October 22, 1980

TO: Rich Powers, Director, Office of Toxic Materials Control

FROM: Larry Fink, Chemist, Office of Toxic Materials Control

SUBJECT: Public Health Risks from BASF Wyandotte Corporation North Works Discharges - Wyandotte, Michigan
Propylene Oxide and Ethylene Oxide

Based on the evaluation of the physical, chemical and toxicological properties of propylene oxide (PO) and ethylene oxide (EO) and the quantities of these substances released to the Trenton Channel by the BASF Wyandotte Corporation - Wyandotte, Michigan from its North Works outfalls, I believe that populations obtaining drinking water from the Trenton Channel downstream of those discharges were and are at some increased risk of hereditary mutations, birth defects and cancer which may be significant. BWC indicated in its Critical Materials Report for 1978 that 10,000-100,000 pounds of EO were discharged from its North Works outfalls 001-N and 003-N. EO was dropped from the 1979 Critical Materials Register. Since PO has never been included on Michigan's Critical Materials Register and is not a Section 307(a) toxic pollutant, BWC has never been required to report the discharge of this substance. However, since both EO and PO are used in the manufacture of polyols, it is reasonable to assume that between 10,000-100,000 pounds of PO are also being discharged each year as a result of polyol manufacture. The mass loadings to the Trenton Channel which resulted from the manufacture of 175 million pounds of PO each year at BWC's South Works are unknown.

Attached find calculations quantifying the concentrations of EO and PO in City of Wyandotte raw water under various loading and dilution assumptions, labeled I.

I recommend that highest priority be given to the evaluation of the risks of injury to public health and to the designated uses of the Detroit River resulting from the release of PO and EO by BWC-Wyandotte. The presence of these substances in Wyandotte's raw water intake may compound the risks associated with the discharge of 80,000 lbs/year of acrylontrile from BWC discussed in a 9/5/89 memo to you.

Until it closed its South Works production facilities in May of 1980, the BASF Wyandotte Corporation of Wyandotte, Michigan produced 175 million pounds of PO per year via the propylene chlorohydrin process[1]. This product was used in the manufacture of polyoxyethylene-polyoxypropylene block copolymer polyols at BWC's North Works. Propylene dichloride, a by-product of propylene oxide production, was recovered at the South Works via fractional distillation.

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A joint U.S. EPA/Michigan DNR waste stream survey conducted at BWC's North and South Works in October-November 1979 revealed that outfall 005-S effluent was contaminated with bis(chloroisopropyl)ether and bis(chloroethyl)ether at 5.4 ppm and 1.3 ppm respectively[2]. These molecules are believed to be formed in the synthesis of propylene oxide via the propylene chlorohydrin process. A letter of 8/28/80 from Sandra Gardebring, Director, Enforcement Division, U.S. EPA - Region V identified concerns associated with the presence of these suspect carcinogens in BWC effluent. Since 005-S served the Propylene Dichloride recovery plant, and since the chloroalkyl ethers are unintended by-products of the propylene chlorohydrin process, their association with processes designed to recover by-products of propylene oxide production is unremarkable.

Lime residues from the PO production process were piped to Fighting Island (FI). PO still bottom residues were also conveyed to FI for disposal. Effluent and residues taken 10/3/79 and 10/29/79 from the South settling Beds were analyzed by the Ontario Ministry of the Environment and found to be contaminated with bis(chloroisopropyl)ether, as well[3].

PO is the second member of the homologous series of alkyl epoxides, of which EO is the first. Like EO, PO is not immediately hydrolyzed upon contact with natural waters. EO has a measured half-life of approximately 12 days in water at 25°C and neutral pH. PO has a measured half-life of 14.6 days under those same conditions[4]. The hydrolysis products of the alkyl oxides are alkyl diols: EO and PO are hydrolyzed to ethylene glycol and propylene glycol, respectively.

EO and PO are soluble in water and are not expected to be removed from the water column via volatilization/codistillation. EO and PO are not expected to strongly adsorb on the surfaces of settleable solids. Thus, the PO and EO released to natural waters are expected to remain in solution in the water column. Both PO and EO have negative logarithims of their n-octanol/water partition coefficients and are thus not expected to bioaccumulate[5].

PO reacts with DNA to form N-7-(2-hydroxypropyl)guanine and N-3-(2-hydroxypropyl)adenine[6] and, like EO, is a potent bacterial mutagen.[7] PO has been further demonstrated to induce recessive lethal mutations in Drosophila melanogaster[8]. Sub-cutaneously administered to rats, it was demonstrated to be carcinogenic[9].

While exposure to EO is now strongly associated with human chromosomal damage,[10] PO has yet to be demonstrated to have a similar effect. Based on its chemical similarity to EO, it is expected that exposure to PO will eventually be demonstrated to cause human chromosomal aberrations.

When alkyl oxides are exposed to dissolved chlorine gas in aqueous solution, corresponding chlorinated alcohols are formed. Ethylene oxide is believed to react to form ethylene chlorohydrin (2-chloroethanol) while propylene oxide is believed to react to form propylene chlorohydrin (2-chloropropanol). Ethylene chlorohydrin is a mutagen[11]. The carcinogenicity or mutagenicity of propylene chlorohydrin is not reported in the literature reviewed.

