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ANALYSES OF IMPACTS OF BOTTOM SEDIMENTS FROM GRAND CALUMET RIVER AND INDIANA HARBOR CANAL ON WATER QUALITY

by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) At the request of the Chicago District, the influence of polluted bottom sediments on the quality of water in the Grand Calumet River/Indiana Harbor Canal (GCR/IHC) was investi- gated. The approach used in this study consisted of obtaining and analyzing existing information on sediment-water interactions and their relationship to water quality, methods for estimating impacts of sediment-water interactions on water quality, and sediment and water quality data for the GCR/IHC system. Limited field data were collected by the Chicago District in support of this study. In order to understand the role of sediment as a source of contaminants in the GCR/ IHC, it is necessary to understand the relative importance of sediment and water from the GCR/IHC as contaminant sources to Lake Michigan. To accomplish this, data available on sources of pollutants to the GCR/IHC were examined, and a wasteload allocation model devel- oped for the GCR/IHC was evaluated. (Continued)					
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Contaminant models	In-place sediment assessment	Sediment transport
Grand Calumet River	Metals	Sediment/water interaction
Indiana Harbor	Polychlorinated biphenyls	

19. ABSTRACT (Continued). Evaluation of the wasteload allocation model developed for the Grand Calumet River system by the Indiana State Board of Health showed that the model simulates field water quality data for dissolved oxygen and conservative pollutants within a reasonable range of accuracy. At present, the model is unsuitable for nonconservative (subject only to transport) contaminants such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), and heavy metals. Weaknesses identified in the existing database included unmonitored loadings and limited flow data for the stream and harbor, as well as surprisingly low values of sediment oxygen demand. Other wasteload allocation models currently in use show similar weaknesses and are of limited value for evaluating the transport of sediment contaminants out of the GCR/IHC system or for quantifying the impacts of contaminated sediment on water quality.

Results of equilibrium partitioning calculations made using data specific for the GCR/IHC system indicate that Food and Drug Administration limits on PCB concentrations in fish tissue for human consumption would be exceeded if the fish survived in the canal for a sufficient period to come to equilibrium with sediment PCBs. However, estimated diffusion rates of PCBs in the Indiana Harbor Canal sediments indicate that, in the absence of disturbances, movement of soluble PCBs from the sediment into the overlying water is relatively minor.

The relative importance of mechanisms controlling contaminant movement from sediment in the GCR/IHC is in the order: transport of contaminants associated with particulates > transport of contaminants desorbed from suspended particulates > transport of soluble contaminants released from deposited sediment. Bioaccumulation, another mechanism for contaminant movement, is of minor importance in the GCR/IHC. The existing aquatic life is limited to pollution-tolerant species of variable numbers and lower numbers of less pollution-tolerant fish species. Therefore, before other than a rough approximation of the benefits of dredging the Indiana Harbor Canal can be made, a thorough knowledge of the sources of sediment and how these sediments move through the system is needed.

Results of this study have shown that the data available allow only rough estimates, such as those made by the Chicago District for the Indiana Harbor Environmental Impact Statement, of sediment loadings and sediment yield. However, historical data suggest that dredging the Indiana Harbor Canal would allow it to act as a sediment trap, retaining contaminated sediment that would otherwise be transported into Lake Michigan. More detailed hydrodynamic and suspended sediment transport data are necessary to allow use of more sophisticated analytical techniques for evaluating sediment sources and for quantifying resuspension and sediment transport in the system. Additional data must also be collected before analytical techniques more sophisticated than those already conducted can be applied to the GCR/IHC system for either metals or toxic organics. Therefore, the immediate detailed application of either hydrodynamic or contaminant models is not recommended.

Any studies conducted in the GCR/IHC system require a knowledge of the system's hydrodynamic and sediment transport properties. The information required for an assessment of GCR/IHC system hydrodynamics and sediment transport will necessitate both short-term (on the order of a day) and long-term (on the order of 4 to 6 days) field data sets. Following these hydrodynamic studies, one or more options presented in this report can be utilized. These include (a) quantifying mass loadings to the water column during dredging and non-dredging conditions; (b) determining relative loadings from sediments prior to and following dredging operations and between sediment and nonsediment loading to the GCR/IHC; and (c) determining the long-term fate of contaminants in the GCR/IHC system.

