylbenzimidazone by the mercuric ion (DeSimone et al., 1972; Ridley et al., 1977).

Nucleophilic transfer of methyl groups occurs when S-adenosylmethyionine serves as the methyl donor. The methyl group is transferred as a positively charged ion to form a methylmetal and S-adenosylhomocysteine. This reaction would

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most likely occur in anaerobic environments and produce volatile products (Ridley et al., 1977). N5-methyltetrahydrofolate also donates positively charged carbonium ions.

Methylation of heavy metals can occur in both the acetate and methane formation processes. Both cobalamins and folates are involved in these processes, and as mentioned above, cobalamins and folates are capable of alkylating metals. The methanogens and acetate forming microorganisms are both capable of synthesizing methylcorrinoid compounds (Stadtman, 1967).

Methylation of mercury has been reported in both the aquatic and terrestrial environment under a variety of conditions. A brief review of the literature on mercury methylation in the aquatic environment is presented below:

Wood et al. (1968) described the production of dimethylmercury by an extract from a methanogenic bacterium, Methanobacterium strain M.o.H. Methyl groups from cobalt(II) compounds (methylcobalamin) were transferred to mercury both as a biological process and abiotically. Wood et al. (1968) concluded that biological transmethylation would be enhanced by anaerobic conditions and by increasing numbers of alkylcobalamin synthesizing bacteria.

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Jensen and Jernelov (1969) found the $HgCl_2$ in bottom sediments was methylated to methylmercury and dimethylmercury in an aquarium and a lake in Sweden. Methylmercury production was proportional to Hg(II) addition up to concentrations of 100 ug Hg/g sediment, after which methylmercury production was inhibited.

The biological methylation of mercury has been proposed to be a microbial detoxification reaction. Landner (1971) investigated the methylation of mercury by Neurospora crassa and proposed the following model. Methylation of mercury occurs in the methionine biosynthesis pathway. A mercury atom is bound to homocyseteine followed by the attachment of a methyl group to the mercury-homocysteine complex. Feedback inhibition is not initiated by the methylmercury-homocysteine complex, and this reaction continues until sufficient mercury-free methionine is produced. Methionine initiates feedback inhibition and the production of methylmercury homocysteine stops. Through this process, the cell rids itself of mercury.

Dunlap (1971, citing the work of Wood), stated that methylcorrinoids are involved in mercury methylation by three enzyme systems: methionine biosynthesis, acetate synthetase, and methane synthetase. Methionine synthetase is used by a number of organisms, including a strain of E. coli, to

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sythesize the amino acid methionine. This enzyme is present in some aerobes, some anaerobes, and in mammalian livers. Aerobes and facultative anaerobes which use cobalamin-dependent methionine synthetase can therefore synthesize methylmercury. Anaerobic bacteria which synthesize acetic acid from carbon dioxide using acetate synthetase (e.g., Clostridium thermoaceticium and Clostridium stricklandii) can also methylate mercury. Anaerobic organisms which use methane synthetase are also capable of mercury methylation.

Methylcobalamin was found to rapidly methylate mercury nonenzymatically by Bertilsson and Neujahr (1971). Under Hg(II) excess conditions, the methylation of mercury was 50% completed within as little as four minutes. The reaction was found to decrease as the mercuric ion concentration (relative to methylcobalamin) decreased. Monomethylmercury was formed substantially faster than dimethylmercury, and thiols, cell proteins, and phosphate buffers inhibited mercury methylation.

Imura et al. (1971) also reported the rapid methylation of mercuric chloride by methylcobalamin. Dimethylmercury was proposed as the initial reaction product, with methylmercuric chloride formed by decomposition of dimethylmercury to monomethylmercury by mercuric chloride. Transmethylation was

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nearly completed after five hours. Imura et al. (1971) also attempted to methylate mercury with S-adenosylmethionine as the methyl donor; however, transmethylation with S-adenosylmethionine did not occur.

Formation of methylmercury from mercuric sulfide under aerobic conditions were reported by Fagerstrom and Jernelov (1971). Under aerobic conditions, sulfide ions can be oxidized to sulfate ions. The rate of methylmercury formation, however, was considerably slower than occurs when divalent is more readily available. The amount of methylmercury produced was proportional to the amount of mercuric sulfide added which indicated that processes in addition to chemical equilibrium were involved in the availability of mercury from mercuric sulfide for methylation.

Bishop and Kirsch (1972) reported biological methylmercury formation in anaerobic pond sediments. Production of methylmercury was increased by increasing the inorganic mercury dosage and temperature, and by the addition of nutrients. Methylmercuric chloride was the principle form of methylmercury generated, while gaseous dimethylmercury was not detected.

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Yamanda and Tonomura (1972) found that Clostridium cochlaerium (an anaerobic spore-former) produced methylmercury from HgI_2, $HgCl_2$, $HgNO_3$, HgO, Hg(CN), $Hg(SCN)_2$, and $Hg(CH_3COO)_2$. Addition of vitamin B-12 increased mercury methylation; whereas, methylmercury was not produced from HgS. Other researchers have found that methylmercury can be produced aerobically from mercuric chloride by Enterobacter aerogenes and Pseudomonas flourescens (Vonk and Sijpesteijn, 1973).

Organic matter concentration, temperature, pH, microbial activity, and mercury concentration were all cited by Langley (1973) as factors affecting the methylation rate in river sediments. Downstream of the outfall from a chlor-alkali plant, methylmercury production in the sediments ranged from 0.12 to 4.83 ng of CH_3Hg-Hg(as Hg) per cm^2 per week. Dimethylmercury production ranged from approximately 2 to 11.7 percent of the methylmercury production.

Methylmercury formation in river sediments in situ was reported by Jacobs and Keeney (1974). Mercury was added to sediments as phenylmercuric acetate (PhHgAc) and mercuric chloride ($HgCl_2$). Greater methylmercury production was found with PhHgAc than with $HgCl_2$, which lead Jacobs and Keeney to hypothesize that different pathways were involved in the methylation of these two forms of mercury. Methylmercury

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formation was again found to be positively related to the mercury dosage for both PhHgAc and $HgCl_2$. Decreasing pH and sulfide concentration and increasing organic content may also enhance methylation by keeping mercury in solution.

Holm and Cox (1974) found that both elemental and divalent mercury could be methylated in aerobic and anaerobic sediment-water systems. Methylmercury concentrations, however, never exceeded 1% of the total mercury concentration, and dimethylmercury formation was not found at all. Methylmercury formation was roughly the same under both anaerobic and aerobic conditions. The release of elemental mercury, however, was approximately three times greater under aerobic than anaerobic conditions.

Hamdy and Noyes (1975) tested twenty-three mercury resistant bacterial cultures from the sediments of the Savannah River in Georgia. Enterobacter aerogenes was found to be resistant to 1,200 ug-Hg/ml of culture media and to produce methylmercury from mercuric chloride. Methylmercury was produced under both aerobic and anaerobic conditions; however, slightly more methylmercury was produced under aerobic conditions. Methylcobalamin was found to increase the production of methylmercury, which was cyclic in nature, Hamdy and Noyes (1975) also concluded that mecury methylation may have been a means of resistance and detoxification of

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mercury by the microorganisms. Degradation of methylmercury to methane and elemental mercury was not found.

The production of methylmercury in human feces incubated anaerobically with mercuric chloride was reported by Edwards and McBride (1975). Production of methylmercury was proportional to the initial mercury(II) concentration, with the maximum levels of methylmercury occurring within two days of incubation. No correlation between methane formation and methylmercury biosynthesis was found. High levels of methylmercury were found even in samples which did not generate methane. Methylmercury degradation was found to occur at a relatively constant rate. Since methane production was not found in some of these samples, the loss of methylmercury was not from reductive demethylation.

Reduction of mercuric chloride to elemental mercury by acetylene and ethylene was reported by DeFilippis and Pallaghy (1975). Depending upon the relative amounts of mercuric ion and unsaturated hydrocarbons, mercury could either be reduced or methylated by unsaturated hydrocarbons. Microorganisms capable of synthesizing unsaturated hydrocarbons may, therefore, be involved in the methylation of mercury.

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Mercury methylation in wastewater sludge was found to be minor by van Faassen (1975). After the addition of 650 ug/kg (as Hg) of phenylmercuric acetate and mercuric chloride, a maximum of 1.5 ug/kg of methylmercury was found after 8 and 21 days of anaerobic digestion. During this time period, degradation of methylmercury could have occurred as found by Edwards and McBride (1975).

Cross and Jenkins (1975) investigated the cleavage of the methyl group from methylmercury by thiols and found that monomethylmercury was relatively stable. Methylcobalamin was also found to be the only environmental agent capable of methylating monomethylmercury to dimethylmercury. Furthermore, methylation of monomethylmercury would occur only when the concentration of methylcobalamin exceeded the mercuric ion concentration.

Methylmercury production by whole methanogenic bacteria cells was not found; whereas, cell extracts did methylate mercury when methylcobalamin was present (McBride and Edwards, 1977). Under anaerobic conditions, methylmercury was formed in sewage sludge and fecal material; however, methane biosynthesis was not involved in this reaction. Based upon previous research (Edwards and McBride, 1975) and the finding that 14-C from 14-CO_2 was not incorporated into methylmercury, methanogenic bacteria do not appear to be

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responsible for mercury methylation. Methylation may, therefore, occur during the formation of volatile acids.

S-adenosylmethionine and tetrahydrofolate were found to increase the formation of methylmercury from methylcobalamin by Clostridium cochlearium by Imura et al. (1977). These researchers, however, did not determine the mechanism by which S-adenosylmethionine and tetrahydrofolate stimulate mercury methylation. In fish, the formation of methylmercury was found to be correlated with the vitamin B-12 content of the liver. Since methylcobalamin is a vitamin B-12 analog, these results tend to indicate that methylcobalamin is a major factor in mercury methylation.

Bisogni (1973) and Bisogni and Lawrence (1975) investigated the formation of methylmercury in bench scale aerobic and anaerobic reactors and developed a simple model to describe the formation of organomercury complexes. Their reactors were fed a glucose-nutrient broth and were seeded with anaerobic and activated sludge. Reduction of the divalent mercury to elemental mercury was the major mercury transformation. Dimethylmercury formation was minor in both the anaerobic and aerobic reactors. A maximum of 0.2 and 0.3 percent of the added mercury was transformed into dimethylmercury in the aerobic and anaerobic reactors, repectively. From 8.4 to 71.9 percent of the mercury was

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converted to elemental mercury in the anaerobic reactors. In the aerobic systems, 71.1 to 95.8 percent of the added mercury was reduced to the elemental form. Monomethylmercury production ranged from less than 0.1 to 15.7 percent in the aerobic reactors, and from less than 0.1 to 5.9 percent under anaerobic conditions. In the anaerobic reactors, a significant percentage of the added mercury remained in the divalent state (14.3 to 84.4 percent), while only 0.4 to 2.4 percent remained in the divalent form in the aerobic systems. Bisogni and Lawrence (1975) also found that while increasing the sulfide concentration did not prevent the formation of methymercury from divalent mercury, the amount of methylmercury formed, however, was decreased by approximately 50%.

More methylmercury was found to be produced under anaerobic conditions than under aerobic conditions in San Francisco Bay sediments (Olson and Cooper, 1976). Methylmercury production was proportional to organic content and was limited in sterile sediments. The higher methylmercury concentration under anaerobic conditions may have been due to more limited methylmercury degradation than occurred aerobically.

Gardner et al. (1978) reported that mercury methylation was occurring in a salt marsh ecosystem receiving chlor-alkali wastes, but were unable to determine where methylation

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occurred (i.e. sediments, biota, water column). Methylmercury was not found in the sediments; whereas, trace levels were found in plants. The relative concentration of methylmercury was found to increase with trophic level.

The formation of methylmercury in anaerobic marine sediments was reported by Berdicevsky et al. (1979). In their experiments, methylation was not found in sterile controls; therefore, microbial activity was believed to be responsible for the methylation. Increasing mercury concentration within the range of 100 to 3000 ug/l decreased methylation, probably as a result of inhibition of the microorganisms. At the lower concentration (100 ug/l), the methylmercury levels peaked at 98 percent of the initial mercury concentration; whereas, at 3000 ug/l, the methylmercury concentration peaked at 0.068 percent. These researchers also found methylation to occur in aerobic sediments; however, an extensive investigation of this process was not conducted.

Increasing salinity was found to decrease mercury methylation in anaerobic estuarine sediments. At 0.1% salinity, methylmercury concentrations were found to reach 2.3% of the added mercury concentration; whereas, at 3% salinity, only 0.05% of the added mercury was present as methylmercury. Above 2% salinity, the effect of increasing salinity on decreasing methylmercury formation was minimal.

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Methylmercury levels were also found to peak at 15 to 20 days of incubation followed by a decrease in methylmercury concentration (Blum and Bartha, 1980).

The redox potential is an important factor in controlling the concentration of methylmercury in sediments. The highest levels of methylmercury are present between redox potentials of +100 and -100 mV. Within this redox range, HgS is unstable; thus, sulfides are not a substantial sink of mercury. More mercury is available for methylation, and the organisms responsible for this conversion are most efficient in this range. At redox potentials above 100 mV, the microorganisms responsible for demethylation (i.e. Pseudomonas) are most efficient, and sulfide levels are negligible. Below -100 mV, high levels of H_2S may exist. As a result, mercuric sulfide forms, thereby limiting methylation. Also, the reaction of methylmercury with H_2S forms dimethylmercury which is volatile. Methylmercury concentration was also found to be related to the total mercury concentration, the organic carbon content, and the silt content of the sediment (Bartlett and Craig, 1981).

The pH also affects the relative amounts of monomethyl and dimethylmercury formed. Monomethylmercury is more likely to form in the pH range of approximately 5.2 to 7.8, reaching a maximum near pH 6.0. Dimethylmercury is more likely to form

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between approximately pH 7.8 to 10.0, with a maximum near pH 9.0 (Fagerstrom and Jernelov, 1972). Under acidic conditions, dimethylmercury will dissociate, and in the presence of excess mercuric ions, dimethylmercury will dissociate to form a monomethylmercuric salt (Bisogni, 1973). Furthermore, the pH affects the partitioning of methylmercury between the water column and the sediments. Decreasing pH 1 to 2 units can double the methylmercury concentration in the water column. The amount of methylmercury generated in the sediments, however, is not affected by pH (Miller and Akagi, 1979). Sulfide and bicarbonates reduce mercury methylation in seawater, while light can cause demethylation (Compeau and Bartha, 1983).

Methylation of mercury in both a lake water column and sediments was reported by Furutani and Rudd (1980). Microbial activity was found to be related to methylation; a higher rate of methylation occurred during periods of high microbial activity. Methylation also occurred despite the presence of bound hydrogen sulfide. It was believed that the disassociation of bound sulfides from compounds such as iron sulfide (followed by the formation of mercuric sulfide) did not occur rapidly enough to prevent methylation from occurring.

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Methylmercury formation in the water column was demonstrated by Topping and Davies (1981). Increasing mercury and organic carbon concentrations were found to increase methylmercury formation, which ranged from 1 to 10 ug/l. Based upon this data and the literature, Topping and Davies concluded that methylation occurred at approximately the same rate in both marine sediments and the water column.

A strain of Chlostridium cochlearium T-2C which was incapable of methylating mercury was found to be more sensitive to mercuric ions than was a strain of the same microorganism which could methylate mercury. Sensitivity to methylmercury, however, by both strains was roughly the same. Therefore, Pan-Hou and Imura (1982) concluded that microbial mercury methylation was a means of resistance and detoxification of mercuric ions.

Degradation of Methylmercury

Degradation of methylmercury can occur biologically and abiotically. Furukawa et al. (1969) found that Pseudomonas was able to degrade methylmercuric chloride and other organic mercurials. Methane and metallic mercury vapor were found to be the principle products of methylmercury degradation. The decomposition of phenylmercuric acetate by this microorganism was also found (Tonomura and Kanzaki, 1969).

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Spangler et al. (1973a) also reported the formation of methane and metallic mercury from the degradation of methyl mercury Although a positive identification was not made, Pseudomonas sp. appeared to be the microorganism responsible for methylmercury degradation. Spangler et al. (1973b) examined 207 bacterial cultures for the ability to degrade methylmercury. Thirty of these cultures could degrade methylmercury aerobically. Twenty-two of these thirty could facultatively degrade methylmercury, and twenty-one could anaerobically degrade methylmercury. Twenty-six of these isolates appeared to be Pseudomonas; although, positive identification of any of the isolates was not performed. Methane and metallic mercury were again found to be the principle degradation products.

Billen et al. (1974) found demethylation to occur in the sediments of a river highly contaminated with inorganic mercury. Increased concentrations of methylmercury tended to increase the capacity of the sediment microbiological community to demethylate methylmercury, perhaps due to selection of methylmercury resistant bacteria.

Hydrogen sulfide reacts with methylmercury to form a volatile mercury compound. Although this volatile product was not identified, it was believed to be a sulfur derivative of methylmercury. The rate of volatilization of methylmercury

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by hydrogen sulfide was found to be directly related to both temperature and hydrogen sulfide concentration (Rowland et al., 1977). Deacon (1978) and Craig and Bartlett (1978) also found that hydrogen sulfide can volatilize methylmercuric chloride, and both groups of researchers state that dimethylmercury is the volatile product of this reaction.

Shariat et al. (1979) tested 40 microorganisms and found that 21 could demethylate methylmercury chloride. One of the end products may have been elemental mercury. Percent methylmercury reduction ranged for 1 to 84%. Rapid photodecomposition of methylmercuric salts can occur in the presence of iodine or bromine (Talmi and Mesmer, 1975). Within the pH range of 6-8, the rate demethylation is approximately first-order (Mason et al., 1979).

Degradation of methylmercury can also occur abiotically. Ethylene and acetylene were found to reduce phenylmercury to elemental mercury. Light and alkaline conditions favored this reaction; whereas, the presence of excess sulfide ions inhibited this reaction. (DeFillippis, 1979). Photolysis of organomercurials has also been reported (Inoko, 1981).

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Other Microbial Mercury Transformations

A mercury resistant microorganism, believed to be *Pseudomonas,* was found to be able to volatize phenylmercuric acetate (PMA). This microoganism was able to volatize PMA of concentrations as high as 150 ppm. The mechanism of PMA volatilization was not identified, nor was the volatile product; although, the volatile mercury product was believed not to be PMA (Tonomura et al., 1968).

Mercury resistant *Escherichia coli* were found to be able to reduce mercuric mercury (10^{-5} M) to elemental mercury. This reaction rate was approximately 4 to 5 nmoles of Hg(II) per min. per 10^8 cells. Subsequent volatilization of the elemental mercury from solution then occurred. Gold, silver, and sulfhydryls significantly inhibited this reaction. The inhibitory mechanism of sulfhydryls was proposed to be the result of the formation of a stable Hg-S complex (Summers and Silver, 1972).

Several microorganisms containing a gene conferring mercury resistance were found to be able to convert divalent mercury to a volatile mercury form believed to be elemental mercury. *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* containing the resistant gene were found to be able to perform this transformation. On the other hand, this

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transformation did not occur if these same microorganisms did not contain the resistant gene (Summers and Lewis, 1973).

A similar transformation in yeasts was reported by Brunker and Bott (1974). The reduction of mercuric chloride present in concentrations up to 180 mg/l to elemental mercury in the yeast Cryptococcus by these researchers. These microorganisms were found to accumulate the mercury to concentrations 10 to 30 times that of the media. This ability to concentrate mercury was believed to be due to the microorganism's transformation of divalent mercury to relatively non-toxic elemental mercury. This elemental mercury was then associated with the yeast cell wall, membrane, and vacuoles. Significant mercury concentrations were not present in the yeast cell cytoplasm.

Aspergillus niger and Penicillium notatum, two fungi, have been found to absorb both methylmercuric chloride and mercuric chloride. Mercuric chloride uptake was approximately 25 times the methylmercury chloride uptake; thus, it was hypothesized that organic mercury was more toxic to these fungi than the inorganic mercury. Significant uptake of both forms of mercury by these fungi, however, was found (Hardcastle and Mavichakana, 1974a,b). These two fungi were previously found to be capable of degrading organic mercury fungicides. This breakdown reaction was believed to

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occur in three steps: uptake or sorption of the mercury compound, degradation of the fungicide, and utilization of the breakdown products (Spanis et al., 1962).

Konetzka (1977) reported that microorganisms carrying the penicillinase plasmid are resistant to mercury as well as cadmium, chromium, lead, arsenate, arsenite, thallium, zinc, and other metals. The ability of the plasmid to convert mercuric compounds to a volatile form was believed to be responsible for the increased resistance of these microorganisms to mercury. These resistance plasmids have been found in many diverse organisms such as E. coli, Aerobacter aerogenes, serrati marcescens, Pseudomonas aeruginosa, Proteus vulgaris, Providencia, Shigella dysenteriae,and Staphylococus aereus. A more detailed description of a plasmid conferring resistance to both mercuric ions and sulfonamides is presented by Stanisich et al. (1977).

Aerobic, heterotrophic bacteria can play a significant role in the mobilization of mercury in a marine environment by reducing mercuric and phenylmercuric ions to elemental mercury. In the Chesapeake Bay water and sediments, the potential for mercury mobilization was found to be related to the proportion of mercury-resistant bacteria to the total number of viable aerobic and heterotrophic bacteria.

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Reduction of mercuric mercury to elemental mercury in Chesapeake Bay peaked in spring and was directly correlated with the total Hg sediment concentration and to the water dissolved oxygen concentration. The increase in mercury mobilization in spring could seriously impact the life cycles of marine organisms (Colwell and Nelson, 1975).

Mercury Sinks

In aquatic systems, mercury is primarily associated with the sediments and suspended particulate matter. Cranston and Buckley (1972) found that mercury adsorption to particulate matter was significantly affected by particle size. Adsorption of mercury was found to increase with decreasing particle size, presumably because the increased specific surface area of smaller particles. Mercury released to the aquatic system in a dissolved form was found to be rapidly adsorbed by suspended and sediment particulate matter. Dissolved mercury concentrations ranged from 0.036 to 0.38 ppb; whereas, suspended particulate matter contained 3.59 to 34.4 ppm of Hg, and bottom sediments contained 0.09 to 1.06 ppm.

Alkaline pH conditions have been found to favor the release of mercury from sediments to the water column (Matsumura et

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al., 1972). Although alkaline conditions promote the release of mercury to the water column, acidic pH conditions favor the accumulation of mercury by fish. Under alkaline conditions, mercury forms relatively unreactive forms which may account for the decreased uptake by fish at higher pH values.

Bacteria can increase mercury desorption from river sediment and can effectively compete with the sediments in accumulating mercury. The bacteria can then cause significant (58%) losses of mercury from the system by the formation and subsequent volatilization of elemental mercury (Ramamoorthy et al., 1977). Both mercuric and methylmercury compounds will readily bind to sulfhydryl groups in organics in the sediments as well as to some inorganic sediments particles. Chloride, however, decreases adsorption. Because mercury will bind to sediments, sediment transport may be a significant factor in mercury mobility. In running waters, the dry weight mercury concentration in sediments may not be a good indicator of mercury contamination due to differences in the organic content. Instead, the ash-free dry weight mercury concentration may be a better indicator of mercury contamination. The sediment concentration also does not necessarily reflect the availability of mercury to the stream organisms (Kristensen and Hansen, 1980).

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Over 95 percent of the mercury present in a river system may be associated with the sediments. Uptake of mercury by river sediments is dependent both upon the mercury concentration and form in the water column and the water velocity above the sediments. Greater uptake of mercury occurs in sediments in contact with moving water than in those sediments in stagnant waters. The presence or absence of oxygen, however, does not affect mercury uptake (Kudo and Hart, 1974). The majority of the mercury present in sediments is associated with the organic matter and small size particles (fines). The partition coefficient for sand sediments from the Ottawa River (sediment/water) was found to be 2,091; whereas, the fine material in these sediments had a partition coefficient of 215,000. The river biomass (i.e. fish, plants) accounted for only 0.02 percent of the total mercury present. Organic mercury, however, was the primary form of mercury present in the biomass (Kudo et al., 1977).

Kudo (1976) reported a half-life of mercury in bed sediments of 12 to 20 years. Uptake of mercury by fish (guppies) in contact with mercury contaminated sediments occurred, but the concentration in the fish varied widely. The half-life for mercury in the fish ranged from 38 to 75 days.

Frenet (1981) also found significant Hg adsorption to suspended matter in fresh and brackish waters. In salt

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water, however, the sodium ions successfully competed for the exchange sites on the suspended matter. Mercury thus tends to stay in solution in salt water. These results support those of Feick et al. (1972) who found that high concentrations of salt can release mercury from sediments.

Dilution and adsorption onto suspended particulate matter were found by Cranston and Buckley (1972) to be the primary fate of mercury discharges from industries in a river and estuary system. As the salinity of the river-estuary system increased, the ratio of particulate to dissolved mercury also increased. Cranston and Buckley (1972) thus concluded that only small particles with a high adsorbed mercury concentration persist in saline water. The large particles would be deposited in the estuary.

Carr and Wilkniss (1973) reported that 80% of the total mercury in a sample from Chesapeake Bay was associated with particulate matter (5% salinity). At the interface between a river and saltwater, flocculation, coagulation, and sedimentation of the fine suspended matter occurs. Since mercury adsorbs to suspended particles, higher mercury concentrations would occur in the sediments where river and saltwater mix (e.g., an estuary). Organic matter also tends to settle in such areas due to similar mechanisms; thus, the mercury and organic matter content of the sediment may not be directly related (Cranston, 1976).

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Rae and Aston (1982) found that the mercury concentration in the suspended particulate matter of an estuary decreased significantly during the high chlorinity periods of the tidal cycle. The decrease in mercury concentration, however, was due to changes in the particulate sizes during these period of the tidal cycle and not to desorption. Mercury was found to bind tightly to the suspended particulate matter and also to be highly correlated with the organic carbon concentration in the particulates.

Mercury concentrations in the Tagus (Portugal), Geronde, Loire, and Rhone (France) estuaries were investigated by Figueres et al. (1985). Mercury concentrations in the suspended matter were found to decrease with increasing salinity due to dilution and remobilization. Dissolved mercury concentrations ranged from 3-300 ng/l, and with the exception of areas near waste discharges, the dissolved mercury was primarily organic.

Uptake of mercury by sediments in natural waters is affected by pH and Eh and is nearly complete except when the levels of mercury contamination are very high. Humic acids in the sediments can reduce divalent mercury to elemental mercury. Sulfides, however, inhibit this reaction (Schindler and Alberts, 1977).

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Fluxes of mercury to the sediments of a fjord were found to decrease once the source of mercury contamination was reduced. The decrease in flux was greatest nearer the source of contamination. The residence time of mercury in the water column was found to range from less than one month near the head of the fjord to a maximum of 5-10 years in the deep water portions of the fjord. Approximately one-half of the mercury was deposited near the headwaters of the fjord, while the remainder was deposited in the deep waters of the fjord (Smith and Loring, 1981).

Ocean sediments near a sewage treatment plant effluent outfall were found to be enriched with mercury. The mercury, however, was complexed in refractory forms not readily available for uptake by biota. As the distance from the outfall increased, mercury complexed more with degradable organic matter and thus may be more available for uptake. Scavenging of mercury by sulfides produced in the sediments was postulated as the cause of mercury enrichment near the sewage treatment plant (Eganhouse et al., 1978). Effluent from the Seattle, Washington wastewater treatment plant was found to contribute only 1.5% of the total mass of heavy metals entering Puget Sound. Increases in the concentration of mercury in the water as compared to open sea water were not found. Locally high concentrations of mercury in sediments were found, however. Dumping of sludge from the

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treatment plant may have accounted for the sediment contamination (Schell and Nevissi, 1977).

Both mercuric and methylmercury compounds will readily bind to sulfhydryl groups of organics in the sediments as well as to some inorganic sediment particles. Chloride, however, decreases adsorption. Because mercury will bind to sediments, sediment transport may be a significant factor in mercury mobility. Jackson (1979) also reported that the ratio of mercury to the organic content of the sediment could be used to indicate sources of contamination.

The concentration of dissolved mercury in the interstitial water of estuarine sediments was found to be 2.6 to 36 times greater than the concentration in the overlying surface waters. Dissolved organic matter can increase the solubility of mercury, however, increasing salinity can reduce the mercury complexing ability of the dissolved organics (Lindberg and Harris, 1974).