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The BWC North Works outfalls are some 3,750 feet upstream of the City of Wyandotte public drinking water supply intake. By virtue of the tendency of warm plumes to maintain their integrity in cold surrounding water and reports in the WQD files that foaming at the City of Wyandotte power plant intake resulted from a BWC polyol spill at the North Works, it can be inferred that plumes contaminated with PO and EO may enter the cone of withdrawal of the City of Wyandotte public drinking water supply intake in quantities of concern. Since neither settling nor aeration are expected to effectively remove these substances from water, much of the PO and EO entering the raw water intake would be expected to survive treatment up to chlorination. The yield of propylene chlorohydrin and ethylene chlorohydrin resulting from drinking water chlorination is not known.

Recommendations:

1. BASF Wyandotte Corporation should be requested to submit all relevant information regarding the concentrations and quantities of ethylene oxide and propylene oxide discharged to the Trenton Channel since corporate takeover.

2. Appropriate WQD staff should conduct plume studies employing dye tracers and conductivity probes to establish the spatial distribution and rate of dilution of North Works plumes with distance downstream and to determine if North Works plumes enter the cone of withdrawal of the City of Wyandotte public drinking water supply intake.

3. The concentrations of ethylene oxide, ethylene chlorohydrin, propylene oxide and propylene chlorohydrin in intake water, prior to chlorination, following chlorination, and at the tap should be established using approved analytical protocols or calculated using mass balance techniques.

4. The risks of hereditary mutation, birth defects, and cancer should be estimated for the concentrations of each substance found or estimated to be present in tap water. Synergistic effects due to the presence of chlorinated methanes, ethanes, ethylenes, propanes and propylenes and acrylonitrile should be considered in such a risk assessment.

5. BWC's North Works NPDES permit should be immediately modified to require monitoring of ethylene oxide, propylene oxide, ethylene chlorohydrin, and propylene chlorohydrin at 001-N and 003-N; and, following risk assessment, effluent limits designed to protect the population served by the City of Wyandotte drinking water supply from unacceptable risks of cancer, mutation or birth defects should be calculated and established as permit conditions.

I believe this situation warrants your immediate attention.

Should you have any questions concerning the nature of the public health risks or the recommendations, I am available to answer them at your earliest convenience.

cc: J. Grant/OTMC Files

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Attachment I

Concentration at City of Wyandotte Intake:

| | | |
|---|---|---|
| 1. | assuming plume is not diluted | .32 ppm - 3.2 ppm |
| 2. | assuming plume is diluted by flow in mixing zone (right 100 feet of 850 foot channel) | 1 ppb - 10 ppb |
| 3. | assuming plume is diluted by entire flow of Trenton Channel | .12 ppb - 1.2 ppb |

vls

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References


1. Chemical Week, October 1, 1980: 46

2. BASF Wyandotte Corporation North and South Works Survey (10/29/80 - 11/2/80; 11/5-9/80), Office of Great Lakes Programs, Region V, U.S. EPA, Chicago, Illinois: June 25, 1980

3. Data conveyed in letter form John Luyt, Ontario Ministry of the Environment, to D. Batchelor, Michigan DNR, dated 3/25/80.

4. Radding, S.B., D.H. Liu, et al., Review of the Environmental Fate of Selected Chemicals, Stanford Research Institute, Palo Alto, California, May, 1977: 24

5. Ibid; p. 30

6. IARC Monograph

7. Ibid.

8. Ibid.

9. Ibid.

10. Chem Reg Reporter 5-2-80: 128

11. 21 CFR Parts 211 and 821: Ethylene Oxide - Rebutable Presumption Against Registration. USEPA, USFDA: 3801-3815


LF/vls

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October 9, 1980

TO: Rich Powers, Director, Office of Toxic Materials Control

FROM: Larry Fink, Office of Toxic Materials Control

SUBJECT: BASF Wyandotte Corporation - Wyandotte, Michigan
Toxic Substances Discharges

Because the BASF Wyandotte Corporation (BWC) in Wyandotte, Michigan is known to be discharging substances which are toxic or otherwise injurious or potentially injurious to the public health, safety and welfare and the designated uses of the Detroit River; because the proposed settlement of outstanding litigation does not address the toxic substances problem at BWC - Wyandotte; and because the second-round NPDES permit for BWC - Wyandotte cannot be issued until revised applications are received and settlement reached, I am recommending that the existing NPDES permit be re-opened immediately and modified to require monitoring of those toxic substances which are Michigan Critical Materials and to limit the discharge of those substances known to be injurious or potentially injurious to the public health, safety and welfare: acrylonitrite, ethylene oxide, toulene diamine, etc., to quantities which represent an acceptable risk of injury to the public health, safety and welfare.

Had the permit application been processed in a timely fashion and had a draft permit been issued soon after it became apparent that toxic substances were being discharged by BWC - Wyandotte in toxic or potentially toxic amounts, the need for modification of the existing permit would have been less urgent. Since I brought the discharge of Critical Materials in quantities of concern to the attention of Scott Ross of the Surface Water Compliance Section and Chang Bek of Engineering & Technical Services Section in February of 1979, twenty months have elapsed, during which time BWC - Wyandotte has discharged on the order of 130,000 lbs of acrylonitrile to the Detroit River some 3,750 feet upstream of the City of Wyandotte public drinking water supply intake. To date, no action has been taken regarding the presence of such substances in BWC's discharges. The risk of injury to the public health, safety and welfare resulting from on-going uncontrolled discharges from BWC - Wyandotte's North Works is discussed in my memorandum to you dated September 5, 1980.