PREFACE

This study was sponsored by the US Army Engineer District (USAED), Chicago. The work was conducted by the Environmental Laboratory (EL) and Hydraulics Laboratory (HL), US Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss. The study was conducted under the direction of Dr. John Harrison, Chief of EL, and Mr. Frank A. Herrmann, Jr., Chief of HL, and under the general supervision of Dr. Thomas L. Hart, Chief of the Aquatic Processes and Effects Group; Mr. Norman R. Francingues, Jr., Chief of the Water Supply and Waste Treatment Group; Mr. Mark S. Dortch, Chief of the Water Quality Modeling Group; Mr. William R. Martin, Chief of the Estuarine Engineering Branch; Mr. Donald L. Robey, Chief of the Ecosystem Research and Simulation Division (ERSD); Dr. Raymond L. Montgomery, Chief of the Environmental Engineering Division (EED); and Mr. William H. McAnally, Chief of the Estuaries Division (ED).

The study was conducted by Drs. James M. Brannon, Douglas Gunnison, James L. Martin, and Rex L. Chen of ERSD, Mr. Daniel E. Averett of EED, and Mr. Robert F. Athow, Jr., of ED. The USAED, Chicago, Project Manager was Mr. Jan Miller.

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CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
feet	0.3048	metres
gallons (US liquid)	3.785412	cubic decimetres
inches	2.54	centimetres
miles (US statute)	1.609347	kilometres
square feet	0.09290304	square metres
square miles	2.589998	square kilometres

ANALYSES OF IMPACTS OF BOTTOM SEDIMENTS FROM GRAND CALUMET RIVER
AND INDIANA HARBOR CANAL ON WATER QUALITY

PART I: INTRODUCTION

Background

1. Bottom sediments contaminated with organic matter, heavy metals, oil and grease, nutrients, and organic chemical contaminants are present in almost all urban waterways with Federal navigation channels often acting as catchment basins for these polluted sediments. The Corps, under Federal environmental regulations, must determine the environmental impacts of dredging and disposing of these sediments as part of its assessment before authorizing dredging operations. To date, Corps analysis of sediments has examined the effects of dredging and disposal of these materials with limited attention to the environmental effects of sediments on the overlying water column or the environmental benefits of maintenance dredging on a waterway.

2. Many environmentalists and concerned citizens strongly object to the Corps' dredging and disposal of polluted sediments with the belief that they are better left on the river bottom, out of sight and out of mind. Contaminated sediments, however, are neither stationary nor inert. The very presence of heavily contaminated sediments can exert a significant oxygen demand, support a poor diversity of benthic organisms, and provide a continuing source of contaminants even when all contaminant inputs to the waterway have ceased. The resuspension of polluted sediments can greatly affect the quality of the overlying water column and the water quality downstream. Although Federal channels are specifically authorized for navigation, the maintenance of these channels may provide long-term environmental benefits through the removal and confinement of heavily contaminated sediments. If the Corps can demonstrate or quantify these benefits, it can then offer them as a form of mitigation to the short-term impacts of dredging and disposal.

Objective

3. The objective of this study was to assess the influence of polluted bottom sediments on the quality of water in the Grand Calumet River and Indiana Harbor Canal (GCR/IHC) system.

Approach

4. The approach used for the initial evaluation consisted of obtaining and analyzing existing information on sediment-water interactions and their relationship to water quality, methods for estimating impacts of sediment-water interactions on water quality, and sediment and water quality data for the GCR/IHC system. Limited field data were collected during this study. The following items were evaluated based on existing information and data:

- a. Mechanisms involved in controlling the movement of contaminants and methods for evaluating the magnitude of these mechanisms, such as water quality models.
- b. The relative importance of these mechanisms in the GCR/IHC system.
- c. The need for future studies.