Methylmercury is only a small fraction of the total mercury in river sediments. Batti et al. (1975) found that the methylmercury concentration did not exceed 0.06% of the total mercury concentration. Thompson et al. (1980) also reported that methylation in sediments was small and not a significant mechanism for mercury removal from the sediments.

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Methylmercury comprised less than 1% of the total mercury in the sediments of Howe Sound, British Columbia. Organic mercury compounds in sediments were found to be more available to rooted aquatic plants than are inorganic mercury compounds perhaps because of the insolubility of mercuric sulfides. Uptake by plants occurs both by metabolic uptake and by physical absorption. Thus, rooted aquatic plants could be an important factor in the removal of mercury from sediments (Dolar et al., 1971). Sediment mercury concentrations from the Gulf Coast of Saudia Arabia were reported by Sadig and Zaidi (1985).

Andren and Harris (1973) reported methylmercury concentrations of 0.06 and 0.19 mg/Kg in the sediments of Mobile Bay. Approximately 0.03% of the total mercury was present as methylmercury. The methylmercury concentration decreased with depth in the sediments, perhaps as a result of anoxic conditions.

Akagi et al. (1979) reported that more methylmercury was formed in organic sediments than in sandy sediments. The partition coefficients for these sediments, however, were such that the methylmercury concentrations in the overlying water were approximately the same. Based upon a laboratory study, Akagi et al. (1979) concluded that sediment and water characteristics primarily affected the equilibrium partition

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for methylmercury, and not the methylation rate. Instead, the methylation rate in the sediments appeared to be controlled by the rate of removal of the methylmercury (e.g., by fish uptake) from the water.

Herrick et al. (1982) developed a four compartment model (sediments, detritus, invertebrates, and fish) for mercury contamination in a stream. Based upon this model, Herrick et al. concluded that the effluent discharge standard for mercury should be below 1 ug/kg (ppb) to prevent mercury levels in fish from exceeding the U. S. Food and Drug Administration guideline of 0.5 ppm.

Mercury in the Atmosphere

Because elemental and divalent mercury compounds are volatile, mercury can be lost from the aquatic environment to the atmospheric. Publications directly related to the loss of mercury from natural aquatic systems, however, were not found in the literature during a cursory literature review. References related to the loss of mercury from laboratory samples were found, but were not believed to be directly relevant to this project. Numerous publications of the fate of mercury in the atmosphere, however, do exist; a few of which are summarized below.

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The input of mercury to the atmosphere has increased in recent decades. Volatilization of mercury from the earth's crust is the primary source of mercury to the atmosphere; although, man's activities may have increased the rate of volatilization (Weis et al. 1971). The principle forms of mercury in the atmosphere are elemental mercury, volatile inorganic compounds such as mercuric chloride, organomercury compounds (e.g., dimethylmercury), and particulate mercury. Concentrations of mercury are normally in the part per trillion range (Schroeder, 1982).

Atmospheric mercury emissions have also been documented from chlorine production solid wastes (Lindberg and Turner, 1977), coal combustion (Environment, 1971), and paint (Battigelli, 1960a). Dispersion generally reduces the mercury concentration so that inhalation of the mercury does not pose a signficant health risk. Once emitted, gaseous mercury is quite mobile in the environment. Lockeretz (1974) modelled mercury deposition from power plant and incinerator emissions and predicted that although some local mercury deposition would occur, most of the mercury would remain airborne for distances on the order of tens of kilometers. Lindberg (1980) confirmed this prediction, finding that 92 to 99% of the mercury emitted from a power plant was present as elemental mercury vapor. Gas to particle conversion during plume transport did not occur. Elevated mercury levels were

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found at 22 km from the plant, which was the most distant sampling point. Precipitation scavenging was predicted to be the major mercury removal mechanism.

Williston (1968) monitored the atmospheric mercury concentrations in the San Francisco Bay area and reported mercury concentrations ranging from 0.5 to 25 ng/m^3 (winter) and from 1 to 50 ng/m^3 (summer). Wind direction, temperature, sunlight, and wind speed were all found to affect the mercury concentration.

Elevated atmospheric mercury concentrations have been found above mineral deposits containing mercury. Mercury concentrations 5 to 20 times background levels were found 200 feet above the ground surface over several mercury containing ore deposits. A maximum average of 62 ng/m^3 of mercury was found at an elevation of 200 feet. The range of mercury concentrations was 12 to 66 ng/m^3 compared to background concentrations ranging from 1.6 to 7.6 ng/m^3 (4.5 average). In the soil gas above these deposits, mercury concentrations were as high as approximately 7:1 compared to background levels (200 ppb compared to 30 ppb background). Barometric pressure was found to control mercury emissions from the soil gas to the atmosphere, with the greatest release of mercury occurring at lower pressures (McCarthy et al., 1969).

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Jernelov and Wallin (1973) investigated the atmospheric mercury concentration surrounding five chloralkali plants in Sweden. Although a rapid decrease in mercury concentration with distance was found, only a small amount of mercury was deposited locally (within 5 km). Wallin (1976) investigated mercury deposition from six chloralkali plants and found that less than 10% of the released mercury is deposited within 5 km.

Fungi and mosses have also been found to absorb mercury from the atmosphere. Huckabee (1973) found an average of 1.13 ppm of mercury in mosses 2 km from a power plant compared to 0.066 ppm approxmately 100 km from the power plant. Wet and dry deposition of mercury at 2 km from the plant was estimated to be 20 to 30 ug of mercury per square meter per year. Mosses were also found to accumulate mercury to a greater extent than other forms of vegetation, typically containing an order-of-magnitude greater concentration.

The majority of atmospheric mercury is present in a volatile mercury form. Particulate mercury generally accounts for less than 10% of the total mercury. In the Tampa Bay, Florida area, total atmospheric mercury concentrations range from approximately 0.1 to 116 ng/m^3. Particulate mercury accounted for only 4% of the total mercury present. Volatile, elemental mercury accounted for 49% of the total

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mercury present, while volatile mercuric and monomethylmercuric-type compounds accounted for 25 and 21%, respectively. Only approximately 1% of the mercury was present as dimethylmercury-type compounds. The relative concentrations of each mercury species in the atmosphere may be controlled by microbiological process in the local soils or aquatic environments, in addition to human sources (Johnson and Braman, 1974).

Soldano et al. (1975) investigated the atmostheric mercury concentrations surrounding sewage treatment plants and found the treatment plants to be significant sources of mercury. Both organic and elemental mercury compounds were found in the atmosphere surrounding the treatment plants; however, the organic mercury compounds were transported greater distances.

Mercury vapor can stress vegetation. Sugar beets were reported by Waldron and Terry (1975) to be very sensitive to mercury vapor. Concentrations of mercury vapor as low as 0.28 mg/m^3 produced visible vegetation stress within five hours.

Lodenius and Herranen (1981) found that fungi 0.2 km from a chloralkali plant contained 120 times as much mercury as fungi collected from a control area. The decrease in fungal mercury concentration with distance was found to be

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approximately exponential. Wallin (1976) also found an exponential decrease in mercury concentration with distance from four chloralkali plants.

Brossert (1982) presented data from a Swedish air monitoring network for mercury and determined that atmospheric mercury resulted from two sources: natural and anthropogenic emissions. Background sources include mercury emissions from soils and natural waters; whereas, anthropogenic sources include industrial emissions. Mean total airborne mercury concentrations ranged from 1.5 to 6.3 ng/m^3. All of the air monitoring stations were remote from any anthropogenic mercury sources.

Galloway et al. (1982) conducted a review of atmospheric heavy metal data and found reported atmospheric deposition rates for mercury ranging from approximatley 2×10^{-4} kg/ha/yr to remote areas to 1.5×10^{-2} kg/ha/yr for urban areas. The median mercury concentration in wet deposition ranged from 0.079 ug/l for remote areas (range 0.011 to 0.428) to 0.745 ug/l for urban areas (range 0.002 to 3.8). Total anthropogenic mercury emissions were estimated to be 110×10^8 g/year versus a natural emission rate of 250×10^8 g/year.

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Mercury in the Terrestrial Environment

Wet and dry deposition as well as soil sorption are the primary removal mechanisms for mercury from the atmosphere. Thus, mercury released from an aquatic environment can, via the atmosphere, contaminate the soil environment. Similarly, transformations of mercury in the soil can release mercury to the atmosphere, thereby returning mercury to the aquatic environment.

Fate in Soil

Mercury concentrations in soils are generally low unless the parent material contained mercury or there is an external source of mercury contamination. Jonasson and Boyle (1971) report that the normal range for mercury in soils is 20 to 150 ug/kg. Gracey and Stewart (1974) report mercury levels to be less than 60 ug/kg in non-mineralized (with respect to mercury) soils compared to mineralized areas which contained up to 250 ug/g. The mercury content in non-contaminated soils was found to be directly related to the soil clay content; whereas, no relationship between mercury and soil organic matter content was found.

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The mean mercury concentration in United States soils is 71 ug/kg (ppb). Samples from the Eastern U. S. contained an average of 96 ppb; whereas, western soils contained 55 ppb. Several soils in the United States, however, contained 1 mg/kg (ppm) or more (Woolrich, 1973).

Increased soil and plant mercury concentrations were reported by Lindberg et al. (1979) near the Almaden, Spain mercury mine and smelter. Mercury has been mined at this location for approximately 2,000 years. The major source of mercury emissions at the mine is the smelter; however, mercury vapor is also emitted to the atmosphere from the mine ventilation system and the mine tailings. Soils near the mine (1 km) were found to contain an average of 97 ug/g of mercury; whereas, background soil samples contained an average mercury concentration of only 2.3 ug/g. Mercury emissions from the soils near the mine were approximately 0.33 ug mercury/m^2-hour compared to 0.13 ug/m^2-hour for the background soils (at 25°C). Temperature was found to affect emission rates, with higher emissions occurring at higher temperatures. Alfalfa grown in soils near the mine area was found to accumulate mercury in both the roots and foliage. The mercury concentration in the roots was found to be related to the total mercury levels in the soil. The foliage absorbed elemental mercury vapor directly from the atmosphere. Lindberg et al. (1979) concluded that mercury is

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transformed from various forms in the soil to elemental mercury and is then emitted as mercury vapor.

Crockett and Kinnison (1979) did not detect any increased soil mercury concentrations around a large coal-fired power plant. Increased mercury concentrations were found in the soils, grass, earthworms, and several small mammals near a chloralkali plant. Atmospheric fallout from the plant is believed to have been responsible for the mercury contamination (Bull et al., 1977).

Soil Sorption/Desorption

The adsorption of phenylmercuric acetate (PMA) to soils is dependent upon soil solution pH. Maximum adsorption occurs in the pH range of approximately 5 to 7, rapidly decreasing outside of this range. Under alkaline conditions, adsorption is limited by the formation of phenylmercuric hydroxide complexes; whereas, under acidic conditions, the adsorption sites are increasingly occupied by hydronium ions (Inoue and Aomine, 1969). Conversion of PMA to elemental mercury with subsequent volatilization has also been reported (Kemura and Miller, 1964).

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Sorption of elemental mercury vapor by soils has been shown to occur by Fang (1978) and Landa (1978a). Fang (1978) found that mercury sorbed by the soil could be accumulated by plants and that mercury was either very tightly bound to the soil or was transformed into a nonvolatile form. Only a small amount of the elementary mercury (Hg^{o}) sorbed was converted to the mercuric state. The major form of mercury in the soil was not identified however. The investigation conducted by Landa (1978c) suggested that the mercury was bound to the soil as an organo-complex.

Adsorption of both inorganic and organic mercury compounds from solution to soils occurs and can be described by Langmuir adsorption isotherms. Binding to soil is fairly rapid as vertical migration of any of the mercury compounds through the soil column beyond 20 cm did not occur. Losses of mercury due to volatilization ranged from 7 to 31% (Hoggs et al., 1978), which is similar to the 5 to 40% volatile mercury losses from soil reported by Landa (1978b). MacLean (1974) reported 3 to 59% mercury volatilization from soils. The addition of sulfur to the soil, however, prevented the volatilization of mercury from several soils.

The form of the mercury and the soil type affect the rate of mercury volatilization from soil. Greater volatile losses of mercury occur in sandy soils than in clay soils, probably as

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a result of the decreased sorptive capacity of the sand. The solubility of the mercury compound also affects the volatilization. Losses ranging from 26.4 to 38.3% of the applied mercury were found when relatively soluble mercury compounds were applied (e.g., $HgCl_2$, $HgNO_3$; sandy soil); whereas, only 0.2% of the applied mercuric sulfide was lost by volatilization (Rogers, 1979). Landa (1978b) reported the loss of mercury from soils amended with $Hg(NO_3)_2$. Five to 40% of the initial mercury was lost via volatilization, and soil microbes were a major factor in this volatilization reaction. The form of the volatile mercury, although not identified, was believed to be elemental mercury. Losses of methylmercury from soil were investigated by Landa (1979) who found that increasing soil temperature increased mercury losses.

Sorption of mercury vapor by soil increases with soil moisture to a maximum value and then decreases with moisture content. As moisture content increases, the soil pores become increasingly filled with water, thereby decreasing the surface area available for adsorption. At high moisture contents, the effect of decreased surface area becomes significant. Microbial activity also influences mercury sorption as 20 to 30% more sorption occurs in nonsterile soils as opposed to sterile soils (Fang, 1981).

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Once in the soil, methylation of mercury can occur and has been documented by Rogers (1976). In addition, uptake of mercury from the soil by plants occurs and can provide a pathway for human exposure (food consumption).

Methylation

Beckert et al. (1974) found that mercury salts could be methylated in soils. Due to the soil extraction process, it was not possible to determine if mono- or dimethylmercury was formed. Elemental mercury was formed, however. Rogers (1976) investigated mercury methylation in soils. Sterile soils were found to contain higher concentrations of methylmercury than non-sterile soils suggesting an abiotic methylation mechanism. Biological degradation of methylmercury was also found and may have been a factor in the lower methylmercury concentration in sterile soils. Increasing temperature, mercury dosage, clay content, and moisture content increased methylmercury production.

The compound responsible for the abiotic methylation of mercury in soils was extracted from soil but not identified by Rogers (1977). The methylating factor had a molecular weight similar to that of a fulvic acid. This factor was not heat sensitive (to 120°C), but was inactivated by

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ultraviolet light. A pH below 5.5 favored methylation as did increasing mercury concentration and temperature.

Uptake and Release by Plants

John (1972) investigated the uptake of mercury by eight food crops and found spinach and radishes to accumulate the most mercury in the edible portions. Mercury levels of 0.695 and 0.663 ug-Hg/g of dry plant were found in the spinach leaves and radish tubers grown in soil containing 20 ug/g of $HgCl_2$.

On the other hand, Bache et al. (1973) found no appreciable uptake of $HgCl_2$ by plants. Instead, appreciable uptake of mercury by plants were found only in soils treated with 1 to 10 ppm of methylmercury dicyandiamide. In general, the mercury concentrations in the edible portions were less than 0.1 ppm, with the exception of onions which contained approximately 1.1 ppm of mercury.

Mercury levels of 450 ppm in soil were found not to be toxic to turf grasses. Mercury levels in turf grass averaged only 1.68 ppm. Complexation of the mercury by the soil may have prevented the high soil mercury levels from being phytotoxic (Estes et al., 1973).

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The distribution of mercury in the soil can affect plant uptake. Lee (1974) reported greater mercury uptake by plants if the source of mercury contamination was mixed in the soil than if the contamination was localized. Uptake of mercury by wheat and barley from mixed soil containing 0.5 ug-Hg/g soil, however, was small. Plant tissues contained only 0.01 to 0.03% mercury per gram of plant tissue. Soil pH was also found not to affect Hg uptake by these plants.

Mercury uptake by plants from sewage sludge was reported by van Loon (1974). Tomatoes grown in sludge amended soils containing 15 ppm of mercury had mercury concentrations as high as 12.2 ppm in the fruit. Tomatoes grown in control areas contained only approximately 0.25 ppm of mercury. Bean pods also appeared to show significant mercury uptake, however, sufficient samples were not available for a definitive conclusion. Anderson and Nilsson (1976) also found uptake of mercury by plants from sewage sludge. Decreasing soil pH increased mercury uptake by plants.

Beaufort et al. (1977) reported that the log of plant mercury concentration was directly related to the log of the mercury concentration in the growth media within the range of 0.001 to 10 mg Hg/Kg. Plant growth, however, was affected by mercury concentrations above 5 mg/kg. Approximately 95% of the plant mercury was present in the roots, and the plant

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cell walls bound most of the mercury. The presence of mercury in the plant roots was believed to limit further uptake of mercury by the plant.

Methylmercury content of vegetables grown in sludge-amended soils averaged 14% of the total mercury content compared to only 4% for control soils. Methylmercury content ranged from 0 to 33.3% of the total mercury in the vegetables from the sludge-amended soils. Total mercury concentration ranged from 0.4 to 40.5 ng/kg in the sludge soils compared to 0.1 to 6.7 ng/kg in control soils (Cappon, 1981).

Release of mercury by plants can also occur. Siegel et al. (1974) report the loss of a volatile mercury compound from the foliage of garlic, Koa, and Avocado. Dimethylmercury was found not to be the volatile form of mercury released, nor was elemental mercury believed to be the volatile form.

Vegetation may be a major factor in the environmental distribution of mercury. Low levels of soil mercury were found near a volcanic site in Antarctica compared to similar areas in Hawaii and Iceland. Atmospheric mercury concentrations, however, were similar at all three sites. The lack of vegetation was believed to be a major factor in the low soil mercury levels at the Antarctic site (Siegel et al., 1980).

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Weaver et al. (1984) reported that the concentration of mercury in Bermuda grass grown in mercury contaminated soils was sufficiently high to pose a potential threat to foraging animals. The mercury concentration in plants required to pose a threat to foraging animals, however, was not reported. Siegel et al. (1985) investigated the distribution of mercury in plants and soil around a former mercury mine and concluded that the mining activities caused extensive local pollution, horsetail, plantain, and dandelion were found to be useful indicator plants.

Mercury vapor did not substantially inhibit either seed germination or early plant growth. Inhibition of plant growth, however, increased with time (Siegel et al., 1984). Wang et al. (1984) found that the rate of decomposition of plant residues was not affected by the mercury concentration in soil. Concentrations as low as 1 ug/L of mercury ($HgCl_2$) were found to adversely affect plant growth, and the leaf injury index was found to be a good indicator of susceptibility to mercury toxicity (Mhatre and Chaphekar, 1984).

Lodenius and Tulisolo (1984) investigated the distribution of mercury within a 100 km radius of a chlor-alkali plant. Approximately 6% of the mercury emitted to the atmosphere was

deposited within 5 km of the plant; whereas, 60% of the emitted mercury was deposited within 20-100 km of the plant. Huckabee et al. (1983) conducted a survey of the distribution of mercury in vegetation near the Almaden, Spain mercury mine. Mercury concentration in plants decreased with increasing distance from the mine; however, plants collected 25 km in predominantly upwind direction contained higher mercury concentrations than reported background concentrations. Mosses accumulated higher total mercury concentrations than did vascular or woody plants, and traces of methylmercury (not quantifiable) were found in some plants.

Summary

Mercury enters the aquatic environmental primarily as elemental and mercuric mercury. Sorption to sediment, volatilization, and biological uptake are the primary fates of mercury in the aquatic environment. Methylation of mercury can occur in the aquatic environment under aerobic and anaerobic conditions, and in fresh, brackish, or salt water. The relative amount of methylmercury formed, however, is generally very small. Increasing the mercury concentration will increase methylation as long as inhibition of the microorganisms due to mercury toxicity does not occur.

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Methylation is decreased by increasing sulfide concentration and salinity. Other factors which can affect methylation include the pH and redox potential.

The amount of mercury associated with organisms (i.e. fish) is generally a small percentage of the total mercury in an aquatic system. Most of the mercury present in aquatic organisms is present as methylmercury. In saltwater, the presence of excess selenium in the organisms may reduce the use of toxicity effects resulting from consumption of marine fish.

The primary fate of mercury in the aquatic environment is generally sorption to particulate matter or precipitation with subsequent sedimentation. Windom (1973) analyzed the fate of mercury in an estuary and concluded that mercury could be lost from the system by four mechanisms: (1) Dilution of mercury with seawater, (2) removal of mercury by sedimentation, (3) removal of plant detritus from the estuary to the sea by water currents, and (4) migration of organisms from the estuary. At steady state, approximately one-half of the particulate mercury which enters the estuary will be removed by sedimentation. Plant growth thus becomes a significant mechanism for returning mercury to the system. If a significant percentage of the mercury in the plant detritus is re-cycled, high concentrations of mercury may be

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maintained in the system long after the source of contamination has stopped.

Mercury released from the aquatic environment through volatilization can be transported great distances from the contaminated water. Dispersion will generally prevent such an atmospheric release from posing a potential health risk. Wet and dry deposition and soil sorption are the primary means of removal of mercury from the atmosphere. Once in the soil, plant uptake, leaching (usually minimal), and chemical transformation and fixation can occur. Volatilization can also occur resulting in losses of up to 40% of the applied mercury.

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SECTION 5

UPTAKE AND BIOACCUMULATION

Aquatic Environment

Methylmercury transfer from benthic fauna to fish was reported to be small by Jernelov and Lann (1971). By examining the mercury content of benthic animals, release of mercury from sediments can be detected. Knauer and Martin (1972) did not find any evidence of biomagnification of mercury in a food chain consisting of phytoplankton, zooplankton, and anchovies. Temporal variations in the mercury levels in both phytoplankton and zooplankton were found, but season variations were not apparent. These researchers concluded that unless natural levels were grossly exceeded, many organisms should be able to maintain mercury levels at physiologically safe levels.

Tsai et al. (1975) found pH to be an important factor in the accumulation of mercury by fish. Increased accumulation of mercury was found to occur at lower pH values even though the release of mercury from sediments into the water is enhanced by alkaline pH conditions.

Biomagnification of methylmercury in a food chain consisting of *Chlorella vielgarus, Daphnia Magna,* and *Gambusia affinis* was reported by Boudou et al. (1979). After 30 days, the mercury concentration in *Gambusia affinis* was as much as

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27,000 times the concentration in the water. Increasing temperature increased bioaccumulation. Methylmercury is more easily accumulated by fish than other forms of mercury because the liposolubility of methylmercury facilitates absorption and storage in the organism.

Mussels and shrimp accumulate methylmercury faster than inorganic mercury and excrete methylmercury slower than inorganic mercury. Increasing temperatures (8° - $18^{o}C$) slightly increases both accumulation and excretion. Excretion may occur more rapidly in the natural environment than in the laboratory (Fowler et al., 1978). Mercury accumulation by Salmo gairdneri can occur as much as six times faster when exposed to methylmercury than to inorganic mercury. The concentration of both forms of mercury in the fish tissues, however, was approximately equal (Ribeyre and Boudou, 1984a,b)

The concentration of mercury in croakers (Argyrosomus Argentatus) was found to be a good indicator of mercury contamination in Minamata Bay and in the Yatsushira Sea. Migration of mercury to the croaker from the sediment occurred via zooplankton and suspended particulate matter. Methylation was believed to occur in the zooplankton, however, direct input of methylmercury into these aquatic environments may have occurred (Nishimura and Kumagai, 1983).

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Ribeyre et al. (1980) investigated methylmercury transfer in a four-level aquatic trophic chain consisting of Chlorella vulgaris, Dapnia magna, Gambusia affinis, and Salmo gairdneri (trout). At the lower two elements of the tropic chain, methylmercury transfer between elements was high, ranging from 84 to 100%. At the higher two trophic levels, methylmercury transfer was less complete and was temperature dependent. Transfer rates from the lower to higher trophic levels ranged from 25 to 69 percent. At the highest trophic level (trout), mercury levels averaged 736 ug/kg. The temperature effect is believed to have resulted from differences in fish food consumption with temperature.

The presence of mercury can also increase the uptake of other heavy metals by microorganisms in brackish waters (Guthrie et al., 1977). Accumulation of methylmercury by filamentous algae is also enhanced by decreasing pH (Stokes et al., 1983).

Titus et al. (1980) investigated mercury translocation in a model ecosystem after elemental mercury was added to the sediments. The trophic elements used were plankton, snails, and goldfish. The accumulation of mercury by the organisms followed a logical sequence up through the food chain finally affecting the last organism in the food chain. During this investigation, an increase in the number of mercury resistent microorganisms occurred.

The mercury concentration in fish from Lake St. Clair, Michigan was found to have increased with time since 1920, presumably as a result of increased contamination (Evans et al., 1972). Burrows and Krenkel (1973) reported that uptake of methylmercury from water by bluegills can occur and that methylmercury accounted for 73% of the total mercury present. When the bluegills were removed from the contamination, rapid excretion of 40% of the methylmercury occurred. The remaining mercury concentration then decreased slowly with an approximate half-life of five months. Accumulation of selenium and mercury concentrations in fish from a Norwegian lake were reported by Froslie et al. (1985).

Fish uptake of methylmercury increases with increasing temperature and is also dependent upon the chloride concentration. The highest methylmercury uptake by fish and occurred at chloride concentrations of about 200 mg/L. It will, therefore, apparently take a considerably longer period of time to cleanse the mercury in oceanic environments than in fresh water environments are to the higher levels of chloride (assuming the same degree of mercury contamination; Shin and Krenkel, 1976).

Within the range of 0.2 to 50 ug/L of mercury (in the form of methylmercury) the bioconcentration factor for bluegill sunfish was found to be independent of the mercury

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concentration. The bioconcentration factor did, however, increase exponentially with water temperature. At 50 ug/L of mercury, the fish moved erratically, became disoriented and died within one month (Cember et al., 1978).

The mercury concentration of marine fish was found to be most related to the size and to the position of the food chain. Carnivorous fish were generally found by Yannai and Sachs (1978) to contain higher mercury concentrations than either herbivorous or omnivorous fish. From 77 to 100% of the total mercury in fish containing more than 0.5 mg/kg of mercury was in the form of methylmercury. The mercury concentration in benthic invertebrates were also found to reflect the concentration of the sediment. Kudo and Mortimer (1979) reported that fish in contact with mercury contaminated sediments accumulated higher mercury concentrations than fish exposed to the same mercury concentration, but which did not come in contact with the sediments.

If the source of mercury contamination to an aquatic system is removed or contamination is reduced, the mercury levels in an aquatic system can gradually decline. The half-life for methylmercury in marine fishes ranges from approximately 400 to 1,000 days, depending upon species (Wood, 1971). In freshwater fish, the half-life for total mercury is reported to be approximately 44 days (Krenkel, 1971).

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The mercury content of freshwater fish was found to decrease after the input of mercury into the system was decreased. The reduction of mercury concentrations in the fish was believed to be due to decreased mercury concentrations in the water column since the time period over which the reduction in fish concentration occurred was too brief for a reduction in the sediment mercury concentration to occur. Thus, reduction in the source of mercury without controlling the sediment concentration can reduce mercury levels in fish (Armstrong and Scott, 1979).

Suckchaeroen and Lodenius (1980) collected samples from a drainage system in Thailand one and four years after the initial operation of a waste treatment system at a caustic soda plant. The mercury levels in fish decreased by more than 50% between the two sampling periods. Significant levels of mercury, however, were still present in the fish and sediments. For example, fish from contaminated areas contained 0.1 to 1.38 ppm; whereas, fish from control areas contained only 0.1 to 0.30 ppm of mercury.

Uptake of mercury by sandworms, hard clams, and grass shrimp from contaminated sediments was not found by Rubinstein et al. (1983). The high sulfur and organic content of the sediments may have reduced the availability of the mercury.

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Methylmercury comprises approximately 90% of the total mercury present in the edible portions of marine and freshwater fish. Methylmercury concentrations ranged from 0.08 to 0.73 mg/kg in marine fish. By comparison, the U. S. FDA has established 1.0 mg/kg as the recommended maximum level for mercury in fish (Luten et al., 1980). Westoo (1973) reported that methylmercury comprised approximately 93% of total mercury in the flesh of Salmon and Sea Trout. Age was not a factor in determining the proportion of methylmercury.

Turner et al. (1980) found significantly higher blood methylmercury concentrations in populations consuming large quantities of marine fish. The study group consumed an average of 1.6 kg of fish per person per week compared to a control group which consumed 0.3 kg of fish per person per week. The average blood methylmercury concentration averaged 82 ng/ml in the study group, and 9.9 ng/ml in the control group. No evidence of methylmercury intoxication, however, was found.