The proposed conditions of settlement of the litigation with BWC - Wyandotte do not address violations of Section 6(a) of 1929 PA 245, permitting the DNR to take action where environmental damages can be demonstrated to result from a discharge of an injurious substance. But to take action only after the fact of environmental damages precludes the DNR from protecting the Detroit River from pollution, impairment and destruction which is our constitutional mandate. Paul Zugger has informed me that only if the discharge was presently resulting in the violation of a promulgated Water Quality Standard could the DNR take action under Section 6(a) without environmental damages. Since no promulgated standards for toxic substances exist, we can take no action under Section 6(a).

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It is my opinion that the discharge of wastewaters contaminated with carcinogenic, mutagenic or teratogenic substances to a segment of the Detroit River protected as a public drinking water supply is injurious to that designated use, whether or not a specific standard has been promulgated for toxic substances to protect that use, and is thus unlawful under the intent and meaning of Section 6(a), 1929 P.A. 245. The lack of a standard does not preclude the existence of a hazard.

We would be negligent in our duty if we did not address the discharge of such substances into a public drinking water supply until appropriate standards were promulgated or until existing permits were conveniently reissued routinely.

I would appreciate the opportunity to discuss this situation more fully with appropriate representatives of the Water Quality Division, Environmental Services Division, and Enforcement Division, MDNR; and the Chemicals and Health Center and Water Supply Division, MDPH at their earliest collective convenience.

Your assistance in addressing this situation is appreciated.

LF/vls
cc: J. Grant
OTMC Files

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September 5, 1980

TO: Richard Powers, Director, Office of Toxic Materials Control

FROM: Larry Fink, Office of Toxic Materials Control

RE: Exposure of populations downstream of BASF Wyandotte Corporation to the animal positive carcinogen - acrylonitrile

Attached to a letter from Sandra S. Gardebring, Director, Enforcement Division, Region V EPA, to Karl Zollner, Jr., dated August 28, 1980, was a recommended

BASF Wyandotte Corporation (BWC) North Works effluent limitation for bis(chloroisoprop ether, a suspect carcinogen found present in 003-N effluent at 4.5 ppm in the October-November 1979 joint EPA/DNR BWC survey.

The effluent limitation was based on the assumption that the 003-N plume completely mixes with the average flow of the Trenton Channel of the Detroit River, resulting in bis(chloroisopropyl) ether being present in the water withdrawn from the Trenton Channel to supply drinking water to the City of Wyandotte. To protect populations served by this drinking water supply from an increased risk of cancer not to exceed one-in-one million, no more than 182 lbs/day could be discharged, according to EPA calculations.

Attached find a copy of that letter.

Since the EPA method did not consider the potential for co-carcinogenic and synergistic effects between acrylonitrile, an animal positive carcinogen of which BWC discharges 80,000 lbs/yr., and bis(chloroisopropyl)ether, the recommended EPA effluent limit does not appear to adequately protect exposed populations from an increased incidence of cancer not to exceed $10^{-6}$.

However, employing EPA's assumptions and methodologies; the acrylonitrile risk model developed in 40 FR 191 Monday October 1, 1979; and assuming that all the acrylonitrile remains dissolved in water, it can be calculated that the populations served by the City of Wyandotte may be placed at an increased risk of cancer resulting in an incidence of approximately one-in-ten thousand.

Attached find an explanation of the assumptions made and the calculations.

This risk is 100 times greater than EPA's design risk of one-in-one million. If EPA's assumptions can be justified as a worst-case best guess, then the resulting risk estimate of one-in-ten thousand is reasonably accurate.

Because a risk of one-in-ten thousand appears to be unacceptably high, I am recommending that the following agencies be contacted to determine if an immediate reduction of the acrylonitrile discharge from the BWC North works is advisable:

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John Hesse, Chief, Chemicals and Health Center, DPH
Robert Courchaine, Chief, Water Quality Division, MDNR
Jack Bails, Chief, Environmental Enforcement Division, MDNR
Sandra Gardebring, EPA Region V
Howard Zar, Great Lakes National Program Office, EPA Region V

I believe this requires your immediate attention.

ma
Attachments
cc: J. Grant/OTMC Files

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Attachment II

Acrylonitrile risk assessment from 44 FR 191 October 1, 1979

| | | |
|---|---|---|
| 0.08 ug/l | $10^{-5}$ | [illegible] |
| 0.008 ug/l | $10^{-6}$ | [illegible] |
| 0.0008 ug/l | $10^{-7}$ | [illegible] |

Assumptions:

1. Q(ave) Detroit River = 182,000 cfs
2. Upper Trenton Channel is 25% of Detroit River Q = 45,500 cfs
   = 29,355 MGD
3. Total mixing downstream of 003N = assumption
4. City of Wyandotte water supply intake can be affected by BASF discharges (001,003) and removal of acrylonitrile at water treatment plant is zero = assumption
5. Background of acrylonitrile in Detroit River is zero = assumption
6. WQC for acrylonitrile with a target risk of carcinogenesis level of $10^{-6}$ from U.S. EPA Criterion Document for acrylonitrile = 0.008 ug/l

Calculation

$29{,}355 \text{ MGD} \times 8 \times 10^{-6} \text{ mg/l} \times 8.34 \text{ lbs/MGD} = 1.96 \text{ lbs/day}$

$= 715 \text{ lbs/yr}$

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Attachment III

Acrylonitrile

P = risk probability
70 kg person is the design person

1. $I = 70 \times P/B$ = intake (from 44 FR 15926 March 15, 1979)

2. I (mg/day) = C(mg/1) x R(1/kg fish) x0.0187 kg fish/day
   + C(mg/1) x 2 l/day

3. $C = 70 \times P/B(2 + R \times 0.0187)$ (from 44 FR 15926)

4. $P = \frac{B \times I}{70} = \frac{B}{70}(2 + R \times 0.0187) \times C$ (rearrangement of (1))

55 : $B_H = 2.045$ (mg/kg/day)-1 (44 CFR 191)

R = 110 bioaccumulation factor (from 44 CFR 191 October 1, 1979)

$$C(\bar{Q}) = \frac{80{,}000 \text{ lbs/yr}}{365 \text{ day/yr} \times 8.34 \text{ lbs/gal} \times 29{,}355 \text{ MGD}} = 8.95 \times 10^{-4} \text{ mg/l}$$

$$P = \frac{2.0455}{70} \times (2 + 110 \times 0.0187) \times \cancel{1.37 \times 10^{-3}} \; 8.95 \times 10^{-4} \text{ mg/l} = 10^{-4}$$

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AUG 28 1980

RECEIVED
SEP 03 1980
ENVIRONMENTAL ENFORCEMENT DIVISION

Mr. Karl J. Zollner, Jr.
Chief, Engineering and Technical
Services Section
Water Quality Division
Michigan Department of Natural Resources
P.O. Box 30028
Lansing, Michigan 48909

Re: BASF Wyandotte Corporation
Wyandotte, Michigan
MI 0000540 (North Works)
MI 0000566 (South Works)

Dear Mr. Zollner:

Region V, U.S. Environmental Protection Agency (U.S. EPA) has been following closely the progress of litigation between your Agency and the above referenced company. Our communications with Messrs. Paul Zugger and Dave Bachelor of the Michigan Department of Natural Resources (MDNR) have indicated that a settlement with a Consent Order is in final preparation covering these BASF facilities.

The U.S. EPA is deeply concerned about the delay by BASF in providing process evaluation information. BASF agreed, following the U.S. EPA letter dated October 20, 1978, to Mr. Grashoff, and again when meeting with U.S. EPA in Chicago on March 27, 1979, to conduct a process evaluation. One year was considered a reasonable time to complete the process evaluation. As a result of this delay it appears obligatory to issue a short term permit in order to initiate a positive program to install base line treatment technology on all wastewater streams discharging from organic chemical production or operations. This Agency has not been informed officially of the closure of the South Works. We assume that the MDNR is taking measures to assure that all environmental problems presently known or those that could result from shutdown practices are addressed, and that the U.S. EPA will be kept informed. We are aware that your staff and others in the MDNR have experienced difficulty in obtaining specific, updated process information regarding BASF's closure of some operations and curtailment of others.

Our interest centers on the reissuance of a permit for BASF North Works (MI 0000540), particularly the discharge limitations on outfalls 001, 002, and 003. Our concerns were found to be justified following a review of (1) the existing discharges as shown on the company's Monthly Operating Reports (MORs) for the period March 1979 through February 1980,

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(2) reapplication forms dated August 8, 1979, and October 11, 1979, which indicated no anticipated reduction of organic manufacturing, (3) bioassay test results at outfall 001 for the corresponding period, and (4) other information including results of our joint sampling survey of BASF facilities presented in the "U.S. Environmental Protection Agency Analytical Report" by Environmental Research Group (ERG), dated April 22, 1980, a copy of which was sent to the MDNR.

In summary, outfalls 001 and 003 are discharging large loadings of COD (chemical oxygen demand) representing more than 200 mg/l and 50mg/l, respectively, over Detroit River background. Waste discharges are variable with daily maximums exceeding, at times, 500 mg/l and 400 mg/l COD for outfalls 001 and 003, respectively. Secondly, bioassay tests on outfall 001 effluent (a monthly permit requirement) show the effluent to be acutely toxic six times out of the seven tests completed during a 1-year period. Lastly, there is presently inadequate treatment in place at outfall 001 and little, if any, at outfall 003. It was indicated in the recent ERG report that duplicate samples of the effluent from outfall 003 contained high levels of Bis(2-chloroisopropyl)ether, a potent mutagen and suspected carcinogen, in the mg/l range.

Consequently, this Agency feels that positive steps should be taken now to issue a permit to the North Works incorporating effluent limitations requiring basic treatment along with limited toxicant control and a compliance schedule to meet the conditions at the earliest possible date. Since it is not advisable to issue a 5-year permit with BAT limitations without the benefit of the company's completed process evaluation, it is recommended that a short term permit expiring on June 30, 1981, be issued with a full compliance schedule with the provision that the effluent limitations and compliance schedule will be adjusted when BAT and toxicant control limitations are finalized. The date of the submission of a preliminary engineering report and basis of design for the facility will fall within the term of this permit. The recommended date for submission of final plans for approval was selected to parallel the completion phase of the facility process evaluation so that the process evaluation can be included in the review of the final plans.

The proposed discharge limitations for the significant parameters for outfalls 001 and 003 at BASF North Works (MI 0000540), the rationale, and a proposed schedule of compliance are presented in the attachment to this letter. Additional discharge limitations for phenol, total residual chlorine, phosphates, total chloride, and any other parameter should be developed based on the latest information. Interim conditions on outfall 005 (inorganic operations if discharging) and outfalls 006, 007, and 008 (boiler house discharges originally covered in permit number MI 0001805) should also be included in this short term permit.

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I urge that the MDNR seriously consider this draft permit proposal as the basis for the development of a permit requiring a real commitment by BASF, and that such a permit be public noticed shortly. May I also suggest that you might find it appropriate to incorporate certain provisions of our proposal into your Consent Order with the company. If you have any questions regarding this matter, call the Permit Branch, Industrial Unit, at (312) 353-2105.