Terrestrial Environment

Bioaccumulation of methylmercury can also occur in the terrestrial food chain. Rats (*Sigmodon hispidus*) fed grass

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(Festuca sp.) containing 0.6 ng/g of methylmercury had methylmercury concentrations of 1.4 (muscle) and 1.3 (liver) ng/g. Methylmercury transfer from the grass to the rats was 99% efficient, and once in the rats, methylmercury had a half-life of 9.5 days. Elemental mercury also accumulated in the rats. The grass contained 71 ng/g of mercury; whereas, the rats' muscle and liver tissue contained 119.4 and 34.6 ng/g, respectively (Huckabee et al., 1981).

Intestinal microorganisms appear to enhance the excretion of ingested mercury. Germ-free mice were found to excrete roughly one-half of the amount of mercury excreted by control mice. Accumulation of mercury in the organs was higher in the germ-free mice as opposed to the control mice (Nakamura et al., 1977).

The position of freshwater and marine birds in their food chain may be a significant factor in the accumulation of mercury by birds. Generally, the higher the bird is in the food chain, the higher the levels of mercury that re present. Fimreite (1974) found that carniovorous birds (e.g., raven) accumulated as much as ten times more mercury than surface feeding firds (e.g., ducks). Norheim and Kjos-Hanssen (1984) studied mercury accumulation in birds and found that the

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trophic levels of the birds and the mercury concentration in the birds were not related. Fimreite (1979) received the literature on mercury accumulation in birds.

Bioaccumulation in a terrestrial food chain consisting of tomatoes, aphids, and green lacewing larvae was investiated by Haney and Lipsey (1973). Lacewings accumulated 4,128 times the mercury concentrations in which the tomatoes were grown. In general, mercury does not enter the terrestrial food chain in significant quantities. Binding of mercury to the soil and the cell walls of plant roots limits entry of mercury into the food chain. On the other hand, significant quantities of mercury can enter the aquatic food chain, primarily as a result of mercury methylation (Lorenz, 1979).

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APPENDIX 1

EXCERPT FROM THE U.S. EPA (1983)
WATER QUALITY CRITIERIA DOCUMENT FOR MERCURY

NATIONAL CRITERIA

To protect freshwater aquatic life and its uses, in each 30 consecutive days: (A) the average concentration of active mercury (operationally defined as the mercury that passes through a 0.45 um membrane filtered after the sample is acidified to pH = 4 with nitric acid) should not exceed 0.20 ug/l; (b) the maximum concentration should not exceed 1.1 ug/l; and (c) the concentration may be between 0.20 and 1.1 ug/l for up to 96 hours. these values are based on tests on divalent inorganic mercury and will be too high if a substantial portion of the active mercury is methylmercury. These values will also be too high if bioaccumulation is greater in a field situation than in laboratory tests. In addition, the value of 0.20 ug/l may not protect some salmonids and centrarchids from chronic toxicity and some species will be at the FDA action level of 1.0 mg/kg.

To protect saltwater aquatic life and its uses, in each 30 consecutive days: (a) the average concentration of active mercury should not exceed 0.10 ug/l; (b) the maximum concentration should not exceed 1.9 ug/l; and (c) the concentration may be between 0.10 and 1.9 ug/l for up to 96 hours. these values are based on tests on divalent inorganic mercury and will be too high if a substantial portion of the active mercury is methylmercury. These values will also be too high if bioaccumulation is greater in a field situation than in laboratory tests.

Table 1. Acute toxicity of mercury to aquatic animals

Species	Method*	Chemical	LC50 or EC50 (µg/l)**	Species Mean Acute Value (µg/l)**	Reference
		FRESHWATER SPECIES			
		Divalent Inorganic Mercury			
Rotifer, *Philodina acuticornis*	S, U	Mercuric chloride	518	-	Bulkema, et al. 1974
Rotifer, *Philodina acuticornis*	S, U	Mercuric chloride	1,185	783.4	Bulkema, et al. 1974
Worm, *Nais* sp.	S, M	Mercuric nitrate	1,000	1,000	Rehwoldt, et al. 1973
Snail (adult), *Amnicola* sp.	S, M	Mercuric nitrate	80	80	Rehwoldt, et al. 1973
Snail, *Aplexa hypnorum*	S, U	Mercuric chloride	370	370	Holcombe, et al. Manuscript
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	5	-	Biesinger & Christensen, 1972
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	3.177	-	Canton & Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	3.177	-	Canton & Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	1.330	-	Canton & Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	1.626	-	Canton & Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	2.291	-	Canton & Adema, 1978
Cladoceran, *Daphnia magna*	S, U	Mercuric chloride	2.069	2.442	Canton & Adema, 1978

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Table 1. (Continued)

Species	Method[a]	Chemical	LC50 or EC50 (µg/l)[aa]	Species Mean Acute Value (µg/l)[aa]	Reference
Cladoceran, *Daphnia pulex*	S, U	Mercuric chloride	2,217	-	Canton & Adema, 1978
Cladoceran, *Daphnia pulex*	S, U	Mercuric chloride	2,217	2,217	Canton & Adema, 1978
Scud, *Gammarus* sp.	S, M	Mercuric nitrate	10	10	Rehwoldt, et al. 1973
Crayfish (male, mixed ages), *Faxonella clypeatus*	R, M	Mercuric chloride	20	20	Holt & Fingerman, 1977; Holt, 1981
Crayfish, *Orconectes limosus*	S, U	Mercuric chloride	50	50	Boutet & Chaisemartin, 1973
Mayfly, *Ephemerella subvaria*	S, U	Mercuric chloride	2,000	2,000	Warnick & Bell, 1969
Damselfly, (Unidentified)	S, M	Mercuric nitrate	1,200	1,200	Rehwoldt, et al. 1973
Stonefly, *Acroneuria lycorias*	S, U	Mercuric chloride	2,000	2,000	Warnick & Bell, 1969
Caddisfly, *Hydropsyche betteni*	S, U	Mercuric chloride	2,000	2,000	Warnick & Bell, 1969
Caddisfly, (Unidentified)	S, M	Mercuric nitrate	1,200	1,200	Rehwoldt, et al. 1973
Midge, *Chironomus* sp.	S, M	Mercuric nitrate	20	20	Rehwoldt, et al. 1973
Coho salmon (juvenile), *Oncorhynchus kisutsch*	R, M	Mercuric chloride	240	240	Lorz, et al. 1978
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Mercuric chloride	400	-	MacLeod & Pessah, 1973

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Table 1. (Continued)

Species	Method*	Chemical	LC50 or EC50 (µg/l)**	Species Mean Acute Value (µg/l)**	Reference
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Mercuric chloride	280	-	Macleod & Pessah, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Mercuric chloride	220	-	Macleod & Pessah, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Mercuric chloride	155	-	Matida, et al. 1971
Rainbow trout (juvenile), *Salmo gairdneri*	FT, M	Mercuric chloride	275	275	Lock, et al. 1981
Fathead minnow, *Pimephales promelas*	FT, M	Mercuric chloride	150	-	Call, et al. 1982
Fathead minnow, *Pimephales promelas*	FT, M	Mercuric chloride	168	158.7	Snarski & Olson, 1982
Mosquitofish (female), *Gambusia affinis*	S, U	Mercuric chloride	180	180	Joshi & Rege, 1980
Guppy (116-157 mg), *Poecilia reticulata*	R, U	Mercuric chloride	30	-	Deshmukh & Marathe, 1980
Guppy (363-621 mg), *Poecilia reticulata*	R, U	Mercuric chloride	54	40.25	Deshmukh & Marathe, 1980
Bluegill (juvenile), *Lepomis macrochirus*	S, U	Mercuric chloride	160	160	Holcombe, et al. Manuscript
		Methylmercury			
Rainbow trout (larva), *Salmo gairdneri*	R, U	Methylmercuric chloride	24	-	Wobeser, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	R, U	Methylmercuric chloride	42	-	Wobeser, 1973
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Methylmercuric chloride	25	-	Matida, et al. 1971

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Table 1. (Continued)

Species	Method*	Chemical	LC50 or EC50 (µg/l)**	Species Mean Acute Value** (µg/l)	Reference
Rainbow trout (juvenile), *Salmo gairdneri*	FT, M	Methylmercuric chloride	24	27.89	Lock, et al. 1981
Brook trout (juvenile), *Salvelinus fontinalis*	FT, M	Methylmercuric chloride	84	-	McKim, et al. 1976
Brook trout (yearling), *Salvelinus fontinalis*	FT, M	Methylmercuric chloride	65	73.89	McKim, et al. 1976
		Other Mercury Compounds			
Rainbow trout (juvenile), *Salmo gairdneri*	FT, U	Phenylmercuric acetate	5	5	Matida, et al. 1971
Rainbow trout (2 mos), *Salmo gairdneri*	FT, M	Mercurous nitrate	33.0	33.0	Hale, 1977
Goldfish, *Carassius auratus*	S, U	Phenylmercuric lactate	82	82	Ellis, 1947
Fathead minnow, *Pimephales promelas*	S, M	Mercuric acetate	40	40	Curtis, et al. 1979
Fathead minnow, *Pimephales promelas*	S, M	Mercuric thiocyanate	115	115	Curtis, et al. 1979
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Ethylmercuric p-toluene sulfonanilide	51	51	Clemens & Sneed, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Ethylmercuric phosphate	49	49	Clemens & Sneed, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Phenylmercuric acetate	1,970	1,970	Clemens & Sneed, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Phenylmercuric acetate	28	28	Clemens & Sneed, 1958a, 1959
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Pyridylmercuric acetate	<176	-	Clemens & Sneed, 1958b

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Table 1. (Continued)

Species	Method*	Chemical	LC50 or EC50 (µg/l)**	Species Mean Acute Value** (µg/l)	Reference
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Pyridylmercuric acetate	224	-	Clemens & Sneed, 1958b
Channel catfish (juvenile), *Ictalurus punctatus*	S, U	Pyridylmercuric acetate	<153	<182	Clemens & Sneed, 1958b
Mosquitofish (female), *Gambusia affinis*	S, U	Methoxy ethyl mercuric chloride	910	910	Holcombe, et al. Manuscript
Mosquitofish (female), *Gambusia affinis*	S, U	Phenylmercuric acetate	37	37	Joshi & Rege, 1980
Mosquitofish (female), *Gambusia affinis*	S, U	Phenylmercuric acetate (Ceresan)	44	44	Joshi & Rege, 1980
		SALTWATER SPECIES			
		Divalent Inorganic Mercury			
Polychaete worm (adult), *Neanthes arenaceodentata*	S, U	Mercuric chloride	96	-	Reish, et al. 1976
Polychaete worm (juvenile), *Neanthes arenaceodentata*	S, U	Mercuric chloride	100	97.98	Reish, et al. 1976
Sand worm (adult), *Nereis virens*	S, U	Mercuric chloride	70	70	Eisler & Hennekey, 1977
Polychaete worm (larva), *Capitella capitata*	S, U	Mercuric chloride	14	14	Reish, et al. 1976
Blue mussel, *Mytilus edulis*	S, U	Mercuric chloride	5.8	5.8	Martin, et al. 1981
Bay scallop (juvenile), *Argopecten irradians*	S, U	Mercuric chloride	89	89	Nelson, et al. 1976
Pacific oyster, *Crassostrea gigas*	S, U	Mercuric chloride	6.7	-	Martin, et al. 1981

Table 1. (Continued)

Species	Method*	Chemical	LC50 or EC50 (µg/l)**	Species Mean Acute Value (µg/l)**	Reference
Pacific oyster, *Crassostrea gigas*	S, M	Mercuric chloride	5.7	-	Glickstein, 1978
Pacific oyster, *Crassostrea gigas*	S, M	Mercuric nitrate	5.5	5.944	Glickstein, 1978
Eastern oyster, *Crassostrea virginica*	S, U	Mercuric chloride	5.6	-	Calabrese & Nelson, 1974; Calabrese, et al. 1977
Eastern oyster, *Crassostrea virginica*	S, U	Mercuric chloride	10.2	7.558	MacInnes & Calabrese, 1978
Brackish water clam (adult), *Rangia cuneata*	S, M	Mercuric chloride	58	-	Dillon, 1977
Brackish water clam (adult), *Rangia cuneata*	S, M	Mercuric chloride	122	84.12	Dillon, 1977
Quahog clam, *Mercenaria mercenaria*	S, U	Mercuric chloride	4.8	4.8	Calabrese & Nelson, 1974; Calabrese, et al. 1977
Soft-shell clam (adult), *Mya arenaria*	S, U	Mercuric chloride	400	400	Elsler & Hennekey, 1977
Copepod, *Pseudodiaptomus coronatus*	S, U	Mercuric chloride	79	79	Gentile, 1982
Copepod, *Eurytemora affinis*	S, U	Mercuric chloride	158	158	Gentile, 1982
Copepod, *Acartia clausi*	S, U	Mercuric chloride	10	10	Gentile, 1982
Copepod (adult), *Acartia tonsa*	S, U	Mercuric chloride	10	-	Sosnowski & Gentile, 1978
Copepod (adult), *Acartia tonsa*	S, U	Mercuric chloride	14	-	Sosnowski & Gentile, 1978

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Table 1. (Continued)

Species	Method[a]	Chemical	LC50 or EC50 (µg/l)[**]	Species Mean Acute Value (µg/l)[**]	Reference
Copepod (adult), *Acartia tonsa*	S, U	Mercuric chloride	15	-	Sosnowski & Gentile, 1978
Copepod (adult), *Acartia tonsa*	S, U	Mercuric chloride	20	14.32	Gentile, 1982
Copepod, *Nitocra spinipes*	S, U	Mercuric chloride	230	230	Bengtsson, 1978
Mysid, *Mysidopsis bahia*	FT, M	Mercuric chloride	3.5	3.5	Gentile, et al. 1983
White shrimp (adult), *Penaeus setiferus*	S, U	Mercuric chloride	17	17	Green, et al. 1976
American lobster (larva), *Homarus americanus*	S, U	Mercuric chloride	20	20	Johnson & Gentile, 1979
Hermit crab (adult), *Pagurus longicarpus*	S, U	Mercuric chloride	50	50	Eisler & Hennekey, 1977
Dungeness crab (larva), *Cancer magister*	S, U	Mercuric chloride	8.2	7.4	Martin, et al. 1981
Dungeness crab (larva), *Cancer magister*	S, M	Mercuric chloride	6.6	7.4	Glickstein, 1978
Green crab (larva), *Carcinus maenas*	S, U	Mercuric chloride	14	14	Connor, 1972
Starfish (adult), *Asterias forbesii*	S, U	Mercuric chloride	60	60	Eisler & Hennekey, 1977
Haddock (larva), *Melanogrammus aeglefinus*	S, U	Mercuric chloride	98	98	Cardin, 1982
Mummichog, *Fundulus heteroclitus*	S, U	Mercuric chloride	300	-	Dorfman, 1977

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Table 1. (Continued)

Species	Method[a]	Chemical	LC50 or EC50 (µg/l)[b]	Species Mean Acute Value (µg/l)[b]	Reference
Mummichog, *Fundulus heteroclitus*	S, U	Mercuric chloride	200	-	Dorfman, 1977
Mummichog, *Fundulus heteroclitus*	S, U	Mercuric chloride	300	-	Dorfman, 1977
Mummichog, *Fundulus heteroclutus*	S, U	Mercuric chloride	300	-	Dorfman, 1977
Mummichog (adult), *Fundulus heteroclitus*	S, U	Mercuric chloride	800	-	Eisler & Hennekey, 1977
Mummichog (adult), *Fundulus heteroclitus*	S, U	Mercuric chloride	2,000	453.0	Klaunig, et al. 1975
Atlantic silverside (larva), *Menidia menidia*	S, U	Mercuric chloride	144	-	Cardin, 1982
Atlantic silverside (larva), *Menidia menidia*	S, U	Mercuric chloride	125	-	Cardin, 1982
Atlantic silverside (juvenile), *Menidia menidia*	S, U	Mercuric chloride	86	115.7	Cardin, 1982
Fourspine stickleback (adult), *Apeltes quadracus*	S, U	Mercuric chloride	315	315	Cardin, 1982
Winter flounder (larva), *Pseudopleuronectes americanus*	S, U	Mercuric chloride	1,820	-	Cardin, 1982
Winter flounder (larva), *Pseudopleuronectes americanus*	S, U	Mercuric chloride	1,560	-	Cardin, 1982
Winter flounder (larva), *Pseudopleuronectes americanus*	S, U	Mercuric chloride	1,810	-	Cardin, 1982

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Table 1. (Continued)

Species	Method*	Chemical	LC50 or EC50 (µg/l)**	Species Mean Acute Value (µg/l)**	Reference
Winter flounder (larva), *Pseudopleuronectes americanus*	S, U	Mercuric chloride	1,320	-	Cardin, 1982
Winter flounder (larva), *Pseudopleuronectes americanus*	S, U	Mercuric chloride	1,960	1,678	Cardin, 1982
		Methylmercury			
Amphipod (adult), *Gammarus duebeni*	S, U	Methylmercuric chloride	150	150	Lockwood & Inman, 1975
		Other Mercury Compounds			
Grass shrimp (adult), *Palaemonetes pugio*	S, M	Mercuric acetate	60	60	Curtis, et al. 1979
Grass shrimp (adult), *Palaemonetes pugio*	S, M	Mercuric thiocyanate	90	90	Curtis, et al. 1979
Mummichog, *Fundulus heteroclitus*	S, U	Mercurous sulfate	6,800	-	Dorfman, 1977
Mummichog, *Fundulus heteroclitus*	S, U	Mercurous sulfate	300	1,428	Dorfman, 1977

* S = static, R = renewal, FT = flow-through, U = unmeasured, M = measured.

**Results are expressed as mercury, not as the chemical.

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Table 2. Chronic toxicity of mercury to aquatic animals

Species	Test*	Chemical	Limits (µg/l)**	Chronic Value (µg/l)**	Reference
		FRESHWATER SPECIES			
		Divalent Inorganic Mercury			
Cladoceran, *Daphnia magna*	LC***	Mercuric chloride	0.72-1.28	0.96	Biesinger, et al. 1982
Cladoceran, *Daphnia magna*	LC****	Mercuric chloride	0.91-1.82	1.287	Biesinger, et al. 1982
Fathead minnow, *Pimephales promelas*	LC	Mercuric chloride	<0.26*****	<0.26	Snarski & Olson, 1982
Fathead minnow, *Pimephales promelas*	ELS	Mercuric chloride	<0.23*****	<0.23	Call, et al. 1982
		Methylmercury			
Cladoceran, *Daphnia magna*	LC***	Methylmercuric chloride	<0.04*****	<0.04	Biesinger, et al. 1982
Cladoceran, *Daphnia magna*	LC****	Methylmercuric chloride	0.52-0.87	0.6726	Biesinger, et al. 1982
Brook trout, *Salvelinus fontinalis*	LC	Methylmercuric chloride	0.29-0.93	0.5193	McKim, et al. 1976.
		Other Mercury Compounds			
Cladoceran, *Daphnia magna*	LC****	Phenylmercuric acetate	1.12-1.90	1.459	Biesinger, et al. 1982
		SALTWATER SPECIES			
		Divalent Inorganic Mercury			
Mysid, *Mysidopsis bahia*	LC	Mercuric chloride	0.8-1.6	1.131	Gentile, et al. 1983

Table .. (Continued)

* LC = life cycle or partial life cycle, ELS = early life stage.

** Results are expressed as mercury, not as the chemical.

*** Flow-through

**** Renewal

*****Adverse effects occurred at all concentrations tested.

Acute-Chronic Ratio

Species	Acute Value (µg/l)	Chronic Value (µg/l)	Ratio
	Divalent Inorganic Mercury		
Cladoceran, *Daphnia magna*	5	0.96	5.208
Cladoceran, *Daphnia magna*	5	1.287	3.885
Fathead minnow, *Pimephales promelas*	150	<0.23	>652.2
Fathead minnow, *Pimephales promelas*	168	<0.26	>646.2
Mysid, *Mysidopsis bahia*	3.5	1.131	3.095
	Methylmercury		
Brook trout *Salvelinus fontinalis*	74	0.5193	142.5

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Table 3. Summary of data in Tables 1 and 2 on acute and chronic toxicity of mercury to aquatic animals

Rank[a]	Family	Family Mean Acute Value (µg/l)	Species	Species Mean Acute Value (µg/l)	Species Mean Acute-Chronic Ratio
			FRESHWATER SPECIES		
			Divalent Inorganic Mercury		
16	Perlidae	2,000	Stonefly, *Acroneuria lycorias*	2,000	-
15	Ephemerellidae	2,000	Mayfly, *Ephemerella subvaria*	2,000	-
14	Hydropsychidae	1,549	Caddisfly, *Hydropsyche betteni*	2,000	-
			Caddisfly, (Unidentified)	1,200	-
13	Coenagrionidae	1,200	Damselfly, (Unidentified)	1,200	-
12	Naididae	1,000	Worm, *Nais* sp.	1,000	-
11	Philodinidae	783.4	Rotifer, *Philodina acuticornis*	783.4	-
10	Physidae	370	Snail, *Aplexa hypnorum*	370	-
9	Salmonidae	256.9	Coho salmon, *Oncorhynchus kisutch*	240	-
			Rainbow trout, *Salmo gairdneri*	275	-
8	Centrarchidae	160	Bluegill, *Lepomis macrochirus*	160	-
7	Cyprinidae	158.7	Fathead minnow, *Pimephales promelas*	158.7	>649.2
6	Poeciliidae	85.12	Mosquitofish, *Gambusia affinis*	180	-

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Table 3. (Continued)

Rank[a]	Family	Family Mean Acute Value (µg/l)	Species	Species Mean Acute Value (µg/l)	Species Mean Acute-Chronic Ratio
			Guppy, *Poecilia reticulata*	40.25	-
5	Bithynilidae	80	Snail, *Amnicola* sp.	80	-
4	Astacidae	31.62	Crayfish, *Faxonella clypeatus*	20	-
			Crayfish, *Orconectes limosus*	50	-
3	Chironomidae	20	Midge, *Chironomus* sp.	20	-
2	Gammaridae	10	Scud, *Gammarus* sp.	10	-
1	Daphnidae	2.327	Cladoceran, *Daphnia magna*	2.442	4.498
			Cladoceran, *Daphnia pulex*	2.217	-
			SALTWATER SPECIES		
			Divalent Inorganic Mercury		
24	Pleuronectidae	1,678	Winter flounder, *Pseudopleuronectes americanus*	1,678	-
23	Cyprinodontidae	453.0	Mummichog, *Fundulus heteroclitus*	453.0	-
22	Myidae	400	Soft-shell clam, *Mya arenaria*	400	-
21	Gasterosteidae	315	Fourspine stickleback, *Apeltes quadracus*	315	-
20	Canthocamptidae	230	Copepod, *Nitocra spinipes*	230	-
19	Temoridae	158	Copepod, *Eurytemora affinis*	158	-

829930151

Table 3. (Continued)

Rank[a]	Family	Family Mean Acute Value (µg/l)	Species	Species Mean Acute Value (µg/l)	Species Mean Acute-Chronic Ratio
18	Atherinidae	115.7	Atlantic silverside, *Menidia menidia*	115.7	-
17	Gadidae	98	Haddock, *Melanogrammus aeglefinus*	98	-
16	Pectinidae	89	Bay scallop, *Argopecten irradians*	89	-
15	Mactridae	84.12	Brackish water clam, *Rangia cuneata*	84.12	-
14	Nereidae	82.82	Polychaete worm, *Neanthes arenaceodentata*	97.98	-
			Sand worm, *Nereis virens*	70	-
13	Pseudodiaptomidae	79	Copepod, *Pseudodiaptomus coronatus*	79	-
12	Asteriidae	60	Starfish, *Arterias forbesii*	60	-
11	Paguridae	50	Hermit crab, *Pagurus longicarpus*	50	-
10	Nephropsidae	20	American lobster, *Homarus americanus*	20	-
9	Penaeidae	17	White shrimp, *Penaeus setiferus*	17	-
8	Portunidae	14	Green crab, *Carcinis maenas*	17	-
7	Capitellidae	14	Polychaete worm, *Capitella capitata*	14	-
6	Acartiidae	11.97	Copepod, *Acartia clausi*	10	-

8299930152

Table 3. (Continued)

Rank[a]	Family	Family Mean Acute Value (µg/l)	Species	Species Mean Acute Value (µg/l)	Species Mean Acute-Chronic Ratio
			Copepod, *Acartia tonsa*	14.32	-
5	Cancridae	7.4	Dungeness crab, *Cancer magister*	7.4	-
4	Ostreidae	6.703	Pacific oyster, *Crassostrea gigas*	5.944	-
			Eastern oyster, *Crassostrea virginica*	7.558	-
3	Mytilidae	5.8	Blue mussel, *Mytilus edulis*	5.8	-
2	Veneridae	4.8	Quahog clam, *Mercenaria mercenaria*	4.8	-
1	Mysidae	3.5	Mysid, *Mysidopsis bahia*	3.5	3.095

[a] Ranked from most resistant to most sensitive based on Family Mean Acute Value.

Divalent Inorganic Mercury

Final Acute-Chronic Ratio = 3.731 (see text)

Fresh water

Final Acute Value = 2.165 µg/l

Criterion maximum concentration = (2.165 µg/l) / 2 = 1.082 µg/l

Final Chronic Value = (2.165 µg/l) / 3.731 = 0.5803 µg/l

Salt water

Final Acute Value = 3.848 µg/l

Criterion maximum concentration = (3.848 µg/l) / 2 = 1.924 µg/l

Final Chronic Value = (3.848 µg/l) / 3.731 = 1.031 µg/l

829930153

Table 4. Toxicity of mercury to aquatic plants

Species	Chemical	Effect	Result (µg/l)[a]	Reference
		FRESHWATER SPECIES		
		Divalent Inorganic Mercury		
Alga, *Chlorella vulgaris*	Mercuric chloride	33-day EC50, cell division inhibition	1,030	Rosko & Rachlin, 1977
Blue alga, *Microcystis aeruginosa*	Mercuric chloride	8 day incipient inhibition	5	Bringmann, 1975; Bringmann & Kuhn, 1976, 1978a,b
Green alga, *Scenedesmus quadricauda*	Mercuric chloride	8 day incipient inhibition	70	Bringmann, 1975; Bringmann & Kuhn, 1976, 1978a,b, 1979, 1980b
Water milfoil, *Myriophyllum spicatum*	Mercuric chloride	32-day EC50, root growth inhibition	1,200	Stanley, 1974
		SALTWATER SPECIES		
		Divalent Inorganic Mercury		
Seaweed, *Ascophyllum nodosum*	Mercuric chloride	10-day EC50, growth	100	Stromgren, 1980
Diatom, *Ditylum brightwellii*	Mercuric chloride	5-day EC50, growth	10	Canterford & Canterford, 1980
Seaweed, *Fucus serratus*	Mercuric chloride	10-day EC50, growth	160	Stromgren, 1980
Seaweed, *Fucus spiralis*	Mercuric chloride	10-day EC50, growth	80	Stromgren, 1980
Seaweed, *Fucus vesiculosus*	Mercuric chloride	10-day EC50, growth	45	Stromgren, 1980
Giant kelp, *Macrocystis pyrifera*	Mercuric chloride	4-day EC50, growth	50	Clendenning & North, 1959
Seaweed, *Pelvetia canaliculata*	Mercuric chloride	10-day EC50, growth	130	Stromgren, 1980

[a] Results are expressed as mercury, not as the chemical.