Very truly yours,

Original Signed by Sandra S. Gardebring

Sandra S. Gardebring
Director, Enforcement Division

Attachment

cc: Robert Courchaine, MDNR
Jack Bails, "
Stewart Freeman
Asst. Michigan AG
Dave Bachelor, MDNR
Paul Zugger, "

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ATTACHMENT to Letter of AUG 28 1980

The U.S. Environmental Protection Agency (U.S. EPA) is recommending certain effluent limitations and requirements to be incorporated into a permit to be issued to BASF Wyandotte, North Works (MI 0000540), to supersede the permit that expired on September 30, 1979. The revised effluent limitations for chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$), and Total Suspended Solids (TSS) are based on the following:

Note: Effluent limitations for outfalls 001, 002, and 003, are presented in sections 7 and 9b below. Biomonitoring requirements are presented in sections 8 and 9a below.

1. Current waste abatement practiced at outfalls 001 and 003 is minimal and large loadings of COD and $BOD_5$ over the Detroit River background are consistently being discharged.

2. The effluent discharged from outfall 001 is acutely toxic as shown by company bioassay tests. The wastewater characteristics of the discharge from outfall 003 are variable and a recent survey (ERG report dated April 22, 1980) indicated high levels of a chlorinated alkyl ether in the effluent, as well as the presence of other organic contaminants of concern.

3. Best Practicable Control Technology Currently Available (BPT) on end-of-process treatment for the Major Organic Products point source category is defined in the Development Document (April 1974) as: ".... biological treatment as typified by current exemplary processes: activated sludge, trickling filters, aerated lagoons, and anaerobic lagoons. These systems will be adequately equipped with pH control and equalization in order to control variable waste loads with the addition of chemicals to aid in removing suspended solids where this is required." The BASF facility lacks this basic treatment technology.

4. From information in the Treatability Manual, Vol. III, Technologies, U.S. EPA, Washington, D.C. (January 1980), the average removal efficienies of organic manufacturing facilities with biological treatment were calculated to be:

   >70% removal of COD (average of 10 facilities)

   >80% removal of $BOD_5$ (average of 11 facilities)

5. The originally issued permit with TSS (net 20 mg/l average, net 60 mg/l maximum) as the controlling parameter is too lenient. It is proposed that COD and TSS be the controlling parameters.

6. The final limitations for COD, $BOD_5$, and TSS were calculated on information from the company's MORs for March 1979 through February 1980. Production was not used directly in calculating any loadings.

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(a) For 001, the average flow used for the calculations was 8.5 MGD. Assuming minimal to no removal of $BOD_5$ and COD with primary settling only, the reported average discharge levels were assumed to be the raw waste load (RWL). The yearly daily average discharges of COD and $BOD_5$ were calculated to be:

COD- 17,395 lbs/day (assumed the RWL)
$BOD_5$- 2,840 lbs/day ( " " "

Assuming allowable residuals for COD, $BOD_5$, (see item 4 above), average kg/day (lbs/day) loadings were calculated. Assume the discharge limitations for TSS is 1.5 times the $BOD_5$ limitation. The daily maximum values were calculated to be 2.0 times the daily averages.

b. For 003, the average flow used for the calculations was 1.9 MGD. It was assumed that the average discharge values for COD are equivalent to the raw waste load. The yearly daily average discharge of COD was calculated to be:

COD- 1,568 lbs/day (assumed the RWL)

Assuming the allowable residual for COD (item 4 above), an average kg/day (lbs/day) loading was calculated. Loadings for $BOD_5$ are assumed to be 0.16 times the COD loadings (based on the average $BOD_5$ to COD ratio from data on outfall 001). Again, assume the discharge limitation of TSS is 1.5 times the $BOD_5$ limitation. Daily maximums were calculated to be 2.0 times the daily averages.

7. Proposed Final Effluent Limitations

| | Combined Loading for Outfalls 001 and 002* kg/day (lbs/day) | | Other Limitations |
|---|---|---|---|
| | Daily Avg. | Daily Max. | Daily Maximum |
| COD | 2,370 (5,220) | 4,750 (10,400) | |
| Total Suspended Solids | 387 (852) | 775 (1,700) | |
| $BOD_5$ | 258 (568) | 516 (1,140) | |
| Oil & Grease | - | - | 10 mg/l |
| pH (S.U.) | - | - | 6.0-9.0 range |

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| | Discharge Limitations (Outfall 003) ** kg/day (lbs/day) | | | | Other Limitations |
|---|---|---|---|---|---|
| | Daily Average | | Daily Maximum | | Daily Maximum |
| COD | 218 | (480) | 436 | (960) | |
| Total Suspended Solids | 57 | (125) | 114 | (250) | |
| $BOD_5$ | 38 | ( 83) | 76 | (166) | |
| Oil & Grease | - | | - | | 10 mg/l |
| pH (S.U.) | - | | - | | 6.0-9.0 range |

* All loadings are gross limitations for 001 and 002.

** COD loading is gross, TSS and $BOD_5$ were corrected for average intake values for 003.

As stated earlier, production was not directly used in calculating any loadings. If production is reported to change significantly, corresponding modifications would have to be made in the permit loadings. This need for adjustments was expressed by Karl Zollner in a telephone conversation on July 31, 1980, with the U.S. EPA Permit Branch, when U.S. EPA explained that 1979-1980 effluent discharge data were used in the above calculations. The company "unofficially" has been reported operating presently at 40 percent of normal production.

8. Biomonitoring Requirement

Without any toxicity limitation at this time, the company should be required to perform on a monthly basis a 96-hour continuous flow bioassay in accordance with approved methods. This will continue the present monitoring of combined discharges from outfalls 001 and 002, and establish biomonitoring on outfall 003. A short schedule, i.e., 90 days after permit issuance, is recommended before the permittee shall achieve compliance with the biomonitoring requirement on outfall 003.

9. Toxicant Monitoring and Limitations

a. Monitoring

Due to the recent results of the joint U.S. EPA-MDNR survey (ERG report dated April 22, 1980), indicating the presence of high levels of a chloralkyl ether, specifically, Bis(2-chloroisopropyl)ether (BCIE) and the potential presence of other related chloroalkyl ethers in discharges from North Works operations, the company should be required to perform monitoring to establish the absence or presence of these products. The City of Wyandotte water supply plant intake

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is located about 3,700 feet directly South of 003N, adjacent to the Trenton Channel of the Detroit River. In a worst case situation (cross channel mixing) mg/l quantities of BCIE could affect the water supply. Due to the extreme potency of these products as mutagens or carcinogens, or both, it is vital to have this information as soon as possible. In the full process evaluation, qualitative aspects (phase II) of the evaluation to be performed under the Consent Order is not expected before December 31, 1980, and quantitative information (Phase III) before August 31, 1981. It is suggested that the following options be evaluated for initiating monitoring and reporting for any critical parameters at the earliest possible date: (1) issue a 308 letter, (2) issue a permit with monitoring before November 30, 1980, or (3) revise the proposed Consent Order to include selected monitoring requirements at an early date.

Unless sufficient information is already available from the company, as a minimum, monitoring for the following chloroalkyl ethers should be performed:

Bis(2-chloroisopropyl)ether (BCIE)
Bis(2-chloroethyl)ether (BCEE)
Bis(1-chloroethyl)ether (BCEE isomer)

Monitoring should be performed on outfalls 001 and 003 on a Weekly basis for the term of the permit or order until modified. BCIE and BCEE have been identified in discharges from BASF Wyandotte operations. A potential exists for the presence in BASF discharges of the other chloroalkyl ethers.

b. Limitations

The only chloroalkyl ether positively identified in discharges from the North Works is Bis(2-chloroisopropyl)ether (BCIE). Two grab samples of 003N (ERG report dated April 22, 1980) analyzed at 4.55 mg/l and 17.70 mg/l. Since these values represent significant amounts for this suspected carcinogen, we propose the following interim discharge limitation on a total plant basis:

| Effluent Characteristic * | Total Plant Loading for Outfalls 001, 002, and 003 kg/day (lbs/day) Daily Maximum * | Monitoring Requirements |
|---|---|---|
| Bis(2-chloroisopropyl)ether (BCIE) | 128 (282) | Weekly, 24-hour Composite |

* Effluent characteristics and limitations are subject to revision based upon a determination that the discharge is harmful to human health or the aquatic environment.

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The 282 lbs/day was derived as a water quality based limitation using the following data and assumptions:

(1) Monthly average flow of the total Detroit River = 182,000 cfs

(2) "Upper Trenton Channel" flow is 25% of total Detroit River = 45,500 cfs
= 29,355 MGD

(3) Total mixing downstream of 003N (width from shoal to Michigan shoreline) = assumption

(4) City of Wyandotte water supply intake can be affected by BASF discharges (001, 003), and the removal of BCIE at water treatment plant is zero = assumption

(5) Background of BCIE in Detroit River is zero = assumption

(6) Water quality criterion for BCIE as a mutagen/carginogen with a target risk level (for cancer) of $10^{-6}$ from U.S. EPA Criterion Document for chloroalkyl ethers = 1.15 ug/l (ppb)

(7) Calculation

$$\text{MGD} \times \text{mg/l} \times 8.34 = \text{lbs/day}$$
$$29{,}355 \times 1.15 \times 10^{-3} \times 8.34 = 281.5 \text{ lbs/day}$$

For the maximum protection of human health from the carcinogenic effects of exposure to BCIE (and related compounds) this Agency feels it is imperative to place immediately an interim limitation on BCIE based on the above assumptions. Based on a review of other information available to MDNR biologists, analysis of Detroit River water, and results of analyses of the City of Wyandotte's intake and finished water supply (currently proposed to be sampled by U.S. EPA), a more stringent limitation may be necessary.

10. Schedule of Compliance

For achieving compliance with the final effluent limitations specified for outfall(s) 001, 002, 003, see the attached proposed schedule of compliance. It is recommended that the biomonitoring proposed under sections 8 and 9a above and the imposition of a limitation for BCIE be required at the earliest possible date.

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Proposed Schedule of Compliance for Meeting

Final Effluent Limitations

C. SCHEDULE OF COMPLIANCE

1. The permittee shall achieve compliance with the effluent limitations specified for outfall(s) 001, 002, 003 in accordance with the following schedule:

a. Submit progress report to the Chief Engineer of the Michigan Water Resources Commission on or before December 31, 1980.

b. Submit a preliminary engineering report and basis of design for said facilities to the Chief Engineer of the Michigan Water Resources Commission and obtain his approval thereof on or before February 28, 1981.

c. Submit progress report to the Chief Engineer of the Michigan Water Resources Commission on or before N/A

d. Submit final plans and specifications for said facilities to the Chief Engineer of the Michigan Water Resources Commission and obtain his approval thereof on or before May 31, 1981

e. Commence construction of said facilities on or before August 31, 1981.

f. Submit progress report to the Chief Engineer of the Michigan Water Resources Commission on or before Jan. 31, 1982.

g. Submit progress report to the Chief Engineer of the Michigan Water Resources Commission on or before June 30, 1982.

h. Complete construction of said facilities on or before November 30, 1982.

i. Attain operational level necessary to meet the limitations specified herein on or before December 31, 1982.