829930154

Table 5. Bioaccumulation of mercury by aquatic organisms

Species	Tissue	Chemical	Duration (days)	Bioconcentration Factor*	Reference
		FRESHWATER SPECIES			
		Divalent Inorganic Mercury			
Fathead minnow, *Pimephales promelas*	Whole body	Mercuric chloride	287	4,994**	Snarski & Olson, 1982
		Methylmercury			
Brook trout, *Salvelinus fontinalis*	Muscle	Methylmercuric chloride	273	19,000	McKim, et al. 1976
Brook trout, *Salvelinus fontinalis*	Whole body	Methylmercuric chloride	273	13,000	McKim, et al. 1976
Brook trout, *Salvelinus fontinalis*	Muscle and whole body	Methylmercuric chloride	756	12,000	McKim, et al. 1976
Fathead minnow, *Pimephales promelas*	Whole body	Methylmercuric chloride	336	64,000	Olson, et al. 1975
		SALTWATER SPECIES			
		Divalent Inorganic Mercury			
Eastern oyster (adult), *Crassostrea virginica*	Soft parts	Mercuric chloride	74	10,000	Kopfler, 1974
American lobster (adult), *Homarus americanus*	Tail muscle	Mercuric chloride	30	129	Thurberg, et al. 1977
		Methylmercury			
Eastern oyster (adult), *Crassostrea virginica*	Soft parts	Methylmercuric chloride	74	40,000	Kopfler, 1974
		Other Mercury Compounds			
Eastern oyster (adult), *Crassostrea virginica*	Soft parts	Phenylmercuric chloride	74	40,000	Kopfler, 1974

* Results are based on mercury, not the chemical.

**From concentrations that caused adverse effects in a life cycle test.

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Table 5. (Continued)

Maximum Permissible Tissue Concentration			
Species	Action Level or Effect	Concentration (mg/kg)	References
Man	Edible fish or shellfish	1.0	U.S. FDA Guideline 7408.09, 1978
Mink, *Mustela vison*	Histological evidence of injury	≤1.1	Wobeser, 1976
Brook trout, *Salvelinus fontinalis*	Death (700 days)	5-7	McKim, et al. 1976

Methylmercury

Freshwater Final Residue Value = (1.0 mg/kg) / 23,000 = 0.000043 mg/kg = 0.043 µg/l

Saltwater Final Residue Value = (1.0 mg/kg) / 40,000 = 0.000025 mg/kg = 0.025 µg/l

Divalent Inorganic Mercury

Freshwater Final Residue Value = (1.0 mg/kg) / 4,994 = 0.00020 mg/kg = 0.20 µg/l

Saltwater Final Residue Value = (1.0 mg/kg) / 10,000 = 0.00010 mg/kg = 0.10 µg/l

829930156

CHAPTER B

REMEDIAL INVESTIGATIONS AT RELATED SITES

SUMMARY

A total of 17 related studies were intensively reviewed. Information was collected from articles available in academic publications; general government documents, such as proceedings of meetings; documents specific to a site. such as Environmental Impact Statements (EIS) and Remedial Action Plan/Feasibility Studies (RAP/FS) and personal communications. Relevant information was then summarized to indicate the type and extent of the contamination; health and environmental impacts; the research studies conducted; the remedial action review process and selection; the status of remediation and the monitoring requirements.

At most areally large sites, such as rivers, estuaries, large lakes or large bays, no action has been taken or is planned. At those sites where action has been taken or is planned dredging is the preferred remedial method. Due to the very high cost of remediation the original dredging plan for the Hudson River and Waukegan Harbor were scaled down. However, even these scaled-down plans have yet to be initiated due to funding problems.

With the exception of the North Holston River the majority of remedial plans for the clean-up of mercury contamination have been developed and implemented at sites outside the United States. Japan has been especially active in the remediation of mercury-contaminated sediments, examples being Minamata Bay and Kitakyusyu Port.

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INTRODUCTION

In order to assess what remedial action(s) will be the most effective remedy for the contamination at the Berrys Creek site, related sites were reviewed. These sites are contaminated with mercury, other heavy metal and/or organics that have properties similar to mercury, such as slow or no degradation, low water solubility, an affinity for soil and the potential for significant bioaccumulation.

The review consisted of determining what, if any, remedal action was selected, the rationale behind the choice, the status of implementation and the ultimate effect of the implementation. Any research studies and findings of the studies were also reviewed.

In addition to the development of a summary document for each related site; recommendations, based on studies conducted concerning these sites and the potential usefulness of the studies, are made for site specific field and research investigations at Berrys Creek. Long-term monitoring activities are also recommended.

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SUMMARY OF SITE HISTORIES AND MAJOR FINDINGS

The sites inventoried range from very large sites such as the Hudson River, New York and James River, Virginia to relatively small sites such as Lake Trummen, Sweden and Outboard Marine Corporation, Waukegan, Illinois. The Berrys Creek site, while constituting a significant area would be considered as a small to moderate site when compared to the large related sites.

Based on the limited information available on contaminate concentrations Berrys Creek would be considered highly contaminated, particularly in the area immediately downstream of the former outfall.

In the majority of sites, after a study as to what would be the preferable remedial alternative, it was decided the no action alternative was preferable or the alternative selected has not as yet been implemented. The reason for the choice of the no action alternative was typically the large area contaminated which coincided with prohibitive costs. The reason for non-implementation of a selected remedy is typically lack of funding.

A summary of the sites investigated and the status of the sites are identified in Table B-1. The review of related sites includes a comprehensive computer base search as well as numerous calls to project leaders with state agencies and other organizations to obtain the details of each study. Through the progress of this study considerable effort was made to find as much detail on as many closely related studies as possible. While gaps may exist in some of the study

summaries as relates to the items "suggested" in the consent decree, the summaries represent a vast accumulation of literature and summarize the most pertinent information available.

This review of related sites indicates a lack of the implementation of novel remedial technologies, the two alternatives that have been utilized are dredging and no action. However, as previously stated, in the United States in all except one site reviewed, remediation is pending due to the high cost and unavailability of funds. The initially recommended remedy for the Hudson River and Waukegan Harbor were revised downward in scope due to their very high cost and have not as yet been implemented.

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TABLE B-1

RELATED SITES REVIEWED AND THE RECOMMENDED REMEDIAL ACTION

Site Name	Pollutant	Recommended Remedy	Status
San Francisco Bay, California	Hg, heavy metals & organics	no action	
Lake Trummen, Sweden	Hg & organic sludge	dredging	complete
James River & Estuary, Virginia	Kepone	no action	
Hudson River, New York	PCBs	hot spot dredging	pending
Brunswick River Marsh, Georgia	Hg	no action	
Ottawa River, Canada	Hg & organic sludge	no action	
Wagiboon-English River, Canada	Hg-organic sludge	in place cover	pending
Flin Flon, Canada	Zn, Cd, Cu & Hg	no action	
OMC, Illinois	PCBs	dredging	pending
Holston River, Virginia	Hg	erosion control & hot spot dredging	complete
Detroit area of Great Lakes, Michigan	Hg	no action	
Mobile River, Alabama	Hg	no action	
Shenandoah River, Virginia	Hg	no action	
Everglades, Florida	Hg	no action	
Bellingham Bay, Washington	Hg	no action	
Kitakyusyu Port, Japan	Hg & oil and grease	dredging	complete
Minamata Bay, Japan	Hg	dredging	pending

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RECOMMENDED FIELD & RESEARCH INVESTIGATIONS

Based on the research studies performed in conjunction with related sites the following potentially useful studies are recommended:

1. A comprehensive and applicable mapping of the contamination in Berrys Creek.
2. An assessment of the potential for continuing releases of contaminants into Berrys Creek.
3. Modeling of predictions of the potential movement of mercury in the environment and in the food chain. Included in this recommendation would be the acquisition of those data needed to properly develop these models. The needed data would likely include the following general information:
   a. information on sediment transport (bed load and suspended)
   b. movement of mercury to and from the marshlands
   c. information on uptake and depuration rates of mercury in organisms of interest needed to develop a food web model.
4. An assessment of the hydraulics in the area and the impact a severe flood and or surge tide would have on the mercury in the area.
5. A more complete understanding of mercury methylation and how this phenomena influences and is influenced by the conditions in Berrys Creek. It is noted attention is already being given to this recommendation.

6. A more detailed assessment of those sites where remediation activities have occurred or are occurring at this time. The success these remedies are having in controlling the movement of contaminates in the environment and food chain must be assessed.

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RECOMMENDATIONS FOR IMMEDIATE AND LONG-TERM MONITORING

These monitoring recommendations are based on environmental impacts that occurred at other sites. Monitoring necessary for the development of a model are not included, however, there will be overlap between monitoring to assess environmental impact and monitoring used to develop a model.

1. Monitor the movement of contaminated sediments down the creek.
2. Monitor the potential for sediment deposition over existing sediments.
3. Monitor the accumulation of mercury in resident and transient species; with particular emphasis on those species considered important to man or that are especially sensitive to the effects of mercury.
4. Monitor water quality (ongoing).
5. Monitor development
6. Monitor persons who are at risk to contamination either through proximity to the site or through ingestion of foods (i.e., fish and shell fish) from the contaminated area. It is possible no one or very few persons will be members of the latter at risk category. If it is determined persons are being contaminated a more scientific design should be developed including a control population. Also an effort should be made to identify the mechanism of contamination.

SAN FRANCISCO BAY

SITE SPECIFIC CONTAMINATION

Natural and anthropogenic sources of heavy metals have resulted in water borne and sediment concentrations of heavy metals, including mercury, being significantly higher than background in isolated areas of the bay. However, other areas in the bay are at background level.

The reasons for the difference between areas are not completely understood but are believed to be at least partially based on circulation patterns, point source discharges and naturally occurring cinnabar deposits.

HEALTH AND ENVIRONMENTAL IMPACTS

At present, the majority of shellfish beds are closed due to pathogenic contamination. Of the three beds not closed because of pathogens in 1984 one was closed due to high levels of lead in tissue. Frequently in areas with elevated water borne and sediment heavy metals levels shellfish have elevated tissue metals levels.

Stressed shellfish growth has been correlated with elevated water and sediment heavy metals levels. However, no definite cause-effect relationship was established.

An advisory has been issued relative to the consumption of striped bass by pregnant women and children because of mercury contamination.

RESEARCH STUDIES

Various studies have been undertaken relative to heavy metal concentrations and movement in San Francisco Bay.

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The Corps of Engineers conducted a detailed study on the impact of dredging on heavy metals movement. Bioavailability studies have been undertaken to measure the concentration of heavy metals in all environmental compartments.

The bay's hydraulics and sediment transport have been extensively studied. As previously referenced the impact of heavy metals on shellfish growth has been assessed.

REMEDIATION

At present remediation activities involve the regulation and treatment of point source discharges in order to limit their release of heavy metals.

There are also in some areas limited programs to remove contaminants from city streets.

MONITORING

Point source discharges to the bay are monitored as a part of NPDES requirements. The shell fish in the bay are monitored as a part of a state wide program. Fin fish are monitored by Wildlife and Fisheries.

The waters and sediments of the bay are monitored intermittently in special studies.

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LAKE TRUMMEN, SWEDEN

SITE SPECIFIC CONTAMINATION AND ENVIRONMENTAL IMPACT

Lake Trummen is situated close to the town of Vaxjo in the South Swedish Uplands; it has an area of 1 km^2 and a maximum depth of 2.2 m. The lake received municipal waste from the early 1930s to 1958, and from 1941 to 1957, Trummen received additional pollution from a flax factory. It did not recover after the inflow of wastewater was cut off in 1957-1958; instead, it maintained the characteristics of an overexploited recipient of waste (eutrophic) during the 1960s. The lake deteriorated to such an extent that the inhabitants of Vaxjo considered filling in the basin.

INVESTIGATIVE STUDIES

Due to pollution, the sediments in the lake became heavily loaded with nutrients and heavy metals including mercury. The increased organic load induced high microbial activity with oxygen-poor water conditions and a reduced sulphide-rich sediment layer. Additionally, investigations showed mercury levels of the sediments to be well above the natural background (1.0 to 1.5 ppb) in the contaminated range of 0.5 to 1.8 ppm dry weight. The highest mercury concentrations were at a sediment depth of about 0.2 m. Levels of methyl mercury concentrations in pike and other fish were low. The total mercury content of the lake water was within the range 0.05-0.15 ppb.

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REMEDIAL ACTION

In 1969 and 1970 a rehabilitation plan was developed by the Lake Restoration Research Team at the University of Lund, Sweden. The team, consisting of geologists, limnologists, microbiologists, and plant ecologists, developed a comprehensive plan to restore the lake and measure the success of their effort. The plan was primarily developed due to the partial filling of the lake with organic sludge. In 1970, the top half meter of black gyttja type sediment was suction dredged uniformly from the main lake basin. The company Skanska Cement AB constructed, with the aid of the limnologists, a suction pumping nozzle which would make it possible to suck in the sediment without making the lake water turbid and with very little mixing of lake water. In 1971 another half meter of sediment was removed from the same area. Altogether, approximately 600,000 m^3 of sediment and an additional 300,000m^3 of water were removed.

Part of the gyttja dredge material was disposed of in three diked-off bays which were overgrown with macrophytes. The remainder of the dredge spoil was pumped to diked settling ponds on an old farm area from which the top soil had been removed. The return flow water was treated with aluminum sulfate to remove phosphorus and suspended solids. The restoration processes ended in October 1971 with the final remedial action being the establishment of green belts and parks around the lake. The total cost of bringing Lake Trummen back to health was $500,000(U.S.)

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MONITORING MEASURES

As was foreseen, the changes in Trummen's ecosystem have been dramatic. Information pertaining to water and sediment chemistry, phytoplankton, macrophytes, zooplankton, bottom fauna, and fish populations has been collected since 1972. Bengtsson, et al.[2] indicate that phosphorus and nitrogen have decreased dramatically and that the role of sediment in recycling nutrients has been minimized. Cronberg et al.[3] found that nutrient concentrations and phytoplankton biomass were drastically reduced. Eutropic species disappeared and more oligotrophic species returned to the lake. The study covers a 12 years - monthly - bimonthly counting of algae together with election microscopical studies of taxonomically difficult taxa. Andersson et al.[1] studied the effects of dredging upon the lake's benthic community and found no adverse repercussions. None of the subsequent monitoring investigations say anything about 1970-1980 mercury concentration levels; therefore, it may be assumed that the mercury in the lake basin's sediments was recovered sufficiently and that no further problems exist, to date.

Lake Trummen is now accessible for fishing and bathing, and it can be considered to be a valuable recreational asset.

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KEPONE CONTAMINATION IN AND AROUND HOPEWELL, VIRGINIA

SITE SPECIFIC CONTAMINATION

Kepone, an extremely stable, high molecular weight chlorinated organic compound ($C_{10}Cl_{10}O$), was manufactured from 1966 until 1975 in Hopewell, Virginia. Production was halted due to significant adverse health and environmental impacts in 1975.

Sampling indicated Kepone was present at the production site, Hopewell WWTP and sewage lines and municipal landfill. Kepone was also detected in James River and James River Estuary sediments and in fish and shell fish from the river and estuary.

HEALTH AND ENVIRONMENTAL IMPACTS

Resident fish and shell fish species had mean Kepone levels to a maximum of 2.7 mg/kg (dry weight). Kepone was detected at significant levels throughout the aquatic food chain. In December, 1975 the James River closed to fin and shellfishing. Fishing on a species by species basis has been re-established as kepone body burdens drop below the action level.

Human health impacts were limited to those workers and their household who worked in the production plant.

RESEARCH STUDIES

Research studies can be divided into two classes. One class defined the location and extent of Kepone contamination and the mobility of the contaminates. Toxicity and bioaccumulation/bioelimination rate studies were also conducted. In addition, a computer model was

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calibrated to predict the mobility of Kepone in the James River and Estuary. The model was also used to predict potential threats to Chesapeake Bay. The second class of studies was included in the Kepone Mitigation Feasibility Project. Numerous mitigations approaches (remedial actions) were evaluated for remediation of the contamination.

REMEDIATION

Production of Kepone was halted in September, 1975. A fin and shellfishing ban was imposed in December, 1975. This ban has been almost entirely lifted (May, 1985). Contaminated soils and wastes and raw product were removed from the production area and disposed of. It was decided the "no action" alternative was proper for remediation of sediment contamination due to the large area contaminated.

MONITORING

Finfish and shell fish are monitored for Kepone both in the James River and at the marketplace.

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HUDSON RIVER, NEW YORK

SITE SPECIFIC CONTAMINATION

Over 500,000 lbs of PCBs were discharged to the upper Hudson River during an approximate 30-year period, until 1977 in the wastestreams of General Electric capacitor manufacturing plants at Ft. Edward and Hudson Falls, New York. It is estimated that 80 percent of the PCBs were Aroclor 1242 with the remaining PCBs being comprised of Aroclor 1016 and 1254. Due to the hydrophobic nature of PCBs, the PCBs were concentrated in sediments. A significant portion of the PCB-contaminated sediment had originally accumulated behind Ft. Edward Dam, however, upon the removal of this dam in 1973 the PCB-contaminated sediments were released downstream and continued to be transported downstream during subsequent flood events. High concentrations of PCBs have been found in Hudson River water, sediments and organisms. Average concentrations of PCBs in water sampled near hot spots have been found to be in the range of 0.568 ug/l to 0.687 ug/l. Data on PCB levels in fish from the upper Hudson River indicate levels ranging up to 500 ppm. General air concentrations of PCBs are reported to be in the range of 0.05 to 0.10 ug/m^3. PCB-contaminated sediments have been found to extend approximately 200 miles downstream of Ft. Edward to New York Harbor. However, a high percentage of the PCBs contained in the sediments are in hot spots located in the upper Hudson River.

REMEDIATION

No specific remedial action has been implemented on the Hudson River to date, however, an original plan to selectively dredge PCB hot

spots and remnant sites was proposed in 1981. A total of 40 PCB hot spots were identified as the result of a $3,000,000 investigation of PCB contamination in the Hudson River. These hot spots were defined as sediments containing greater than 50 ppm PCB. In addition, five PCB-contaminated remnant deposits were identified. These remnant deposits were formed when the removal of the Ft. Edward Dam caused water levels of the river behind the dam to drop significantly. This caused once-submerged bottom sediments to be exposed to the atmosphere.

The original environmental impact statement for the Hudson River detailed a recommended full-scale project for removal of all 40 hot spots and the five remnant deposits. The full-scale project for removing these hot spot areas was estimated to cost approximately $40,000,000. Due to the high cost of this full-scale implementation a reduced-scale project was developed for the removal of 20 of the PCB hot spots with a resulting cost of approximately $26,700,000.

The recommended plan of action was to consist of the dredging of PCB hot spots in the river bed with containment in a secured open site. The actual method of dredging was not specified, however, a review and evaluation was made of the various possible types of dredging alternatives. The open containment site for disposal of the dredged materials was to be designed and constructed to insure a secure site capable of indefinite long-term isolation of the contaminated materials.

Although no remedial action has been undertaken to date, approximately $5,000,000 has been set aside for removal of the remnant sites which would be dredged and disposed in an off-site disposal area. According to the New York State Department of Environmental Conservation

dredging of the hot spots in the river channel is not considered to be cost-effective at this time.

HEALTH AND ENVIRONMENTAL EFFECTS

As previously indicated the entire Hudson River downstream of Ft. Edwards is contaminated with PCBs. Both sediments and fish have been significantly impacted. It is estimated up to 178,700 kg of PCBs are present in sediments in the upper Hudson. An additional 75,700 kg of PCBs are present in the sediments below the Federal Dam (the lower Hudson).

When wide scale testing for PCBs in fish began in 1977, it was found that PCB contamination was extensive. In 1978 monitoring indicated a mean stripped bass PCB concentration of 18 ppm. From 1977 until 1980 the PCB body burden in fishes has been dropping although body burdens still exceed the FDA tolerence level of 5 ppm (1980).

Due to the high body burden of PCBs in fish a ban on commercial and sport fishing has been imposed since 1976.

No direct health effects upon humans have been documented due to the contamination of the Hudson with PCBs. However, no known detailed health impact studies have been conducted.

RESEARCH STUDIES

Detailed studies have been performed on the Hudson. These studies have defined where and to what extent sediments have been contaminated with PCBs. Detailed assessments have also been made of impacts on surface water and ground water, air quality (via PCB volatilization), and impacts upon the fisheries, and the flora and fauna of the area.

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A detailed assessment of remedial alternatives has been performed. The preferred alternative was selected and its implementation recommended. Many of the research projects are included as a part of or summarized in the U.S. EPA Environmental Impact Statement.

As part of the assessment of remedial alternatives a sediment transport model was developed for the Hudson River. The no action and various dredging scenarios were simulated using the model. A food web model was developed to predict the impact of various remedial alternatives on the food chain with respect to time.

ENGINEERING CONSIDERATIONS/RESEARCH STUDIES AND MONITORING

No specific research or engineering studies were recommended as part of this study. The only recommendation for work prior to actual dredging was additional sampling to better define the horizontal area and vertical disposition of the contaminated sediments. Extensive monitoring was recommended during the actual implementation of the dredging operation. This monitoring was to include sampling of air emissions, water, sediment, fish, and macroinvertebrates.

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CONTAMINATED SALT MARSHES NEAR BRUNSWICK, GEORGIA

SITE SPECIFIC CONTAMINATION

A chlor-alkali chemical plant discharged approximately 2.2 lb/day of mercury for a period of 6 years into salt marshes adjacent to the Turtle River northwest of Brunswick, Georgia. The discharge was discontinued in 1976. Mercury was first detected in marsh organisms by the Georgia Department of Natural Resources in 1974.

HEALTH AND ENVIRONMENTAL IMPACTS

Resident invertebrates had total mercury (dry weight) up to 9.4 ppm. Fish samples showed total mercury levels of (0.3 to 2.4 ppm) in muscle and (0.34 to 4.2 ppm) in liver. Most mercury in fish muscle (76%) was in the methyl form. Birds and mammals were reported as having 0.09 to 7.4 ppm mercury in muscle and 3.8 to 37 ppm mercury in liver tissue.

RESEARCH STUDIES

To investigate the distribution and forms of residual mercury samples of sediment, plants, and primary consumers were collected in 1974. Higher more mobile organisms were collected from 1974 to 1976.

REMEDIATION

Discharge levels of mercury were reduced to a daily maximum of 0.138 lb/day and a daily average of 0.06 lb/day.

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MONITORING REQUIREMENTS

Weekly analysis of total mercury in the effluent. No field sampling.

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OTTAWA RIVER

SITE SPECIFIC CONTAMINATION AND ENVIRONMENTAL IMPACTS

Mercury pollution of the Ottawa River proceeded for decades at a constant rate estimated to be between 400 to 800 pounds of mercury per year. The two primary sources were the paper mills at Hull and Gatinean, Quebec; phenylmercuric acetate was used as a slimicide in pulp processing through 1971 in both plants. Moreover, the river received waste in the form of wood chips, wood fibers, and bark refuse from various sources, giving rise to extensive organic deposits integrated within the river's bed sediments. This feature is an important characteristic of the Ottawa River contamination.

INVESTIGATIVE STUDIES

Mercury contamination in the Ottawa River was studied by the Ottawa River Group from 1972 to 1977 (a joint research program of the National Research Council of Canada Laboratories and the University of Ottawa. Departments of Biology, Civil Engineering, and Geology). A field survey was conducted to obtain detailed mercury analysis of representative samples of all components of the river system, namely water, bed sediments, higher aquatic plants, aquatic invertebrates, and fish. A three mile reach of the river, beginning 1.6 km downstream from the city of Ottawa, was chosen to be studied, specifically because of its complicated form and varied environments. The project provided an excellent opportunity to investigate reduction in mercury levels consequent to the cessation of a known source of contamination.

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Some of the individual investigations included detailed studies of: mineral content, sediment transport rates, mercury sorption capacity, ion exchange capacities of various fractions of sand sediment and wood chip sediment, and the proportion of methylmercury to the total amount of mercury. Some average mercury concentration values for the study area:

[1]filtered water	0.013 ppb
suspended solids	1,140 ppb (dry weight)
bed sediments	80.6 ppb (dry weight)
higher plants	14.2 ppb (wet weight)
benthic inverts.	223 ppb (wet weight)
fish	162 ppb (wet weight)

Hart (1972) estimated that bed sediments of the Ottawa River contained 97% of the mercury in the system. Both Miller and Kudo, et al. found similar percentage results as Hart. Dennis G. Waslenchuk (1975);

Department of Geology, University of Ottawa, Ottawa, Canada, determined that both mechanical and chemical mechanisms operate to reduce mercury concentrations in the bed sediments of the contaminated area, mainly by three processes:

1. The transport of unnaturally contaminated sediment grains downstream, which are replaced by grains of lower background mercury levels from upstream of the artifical mercury input.
2. In response to lower aqueous mercury concentrations in the water column, crystalline forms of mercury dissolve slowly to regain equilibrium. The products of dissolution likely will be lost to

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the atmosphere due to high vapor pressures, or will be kept in solution by organic complexing.

3. As a result of the aging of ferric hydroxide grain coatings, adsorbed mercury and other trace-elements will be liberated. Some of the liberated mercury will become associated with fresh ferric hydroxide precipitates in the immediate area, maintaining a strong Fe - Hg correlation. The rest will be transported downstream in solution.

The net rate of the processes above is apparently on the order of a 50 percent annual decrease in mercury. There is evidence that the net loss proceeds exponentially, in which case the half-life is 0.78 to 1.15 years. Therefore, the bed sediments of a fluvial system will slowly recover from unnatural mercury contamination. The liberated mercury will not be lost from the environment, but will, to some extent, enter the atmosphere, and, more importantly, will migrate downstream to the oceans.

Furthermore, Townsend et al (1974) made a laboratory investigation of mercury desorption from Ottawa River sediments and obtained a mercury half-life of 0.82 years for aerobic Ottawa River water (the condition which prevails in the river).

REMEDIAL ACTION

The Ottawa River Programme decided that the Ottawa River will clear itself naturally; and therefore, it proposed a verdict of 'no remedial action necessary.' Personal communication with Don R. Miller varifies the above statement also.

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MONITORING MEASURES

The Ontario Ministry of the Environment conducts annual fish samplings and publishes the results for fishermen.

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WABIGOON-ENGLISH RIVER OF NORTHWESTERN ONTARIO

SITE SPECIFIC CONTAMINATION

A paper mill complex and the Dryden STP have released large quantities of organic waste into the Wabigoon River since about 1913. A chlor-alkali plant that operated from 1963 until 1975 released mercury compounds into the system. At present, mercury levels in fish are declining but are expected to stay above 1.0 ppm for a number of years.

HEALTH & ENVIRONMENTAL IMPACTS

Resident fish in the Wabigoon-English River system have been severely contaminated with mercury (Walleye x = 15.1 ug/g and Northern Pike x = 9.7 ug/g in 1971). Most mercury was in a methylated form. Human blood mercury levels exceeded 100 ppb in some individuals. The higher levels were in the range of 100-500 ppb. A strong correlation was observed between the consumption of fish and elevated blood mercury levels.

Commercial fishing in the river system was banned in 1971; however, sport fishing has continued. The government has been providing recommended consumption information.

RESEARCH STUDIES

A detailed study program was conducted under the auspices of the joint federal-provincial governments. Ths study includes an investigation as to the sources, pathways and fate of total and methyl mercury. A review of remedial measures was also made. Detailed investigations concerning the relationship between sediment mercury and

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biological uptake and selenium concentrations and mercury uptake were conducted.

REMEDIATION

Discharges from the paper mill complex and Dryden STP now receive secondary treatment. The level of mercury in the chlor-alkali plant was significantly reduced starting in 1970. In 1975, the chlor-alkali process was converted to a process that does not use mercury but effluent from the mill complex still carries 5 to 10 kg mercury per year.

Impacted communities, native Indian, have been provided with uncontaminated frozen fish.

Although numerous remedial considerations have been studied no action has been implemented. Recommendations include:

1. Mercury monitoring and fish consumption guideline program be continued.
2. A pilot project for semi-continuous resuspension of non-mercury contaminated sediment into the system at critical points be conducted and assessed.
3. The sediment between Dryden and Clay Lake be removed by dredging.
4. Additional scientific investigations which include loss of mercury to the atmosphere and tests of the effectiveness of selenium on mercury pathways.

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MONITORING

Extensive monitoring of the Wabigoon-English River system has been conducted. This monitoring has included the fishery. water column and sediments for total and methyl mercury. Future monitoring plans involve the monitoring of the fishery for total and methyl mercury.

REFERENCES

Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario and Possible Remedial Measures - Technical Report (1984)

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POLLUTED LAKES & STREAMS AT FLIN FLON, CANADA

SITE SPECIFIC CONTAMINATION

A zinc smelter at the Saskatchewan-Manitoba border near laditude $54^{o}45'$ has released heavy metals (Zn, Cd, Cu and Hg) into surrounding lakes via airborne deposition and process water discharge through a tailings pond. The release of contaminates from the smelter have been significantly reduced due to the installation of proper control technologies and discharge monitoring.