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P = risk probability

70 kg person is design person

6.5 gms fish consumed/person

1. $I = 70 \times P/B$ = intake (44 FR 15926 March 15, 1979)

2. $I(\text{mg/day}) = C(\text{mg/l}) \times R(\text{l/kg fish}) \times 0.0065 \text{ kg fish/day} + C(\text{mg/l}) \times 2 \text{ l/day}$

3. $C = 70 \times P / B(2 + R \times 0.0065)$ (44 FR 15926)

4. $P = \frac{B \times I}{70}$ rearrangement of 1.

5. $B_H = .55$ (mg/kg/day) new data based on change in model from single hit to multi-stage

$R = 110$ bioacc. factor

6. $\bar{C}$(acrylonitrile) ≡ concentration of acrylonitrile under average flow conditions in Trenton Channel

$$\bar{C}(\text{acrylonitrile}) = \frac{4,975 \text{ lbs/yr}}{365 \text{ day/yr} \times 8.34 \text{ lbs/gal} \times 29,355 \text{ MGD}} = .00047 \text{ mg/l}$$

7. $$P = \frac{.55 (\text{mg/kg/day})}{70} \times \left[2 + 110 \frac{\text{l}}{\text{kg fish}}(0.0065 \text{ kg fish/day})\right] \times (.00047 \text{ mg/l})$$

$P = 7.6 \times 10^{-6} \sim 10^{-5}$

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CRITICAL MATERIALS REGISTER MASTER PROGRAM

FACILITY- 820314
BASF WYANDOTTE CORP
NORTH PLANT
1609 BIDDLE
WYANDOTTE MI 48192

DISTRICT: 1
COUNTY: 82
RIVER BASIN: 0613100

OUTFALLS: 05
MAJOR DISCHARGE:
TOT. AVG. DAILY DISC: 15.6000

CRITICAL MAT: Y
SANITARY SEWER: 820198
SIC: 2890

| CRITICAL MATERIAL(S) | CON. | USE. | NCOS. | DIS. | RES. | GPSF OUTFALLS |
|---|---|---|---|---|---|---|
| HEXACHLOROBENZENE (HCB) | X | | | 2 | 2 | 001 |
| FLUCHLORALIN | X | | | 2 | 7 | 003 |
| CHLORINE | X | | | 0 | 0 | |
| BIS (2-ETHYLHEXYL 1) PHTHALATE | X | | | 0 | 0 | |
| ACRYLONITRILE | X | | | 80000 | 5 | 001 |
| STYRENE | X | | | 6 | 3 | 001 |
| DI-N-BUTYL PHTHALATE | X | | | 0 | 5 | |
| 1,1,2-TRICHLOROETHANE | X | | | 0 | 0 | |
| POLYCHLORINATED BIPHENYLS(PCB) | X | | | 0 | 0 | |
| ZINC | X | | | 4 | 7 | 006 007 |
| NICKEL | X | | | 1 | 5 | 007 |
| CYANIDES | X | | | 5 | 0 | 005 |
| COBALT | X | | | 5 | 3 | 003 |
| CHROMIUM | X | | | 2 | 0 | 007 |
| HYPOCHLORITE | X | | | 4 | 0 | 001 003 007 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820315 | % PROCESS: | 62 | AVG. DAILY FLOW: | .0400 |
| TYPE: | 8 | % COOLING: | 33 | MAX. DAILY FLOW: | .0000 |
| DESIGN USE: | | % SANITARY: | 5 | TOT. ANN. FLOW: | 10.0 |
| GPSF: | 010 | | | DROUGHT FLOW: | 999999 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820314 | % PROCESS: | 0 | AVG. DAILY FLOW: | 1.1000 |
| TYPE: | 8 | % COOLING: | 0 | MAX. DAILY FLOW: | .0000 |
| DESIGN USE: | | % SANITARY: | 100 | TOT. ANN. FLOW: | 402.0 |
| GPSF: | 009 | | | DROUGHT FLOW: | 999999 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820232 | % PROCESS: | 90 | AVG. DAILY FLOW: | 1.0000 |
| TYPE: | 1 | % COOLING: | 10 | MAX. DAILY FLOW: | 1.1000 |
| DESIGN USE: | C1 | % SANITARY: | 0 | TOT. ANN. FLOW: | 365.0 |
| GPSF: | 007 | | | DROUGHT FLOW: | 100000 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820180 | % PROCESS: | 10 | AVG. DAILY FLOW: | 9.0000 |
| TYPE: | 1 | % COOLING: | 90 | MAX. DAILY FLOW: | 9.6000 |
| DESIGN USE: | C1 | % SANITARY: | 0 | TOT. ANN. FLOW: | 3285.0 |
| GPSF: | 001 | | | DROUGHT FLOW: | 100000 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820178 | % PROCESS: | 5 | AVG. DAILY FLOW: | 1.2000 |
| TYPE: | 1 | % COOLING: | 95 | MAX. DAILY FLOW: | 1.7000 |
| DESIGN USE: | C1 | % SANITARY: | 0 | TOT. ANN. FLOW: | 401.0 |
| GPSF: | 003 | | | DROUGHT FLOW: | 100000 |