HEALTH AND ENVIRONMENTAL IMPACTS

Resident northern pike had liver Cd x = 3.3 (1.2-12) and liver Hg x = 0.28(0.11-0.56) and resident white sucker had liver Cd x = 10.1 (2.6-23.5) in the most polluted lake. Muscle concentrations were significantly lower than liver concentrations and did not approach action levels. No limits on fishing have ever been imposed.

Heavy metals sediment concentrations were found to be elevated above background although the absolute levels did not indicate severe contamination except for Cd and Cu.

RESEARCH STUDIES

Studies have been conducted using the Flin Flon area as a laboratory to assess the stability of heavy metals in sulfide rich muds and/or in algae blooms. A relationship between Ca in water and heavy metal bioaccumulation was proposed in one study. It was suggested that the higher the Ca level the lower the bioaccumulation potential.

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Fish, sediment and water samples have been collected in order to monitor the extent and severity of contamination.

REMEDIATION

Improved air and effluent discharge controls have been implemented at the smelter. These controls have greatly improved the situation relative to continued contamination.

MONITORING

The smelter must periodically monitor its air emissions and effluent discharge. These sources must meet established discharge limits. No field sampling is currently occurring.

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OUTBOARD MARINE CORPORATION (OMC)
WAUKEGAN, ILLINOIS

SITE SPECIFIC CONTAMINATION

Polychlorinated Biphenyls (PCBs) were discharged with process cooling water and water from floor drains from the OMC plant. PCBs have contaminated three areas around the plant. These areas are Waukegan Harbor sediments, soils and sediments around the drain called the north ditch and the OMC parking lot. Over 1 million pounds of PCBs are contaminating these locations. 300,000 lbs PCBs are contained in 10,000 cu yd in the harbor near OMC; 5,000 lbs PCBs are contained in 35,700 cu yd in the upper harbor; 495,000 lbs PCBs are contained in 70,800 cu yd in soils and sediments in the North Ditch; and 277,000 lbs PCBs are contained in 105,800 cu yd in soils in the OMC parking lot. The OMC site is the largest uncontrolled contributor of PCBs into Lake Michigan.

HEALTH AND ENVIRONMENTAL IMPACTS

Monitoring of the fisheries around Waukegan Harbor and in Lake Michigan indicates PCBs are being bioaccumulated. At present there are no restrictions on fishing around Waukegan. Fishing is prohibited within Waukegan Harbor although the reason for the restrictions is not known and may not be related to PCB contamination.

As previously stated there is extensive PCB contamination in the sediments in Waukegan Harbor. The concentrations are especially high in slip #3. Slip #3 is the area into which OMC discharged. Concentrations as high as 55,000 ppm are present. These concentrations decline rapidly

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averaging approximately 7,500 ppm 300 feet downstream; 550 ppm 500 feet downstream; and 100 ppm 1100 feet downstream.

Computer modeling predicts the contaminated sediments are releasing PCBs into Lake Michigan via sediment transport and as dissolved PCBs. In addition, the model predicted PCBs were being volatilized into the atmosphere although ambient air standards were not being exceeded. The model also predicted fish residing in the harbor would have PCB flesh levels above 5 ppm under present conditions.

RESEARCH STUDIES

Research studies have consisted of precisely defining what the extent of PCB contamination is in the harbor and surrounding waters. Extensive sediment sampling and analysis has been conducted. Surface water and fish sampling has also been undertaken. Ground water contamination and flow pattern investigations have been performed. In addition, a remedial action plan/feasibility study (RAP/FS) has been developed by U.S. EPA.

Studies assessing the PCB levels observed in sedments and fish through southern Lake Michigan also provide useful information on the movement of PCBs out of Waukegan Harbor.

REMEDIATION

Over 50 alternatives were reviewed in the decision process used in developing the cost-effective remedy.

The classes of alternatives received included:

1. in-place destruction
2. in-place fixation
3. in-place separation and removal

4. removal followed by on-site or off-site disposal

5. bypassing contaminated materials

6. no action

The alternative selected as the best combination of effectiveness and environmental success was the removal, dewatering, fixation and off-site disposal of all soils and sediments contaminated with PCB concentrations above 50 ppm. The estimated cost for this remedy is $74,890,000 (1983).

Due to funding restrictions this remedy was modified as a means of cost reduction. The modified remedy calls for the removal of highly PCB contaminated soils and sediments (>10,000 ppm) and secure off-site disposal. Moderately contaminated (500-10,000 ppm) and less contaminated (50-500 ppm) materials will be dewatered and disposed of on the OMC parking lot. The parking lot will be clay capped and slurry walled down to glacial till. The estimated cost of this remedy is $21,300,000.

To date no work has begun on this reclamation project.

MONITORING

No information concerning monitoring is available. However, it was stated in the Remedial Alternative Selection document that detailed monitoring would occur upon completion of the remedial action. It is expected this monitoring program would include monitoring of ground water, surface water and runoff, sediments, and aquatic life. A monitoring program would likely be established to monitor contaminate release during implementation of the remedial action. This would likely include surface water, runoff and ambient air monitoring.

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REFERENCES

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NORTH FORK HOLSTON RIVER. VIRGINIA

SITE SPECIFIC CONTAMINATION AND ENVIRONMENTAL IMPACTS

From 1895 until its closing in 1972, Olin Corporation operated a chlor-alkali plant and other facilities at Saltville, Virginia along the North Fork of the Holston River. Olin discharged insoluble metallic mercury. In 1970, when sampling results showed that Olin was releasing large amounts of mercury into the environment (more than 80 river miles are polluted), Olin modified its operating procedures to reduce mercury losses from 100 lb/day to 1/4 lb/day. Additionally, Olin disposed of mercuric waste in 'Muck Pond No. 5', which is adjacent to the river. Upstream of Olin the Saltville dump was contaminated by mercury waste from Olin which was found to leach into the North Fork of the Holston River. Aerial fallout is also sited as a source of contamination in the river due to elevated mercury in fish 20-30 miles upstream of known sources. The reach of the river from the Olin plant to the Tennessee border (80 miles) has been closed to fishing as well as 6.2 miles of the river in Tennessee. Faced with the cost of clean-up Olin closed the plant in 1972 and donated all its holdings to the State (7,300 acres).

INVESTIGATIVE STUDIES

Since 1975 the Virginia State Water Control Board (V.S.W.C.B.) has been conducting a regular fish sampling and analysis program. Concentrations of mercury in fish fillets range from 0.11 to 4.8 ppm. Values reveal that mercury concentrations increased right after the plant's shut down (due to chloride concentration reduction), and then they tended to decline at an extremely slow rate to present. Fish

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samples indicate decreasing Hg concentrations with downstream river miles also. Likewise, the V.S.W.C.B. has been monitoring surface and ground water, soil, and sediment concentrations in great detail since 1983.

Olin Chemicals sampled the soil under the former chlorine plant when it installed 12 monitoring wells in November 1981. Mercury levels ranged from 34 ppm to 1,821 ppm at varying depths between 5 and 23 feet. During January and March of 1982, Olin took samples from these wells, revealing that even the water from the wells screened in bedrock contained Hg at 0.16 ppm. The wells screened in alluvium contained water with up to 7.6 ppm Hg.

Additionally, Olin found that surface water samples of the north fork of the Holston River taken from 1970 to the present have concentrations of Hg ranging from less than 0.02 ppb to 17 ppb. The outfall from Muck Pond 5 ranges from 4 to 175 ppb Hg concentrations.

In 1978 the Tennessee Valley Authority (TVA) studied the transport of mercury in the river sediments. In general, at sediment stations below Olin, Hg values in the top one inch were higher than the second inch, and the second inch values were greater than the third inch values. The major conclusion reached was that mercury is readily transported downstream and out of the North Fork Holston River system, with little accumulation in the sediments. However, the re-innoculation of river sediments from the Muck Pond, Saltville dump and aerial fallout make a persistent problem for which remedial action was eventually taken.

REMEDIAL ACTION

On September 25, 1978 Olin began an erosion control project at the old plant site: a project whereby the river bank was stabilized with the emplacement of rip-rap. Olin completed this project in the fall of 1979 at a cost of around $400.000 - the results were rewarding. During the summer of 1982, a portion of the river bank downriver and adjacent to Muck Pond 5 was also rip-rapped at a cost of approximately $240.000. Later in 1982 Olin constructed a $640,000 diversion ditch around the western half of Muck Pond 5 (some 72 acres) to divert surface runoff from this highly contaminated area. As of 1985, the amount of mercury flowing from the Muck Pond into the river has been reduced by about 80%. Pond 5 contributes about 20-30% of the overall Hg problem, with the remaining 70-80% of the Hg being due to river sediments adjacent to and downstream of the plant site for about 1,000 feet.

Additionally in 1982, Olin temporarily diverted a portion of the North Fork Holston River and began dredging the river bottom along a 1300-foot section of the riverbed just below the plant site; the total cost being about $2.2 million. As of January 25, 1983 dredging was completed. The dredged materials were processed to remove mercury prior to disposal. After having been spread atop the old plant site the dredged materials were encapsulated with a clay cap.

MONITORING

Five years of monitoring (fish, water, etc.) began in 1982 and are conducted by both Olin Corporation and V.S.W.C.B.

REFERENCES

A Special Order Issued to Olin Corporation by the V.S.W.C.B. in August of 1982.

EPA Work Assignment #01-3V24.0, contract #68-01-6697, NUS Project #0701.73 "Remedial Action Master Plan, Saltville Waste Disposal Site, Smyth County, VA": June 1984.

Olin Corp update from J.C. Brown to M.G. Ferguson of the V.S.W.C.B. in Richmond; March 1, 1985.

TVA Paper; Div. of Env. Planning, Water Quality, and Ecology Branch, "Transport and Partitioning of Mercury in Sediment of the North Fork Holston River - 1978" by J. D. Milligan, et al.

Personal communication with Mr. Dallas Sizemore of the V.S.W.C.B. in Abingdon, VA, May 1985.

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LAKE ERIE, DETROIT RIVER, LAKE ST.CLAIR AND ST. CLAIR RIVER

SITE SPECIFIC CONTAMINATION AND ENVIRONMENTAL IMPACT

Wyandotte Chemical Co. of Wyandotte, Michigan (Figure B-1) released upwards of 10 to 20 lb/day of mercury into the Detroit River, prior to March 31, 1971. Dow Chemical of Sarnia, Ontario dumped about 65 lb/day of mercury into the St. Clair River and Lake St. Clair prior to 1970. Another chlor-alkali plant, Detrex Chemical Corp. of Ashtabula, Ohio, released as much as 66 lb/day of mercury into western Lake Erie until April of 1970; whereupon monitoring studies revealed a significant reduction in Hg effluent, down to about 2 lb/day. Unfortunately, no accurate information pertaining to total quantities of mercury discharged was ever released.

After the impoundment of fish by Canadian authorities on March 24, 1970, the U.S. Food and Drug Administration lab in Detroit began analyzing fish taken from the St. Clair River, Lake St. Clair, the Detroit River, and Lake Erie. Results showed significant mercury levels ranging above 5 ppm in the flesh of fish taken from all of the aforementioned bodies of water. Thereafter, a fishing ban was emplaced upon Lake St. Clair; and fish taken from the other localities were not to be eaten.

INVESTIGATIVE STUDIES

Sampling of the St. Clair River began on March 26, 1970. Immediately below the Dow Chemical discharge at Sarnia, residuals ranged as high as 2,000 ppm. Beginning another mile further downstream fifteen

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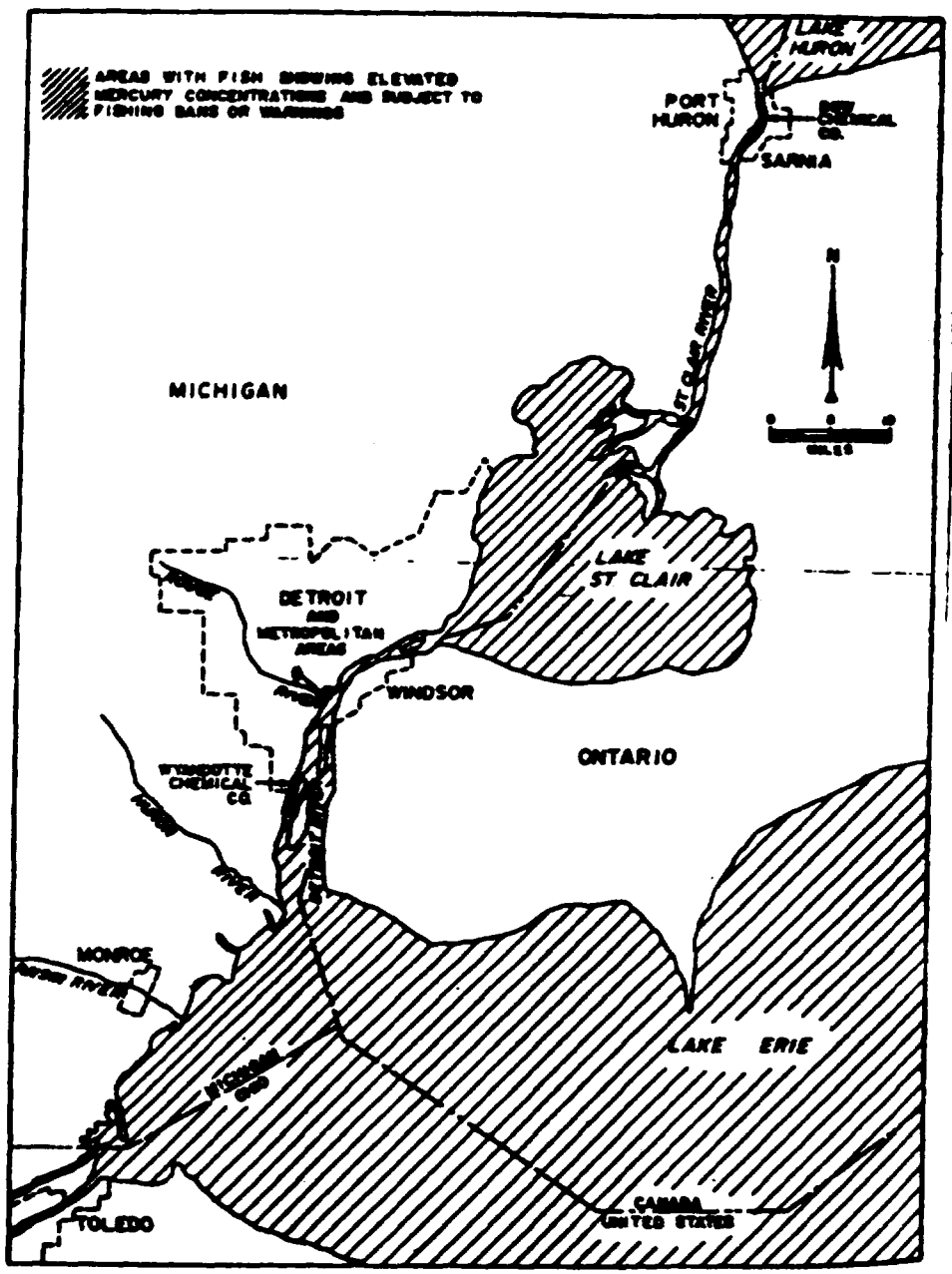

Figure B-1 —Waters affected by mercury contamination. (Miles × 1.61 = km)

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samples of sediment and six water samples were collected. All but one sediment sample contained less than the measurable limit of 0.5 ppm (wet weight). The six water samples contained no measurable concentrations of Hg.

One water sample and 26 sediment samples were collected and analyzed from Lake St. Clair. Six sediment samples in the navigation channel (the thalwag supplies 40% of the St. Clair River flow in a relatively unmixed stream through Lake St. Clair to the Detroit River) contained Hg in concentrations from 0.3 to 9.2 ppm. Two samples from a dredging disposal area contained Hg at concentrations of 1.7 and 2.1 ppm. In the other 18 sediment samples, the presence of Hg was indicated but it was less than the measurable limit. The water sample contained less than the measurable limit.

Sampling of the Detroit River began on March 26, 1970 and continued to April 24, 1970. Hg values ranged from less than the measurable level (0.5 ppm) near the headwaters to 2.0 ppm downstream from the Rouge River. Concentrations in sediments at Grassy Isle and upper F. Island were less than the measurable limit.

In the portion of the Detroit River from Grassy Isle to the mouth at Lake Erie, 78 sediment and 23 water samples were collected between March 26, 1970 and April 16, 1970. The highest levels of Hg occurred in the bottom muds of the Trenton Channel downstream from the Wyandotte Chemical Corporation Works. In a narrow strip from 20 to 100 feet wide along the western shore; the value was 28.0 ppm. Concentrations along the eastern shore of the channel near Grassy Isle were less than the measurable limit of 0.5 ppm. All but one water sampling value were below 0.01 ppm with the exception having a value of 0.03 ppm.

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The monitoring of Lake Erie began on April 6, 1970, with 44 bottom sediment stations being sampled in the western extensions of the lake. Sixteen of these stations had Hg concentrations greater than the measurable limit; they were located in the deep water areas of the western basin of Lake Erie from the mouth of the Detroit River southward and eastward (highest value was 1.0 ppm).

The remainder of Lake Erie was examined (three water samples and 35 sediment samples) with the highest water sample value being 1.06 ppm and the highest sediment sample value being 8.0 ppm. The majority of the water values were less than 0.002 ppm, and the majority of the sediment samples were <1.0 ppm.

Since mercury becomes sorbed onto sediments and therefore resides in dynamic equilibrium with dissolved species in the supradjacent water column, aquatic biota may then ingest mercury. As mercury accumulates throughout the food web, it concentrates in higher life forms, as is explained in detail in Task I - General Literature Topic Summary, Nature of Mercury in the Environment. In a nutshell, it does not take very much mercury contamination to cause methyl mercury poisoning/contamination in game fish.

REMEDIAL ACTION

Other than pollution controls and reductions/cessations of mercurial effluents, no major remedial actions were employed.

MONITORING MEASURES

Continued monitoring of Hg in fish.

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REFERENCES

National Field Investigations Center, Cincinnati, Ohio, "Investigation of Hg in the St. Clair River, Lake Erie Systems," compiled by Federal Water Quality Administration, et al; May, 1970.

Turney, William G., "Mercury Pollution: Michigan's Action Program." Journal WPCF, 1971, 43, #7, 1427, pp. 1, 1438.

Turney, W.G., Personal Communication: Michigan Water Resources Commission, May 1985.

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MOBILE RIVER SYSTEM

SITE SPECIFIC CONTAMINATION

Prior to 1970 a major chlor-alkali plant in southern Alabama discharged approximately 100 lb/day of mercury into the Mobile River System. The State of Alabama analyzed fish and reported mercury concentrations over 0.5 ppm in 1970. In June 1970 a ban on commercial fishing was imposed on the Mobile River below Jackson Lock and Dam. In July the discharge was limited to 0.25 lb/day and continuous monitoring was required. Numerous other industries apparently released mercury and swamps downstream of the chlor-alkali plant were sources of mercury to the river system. Mercury levels in swamp mud were as high as 5.100 ppm (dry weight).

INVESTIGATIVE STUDIES

Investigative studies have included the monitoring of mercury concentration in fish and sediment, a study designed to determine if methylation was occurring in the swamp and at what rate it wa occurring and the impact of mercury contamination on the fish population.

The methylation studies included exposure of fish (gold fish and guppies) to contaminated muds and surficial waters contained in Jenkins Tubes. The mud cores were exposed to different treatments, i.e., mercury spikes, effluent, aerobic environment, oyster shell cover. in order to evaluate impacts on methylation rates. Sampling of sediments was conducted to determine the distribution of mercury contamination.

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REMEDIAL ACTION

No Action.

MONITORING REQUIREMENTS AND CLEANUP

Primarily results indicate that very little methylation was occurring in contaminated sediments. Methylation did occur in specific areas of the swamp, however, these areas could not support significant aquatic life from a water quality standpoint. Following the reduction in mercury discharge to 0.25 lb/day the concentration of mercury in fish tissue decreased. In 1982 all monitoring requirements were lifted because mercury was not detected above background levels in fish (based on routine monitoring program).

REFERENCES

Direct communication; State of Alabama Department of Environmental Management, Mr. Charles Horn and Mr. John Williford, May 1985.

AWARE, Inc., June 1972, Investigation of Mercury Methylation in the Mobile River System.

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SOUTH RIVER AND SOUTH FORK OF SHENANDOAH RIVER

SITE SPECIFIC CONTAMINATION

Mercury contamination has been detected along a 25-mile stretch of the South and South Fork of the Shenandoah River below the DuPont facility. Four separate areas were investigated for contaminant distribution:

1. Sediments - Average total mercury concentration, approximtely 10 ppm with 2 percent of mercury in river sediments and 98 percent in floodplain sediments.
2. Water - Net mercury flux for South River in vicinity of the DuPont plant averages about 7 gm/day (5.6 lb/yr). Mercury emanating from sediments also contributed 16.3 gm/day (13 lb/yr).
3. Biota - Included aquatic plants (0.09 to 2.18 ppm dry weight) macroinvertebrates (0.081 to 2.362 ug/g wet weight), and fish (mean range 0.153 to 1.695 ppm).
4. Plant site - Included ground water (consistently <0.5 ppb), surface soils, and pipelines/outfalls.

REMEDIAL MEASURES EVALUATED

Alternatives addressed for remediation included:

1. No action.
2. Partial sediment removal ("hot spots").
3. Complete sediment removal.
4. Abatement of plant site contributions.

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REMEDIAL MEASURES IMPLEMENTED

No action with continued monitoring.

MONITORING REQUIREMENTS

Continued monitoring of mercury in the sediment, water and fish.

CLEAN-UP CRITERIA

Used 1.0 ppm FDA action limit for fish.

REFERENCES

"Engineering Feasiblity Study of Rehabilitating the South River and the South Fork Shenandoah River"; March 1981; prepared for E.I. DuPont DeNemours & Co., Inc.: prepared by Lawler, Matusky & Skelly Engineers.

ESTUARINE SEDIMENTS IN THE FLORIDA EVERGLADES

SITE SPECIFIC CONTAMINATION

Mercury has been reported in sediments of the western Everglades at concentrations ranging from 0.2 to 2.0 ppm. There has been no point source located as the cause for these levels. Deposition is attributed to physical conditions conducive to sedimentation and particle size. Although mercury concentrations are not high when compared to industrially polluted areas, interstitial water mercury concentrations are high and methylation has been observed at these levels in industrially polluted areas.

ENVIRONMENTAL IMPACTS

Fish and shellfish in the area have been reported with mercury levels near the FDA action limit of 1 ppm.

RESEARCH INVESTIGATIONS

Fish, shellfish, sediment and water sampling associated with the area has taken place, as well as, studies concerning the correlation of mercury with salinity, total dissolved sulfide and dissolved organic carbon in the water and sediment. A study has also been conducted to determine the concentration and distribution of methylmercury in Everglades sediments.

CLEAN-UP REQUIREMENTS

Although some fish in specific areas have become contaminated no clean-up has been recommended due to the fact no source(s) has been

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located and the sporadic frequency of occurrence does not substantiate a hazard. In sum the levels are likely attributable to background conditions.

REFERENCES

Lindberg, S.E., R.C. Harriss, 1974. Mercury-Organic Matter Associations in Estuarine sediments and Interstitial Water. Env. Science & Technology, Vol. 8.

Ardrea, A. W., R. C. Harriss, 1973. Methylmercury in Estuarine Sediments. Nature, Vol. 245.

Don Sessons, 1985, Florida Department of Environmental Regulation. Personal Communication.

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BELLINGHAM BAY, WASHINGTON

SITE SPECIFIC CONTAMINATION & ENVIRONMENTAL IMPACT

Bellingham Bay, located in Northern Puget Sound about 70 miles north of Seattle, Washington, received an estimated 4.5-9.0 kg of mercury a day from August 1965 to August 1970. The source of contamination was a Georgia-Pacific chloralkali plant. In August 1970, the discharges were reduced to about 0.1 kg/day. In the fall of 1970, estuarine sediments between 0.5 and 7.0 km from the plant had mercury concentrations of 2-20 ppm, compared to the naturally occurring concentrations of 0.2 ppm.

INVESTIGATIVE STUDIES

In the fall of 1970, the Department of Oceanography at the University of Washington at Seattle began perodically collecting and analyzing cores of sediment (surface and subsurface) to document the rate of decrease of mercury in the Bellingham Bay area. This study examined specific sites for a two-year period after the nearly complete curtailment of mercury discharged from the chlor-alkali plant. Additionally, the Department measured the flux of dissolved and volatile Hg from contaminated sediments into the overlying water, where its mobility would increase.

In all of the core samples, only the top 10-12 cm of sediment were Hg-contaminated. The highest concentrations, at all depths were observed in cores obtained in 1970. A generally systematic decrease in the Hg concentration was detected in samples collected at later dates, elucidating an apparent half-life of about 1.3 years. Moreover, during

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the study period, the closer the samples taken to the chlor-alkali plant, the higher their respective Hg concentrations.

In the areas having oxidizing surface sediments, the Hg was assumed to be lost while associated with sediments that are resuspended and transported by bottom currents. The flux of dissolved or volatile Hg was not measurable in areas having Hg concentrations of 1-5 ppm in oxidizing surface sediments.

In contrast, the flux of dissolved Hg from highly contaminated anoxic sediments to oxygenated overlying water was about 1.2×10^{-5} $ng/cm^2/sec$. From the same sediments, the flux to overlying water that was allowed to become anoxic was 2.8×10^{-5} $ng/cm^2/sec$. The increased Hg flux observed when bottom waters became anoxic suggests that maintaining oxygenated conditions in waters overyling contaminated sediments is one means of reducing the flux of Hg to other parts of the environment[1].

REMEDIAL ACTION

No action due to immense size of bay.

MONITORING MEASURES

Fish samples taken during the eary 1970s revealed slightly high Hg concentrations relevant to the background levels, but none were found to be above the 1.0 ppm standard limit.

REFERENCES

[1]Bothner, M.H., Carpenter, Roy, et al. "Rate of Mercury Loss from Contaminated Estuarine Sediments," Geochemica et Cosmochimica Octa. 44 (1979), pp. 273-285.

Bothner, M.H. and Piper, D.Z. "The Distribution of Mercury in Sediment Cores from Bellingham Bay, Washington." Mercury in the Western Environment, Corvallis: Oregon State University, 1973.

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Carpenter, Roy, U.S. EPA Corvallis, Oregan. Personal communication, May 1985.

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Kitakyusyu, Port Japan

Site Specific Contamination: Bottom sediments, water and fish in Kitakyusyu (Dokai Bay) Port have been contaminated as a result of the discharge of various organics (oils and greases) and mercury from a petrochemical complex. The bay was found to be heavily contaminated with oils and greases and mercury (average concentration of 50 mg/kg). Considerable amounts of lead, cyanide, chrome and arsenic were also detected. Significant concentrations of tars and sulfides were also present.

Health and Environmental Impacts: No information available.

Research Studies. Extensive studies have been conducted in order to determine the extent of contamination in the sediment of Dokai Bay and the surrounding ocean. The results of these studies were used to determine what areas of the bay were to be dredged.

Once dredging was selected as the cleanup method a research study was conducted to find the best method of stabilizing the dredge spoils. The stabilization method selected was to put the spoils into a lagoon and cap the lagoon with sand. If the spoils were so liquid that a sand cover was impractical, it was discovered that sand lenses layered with bamboo were an excellent cover.

Remediation: The selected remedy involved the dredging of an estimated 2,200,000 m^3 utilizing a centrifugal pump type dredge (50% average solids content) and vacuum type dredge (60-80% average solids content). This was the first project to dispose of mercury containing sediment in Japan. The two dredges were operated in parallel with the

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discharge from each dredge going to a sump rehandler type station barge which pumped the sediment slurry to the disposal site. The criteria of whether to dredge a section of the bay was: if the sediments exceeded 6 ppm total mercury and/or 4,000 ppm hexane extractable oil and grease than the sediment would be dredged. If these contaminant concentrtions were not exceeded the sediments would not be dredged.

The dredged materials were pumped approximately 5 km through a 24-inch diameter pipe to a sedimentation pond. This pond covered about 400,000 m^2 and had a capacity of approximately 2,800,000 m^3. Supernatant from the sediment pond flowed to a 52,000 m^3 settling pond. From the settling pond the water was treated in a treatment system consisting of a flocculation tank, a clarifier and a gravity filter consisting of anthracite and sand. The final disposal of all dredged materials was the sediment pond.

The only major problem reported was the difficulty in completely removing sediments with a high water content. These sediments are liquid enough to flow aside during dredging and therefore not suctioned by the dredge.

Health and Environmental Impacts Associated with Alternative: No information available.

Monitoring: Routine monitoring on a daily (ebb tide) basis occurred at four stations along the port boundaries. The sampling frequency was later reduced to weekly because the mercury results were non-detectable. Samples were collected from depths of 0.5 m, 2 m and 3 m above the bottom with the following parameters being analyzed:

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1. Total mercury

2. pH, DO, COD and n-hexane extractables (oil and grease)

3. Light transmission

Additional monitoring points located between the four routine stations and the dredging site were checked for light transmission. These are typically checked four times a day at a depth 3 m off the bottom. The purpose of this monitoring was to insure the environment was not being degraded by the dredging operation.

Discharge from the treatment system was monitored for the following parameters:

1. Toxic substances as required by the Law Concerning Prevention of Marine Pollution and Maritime Disasters. Total mercury is analyzed daily with other parameters analyzed on a monthly basis.

2. Suspended solids and oil and grease are analyzed once a week.

3. pH, turbidity and oil content are analyzed continuously.

In addition, noxious odors were periodically monitored with the mercury content in fish being investigated three times a year.

No information is available as to what long-term monitoring is now occurring.

References

Hijimi, Ito, 1978. Dredging Toxic Sediments in Yokkaichi Port. In: Proceedings of the Third U.S. - Japan Experts' Meeting on Management of Bottom Sediments Containing Toxic Substances. EPA-600/3-78-084, pp. 65-85.

Fujino, S., 1976, Using Sand Fill to Cover Dredge Spils Containing Mercury. In: Proceeding of the Second U.S. - Japan Expert's Meeting on Management of Bottom Sediments Containing Toic Substances. EPA-600/3-77-083, pp. 144-154.

MINAMATA BAY

SITE SPECIFIC CONTAMINATION AND ENVIRONMENTAL IMPACT

The mercury pollution and the associated methyl mercury poisoning in the vicinity of Minamata Bay (Minamata disease) is the most well known incident of environmental mercury contamination in the world. The salt water bay is located on the southwest shore of Kyusher Island, the southern island of Japan. The bay is about 3 km^2 in area. The bay feeds into the Yalsushiro Sea, a small inland body of water 636 km^2 in area.

The Chisso Chemical factory located near the bay synthesized vinyl chloride and acetaldehyde. Mercury chloride and mercury oxide were used as a catalyst. Wastewater was discharged into Minamata Bay. From February, 1946 until September, 1959, both the vinyl chloride and acetaldehyde plants discharged untreated wastewater to the bay. From September, 1959, until March, 1971, various levels of treatment were employed. In May, 1968, the acetaldehyde plant was closed.

High levels of mercury were found in the sediments of Minamata Bay, the maximum concentration being 908 ppm. However, the most disturbing aspect of this incident was the development of Minamata disease. To date, over 700 patients had been affected by methyl mercury toxicity. Of these over 50 had died. In addition to the incidence of human toxicity, cats, rats and waterfowl living near the bay were also affected. The great majority of cases occurred between 1954 and 1959.

Very significant levels of mercury were found in fish and shellfish from the bay. A value of 178 ppm was measured in a shellfish and 15 ppm in a fish in 1959. By 1961 the average fish body burden had dropped to

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2.3 ppm and to 0.2 ppm in 1970. It is speculated that the reason such high body burdens were observed is that mercury was discharged as methyl mercury directly from the plant. This was due to a reaction between the acetaldehyde and its mercury catalyst.

Bottom sediments in the Bay are highly contaminated by mercury. Sediments 1 km or nearer the former outfall have an average mercury concentration of over 100 ppm (dry wt). The average mercury concentration does not decrease to 1 ppm until 5.5 km from the former outfall. In 1978 it was estimated that more than 1.5×10^6 m^3 of Minamata Bay sediments were contaminated with mercury at a concentration over 25 ppm. An estimated 150 tons of mercury contaminated the sediments.

INVESTIGATIVE STUDIES

Extensive monitoring, epidemiological studies and research studies have been performed in the Minamata Bay area. The environmental monitoring included extensive monitoring of sediments both in the bay and outside of the bay and fish and shellfish monitoring. Epidemiological studies involved assessing the physical conditions of people who live in the Minamata Bay area. Symptoms of methyl mercury toxicity levels were analyzed.

Research studies varied extensively in their objectives and design. Studies that were performed include the following:

In order to assess the movement of mercury out of Minamata Bay, sampling stations were established in Yalsushiro Sea and Minamata Bay. The stations were periodically monitored for mercury. Based on the results of this study it was determined that mercury was being

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transported out of the bay. Investigative work was conducted to determine at what sediment mercury concentration there was a threat to the environment. The ultimate purpose of this work was to decide the extent of the remedial action. After extensive work and discussion, 25 ppm was determined to be the criteria level. In addition to the captive of native fish, caged fish studies were conducted in order to assess the accumulation of mercury by fish from contaminated sediments.

Unfortunately, no detailed information has been located that discusses the rationale used to arrive at the dredging alternative. (This is discussed later in the Remedial Action section of this document.) However, information is available on research studies associated with the implementation of dredging. The rate of suspended soil settling and mercury concentration relative to initial suspended soil concentrations was investigated. The effect of mechanical agitation was investigated as was the effect of pumping agitation. The permeability of impoundment materials to mercury was investigated. Coal fires proved to be the most impermeable material tested.

Once it was determined mercury was firmly bound to sediment particles the control and removal of suspended particulate became important. Various settling tests using coagulants were performed. The most successful combinations of flocculants were PAC and PA-331 (a polyacrylacide.

REMEDIAL ACTION

After years of social, political and scientific controversy, the Japanese government developed a program aiming to accomplish three objectives: 1) decontaminating an area of 1,528,000 m^3 with 25 ppm or

more mercury concentration (150 tons of mercury is deposited) 2) construction of a modern industrial harbor capable of handling 30,000 ton ships, and 3) creating 382,000 m^2 of new land with the dredge spoils.

The original estimated cost of this action was $120 million 1976 dollars. The polluters agreed to pay two-thirds of this cost. The final cost of this remedial action development project was $200 million U.S. dollars.

As previously stated, dredging was the selected remedial action, however, no information on the selection process has been located, nor is there presently any information on the use of 25 ppm mercury in sediments as the criteria level for dredging.

MONITORING

No information has been located on the status of post remedial action monitoring.

REFERENCES

Akira Kudo, Ph.D: National Research Council of Canada, Ottawa, Canada: personal communications, July 1985.

Fiziki Motoo; The Pollutions of Minamata Bay by Mercury and Minamata Disease; In: Contaminants and Sediments, Vol 2: Ann Arbor Science Publishers, 1980, pp. 493-500.

Yoshida, Tatsuo and Ikegaki, Yoshidaza; Study on the Behavours of Mercury Contaminated Sediments in Minamata Bay; In Management of Bottom Sediments Containing Toxic Substances: Proceedings of the Second U.S.-Japan Experts Meeting-October 1976, Tokyo, Japan, pp. 127-143.

R. Hirota, Fujiki, M. Ikegaki, Y. and S. Tajima, Accumulation of Mercury by Fish from Contaminated Sediments; In Management of Bottom Sediments Containing Toxic Substances: Proceedings of the Fourth U.S.-Japan Experts Meeting October, 1978, Tokyo, Japan, pp. 223-240.

Akira Kudo and Miyahura, Shojiro: Migration of Mercury from Minamata Bay; In Toxic Materials Methods for Control. University of Texas at Austin, 1983. pp.265-286.

CHAPTER C

ANALYTICAL METHODOLOGIES

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INVENTORY OF ANALYTICAL METHODOLOGIES

INTRODUCTION

The following is an inventory of the analytical methodologies that were used in generating all Volume III (site specific) data. This is not an exhaustive listing of all the methods used to analyze for mercury. Little emphasis has been placed on the identification of historical methods. Following the inventory of methods is Table C-1. Table C-1 identifies sensitivity and sampling procedures for mercury analyses by matrix. More than one method is suggested for specific matrices as several methods are acceptable for each. The recommended methods to be utilized for future use in the Berrys Creek investigation are listed following this inventory, however, the specific method should be discussed with the contract laboratory based upon their experience and equipment.

DISCUSSION

It is noted almost all methodologies utilized for total mercury incorporate C.V. (cold vapor) detection. In addition, many of the methodologies for tissue and sediments and soils are interconvertible between the two matrices.

The classes of analyses and matrices are:

total mercury - water

total mercury - soils and sediments

total mercury - tissue

total mercury - air

organo mercury - water*

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TABLE C-1

SENSITIVITY AND SAMPLING AND HANDLING PROCEDURES FOR MERCURY ANALYSIS METHODS

Matrix and Parameter	Source and Procedure	Sensitivity	Sampling and Handling Procedures
Total Hg - water	Standard methods; Dithizone	1 ug in a double beam instrument (2 ug/l) detection limit	No sampling procedures are referenced. Preserve sample with 1.5 ml HNO_3 per liter. Strong acid solutions interfere, filtration is sometimes required.
Total Hg - water	Methods for chemical analysis of water and wastes (MCAWW); cold vapor technique	0.2 ug/l detection limit in a 100 ml sample	No sampling procedures are referenced. Preserve sample with HNO_3 to pH<2. If sample to be soluble, filter prior to acidification.
Total Hg - water	Standard methods; cold vapor technique	none referenced, should be same as above	No sampling or handling procedures are referenced, however, should be same as above
Total Hg - water	SW-846, cold vapor technique	0.2 ug/l detection limit	Either plastic or glass containers are acceptable for sampling. Preserve sample to pH$\leq$2. Holding time in glass, 38 days; in plastic, 13 days.
Total Hg- water	Weaver, et al; nuclear activation	none referenced	No sampling or handling procedures are referenced.
Total Hg - soils and sediments	MCAWW; cold vapor technique	0.2 ug/g detection limit	No sampling procedures are referenced except the recommendation to insure sampling devices and containers are not contaminated with mercury. Drying the samples at 60°C is recommended.
Total Hg - soils and sediments	SW-846; cold vapor technique	0.2 ug/l detection limit (this appears high - the author)	Insure sampling devices and containers are mercury-free. Dry sample at 60°C. Both plastic and glass containers are acceptable.
Total Hg - soils and sediments	Knechtel and Fraser; cold vapor techniques	0.01 ug/g using a 0.5 g sample	No sampling or handling procedures are referenced.
Total Hg - tissue	Egaas and Julshamir; cold vapor technique	none referenced	No sampling procedures are referenced. After collection the sample should be ground, freeze dried and homogenized.
Total Hg tissue	Knechtel and Fraser; cold vapor technique	as previous Kenechtel & Fraser	No sampling or handling procedures are referenced.
Total Hg tissue	Uthe, Armstrong and Stainton; cold vapor technique	none referenced, however, equal to or less than 0.2 ug/g	No sampling procedures are referenced. Sample digestion is performed in H_2SO_4 at only 50 60°C

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TABLE C 1 (Cont'd.)

SENSITIVITY AND SAMPLING AND HANDLING PROCEDURES FOR MERCURY ANALYSIS METHODS

Matrix and Parameter	Source and Procedure	Sensitivity	Sampling and Handling Procedures
Inorganic Hg - Air	NIOSH Manual of Analytical Methods, 3rd Ed.; silvered Chromosorb P, Method 6000	detection limit - 0.003 mg/m^3	The sample is collected using a 30 mg silvered Chromosorb P sorbent tube (Ag CP), with a glass fiber pre-filter at a flow rate of 0.01 to 0.2 l/min. Mercury is thermally desorped at 650 to 700°C and analyzed using an U.V. detection. The holding time is 7 days at 25°C. Methyl mercury is a potential interference.
Inorganic Hg - Air	NIOSH Manual, 2nd Ed., V. 5: 3 stage sorbent system, Method 175	detection limit 0.001 ug Hg/sample using 15.5 cm cell	The sample is colleted using a glass fiber filter followed by AgCP followed by Carbosieve B at a flow rate of about 0.2 l/min. Mercury is thermally desorped. Some metallic mercury is found on the Carbosieve B and a connection made.
Inorganic Hg - Air	Rathje and Marcero, hopcalite technique	none referenced but less than 0.026 mg/m^3	The sample is collected using a 0.5 g hopcalite sampling tube at a flow of 1 to 3 l/min. Mercury is dissolved in a 1:1 HNO_3:HCl solution. Analysis is by U.V. detection.
Inorganic Hg - Air	Long, Scott & Thompson; silver wool as the sorbent	detection limit 0.3 ng Hg/sample using 20 cm cell	The sample is collected on 1 to 2 grams of activated silver wool. Mercury is released by thermal desorption. Analysis is by U.V. detection.
Inorganic Hg - Air	Scaringelli, et al; charcoal adsorption	detection limit less than 0.05 ug/m^3 for 24-hr sampling at 0.2 l/min flow rate	The sample is collected on a thermal activated charcoal filter. All species of mercury are reportedly absorbed at a flow rate of 0.2 to 0.6 l/min. Mercury is thermally desorped and converted to elemental mercury. The mercury is then collected on silver, thermally desorped from the silver and quantified using U.V. detection.
Organo Hg - water	Robinson and Skelly; Differential Atomization	detection limit not referenced, however, method may not be sensitive	No sampling procedures are referenced. Mercury differentiated by controlled heating and differences in the volatilization of different mercury compounds. Platinium sloop and glass rod atomizers were used to volatilize compounds. Quantification was done by using U.V. detection.
Organo Hg - water	Goulden and Anthony; different digestion procedures	detection limit: 1 ng/l	No sampling procedures are referenced. Mercury compounds are differentiated by controlling reducing conditions. By using three reagent mixtures, Hg^0 and inorganic Hg can be differentiated from organic mercury compounds. Quantitation is by U.V. detection.

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TABLE C-1 (Cont'd.)

SENSITIVITY AND SAMPLING AND HANDLING PROCEDURES FOR MERCURY ANALYSIS METHODS

Matrix and Parameter	Source and Procedure	Sensitivity	Sampling and Handling Procedures
Organo Hg - water	Longborrom, Dressman, Lichtenberg; GC/EC Method	detection limit: 0.02 ug/l	Samples should be preserved with 1 g $CuSO_4$/l Methyl mercury is extracted from water as methyl mercury iodide. Quantitation is by gas chromatography/electron capture detection.
Organo Hg - soils and sediments	Longbottom, Dressman Linchtenberg; GC/EC technique	detection limit: 0.001 ug/g using a 10 g sample	Samples should be preserved by freezing and homogenized prior to analysis. Methyl mercury is by gas chromatography separation/electron capture detection.
Organo Hg - tissues	Johansson, Ryhage, Westoo; GC/MS Method	detection limit: not referenced but less than 0.14 ug/g	No sampling procedures are recommended. Methyl mercury is extracted as methyl mercury chloride. Quantitation is by GC/EC and GC/MS
Organo Hg - tissues	Cappon and Smith, GC/EC Method	detection limit: less than 1 ug/g using a 2 g sample	No sampling procedures are recommended. Samples are either aquously or alkaline digested. Organic mercury compounds are extracted as chloride derivatives. Inorganic mercury is isolated as methyl mercury upon reaction with tetramethyltion. Quantitation is by GC/EC.
Organo Hg - tissues	Gonzales and Ross; GC/AA Method	detection limit estimated as 1.25×10^{-11} g/g, however, work done using a minimum of 0.1 ug/g	No sampling procedures are recommended. Samples are homogenized and extracted into benzene. The extract is injected into a GC for separation of compounds, the eluant is combusted and sent to a U.V. detector for quantitation.
Organo Hg - tissue	Longbottom, Dressman and Linchtenberg; GC/EC technique	Detection limit: 0.01 ug/g using a 2 g sample	Samples should be frozen; and homogenized before extraction. Methyl mercury is extracted as methyl mercury bromide. Quantitation is by GC separation and EC detection.
Organo Hg - Air	NIOSH 2nd Ed. Carbosieve B, Method S342	detection limit not referenced but less than 0.004 mg/m^3 using a 12 l sample	The sample is collected using a sorbent tube containing 12 mg of Carbosieve B at a flow rate of of 0.01 to 0.2 l/min. The sample is thermally desorped and quantified using U.V. detection.
Organo Hg - Air	Braman and Johnson; chromosorb Wiviter silvered and gold coated beads	detection limit: 0.01 ng Hg therefore 0.1 ng/m^3 for a 0.1 m^3 sample	Separation of particulate Hg, methyl mercury, mercuric chloride, elemental Hg and dimethyl mercury is provided by using a glass wool fiber. Chromosorb W - 3% SE 30, NaOH treated Chromosorb W, silvered glass beads, and gold coated glass beads. The samples are thermally desorbed and quantified using U.V. detection.

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TABLE C-1 (Cont'd.)

SENSITIVITY AND SAMPLING AND HANDLING PROCEDURES FOR MERCURY ANALYSIS METHODS

Matrix and Parameter	Source and Procedure	Sensitivity	Sampling and Handling Procedures
Organo Hg -Air	Henriques, et al; $KMNO_4$ and gold filter	none referenced	Separation of elemental Hg, methyl mercury and dimethyl mercury is made using a partical filter, gold foils, and oxidation vessel. Mercury is quantified using U.V. detection.
Organo Hg -Air	Trujillo and Campbell, Carbosieve B and silvered Chromosorb P	detection limit: 0.3 ng Hg	The sample is collected using a sorbent train containing Carbosieve B followed by AgCP. The sample is thermally desorped and quantified by U.V. detection.

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organo mercury - soils and sediments*

organo mercury - tissue*

organo mercury - air*

* organo mercury analyses include methyl mercury.

The different analytical methodologies evaluated for each class of analyses and matrices as listed. Relevant, important references for each methodology are also listed.

A. Dithizone Method

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp. 229-231 (1975).

B. Cold Vapor Techniques

1. U.S. EPA-EMSL: Methods for Chemical Analysis of Water and Wastes, pp. 245.1-1-245.1-6 (1983).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, pp. 156-159 (1975).
3. U.S. EPA: Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, 2nd Edition, pp. 7470.1-7470.7 (1984).

C. Nuclear Activation

1. J.N. Weaver, Hanson, A., McGaughey J., Steinkruger, F.J.: Determination of Heavy Metals in Municipal Sewerage Plant Sludges by Neutron Activation Analysis: Water, Air and Soil Pollution, V. 3, pp. 327-335, (1974).

II. Total mercury - soils and sediments

A. Cold Vapor Techniques

1. U.S. EPA-EMSL: Methods for Chemical Analysis of Water and Wastes, pp. 245.5-1 - 245.5-4. (1983).

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2. U.S. EPA: Test Methods for Evaluating Solid Waste. Physical/Chemical Methods. 2nd Edition, pp. 7471.1-7471.6 (1984).

3. R. Knechtel and Fraser, J.L.; Wet Digestion Method for the Determination of Mercury in Biological and Environmental Samples: Analytical Chemistry, V. 51, No. 2, pp. 315-317 (1979).

III. Total mercury - tissue

A. Cold Vapor Techniques

1. E. Egaas and Julshamn, K.: A Method for the Determination of Selenium and Mercury in Fish Products Using the Digestion Procedure: Atomic Absorption Newsletters: V. 17, No. 6, pp. 135-138 (1978).

2. R. Knechtel and Fraser, J.L.; Wet Digestion Method for the Determination of Mercury in Biological and Environmental Samples: Analytical Chemistry, V. 15, No. 2, pp. 315-317 (1979).

3. J.F. Uthe, Armstrong, F.U.J., Stainton, M.P.: Mercury Determination in Fish Samples by Wet Digestion and Flameless Atomic Absorption Spectrophotometry, Journal of the Fisheries Research Board of Canada: Vol. 27, No. [illegible] (1970).

IV. Elemental (inorganic) mercury - air

A. Adsorption onto solid sorbent

1. U.S. Department of Health and Human Services; NIOSH Manual of Analytical Methods - 3rd Edition, V. 1, pp. 6000-1 6000-7 (1984). Method uses silvered chromosorb P.

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2. U.S. Department of Health & Human Services: NIOSH Manual of Analytical Methods - 2nd Edition. V. 5. pp. 173-1 - 173-17 (1979(. Method uses three sorbents - a glass fiber filter for particulate Hg, a carbosieve sorbent for organic Hg and Chromosorb P for elemental mercury.

3. A.O. Rathje and Marcero, D.H.; Improved Hopcalite Procedure for the Determination of Mercury Vapor in Air by Flameless Atomic Absorption: Journal of the Association of American Industrial Hygiene, V. 37, pp. 311-314 (1976). The method uses hopcalite as the solid sorbent.

4. S. J. Long, Scott, D.R., Thompson, R. J.; Atomic Absorption Determination of Elemental Mercury Collected from Ambient Air on Silver Wool; Analytical Chemistry, V. 45, No. 13, pp. 2227-2234 (1973). The method uses silver wool as the solid sorbent.

5. F.P. Scaringelli, Puzak, J.C., Bennett, B.I., Denny, R.L.: Determination of Total Mercury in Air by Charcoal Adsorption and Ultraviolet Spectrophotometry; Analytical Chemistry, V. 46, No. 2, (1974). Total mercury is determined by the use of charcoal as the solid sorbent.

V. Organo mercury - water

A. Cold Vapor Techniques

1. J.W. Robinson and Skelly, E.M.: Speciation of Mercury Compounds by Differential Atomization - Atomic Absorption Spectroscopy, Journal of Environmental Science Health, V. A17, No. 3, pp. 391-425 (1982). Method employs

differences in the volatilization temperature of mercury compounds as a means of separation.

2. P.D. Goulden and Anthony, D.H.J.; Chemical Speciation of Mercury in Natural Waters; Analytical Chemica Acta. V. 120, pp. 129-139, (1980). Method uses different digestion conditions to separate forms of mercury.

B. Gas Chromographic Techniques

1. J. E. Longbottom, Dressman. R.C., Lichtenberg, J.J.; Gas Chromatographic Determination of Methyl Mercury in Fish, Sediment, and Water; Journal of the Association of Official Analytical Chemist; V. 56, No. 6, pp. 1296-1303 (1973). Method uses gas chromatography to identify mercury compounds.

VI. Organo Mercury - soils and sediments

A. Gas Chromatographic Techniques

1. J.E. Longbottom, Dressman, R.C., Linchtenberg, J.J.; Gas Chromatographic Determination of Methyl Mercury in Fish, Sediment, and Water; Journal of the Association of Official Analytical Chemist; V. 56; No. 6; pp. 1297-13-3 (1973).

VII. Organo Mercury - Tissues

A. Gas Chromatographic Techniques

1. G. Johansson, Ryhage, R., Westoo, G.; Identification and Determination of Methyl - mercury compounds in Fish Using Combination Gas Chromatography - Mass Spectrometer; Acta Chem. Scand.; V. 24; No. 7, pp. 2349-2353 (1970).

2. C.J. Cappon and Smith, J.C.: Gas-Chromatographic Determination of Inorganic Mercury and Organo-mercurials in Biological Materials: Analytical Chemistry: Vol. 49, No. 3, pp. 365-369 (1977).

3. J.G., Gonzalez and Ross, R.T.; Interfacing of an Atomic Absorption Spectrophotometer with a Gas-Liquid Chromatograph for the Determination of Trace Quantities of Alkyl Mercury Compounds in Fish Tissue: Analytical Letters: V. 5: No. 10, pp. 683-694 (1972).

4. J.E. Longbottom, Dressman, R.C., Lichtenberg, J.J.: Gas Chromatographic Determination of Methyl Mercury in Fish, Sediment, and Water; Journal of the Association of Official Analytical Chemist; V. 56; No. 6; pp. 1297-1303; (1973).

B. Cold Vapor Techniques

1. L. Magos; Selective Atomic - Absorption Determination of Inorganic Mercury and Methylmercury in Undigested Biological Samples; Analyst: Vol. 96; pp. 847-853 (1971).

VIII. Organo Mercury - Air

A. Absorption onto solid sorbents

1. U.S. Department of Health and Human Services; Organo (alkyl) Mercury, Method S342; NIOSH Manual of Analytical Methods - 2nd Edition. Method uses Carbosieve B, Thermal desorption and cold vapor.

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2. R.S. Braman and Johnson, D.L.: Selective Absorption Tubes and Emission Technique for Determination of Ambient Forms of Mercury in Air, Environmental Science and Technology; V. 8: pp. 996-1003 (1974). Method uses Chromosorb-W, silvered and gold-coated glass beads, thermal desorption and cold vapor.

3. A. Henriques, Isberg, J. and Kjellgren, D.: Collection and Separation of Metallic Mercury and Organo-mercury Compounds in Air: Chemica Scripta; V. 4: pp. 139-142 (1973). Method uses $KMnO_4$ solution and a gold filter.

4. P.E. Trujillo and Campbell, E.E.: Development of a Multistage Air Sampler for Mercury: Analytical Chemistry, Vol. 47, NO. 9, pp. 1629-1634 (1975). Method uses Carbosieve B, and Silvered Chromosorb P as sorbents, thermal desorption and cold vapor.

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RECOMMENDED ANALYTICAL METHODS FOR THE
ANALYSIS OF MERCURY

The following is a list of the recommended methods for each matrix and a justification for this recommendation.

Total Mercury in Water: The cold vapor technique as described in SW-846 (Test Methods for Evaluating Solid Waste - Physical/Chemical Methods) is the recommended analytical procedure. The method number is 7470. This method is recommended for the following reasons:

1. It is the standard permanganate digestion followed by stannous sulfate reduction with U.V detection. This method has been used for years with good results. Interferences are well documented and correctable.
2. SW-846 is the document listing testing procedures EPA requires for testing in its hazardous waste programs, therefore, an EPA methodology will be utilized.
3. No specialized equipment except for an atomic absorption spectrophotometer and a cold vapor apparatus are required.
4. The method is quite sensitive and also has good precision and accuracy.

Total Mercury in Soils and Sediments: The cold vapor technique as described in SW-846 (Test Methods for evaluating Solid Waste Physical/Chemical Methods) is the recommended analytical procedure. The method number is 7471. This method is recommended for the following reasons:

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1. This method is based on the cold vapor technique. It incorporates a permanganate/aqua regia digestion procedure, stannous sulfate reduction and U.V. detection. The cold vapor technique has been used for years with good results. Interferences are well documented and correctable.

2. SW-846 is the document listing testing procedures EPA requires for testing in its hazardous waste programs; therefore, an EPA approved methodology will be utilized.

3. No specialized equipment or sample handling except for an atomic absorption spectrophotometer and a cold vapor apparatus are required.

Total Mercury in Tissue: The cold vapor technique as described in Uthe, Armstrong and Staninton: Journal of the Fisheries Research Board of Canada, Vol. 27, No 4, 1970 is the recommended procedure. This method is recommended for the following reasons:

1. The method is a standard acid permanganate digestion followed by stannous sulfate reduction with U.V. detection. Interferences are well documented and correctable.

2. There are no EPA "approved" methodologies for the analysis of mercury in tissues; therefore, a methodology resembling the approved methodologies for water and soils and sediments would seem preferable.

3. No specialized equipment or sample handling is required except for an atomic absorbance spectrophotometer and cold vapor apparatus.

Total Mercury in Air: (There is no single accepted method for total mercury in air; therefore, the recommendation will be for a methodology for the analysis of particulate mercury and elemental mercury vapor.)

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The recommended adsorption, thermal desorption, flameless AA method is described in the NIOSH Manual of Analytical Methods - 3rd Edition, Volume 1, Method 6000. This method is recommended for the following reasons:

1. The sampling device is small, portable and involves no liquid.
2. The silvered Chromosorb P tubes are available on special order from SKC, Inc.
3. The method has been approved by NIOSH following a validation over the range of 0.0456-0-1800 mg/cum. The method, however, can measure smaller amounts
4. Some special equipment and sample handling is required. This included a sampling pump, flow controller, thermal desorption unit and an atomic absorption spectrophotometer.
5. Gold foil detectors such as the Gerome Models would be prohibitively expensive if several stations are monitored simultaneously and would require additional equipment for intergrating results.
6. A potential problem with this method is the possibility that methyl mercury is also retained on the absorbent. If this is so, the method would not be specific to inorganic mercury. It is also the author's understanding the Gerome models cannot differentiate between organic and inorganic mercury.