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CRITICAL MATERIALS REGISTER MASTER PROGRAM

OUTFALL: 820131 % PROCESS: 2 AVG. DAILY FLOW: 4.0000
TYPE: 1 % COOLING: 98 MAX. DAILY FLOW: 6.0000
DESIGN USE: C1 % SANITARY: 0 TOT. ANN. FLOW: 1460.0
GPSF: 005 DROUGHT FLOW: 100000

OUTFALL: 820095 % PROCESS: 30 AVG. DAILY FLOW: .4000
TYPE: 1 % COOLING: 70 MAX. DAILY FLOW: .4000
DESIGN USE: C1 % SANITARY: 0 TOT. ANN. FLOW: 146.0
GPSF: 006 DROUGHT FLOW: 100000

PRODUCTION RESIDUAL 820314P
PHYSICAL STATE: 1 SOLVENT: 3 RESIDUE: 1 AMOUNT: 0000240 P DISPOSAL: 0 STORAGE: 1
ACRYLONITRILE HEXACHLOROBENZENE (HCB)
STYRENE

PRODUCTION RESIDUAL 820314P
PHYSICAL STATE: 4 SOLVENT: 1 RESIDUE: 1 AMOUNT: 0060000 P DISPOSAL: 0 STORAGE: 1
CRITICAL MATERIAL: FLUCHLORALIN

WASTEWATER RESIDUAL 820314W
PHYSICAL STATE: 3 SOLVENT: 1 RESIDUE: 6 AMOUNT: 0001000 C DISPOSAL: 0 STORAGE: 7

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FACILITY- 820315
BASF WYANDOTTE CORP
SOUTH PLANT
4001 RIDGLE
WYANDOTTE MI 48192

DISTRICT: 1 OUTFALLS: 04 CRITICAL MAT: Y
COUNTY: 82 MAJOR DISCHARGE: SANITARY SEWER: 820198
RIVER BASIN: 0613100 TOT. AVG. DAILY DISC: 45.1000 SIC: 2890

| CRITICAL MATERIAL(S) | CON. | USE. | NCOS. | DIS. | RES. | GPSF | OUTFALLS |
|---|---|---|---|---|---|---|---|
| CHLORINE | X | | | 0 | 0 | | |
| TRIS(DIBROMOPROPYL) PHOSPHATE | X | | | 0 | 3 | | |
| BIS (2-ETHYLHEXYL 1) PHTHALATE | X | | | 0 | 5 | | |
| 1-CHLORO-2,3-EPOXYPROPANE | X | | | 0 | 0 | | |
| CARBON TETRACHLORIDE | X | | | 0 | 6 | | |
| POLYCHLORINATED BIPHENYLS(PCB) | X | | | 0 | 0 | | |
| HYPOCHLORITE | X | | | 6 | 0 | | 002 003 004 |

OUTFALL: 820315 % PROCESS: 0 AVG. DAILY FLOW: .2500
TYPE: A % COOLING: 0 MAX. DAILY FLOW: .0000
DESIGN USE: % SANITARY: 100 TOT. ANN. FLOW: 93.0
GPSF: 006 DROUGHT FLOW: 999999

OUTFALL: 820227 % PROCESS: 0 AVG. DAILY FLOW: .5000
TYPE: 1 % COOLING: 100 MAX. DAILY FLOW: .7000
DESIGN USE: C1 % SANITARY: 0 TOT. ANN. FLOW: 183.0
GPSF: 005 DROUGHT FLOW: 100000

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BUREAU OF ENVIRONMENTAL PROTECTION
CRITICAL MATERIALS REGISTER MASTER PROGRAM



| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820185 | % PROCESS: | 2 | AVG. DAILY FLOW: | 7.2000 |
| TYPE: | 1 | % COOLING: | 98 | MAX. DAILY FLOW: | 8.6000 |
| DESIGN USE: | C1 | % SANITARY: | 0 | TOT. ANN. FLOW: | 2628.0 |
| GPSF: | 002 | | | DROUGHT FLOW: | 100000 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820183 | % PROCESS: | 65 | AVG. DAILY FLOW: | 37.0000 |
| TYPE: | 1 | % COOLING: | 35 | MAX. DAILY FLOW: | 49.3000 |
| DESIGN USE: | C1 | % SANITARY: | 0 | TOT. ANN. FLOW: | 13505.0 |
| GPSF: | 003 | | | DROUGHT FLOW: | 100000 |

| | | | | | |
|---|---|---|---|---|---|
| OUTFALL: | 820132 | % PROCESS: | 1 | AVG. DAILY FLOW: | .4000 |
| TYPE: | 1 | % COOLING: | 99 | MAX. DAILY FLOW: | .4000 |
| DESIGN USE: | C1 | % SANITARY: | 0 | TOT. ANN. FLOW: | 146.0 |
| GPSF: | 004 | | | DROUGHT FLOW: | 100000 |

PRODUCTION RESIDUAL 820315P
PHYSICAL STATE: 1 SOLVENT: 3 RESIDUE: 9 AMOUNT: 0010000 G DISPOSAL: 0 STORAGE: 1
BIS (2-ETHYLHEXYL 1) PHTHALATE TRIS(DIBROMOPROPYL) PHOSPHATE

WASTEWATER RESIDUAL 820315W
PHYSICAL STATE: 1 SOLVENT: 3 RESIDUE: 9 AMOUNT: 0009388 G DISPOSAL: 0 STORAGE: 1
CRITICAL MATERIAL: CARBON TETRACHLORIDE

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Background groundwater data and down gradient groundwater samples will also be drilled for and collected.

The Department's concern is based on the following information:

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