Organic Mercury in Water: The recommended method is a gas chromatography/electron captive detector (GC/EC) method. The method is described in Longbottom, Dressman and Lichtenberg in the Journal of the Association of Official Analytical Chemists, (JAOAC), Vol 56, No.6. The method consists of pH adjustment, benzene extraction, solvent

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concentration, clean-up, iodinations of methyl mercury and GC/EC separation and detection. This method is recommended for the following reasons:

1. This is a commonly employed methodology for the quantitation of methyl mercury.
2. There are no EPA approved methodologies.
3. The methodology is relatively simple with only one derivation required.
4. The equipment needed is not highly specialized, being a GC/EC detector and chromatographic columns.

Organic Mercury in Soils and Sediments: The recommended method is a GC/EC method. The method is described in Longbottom, Dressman and Lichtenberg JAOAC, Vol.56, No. 6. The method consists of homogenizing the sample, determine moisture content, brominations, toluene extraction, clean-up, iodination of methyl mercury and GC/EC separation and detection. This method is recommended for the following reasons:

1. This is a commonly employed methodology for the quantitation of methyl mercury.
2. There is no EPA approved methodology for the determination of methyl mercury.
3. The methodology is relatively simple with two derivations required.
4. The equipment needed is not highly specialized, being a GC/EC detector and chromographic columns.

Organic Mercury in Tissue: The recommended method is a GC/EC method. The method is described in Longbottom, Dressman and Lichtenberg JAOAC, Vol.56, No. 6. The method consists of homogenizing the sample, determine moisture content, bromination, toluene extraction, clean-up,

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iodination of methyl mercury and GC/EC separation and detection. This method is recommended for the following reasons.

1. This is commonly employed methodology for the quantitation of methyl mercury.
2. There is no EPA approved methodology for the determination of methyl mercury.
3. The methodology is relatively simple with two derivations required.
4. The equipment needed is not highly specialized, being a GC/EC detector and chromographic columns.

Organic Mercury in Air: The recommended method for the analysis of organic mercury in air is a sampling tube train consisting of a mixed cellulose ester filter followed by a Chromosorb-W absorption tube, followed by a silvered glass bead absorption tube, followed by a gold-coated glass bead absorption tube. This method is published in Environmental Science and Technology, Vol. 8, pp 996-1003. The removal scheme is as follows: particulate bound mercury is removed by the mixed cellulose ester filters, methyl mercury is removed in the Chromosorb-W, elemental mercury is removed by the silvered beads and dimethyl mercury is removed by the gold-coated beads. All tubes are analyzed by thermal desorption and U.V. detection. This method is recommended for the following reasons:

1. The method separates metallic mercury, methyl mercury and dimethyl mercury from each other.
2. The preliminary validations work contained in the publications appears quite promising, although more work will be required before this method is used without restrictions.
3. The method is very sensitive.

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4. The method is relatively complex with four types of absorbents. Relatively complex desorption procedures are required.

5. If additional validation testing demonstrates the effectiveness of this methodology this single method can be used to separate all mercury species of interest and the procedure recommended for the analysis of inorganic mercury can be omited.

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CHAPTER D

MODELS FOR ESTUARY PROCESSES

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MODELS FOR ESTUARY PROCESSES

SUMMARY

A major consideration in evaluating remedial actions to be employed for the Berrys Creek site are the secondary environmental effects associated with the activity. Also of concern is the long term consequences of remedial activities as well as development activities planned for the basin. This task has concentrated on identifying and reviewing tools that may be of use in evaluating the potential for mercury transport that may result from planned or contemplated activities.

The potential for the transport of mercury is dependent on the chemistry of the aquatic environment as well as hydrodynamics. Mercury may be in a soluble or insoluble form depending on the chemistry of the aquatic environment. It may also be strongly or loosely bound to solid or sediment particles depending on the water chemistry and the electrochemical nature of the solid surface.

Present information indicated that, under conditions that have existed in Berrys Creek since the mercury discharge commenced, mercury was deposited in the sediments of the creek, and this sediment mercury is not highly mobile. This is consistent with generalized observations concerning sediment transport within the estuaries along the northern Atlantic coast of the United States. A high percentage of the sediment in the tributaries of these estuaries is deposited within the estuary and is not widely distributed.

At this time, although "candidate" processes have been identified, there is not a complete understanding of the relative significance, or

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the specific parameters that control mercury transport in the creek. The sensitivity of mercury transport to the range of chemical compositions of the water has not been demonstrated. There is also not sufficient data to determine whether the vertical dimension is significant with respect to the hydrodynamic transport of sediments, or whether chemical equilibrium factors are more significant than hydrodynamic factors. These determinations can only be made after additional understanding is developed of

the impact of these phenomena

in Berrys Creek.

It is most likely that this understanding can be most efficiently be obtained from stepwise data acquisition-analysis that will refine the understanding of the significant phenomena and determine the parameters that are most significant to mercury transport. If a more thorough understanding is indicated further efforts can be concentrated on the parameters to which mercury transport is most sensitive.

RECOMMENDED INVESTIGATIVE MODELING

Investigation of the chemical effects on mercury transport should begin with analysis of the existing data. The available data should serve as a basis to estimate the range of concentrations that could be expected in Berrys Creek. Simulations of the chemical equilibrium can then be made to determine the sensitivity of mercury solubility to the range of observed and expected chemical constituent concentrations. This analysis should demonstrate which chemical constituents most affect the solubility of mercury, and therefore which constituents may need to be investigated further with additional data acquisition and analysis.

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Of the computer programs reviewed here, the PHREEQE or GEOCHEM program with their external data bases would be suitable for use in simulating the chemistry of mercury in Berrys Creek. Available information can be used in the preliminary analysis, however, the application of these programs may require extensive literature and possibly laboratory research to determine accurate equilibrium constant data for the interactions of the chemical species found in Berrys Creek.

Investigation of the sediment transport should begin with a study of the hydraulic characteristics of Berrys Creek, and the potential range of hydraulic conditions that may occur in the area. This can be done assuming a one dimensional representation of Berrys Creek. The results can then be compared to the estimated erosion potential of the creek bottom deposits to determine a gross estimate of the potential for transport of sediments from the contaminated area under the range of conditions expected to occur.

Data must also be obtained to determine the propriety of the one dimensional hydraulic assumption; verify the creek physical dimensions used, and characterize the erodibility of the Berrys Creek bottom sediments.

This will require characterization of the water chemistry and velocities throughout the water column under the range of hydraulic regimes that will influence Berrys Creek. Sediment deposits must also be characterized. The characterization should include particle size, density, and shear strength under the range of water quality conditions that will exist under the hydraulic regimes anticipated.

If significant chemical or velocity stratification is found in the lower reaches of the creek, a two-dimensional, laterally averaged model

may be necessary to accurately describe the mercury transport. If no stratification is found in the creek a one-dimensional representation of the creek should accurately describe the hydraulic transport in the system.

Application of a two-dimensional model should only be attempted if a one-dimensional model will clearly fail to predict transport with acceptable accuracy. In the sediment transport model, depending on the sediment characterization, it may be necessary to consider the various sediment fractions separately rather than in an average sense. The selection of a specific sediment transport simulation model for use in Berrys Creek should be based on data and analysis to be done. As a result, it is not possible to make a specific recommendation at this time. The models reviewed here have been designed to simulate sediment transport within specific limitations characteristic of the given model and would be appropriate for those conditions.

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INTRODUCTION

Modeling of estuary processes can be very complex, this is because the number of different phenomena that may be of significance with respect to the process of concern may be many. One of the main reasons for the difficulty in evaluating the relative significance of various processes in an estuary is that an estuary is an area of transition. This is true with respect to hydraulics, water chemistry, and biological regimes.

With respect to hydraulics, the water flow is reducing in velocity and changing from free flow to tidal flow, and also, from water of fresh water density to salt water density. This results in highly complex circulation patterns that are highly individualized and site specific.

Water chemistry also changes dramatically through an estuary. The obvious change in chemistry is the increase in the salinity and chlorinity as the sea water mixes with the fresh water. The changes in salinity can have profound effects on chemical equilibria, chemical complex stability, and clay mineral dispersion. The higher concentrations of anions in the salt water can precipitate the less soluble metal ions. The high sodium ion concentrations will displace the higher valence ions in ion complexes This will result in the destabilization of the ion complex and also result in precipitation. Likewise, the sodium ion concentration will destabilize the dispersed clay minerals and result in clay deposition.

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In many estuaries, a stratification will occur that will result from the less dense fresh water over running the more dense salt water. Measurements have shown (O'Connor and Lung, 1981) that the net mass flow in the salt layer is in the upstream direction. Chemical interactions will occur at the interface where the fresh water and salt water mix. Normally, precipitates from the chemical reactions as the freshwater and sea water mix, (the suspended sediment load from upstream) will settle to the lower layer and be carried upstream (Figure D-1). The resulting cycling creates a substantial suspended solids "peak" or "turbidity maximum". O'Connor and Lung's data indicate that this point occurs at the point in the estuary where the average salinity reaches the 5 to 10 ppt level. The salinity of the lower end of Berrys Creek reaches this salinity range, and therefore the possibility of this phenomena occurring in Berrys Creek should be investigated.

The processes which could possibly affect the heavy metal ion concentration and in particular mercury concentration in an estuary include chemical equilibrium precipitation-dissolution reactions, oxidation-reduction reactions, metal complexation, and cation exchange as well as hydraulic transport. While these processes are all potentially important in describing the movement of the mercury in estuarine conditions, it is highly likely that in Berrys Creek certain processes will be more significant and possibly dominant with respect to being able to describe mercury transport.

In addition, it must also be kept in mind that the factors that may affect processes in Berrys Creek are not expected to be constant. The organic load to the system will be reduced by the removal of STP discharges. Further development of the area will reduce the marsh area.

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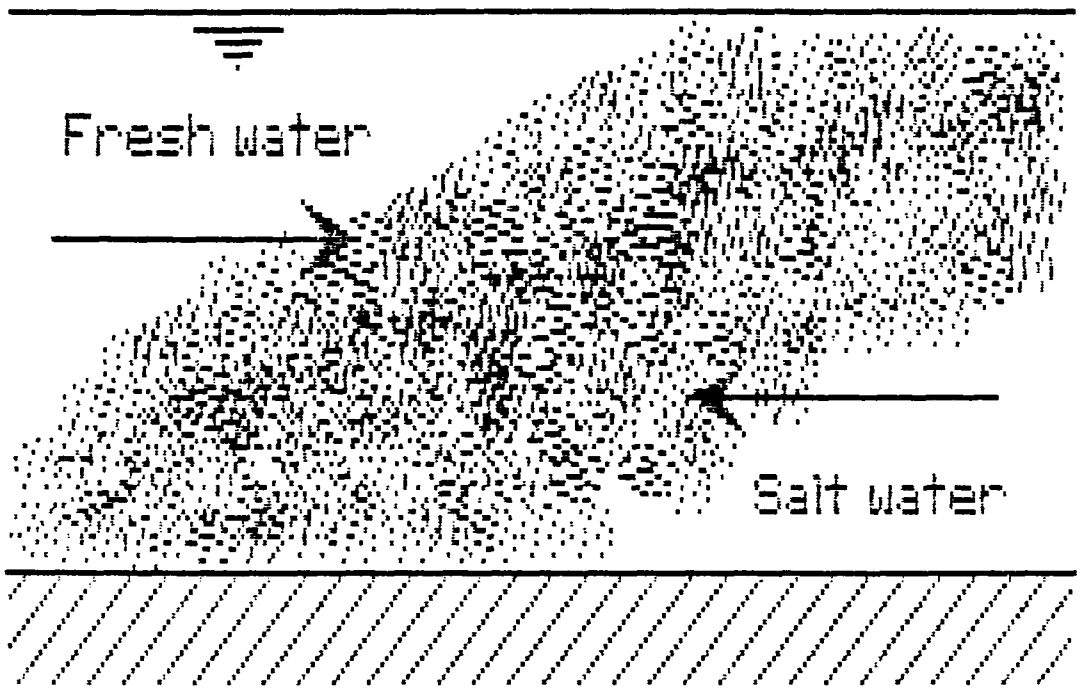

Figure D-1. Accumulation of Solids in an Estuary

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reduce the overall rainfall infiltration rate, change runoff water quality and reduce the runoff time of concentration. These changes could have profound effects on the potential for mercury transport from the sediments and marshes adjacent to Berrys Creek.

MERCURY TRANSPORT IN BERRYS CREEK

From available information it can be assumed that mercury contamination of Berrys Creek began in the 1920s and continued into the 1970s. Extensive deposits of mercury now exist in the sediments of Berrys Creek for approximately 2000 ft. downstream from the original discharge and in addition to limited contamination of the surrounding marshes. Considering that mercury has entered the creek over a long period of time, the lateral migration of mercury has been minimal, and measurements of soluble mercury have been extremely low compared to the concentrations found in the sediments and soils. From this evidence it appears that the transport of the mercury is associated with the transport of the sediments, and also that the transport of sediment in Berrys Creek is very slow.

At this point a conceptual model of the sediment transport in the Berrys Creek area cannot be supported by the available data. There are two possible conceptual models that could explain the limited extent of the occurrence of mercury in the sediments of Berrys Creek, that have considerably different implications with respect to the need and method of remediation.

A possible scenario is suggested by the work of Meade(1982). It was pointed out that sediment transport is not a process that takes place at a slow continuous rate. Rather, it is an "event" type process.

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Fifty percent of the sediment transport takes place in 1% of the time, and roughly 85% of the transport will take place in less than 10% of the time. Mead also points out that 90% of the sediments from east coast streams do not leave the estuaries. This is because of the complex tidal circulation resulting from density differences between fresh and sea water. It could be possible that the Berrys Creek area is a deposition zone where there is a net sediments accumulation. This would be an explanation for the limited extent of mercury migration from the source. Although the net transport of sediment may be into the creek, it must be recognized that there may be hydraulic regimes where sediment is leaving the area. There are four obvious flow circulation regimes where the sediment transport could be substantially different. These are:

1. Tidal flood conditions.
2. Local rainfall runoff events.
3. High Hackensack River flow events with normal tides.
4. "Normal" flow and tidal conditions.

It may be that during tidal flood and local storm conditions a high flushing flow from the headwaters of the creek may transport sediment from the creek, while during normal conditions and high river flow, the complex flow circulation may result in sediment actually being transported in the upstream direction in the lower reaches of the creek. Substantial volumes of sediment may be transported in relatively short time periods during an "event".

While the sediment is transported during relatively short time intervals, chemical and biochemical reactions will probably result in

significant chemical transformations during the periods of time when the sediment transport is currently minimal. Proposed or anticipated changes within the basin that change water quality may result in chemical equilibrium changes that may effect mercury mobility.

An alternative conceptual model of this could be based on the changes in chemical equilibrium that may result from the changes in salinity of the creek water as it mixes with the sea water. In this theory the mercury in the sediments is bound to the ion exchange sites of the clay and organic material. As the sediment bed load is transported downstream, the higher sodium ion concentration of the water will begin to displace the mercury from the ion exchange sites, and release it to the water in very low concentrations. The prediction that would result if this model were accurate would also indicate that the mercury is not migrating extensively from the source of the initial contamination. If the release were slow enough, changes in concentration would not be detectable.

DATA NEEDS

Although there has been considerable effort and analysis of mercury levels in Berrys Creek and the surrounding area, the major goal of this study has been oriented toward evaluating the current extent of the mercury migration and the extent of the biological impact. Although these are important objectives, the resultant data has not shed any light on the mechanisms of mercury transport or the factors that inhibit or promote that transport.

At this point, there is not enough chemical data for Berrys Creek to evaluate the relative significance of the processes that may

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currently be effecting mercury transport in the system or that may be effecting transport in the future. It may be that once the relative significances are understood, the necessary actions will not require extensive transport simulation to evaluate the impact of alternatives under consideration for remedial action.

The types of information that must be obtained include the data necessary to quantify and characterize the sediment that is entering the creek both from the upstream, and, if applicable, from downstream. The characteristics of the sediments must also be known. Important characteristics necessary to evaluate the sediment transport potential include particle size, organic fraction, and clay fraction and minerology. In addition, the mercury associated with the sediment classifications found must be known.

The modeling tools described in this report can be used to simulate the processes that may be significant factors concerning mercury transport and the results compared to known response of the system to determine the significance of process. Currently, however, the available data do not permit the determination of the significant processes, and therefore it is not possible to recommend specific tools to simulate mercury transport.

As an example, the behavior of the sediments and the mercury transporting characteristics of the sediments is dependent on the cohesivity of the sediment grains. Models that simulate cohesive sediments also are significantly more complex and more difficult to use than those that do not. If a model that does not simulate cohesive sediments could accurately reproduce the conditions of Berrys Creek, the modeling tasks would be less difficult. Some of the sediment samples

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from Berrys Creek for which lithology was reported included clay as a constituent. Until the presence of cohesive materials in Berrys Creek sediments is quantified, and its significance related to mercury transport documented, it will not be possible to intelligently decide on the proper sediment transport modeling tool.

Through this process, an understanding of the factors that in Berrys Creek is determined, influence mercury transport can be obtained.

The purpose of this report, therefore, will be to present and describe, in general terms, the modeling tools that are available and may be of value in assessing the impacts of the remedial measures that may be considered and the method of implementing those alternatives.

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CHEMICAL EQUILIBRIUM MODEL

The chemical and physical behavior of aqueous solutions is characterized adequately enough to allow us to build models of natural systems. The creation of the computer programs to implement such models has employed an interdisciplinary approach, drawing on such fields as physical and geochemistry, environmental engineering, numerical analysis and computer programming. The computer programs that have been developed have two main thrusts, calculation of species distribution and testing of solubility hypothesis. Specific programs discussed have their own individual emphasis. Past uses of these programs include: examining the availability of free and reactive ions; determining the potential bioavailability of nutrients or toxic substances; predicting the chemical changes caused by seawater encroachment in a fresh water aquifer; predicting the solubility of minerals in a given solution; examining the effects of the agricultural practices such as irrigation and fertilization on quality; and examining the effects of the addition of pollutants, such as organic ligands, to a given system.

The species distribution problem can be solved in two different ways, the Gibbs free energy approach and the equilibrium constant approach. Programs reviewed here have used the equilibrium constant approach since there are generally more reliable and available data for the equilibrium constant approach.

The equilibrium constant approach is based on the fact that for every chemical equation a unique equilibrium constant exists. The

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equilibrium constant is a function of the temperature and the nature of the reaction. All chemical reactions are also subject to the restraint of mass balance. Roughly mass balance is "chemical bookkeeping" where the computed sum of all free and complexed species must equal the given concentrations. Numerically stated, the system of chemical equations given is a set of non-linear equations. The standard method of solving the problem by equilibrium constant approach is linearized matrix inversion. A more detailed treatment of the numerical methods involved are given by the individual models and publications by Van Zeggeren and Storey (1970) and by Mercer et al. (1981).

REVIEW OF CURRENT GEOCHEMICAL COMPUTER MODELS

Successive Approximation Based Models

Current geochemical models can be divided into two families according to the numerical method used to solve the equations of equilibrium reactions.

The first family of geochemical models evolved from the aqueous model for seawater developed by Garrells and Thompson (1962) and uses successive approximation as its numerical method. The geochemical computer model SOLMNEQ was developed by Kharaka and Barnes in 1973 based on this approach. SOLMNEQ requires the input of temperature (^{o}C), pH, Eh and concentrations of 27 major species (see Table D-1) in ppm, mg/l, or meg/l concentration units. Optional input includes the density of the solution and variations of the measured Eh.

The data base for SOLMNEQ consists of K values over a range of temperatures from 0-350°C in increments of 25°C. The data base was generated from reported data, computer programs (using standard

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TABLE D-1

REQUIRED CHEMICAL ANALYSES

Model Name	Analyses Required
SOLMNEQ	Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Cl^{-}, SO_4^{--}, HCO_3^{-}, SiO_2, Ag^{+}, Al^{+++}, Ba^{++}, Cu^{++}, Fe^{++}, Fe^{+++}, Hg^{++}, Li^{+}, Mn^{+}, Pb^{++}, Sr, Zn^{++}, $As(OH)_4^{-}$, PO_4^{--}, F^{-}, H_3BO_3, NH_3, CO_3^{--}, and NO_3^{-}
WATEQ	Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Cl^{-}, SO_4^{--}, HCO_3^{-}, Fe^{++}, Fe^{+++}, H_2S, CO_3^{--}, SiO_2, NH_4^{+}, B^{+++}, PO_4^{--}, Al^{+++}, F^{-}, and NO_3^{-}
MIX2	Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Cl^{-} and SO_4^{--}

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entropies, enthalpies, free energies and heat capacities) and extrapolation of K values known at single temperature. SOLMNEQ computes activity coefficients using the extended Debye-Huckel equation. SOLMNEQ also uses the Gibbs free energy difference equation to show states of supersaturation, saturation or undersaturation relative to the solid phase.

SOLMNEQ has been extensively updated since 1973. Updated equilibrium constants and correction for pressure effects on equilibrium constants are included. Subsurface pH can be calculated from surface pH of a given sample. The data base has expanded to include several more organic and inorganic complexes (Kharaka 1982).

Another early computer model developed from Garrells and Thompson (1962) is WATEQ by Truesdell and Jones (1973). WATEQ requires the input of temperature, pH, Eh and the concentration of 17 major species (see Table D-1) in units of ppm, mg/l, meg/l or mole/l. Optional input includes density, variations on the Eh measurement, ppm of dissolved oxygen and concentration of certain trace elements (Li, Sr and Ba).

The program corrects for temperature using the Van't Hoff equation. The data base for WATEQ comes from an extensive literature search. Activity coefficients are computed from the extended Debye-Huckel equation with the MacInness assumption for terms a and b (MacInness 1939, Truesdell and Jones 1974). Eh is converted into pE within this program and is used to calculate equilibrium in redox reactions. WATEQ computes degree of saturation by comparing the activity product with the equilibrium constant (see Trusedell and Jones 1974).

From the original WATEQ program, several "second generation" programs have been developed. Many of the changes from WATEQ involve

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the code itself, its error checking ability, and inclusion of additional chemical species. WATEQ2 also includes improved documentation and faster, more reliable numerical methods for checking mass balance. The structure of the program is taken from WATEQF, which is discussed later. WATEQ2 was further updated by Ball et al. (1980)

WATEQ3 (Ball et al. (1981) adds seven species of uranium and further documentation to WATEQ2. There are no other notable differences between WATEQ2 and WATEQ3.

WATEQF is a FORTRAN version of WATEQ developed in Pl/I in 1976 by Plummer et al. WATEQF has added 100 aqueous species including 14 species of manganese to the WATEQ data base. The data base can be directly augmented during the input phase by the user. The program also uses either the extended Debye-Huckel equation or the Davies equation to compute the individual activity coefficients. In addition to calculating pE from dissolved oxygen and Eh (as in WATEQ), pE can be set by the dissolved oxygen relation of Sato (1960) and by the SO_4^{--}/S^{--} ratio. The output has been modified to allow for several print options, thus limiting the volume of output. WATEQF also includes improved numerical methods for checking mass balance resulting in faster execution times.

WATEQF was updated by Lueck (1978) to include 21 species of uranium and improved documentation and data entry.

WATSPEC (Wigley 1977) is a shorter version of WATEQF, designed for distribution of species problems in routine hydrological analyses.

MIX2 (plummer et al. 1975) is a different variation of the WATEQ family. MIX2 uses WATEQ data base and develops its model from reaction progress in closed system. Plummer et al. suggest three general classes

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of problems: 1) mixing of two solutions in fixed volume, 2) titration of one solution into another, 3) addition or subtraction of a net stoichiometric reaction to or from the defined aqueous system. Input includes volume specifications, temperature, specific reactions to be followed, pH, density of solution and concentrations of six species (see Table D-1) and total carbon in concentration units of meg/l, mg/l, ppm or mole/kg.

The input also includes an option to balance the charge of the defined solution using K+ or Cl- (the defined solution must be electrically balanced for the program to work). Activity coefficients are computed from the extended Debye-Huckel equation with given values for parameter b. Output includes volume changes, pH changes and thermodynamic data.

EQ3/6 (Worley 1979) is actually a combination of two geochemical programs. EQ3 is a equilibrium constant/distribution of species program of the type already discussed in this paper. The data base was taken mainly from the work of Hegleson and others (1974, 1978) and covers in 25°C increments and two possible pressures. Input is flexible in this program including such values as pH, several redox parameters, and concentrations of specific ions, either "free" or "total" concentrations. Individual activity coefficients are computed from the extended Debye-Huckel equation. EQ6, the second geochemical program, is a reaction-path model. This is a member of a relatively small family of computer models based on the PATHI (also known as PATHCAL, Hegleson 1970) computer model. A more extensive review of these models and their approach can be found in Mercer et al. (1981)

EQ6 takes the aqueous system defined by EQ3 and checks first for homogenous equilibrium. If there are any supersaturated constituents. they are "precipitated" from the aqueous phase up to their solubility limits. The resulting solids may be retained or discarded from the system. Titration or irreversible reactions are then modeled for either closed to solids or a flow-thru model. The whole system (including O and H present in solvent) is subject to mass and charge balance. All these steps will change such parameters as pH, Eh and distribution of species.

Most members of WATEQ family have been developed by the United States Geological Survey, and the geochemical model PHREEQE (Parkhurst et al. 1980) represents the most recent addition to that family. The authors suggest three general uses of PHREEQE; additions of reactants to a solution, mixing of two waters, and titrating one solution with another.

The data base for PHREEQE is completely external to the actual program. However, a preliminary data base is suggested. Input includes analytical concentrations of defined elements, pE, pH, temperature (in ^{o}C) and density.

Individual activity coefficients are calculated by either the Debye-Huckel, extended Debye-Huckel, or the Davies equation. If specified, PHREEQE can calculate two parameters as reactions progress: 1) pH as defined by electroneutrality and mass balance 2) pE as determined by species whose valence might change in the defined system. Output also includes concentration of each element, distribution of species, mass transfer of specific mineral in and out of solution and

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the saturation state of specific minerals. As suggested above, PHREEQE has limited capacity to model reaction paths, similar to EQ 3/6.

Newton-Raphson Based Models

The second approach to solving the problem of speciation in complex solutions has been developed by Morel and Morgan (1972), resulting in the computer model REDEQL. Based on this initial work, McDuff and Morel (1973) developed REDEQL2. Both models use the Newton-Raphson numerical method to solve the set of nonlinear equations generated by the equilibrium reactions. Since the last update of the REDEQL2 program in 1976, a new generation of programs using the Newton-Raphson method has been developed. These programs differ considerably from REDEQL2.

REDEQL.EPAK is one of these second-generation computer models and it was developed by Ingle et al. (1980). The data base for REDEQL.EPAK comes from a literature survey. The data base can also be directly augmented by the user. Input includes concentration of specified ligands and metals, print options, estimated ionic strength, estimated pH, redox reactions considered, partial pressure of CO_2 and N_2, and pE. Individual activity coefficients are calculated using the Davies equation. For temperature corrections, the Van't Hoff equation is used. There are 24 redox reactions that can take place which must be referenced by the user during the input. The program can calculate pH. The user can specify whether the solution is electroneutral or not. The program includes an adsorption routine using a surface complexation adsorption model. Only the ligand surfaces are considered. A prototype of this model is described by McDuff and Morgan (1976). Output includes saturation data, speciation and various user specified options.

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Another program based on the work of Morel and Morgan (1972) is the chemical computer model GEOCHEM (Mattigod and Sposito 1979). This model is especially suited to the speciation of trace, or "heavy" metals. The data base for GEOCHEM was generated by a literature search and estimation of values for unknown species, based on properties of the unknown species such as electronegativity, radius, charge and coordination number. The individual activity coefficients are calculated from the Davies equation. The program also includes a cation exchange routine for clay materials based on a thermodynamic model.

MINEQL2 (Westhall et al. 1976) is a direct descendant of the original REDEQL models. It includes a "Swiss" adsorption model and an external, user-augmented data base. Several versions of MINEQL2 exist, but no information on any of them was available to include in this report.

Summary of Computer Model Characteristics

Chemical characteristics and computer code information of the discussed models are summarized in Table D-2.

The first page of Table D-2 lists the computer coding characteristics of the models. A comparison of utilized computer languages, program length and availability of user's manual and documentation is given. References including program listing are cited.

The second page of Table D-2 compares the number of elements, species, organic chemicals and redox reactions used in each model.

LIMITATIONS OF GEOCHEMICAL COMPUTER MODELS

It is important to know the limitations of geochemical models. They provide a means for understanding rather than a method for precise

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TABLE D-2

MODEL CODE INFORMATION

Name	SOLMNEQ[1]	WATEQ[3]	WATEQF[3]	WATSPEC[4]	MIX2
Language	PL-1	PL-1	FORTRAN	FORTRAN	FORTRAN
Computer	IBM 3/0	Honeywell[2] 60/68/80	IMB 370	ILL 1903 IBM 370	IMB 370
Number of Statements	2,000	3.000[6]	1,857	423	1,150
Documentation & User's Manual Available?	no	yes	yes	N/A	yes
Is Code Available?	yes	yes	yes	N/A	yes
Code Listing in Reference	Kharaka *et al*. 1973	Ball *et al*. 1981	Plummer *et al*. 1976	Wigley 1977	Plummer *et al*. 1975

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TABLE D-2 (Cont'd.)

MODEL CODE INFORMATION

Name	PHREEQE	EQ 3/6	REDEQI.EPAK	GEOCHEM[4]	MINEQ1.2[4]
Language	FORTRAN-IV	FORTRAN	FORTRAN	FORTRAN	FORTRAN
Computer	Amdahl 470V/7	CDC 6600	IBM 370	IBM 360	CDC CYBER 74
Number of Statements	2,434	30,000	4,000	3,630	1,500
Documentation & User's Manual Available?	yes	included in program	yes	N/A	N/A
Is Code Available?	yes	only from NESC	yes	N/A	N/A
Code Listing in Reference	Parkhurst et al. 1980	N/A	see note 5	N/A	N/A

1 Most recent version (Kharaka 1982)
2 WATEQ3 has been extensively suited in the Honeywell computer (Ball memo 1981). WATEQ2 is available in versions suitable for both the Honeywell 60/68/80 and the IBM 370 (Ball et al. 1979).
3 Plummer et al. (1976) version.
4 From Nordstrom et al. (1979).
5 Code available through COMNET computer system. Instructions given in Ingle et al. (1980).
6 Estimated.

N/A indicates no information obtained.

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solution of a particular, real-world problem. Many of the weaknesses of the discussed models involve critical problems which must be further researched before they become useful in applications involving pollution chemistry.

First of all, no computer program output is any better than the data it is given. Most chemical models rely on chemical data which are easily measured by analytical chemistry techniques, however, a few commonly-encountered chemicals are difficult to measure. Another source of inaccuracy lies in the field analysis of samples. As a result published values for reaction constants for some reactions may vary widely. Therefore, the data base used in applications must be checked closely.

Secondly, a computer equilibrium model assumes that the described solution is at equilibrium. Although generally accurate, this is not always true, especially in regard to systems which involve biological activity (Ingle et al. 1978). Micro-organisms act as catalysts in many reactions, especially redox reactions, and their action is hard to quantify.

Thirdly, equilibrium constants and other data for environmentally important chemicals such as organic (both natural and synthetic) ligands and trace metals are rare. Jenne (1979) points this out as one of the most important problems facing researchers and model builders in quantifying and characterizing natural aqueous systems.

Finally, the aqueous models are constructed with certain assumptions. For example, such equations as the Davies, the extended Debye-Huckel and the Van't Hoff are derived assuming medium or low ionic strength, low temperature and low pressure. Deviations from these

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conditions are a source of error. Related to this problem, the models contain numerical methods which can generate errors. Most programs reviewed here contain warning messages when such problems occur.

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HYDRODYNAMIC TRANSPORT MODELS

A mathematical model of hydrodynamics and sediment transport can be particularly useful as an analytical tool for the simulation of the pertinent physical processes within Berrys Creek.

The transport in many estuaries will be, in general, three-dimensional and transient, thus posing significant problems in the formulation of appropriate equations and in their solution. Major uncertainties in the transport prediction stem from the lack of knowledge of the relevant significance of the various phenomena affecting transport and mixing processes. These will be discussed in more detail in the following section. Subsequently, the mathematical aspects of the problem will be considered. In the specific case of Berrys Creek, the main contaminant of interest is mercury. Because of the nature of mercury, and analytical evidence, it can be expected that a major fraction of the mercury in the system will be associated with the sediments, and that a significant factor in the transport of the mercury will be associated with the transport of the sediments.

Theoretical Considerations

In general, factors affecting the behavior of the water-sediment system in estuaries may be grouped as follows:

a. macroscale hydrodynamic,

b. microscale hydrodynamic related to the mixing processes,

c. sediment characteristics, and

d. external, such as wind.

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These factors, however, should not be thought of as operating independently, since they may exert mutual influences through interactions.

Turbulence-producing mechanisms of importance for flows in estuaries are shearing motions due to currents in the interior of the fluid, air turbulence at the air-water interface, and shear at the water-sediment interface, Lick (1982). Most models used semi-empirical turbulent eddy coefficients (zero-equation turbulence models), whose determination is extremely difficult even in relatively simple cases, e.g., in the absence of stratification, Rodi, (1980).

Of paramount importance in the sedimentation processes are the properties of the sediments. These can vary over a wide range. However, most bottom sediments consist primarily of inorganic particles in matrix with a small amount of organic material. The larger grains (d > 0.00625 mm, sands and gravels) are non-cohesive, while the smaller ones (d < 0.00 mm, clay-size) are cohesive. The latter often aggregate or flocculate as a result of electrochemical forces, Lick (1982).

From field data it is evident that settling velocities can vary over several orders of magnitude. This implies that the effective particle sizes also range over several orders of magnitude, a fact of significance in the prediction of sediment deposition. The deposition rate is usually assumed to be directly proportional to the local concentration at the water-sediment interface, Lick, (1982). The constant of proportionality, which has the dimensions of velocity, should equal the settling velocity for large particles, while for fine grains it should mainly depend on diffusion. For shallow flows,

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diffusion is the dominant factor in distributing the sediment vertically (Lick, Fresh Water Symposium).

Past research on sediment transport has dealt mainly with flows of low concentration of non-cohesive material. Information on the transport of cohesive sediment is more scarce, while our understanding of mixtures of non-cohesive and cohesive sediments is practically rudimentary. Moreover, it should be borne in mind that sediment transport equations have been developed on the basis of the simplest flow configuration, namely, steady, two-dimensional, and uniform flow Vanoni (1977).

Doubts exist also regarding the effect of high sediment concentration on the flow. Whereas the currently accepted opinion is that high concentrations markedly reduce the intensity of turbulence, thus leading to lower values of the von Karman constant compared to the clear water case, i.e., $K < 0.4$, a recently published investigation, which reanalyzes earlier data along with new ones, does not confirm this conclusion, Coleman, (1981).

Mathematical Considerations

The quality and reliability of results that numerical mathematical models for transport can provide are directly related to the degree of understanding of the assumptions and limitations imposed in the formulation of the mixing coefficients contained in the pertinent equations. These express the effects of all processes whose scale is less than that used in the numerical calculations, Fisher, et al. (1979). Therefore, although computational abilities are constantly improving, there remains always the question of how appropriate a chosen

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flow formulation is. Of course, cost aspects, ease of use, and reliability of results are important factors in a model selection. However, the purpose of the computations should determine the most appropriate model rather than the most sophisticated one. The two major issues which need to be discussed first are the temporal and spacial resolution used in the mathematical formulation of the physical processes. Considerations concerning the most desirable type of discrete mathematical formulation will be presented subsequently.

Steady versus Transient

Mead(1982) states that, for many systems, half of the sediment is transported during 1% of the time and that 85% of the transport occurs in 10% of the time. From this it is obvious that sediment transport is a transient phenomena and cannot be accurately described by a steady-state representation. However, complete annual cycle simulation probably will not be necessary to accurately simulate the sediment transport process. Chemical transformations and diffusion processes, on the other hand, will be expected to dominate in significance during the periods when hydraulic transport of sediment is low.

This would suggest that a dynamic sediment transport model could be used for the hydraulic transport of the sediment, and a one-dimensional (vertically-discrete) sediment diffusion-chemical equilibrium model could be used to describe the chemical transformations that occur during the periods of the year when little or no hydraulic transport of sediment is taking place.

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How Many Dimensions?

As already stated, the flow in many estuaries is certainly three-dimensional. However, three-dimensional models have not been tested sufficiently in hydraulic studies to allow for a safe evaluation of their accuracy and reliability, Fisher, et al. (1979). Above all, our deficiencies in the understanding of the sediment-fluid interactions and the mixing characteristics of the flow weigh heavily and cast doubts on the appropriateness of a highly sophisticated model. A three-dimensional model will pose, in all probability, significant problems in the specification of proper internal and boundary conditions. In addition, it will be an order of magnitude more involved with respect to computational requirement, and, therefore, substantially more expensive to run than a two-dimensional model.

Berrys Creek is a tidal tributary stream. The channel is relatively shallow in the upper reaches, but the lower end of the creek has been rerouted and channelized. This section of the creek is considerably deeper than the upper reaches and as a result significant density stratification may exist during certain periods. From the current knowledge of Berrys Creek application of a three dimensional model does not appear to be warranted. If, however, significant density stratification is found in the lower reaches of the creek, a two-dimensional, laterally averaged model may be necessary to accurately describe the mercury transport. If no stratification is found in the creek a one-dimensional representation of the creek should accurately describe the hydraulic transport in the system.

Application of a two-dimensional model should only be attempted if a one-dimensional model clearly fails to predict transport with

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acceptable accuracy. The need for a two-dimensional model may arise from the density stratification of the fluid-sediment mixture caused by the possible high sediment concentration. In the sediment transport model, it may be necessary to consider the various sediment fractions separately rather than in an average sense.

Existing Mathematical Models

Existing mathematical models have in common that they divide the solution domain into a number of computational molecules or grid cells. Major differences in the various models arise from the number of spatial dimensions considered, the terms retained in the equations, and the solution approach. The latter one can be either a finite difference technique or a finite element technique. No model, presently in usable form, employs the recently developed boundary element method.

In general, the hydrodynamic models are more sophisticated than necessary for the project under consideration. The reason for this is that they have been conceived mainly as operational tools for the simulation of complex circulation patterns of larger coastal and estuarine regions and, therefore, account for the complex transient nature of the hydrodynamics. This time-dependent formulation increases the computational effort tremendously, making their routine use prohibitive, particularly in three-dimensions. Fortunately, it appears that the simulation of hydraulic sediment transport in Berrys Creek can be accomplished using a one-dimensional configuration, and require a relatively short dynamic simulation time to account for the majority of the transport. In all hydrodynamic models it is assumed that the concentration of suspended solids is sufficiently small that the

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dynamics of the flow are not affected by the suspended solids. The sediment transport equation thus can be solved separately from the hydrodynamic equations.

The models which can be considered as potentially most useful for simulating transport in Berrys Creek are presented subsequently in a summary form. The availability of sediment transport models is more restricted than that of hydrodynamic models. However, the situation, as far as the suitability of the existing models for our project is concerned, is slightly more favorable. The main limitation lies in the scarce information regarding cohesive sediments. Ariathuai's and Krone's models (1976, 1977) are the only ones explicitly developed for cohesive sediment applications. Onishi's model discusses non-cohesive and cohesive sediments. Summaries of the sediment transport model, which are most appropriate for simulating mercury transport in the Berrys Creek project, are presented below.

In most instances, the development of models for the hydrodynamics and the sediment transport is not parallel. However, we feel that this is not a severe limitation, because independently-developed models can be combined, provided that they are compatible in their spatial dimensionality.

Hydrodynamics Models. The work done at the Rand Corporation by J. Leendertse and co-workers and the developments of W. Lick and J. Paul appear to be among the most comprehensive studies of direct usefulness to this project. They are the result of many years of research and reflect the state of the art in the simulation of free surface multi-dimensional flows. Experience accumulated from the application of these models to real flows is substantial and the documentation is good and

readily available. They are more sophisticated than it is anticipated will be required for simulating sediment transport in Berrys Creek, however, they can be used as standards of reference and as bases for future developments. In addition, more thorough investigation of the Berrys Creek system may reveal that their application in this case is warranted. Consequently, a rather detailed summary of the characteristics and capabilities of these models will be given herein. In addition to that, two recently published and potentially useful models, developed by Baker and by Ponce and Yabusaki, will be discussed briefly. First, we present an overview of these models according to their basic features in Table D-3.

3-D Model by Paul & Lick(1974). The development of this model has been aimed at describing the hydrodynamics in large lakes, near-shore processes, and thermal discharges in a realistic way. Therefore, it accounts for the time-dependent and three-dimensional nature of the flow and for the variable density of the fluid due to temperature changes. The main simplifying assumptions made in the development of the model are hydrostatic pressure variation, rigid-lid approximation (i.e., vertical velocity component at the undisturbed free-surface is zero), Boussinesq approximation (i.e., density variation is included only in the gravity term), and turbulence is modeled via the concept of eddy coefficients (i.e., zero equation turbulence model), assuming coefficients to be constant in the horizontal directions but variable in the vertical.

The solution procedure is based on the finite-difference technique and is a modification of the simplified marker and cell method. The dependent variables are defined in a grid lattice fitting the system's

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TABLE D-3

HYDRODYNAMIC MODELS

Model Developer	Spatial Resolution	Temporal Mode	Solution Tech.	Experience
Leendertse & Co-workers	2-D(V) and 3-D	Transient	FD	Extensive
Paul & Lick	3-D, rigid lid	Transient	FD	Extensive
Baker	2-D(V) and 3-D	Transient/Steady	FE	Minimal
Ponce & Yabusaki	3-D(V)	Transient	FD	Minimal
REVEIV	2-D, link-node	Transient	FD (link-node)	
CAFE	2-D(V)	Transient	FE	
MIT DNM	2-D(V)	Transient	FE (link-channel)	

where:

2-D(V) = two-dimensional, vertically integrated,

3-D = three-dimensional,

FD = Finite Differences, and

FE = Finite Elements.

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geometry and grid cells are defined around each variable in it. The appropriate differential equations are integrated approximately over the volume of grid cells to give the finite-difference equations. Care has been taken to state the differential equations in conservative form. The horizontal spatial increments can be non-uniform, while the vertical spatial increments is based on a normalization of the elevations from the bed, achieved through a coordinate transformation, thus avoiding loss of resolution and accuracy in shallow regions.

A forward time-differencing scheme is utilized for the time derivatives with most terms in the equations evaluated at the known time level. To increase the allowable time step the vertical diffusion terms have been evaluated implicitly, and, in order to avoid possible numerical instabilities, the option for an implicit evaluation of the Coriolis acceleration is also provided. A procedure, based on a modification of the marker and cell method, is employed in the rigid-lid approximation with some terms treated implicitly.

This model is an updated version of a family of multi-dimensional hydrodynamic models whose development and testing has been ongoing in the past decade. It is based on considerable expertise and experience in numerical modeling of complex flows, and its validity is established by practical applications. Boundary conditions can be imposed according to the problem at hand.

At this point it is appropriate to mention that coupling of this model with a sediment transport model is planned. Lick and co-workers have developed, and, to some extent, have applied a three-dimensional transport model for the simulation of sedimentation processes in large lakes.

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The Rand Corporation Models (1967-1979). Two models have been developed by the Rand Corporation for the simulation of water quality in estuaries and coastal seas, a two-dimensional, vertically integrated model (vertically well-mixed fluid), and a three-dimensional model. Both packages incorporate a transient hydrodynamic model and a model for the transport of several dissolved waste constituents in the fluid, which accounts for reactions in the biological and chemical processes involving these constituents. The assumption of hydrostatic pressure distribution is made in both models.

The 2-D Model. The governing equations for the hydrodynamics are solved using an alternating direction implicit finite difference scheme (ADI). The boundary conditions can be specified so as to accommodate open or closed boundaries. A tri-diagonal system of difference equations is obtained and is solved with the double-sweep method (Thomas algorithm). Water level and the two vertically-averaged, horizontal velocity components are evaluated at different points in the spatial grid.

The solution of the transport and reaction models is obtained at the same grid points for which the hydrodynamic parameters have been computed. An implicit finite-difference scheme is used which again leads to a tri-diagonal system of equations that is solved according to the Thomas algorithm. The input data that need to be processed for the models are given in Table D-4. The output information that is obtained in digital and graphical form is listed in Table D-5.

In applications, major difficulties were encountered in the introduction of open boundary conditions. This model has been applied extensively in the U.S. and abroad. Probably the best-known application

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TABLE D-4

INPUT DATA REQUIREMENTS FOR RAND CORPORATION MODELS

Hydrodynamics	Transport	Reaction
Bathymetry	Transport Velocities	Decay Rates
Land-Water Boundary Open Boundaries	Constituent Time Histories at Open Boundaries	First-order reaction rates
		Sources & sinks
Latitude (Coriolis)	Concentrations in Discharges	
Friction Coefficient	Dispersion Coefficients	
Wind	Initial Concentrations	
Discharge Points		

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TABLE D-5

OUTPUT DATA PROVIDED BY THE RAND CORPORATION MODELS

Hydrodynamics	Transport and Reaction
Velocities (U,V)	Mass Densities
Water Level	Constituent Concentration
Water Discharge	Constituent Mass Transport

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case is the simulation of water processes in the Jamaica Bay, New York, where the model was used to analyze the impact of the hurricane barrier across the Rockway Inlet. The numerical experimentations gave insight into the hydrodynamics and the water quality modeling. The sensitivity of results to variations of the roughness coefficient and the wind effects were studied, the operational characteristics, and the computational procedures were explored, and the system of results presentation was perfected.

The calculations are in good agreement with observations. The model conserves mass and the computation of reactions among constituents does not generate any anomalies or pose any numerical difficulties. New diagnostic quantities (net flow and net transport) were evaluated and compared with data from tidal flows. The sophistication of the model requires high quality data for the utilization of its full capabilities.

The 3-D Model. The model predicts three-dimensional, transient circulation patterns. The increments in the vertical leads to a multi-layer scheme with the equations describing the average conditions in each layer. Boundary shear stresses, due to wind action at the free surface and due to friction at the bed are introduced as quadratic expressions.

The numerical integration is performed over a space-staggered grid and the stability of the computation does not depend on the viscosity, as is often the case with models of this type. The leap-frog scheme is used in the formulation of difference equations, after discarding the ADI method because of the excessive size of the computer memory requirements. The leap-frog scheme is presenting difficulties in the determination of the stability condition.

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The model is still under testing and development. In its current state, the exchange coefficient in the momentum and transport equations are related to the computed intensity of turbulence. The vertical exchange coefficients are computed from the subgrid scale energy intensity. The hydrodynamic model is coupled with the transport model, which predicts the movement, interaction, and decay of dissolved substances in areas with either closed or open boundaries.

Experience with this model is limited to simple, idealized cases. The model cannot be considered as field-verified at this stage of its development. However, results of flow and water quality simulations appear to be physically reasonable.

The Baker-Models (1977) The algorithms of these models employ the Finite-Element approximation techniques in connection with the method of weighted residuals (Galerkin) to include non-linearity. Two models have been developed and are in the stage of testing: (1) a vertically-integrated, two-dimensional, transient model, which is applicable to layered hydrodynamic flows yielding average behavior within strata (integral transformation in the vertical), and (2) a three-dimensional steady-state-type model, appropriate for flows with one predominant direction of flow.

Both models can accommodate arbitrary geometries and can be used with various boundary conditions imposed. The basis for these models are the conservation equations for species mass, total mass, linear momentum and energy. Modeling of turbulence is formulated by means of a generalized, non-linear stress-strain law which can be evaluated by the usual eddy diffusivity concept.

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Two examples have been presented for the two-dimensional model. A simulation of diffusion in a meandering stream, and a study of recirculating flows induced by abrupt changes in the geometry and by mass flow perturbation. Results appear to be physically reasonable but no direct comparison with experimental data is available.

The three-dimensional model (parabolic Navier-Stokes equations) is used to simulate the cross-sectional diffusion and three-dimensional convection of the effluent from a wastewater outfall. Results are in good agreement with observations.

The Model by Ponce & Yabusaki (1981) A two-dimensional, vertically-integrated, transient hydrodynamic model has been formulated. The numerical solution is based on the finite-difference technique. The model does not account for wind and geostrophic effects, treats the fluid as incompressible, and assumes hydrostatic pressure distribution. Turbulence is modeled on the basis of the method of pseudo-viscosity rather than on a physical basis. That means the numerical dispersion coefficients are used in place of the turbulent eddy coefficients. Four grid systems are staggered in space, each one having been defined for the four variables of the flow, i.e., two velocity components, a bed- and a free-surface elevation. Two boundary types can be specified in the numerical model, closed and open boundaries.

Testing of the model has been fairly extensive but with no practical applications and, therefore, the model cannot be considered as verified. Results appear to be physically reasonable.

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Transport Models

In this section the models developed by Ariathurai and Krone and expanded by the US Army COE (TABS-2) and that developed by Onishi (FETRA) will be discussed. As stated earlier, although the developmental state of transport models may not be as advanced as that of their hydrodynamic counterparts, they would be suitable for simulating sediment transport in Berrys Creek if the necessary sediment characteristics are known. At this time, both aforementioned models have not been extensively tested. While the FETRA model has only recently been made publicly available, the COE model is still under going inhouse use and testing at this time. The FETRA model is not supplied with its own hydraulic transport capability, but is designed to be coupled with an appropriate hydraulic model for a given application. It has been coupled with both one-dimensional and two-dimensional hydraulic codes. TABS-2, when it becomes available will undoubtedly be a more comprehensive, all-inclusive and more universally applicable. Their basic characteristics are summarized in Table D-6 below.

Onishi's Model (1981). A sediment and contaminant transport model (FETRA) has been developed which utilizes the unsteady, two-dimensional, vertically averaged equations and discretizes by means of the finite-element method after linearizing with Galerkin-weighted residuals. Three submodels were coupled: (1) a sediment transport model; (2) a dissolved contaminant transport model; and (3) a particulate contaminant transport model. The mechanisms taken into account in each model are shown in Table D-7.

Currently, FETRA handles three sediment size fractions or types. Sediment movements and particulate contaminant transport are modeled

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TABLE D-6

SEDIMENT TRANSPORT MODELS

Model Developer	Spatial Resolution	Temporal Mode	Sediment Type	Solution Technique	Experience
TABS-2 &	3-D(V,H)	Transient	Cohesive & Non-cohesive	FE	Limited
FETRA	2-D(V)	Transient	Cohesive & Non-cohesive	FE	Limited
HSPF	2-D(H)	Transient	Cohesive & Non-cohesive	FD	Limited

V = vertically-averaged
H = horizontally-averaged

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TABLE D-7

PROCESSES CONSIDERED IN SUBMODELS

Mechanism	Submodels (1)	(2)	(3)
Advection and diffusion/dispersion	x	x	x
Fall velocities and cohesiveness	x		
Deposition on the riverbed	x		x
Erosion from the riverbed	x		x
Sediment contribution from sources	x	x	x
Adsorption (uptake) of dissolved contaminants by both moving and stationary sediments or desorption from the sediments into water		x	x
Chemical and biological degradation or radionuclide decay of contaminants		x	x

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separately. The governing equation is obtained from the three-dimensional mass-conservation equation by means of a vertical integration. The non-uniform vertical distribution of velocity components and concentrations is represented by the depth-averaged value and a fluctuation about this value. The diffusion coefficients are in the Boussinerg form and are assumed to be the same for all sediments and contaminants. The transport capacity for non-cohesive sediments is estimated according to DuBoy's formula, while the erosion and deposition of cohesive sediments is based on the formulas of Partheniades and Krone. The simulation of processes at the riverbed is modeled through division of the riverbed in layers of variable composition. In the second and third submodel, effects of water quality can be included by changing the partition coefficients of contaminants, Table D-7.

The computer code was applied to simulate the migration of sediment and of a pesticide released from the James River estuary. The principal characteristics of the simulation were:

1. The hydrodynamic parameters were evaluated with a one-dimensional code which gives cross-sectionally averaged velocities and flow depths;
2. Three types of sediments were considered:
   a. Cohesive sediments (clay and silt),
   b. Non-cohesive sediments (sand), and
   c. Organic matter; and
3. Factors affecting riverbed conditions were:
   a. Changes in the river bottom's elevation,
   b. Distribution of sediments and organic matter in the bed; and
   c. Distribution of particular pesticide (kepone) in the bed.

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The computed results and measured data agree rather closely.

The Models of Ariathurai and Krone (1976-1977). These models compute the temporal variation of the concentration of cohesive suspended sediments and the bed surface elevations in an estuary using a finite element formulation in conjunction with Galerkin's weighted residual method.

The governing three-dimensional transport equation has been averaged in one direction to give a vertically-averaged and a laterally-averaged two-dimensional equation.

The result transport models consider convection/diffusion, erosion and deposition. Erosion is related to the critical shear stress and is modeled according to Partheniades, while deposition occurs when the shear stress at the bed is not sufficient to resuspend the particles in contact with the bed, which bond with it, according to Krone's theory. The bed profile is computed by considering a number of layers of known thickness, each having a specific density and resistance to fluid shear.

The validity of the models is tested through comparisons with closed-form solutions of the convection-diffusion equation and through laboratory and field verifications. The following cases have been considered:

1. One-dimensional convection-diffusion: for the steady state, the governing equation reduces to an ordinary differential equation, which is solved using a rectangular grid. Quick convergence to the exact solution is observed.
2. One-dimensional transient heat conduction: using a rectangular grid with spacing of elements increasing in geometric ratio and for runs

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exceeding four time steps, the numerical solution plots in the same curve as the exact solution.

3. Flume test: a computer simulation of the transport of sediment whose properties correspond to those of the San Francisco Bay mud given good agreement between the predicted and observed shoaling patterns and spot heights (bed elevations).

4. Hypothetical problem: flow in a rectangular harbor-like cavity off a uniform mainstream was simulated for three different entrance configurations using a program that solves the velocity equation. The hydrodynamic solution was used with the sediment transport model to predict shoaling patterns and rates.

5. Sedimentation processes in the Savannah Estuary, Georgia, were simulated with some success (1977).

The models of Ariathurai and Krone have been extensively expanded and included in the US Army COE TABS-2 comprehensive hydraulic simulation system. This modeling system is still undergoing final testing and conversion to a standard language. In addition to containing the code to simulate a wide range of hydraulic systems, the TABS-2 system includes many utilities to assist in model development and presentation of results. The system includes the capability of automatic grid generation, data management, summary; or detailed output includes: contour and factor maps, and vector and drogue plots.

HSPF (Imhoff et al., 1981). The HSPF 7.0 (Imhoff et al.,1981) hydrologic simulation program is a comprehensive system of models designed to be capable of simulating transport of contaminants through a watershed. This program includes virtually all hydrodynamic processes including cohesive and non-cohesive sediment fractions. Its use in its

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current form, for simulating conditions in Berrys Creek, however, are limited due to the lack of a capability to simulate tidally influenced stream reaches. The modular structure of the system, however, is well suited importing the code for a tidal hydraulic simulation. As a result the system could be easily modified to include the simulation of estuary hydraulics. The advantages of the HSPF system are its comprehensive and all inclusive nature. Using HSPF it would be possible to completely simulate all aspects of water quality with a single system, once it was initially setup. The disadvantage of the system is that it is extremely large, consisting of over 500 subroutines and 79,000 lines of FORTRAN source code. As a result the initial setup and installation of the program on a new system, it would most likely require extensive effort.

HOTSED (Fields and Hetrick, 1979). The HOTSED (Fields and Hetrick 1979) program was developed to simulate the transport of radioactive non-cohesive sediments in tidally influenced streams. It uses a velocity based non-steady state approach to solve the transport equations. This model separates the sediment into three components; resident stream bed sediments, in transit bed load, and in transit suspended sediment. The sediment itself can be partitioned into as many as 12 size classes. The HOTSED model and the SEDTRN (FIELDS ,1976) sediment transport sub-model have been successfully used to simulate sediment transport in the Hudson and Rio Grande Rivers. Although it has limited capabilities, this program is easy to set up and is inexpensive to run. This program may be a good choice to simulate Berrys Creek if investigations indicate that there is little cohesive sediment in the Berrys Creek Watershed.

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