PART II: GRAND CALUMET RIVER/INDIANA HARBOR CANAL

Flow

5. A description and brief history of the Grand Calumet River are contained elsewhere (Lake Michigan Federation (LMF) 1984). Therefore, this subject will be treated only briefly. The Grand Calumet River originates near Marquette Park Lagoon and flows westward through Gary, East Chicago, and Hammond, Ind., where it intersects the Indiana Harbor Canal prior to reaching the Illinois border. From its headwaters the river flows approximately 13 miles* before joining the Indiana Harbor Canal and its west branch. The Grand Calumet River flows in three directions. East of the Indiana Harbor Canal the river flows westward. However, near the Hammond municipal wastewater treatment plant close to Indianapolis Boulevard, a natural divide exists where the river reverses itself and flows eastward, joining the eastern segment in flowing to Lake Michigan through the Indiana Harbor Canal. These flow patterns are subject to rapid change. Periodic water level changes in Lake Michigan may cause the Grand Calumet River and the Indiana Harbor Canal to reverse their flow direction as often as two to four times daily (US Environmental Protection Agency (USEPA) 1985) with the effect extending upstream to the Kennedy Avenue bridge on the east branch of the Grand Calumet.

6. The volume of flow in the Grand Calumet River is subject to wide variations that depend on winds, wastewater discharges, and storm water runoff (LMF 1984). This variation is especially true in the east branch due to the 368 mgd of wastewater discharged by U.S. Steel. Recent comparisons between flow measurements made by the US Geological Survey (USGS) in the Grand Calumet River and approximate outfall flow from point sources indicated close agreement between the two during dry periods (HydroQual 1984). No comparable data exist for the Indiana Harbor Canal.

* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 4.

Contamination Sources

7. The Grand Calumet River and Indiana Harbor Canal are subject to many sources of contamination. There are 39 permitted outfalls on the Grand Calumet River and Indiana Harbor Canal (HydroQual 1984). It has been reported, however, that measured point source outfall mass discharges do not always account for total contaminant levels (HydroQual 1984), indicating that non-permitted wastes are entering the river and canal. Less is known about the significance of nonpoint pollution sources on water quality in the GCR/IHC system compared with available data on point sources. Nonpoint sources include urban and industrial runoff, combined sewer overflows (CSOs), leachate or overflow from a number of waste fills or ponds, and spills of pollutants in and around industrial operations. Further complicating the problem is the fact that at 15 different CSO points, untreated sewage and industrial wastewater bypass the treatment plants in some cases when rainfall exceeds 0.1 in. in 24 hr. In addition, the Hammond, Ind., sludge storage lagoons are adjacent to the Grand Calumet and are reported to have routinely overflowed (LMF 1984). Also near the river are 11 dumps and landfills and 26 surface impoundments that may contain hazardous materials (LMF 1984). Contaminant problems in the GCR/IHC system are also aggravated by a lack of industrial pretreatment programs and the small size of the upstream drainage basin (68 square miles) of the Grand Calumet River (HydroQual 1984, LMF 1984, USEPA 1985).

Water Quality

8. A number of sources have reported that water quality in the GCR/IHC system has improved in recent years (HydroQual 1984, Polls et al. 1983, LMF 1984). HydroQual (1984) reported a general reduction in the magnitude of concentrations of fecal coliform bacteria, ammonium-nitrogen, cyanides, phenols, total phosphorus, and oil and grease between 1977 and 1983. Polls et al. (1983) reviewed historical chemical water quality monitoring data and concluded that concentrations of ammonium-nitrogen, cyanide, and suspended solids had improved in the Indiana Harbor Canal over the 1970 to 1981 period. They reported that other constituents showed minor or no improvement. Polls et al. (1983) also conducted a water quality survey in 1982. They found decreased concentrations of ammonium-nitrogen, cyanide, iron, and phenol in

Indiana Harbor Canal waters in 1982 compared with 1973 data. Dissolved oxygen concentrations increased over the same time period. HydroQual (1984) reported that compounds such as iron, mercury, chlorides, and sulfates have not shown decreased concentrations over the 1977 to 1983 period (HydroQual 1984). Water quality standards for dissolved oxygen, pH, chlorides, total dissolved solids, and mercury continue to be violated (HydroQual 1984).

9. Surface water contaminant concentrations in Indiana Harbor have been shown to be generally higher than bottom water contaminant concentrations (HydroQual 1984). Water quality data indicate that a weak thermocline exists somewhere near the 20-ft depth. The presence of a thermocline means that canal waters are flowing through the surface water of the harbor and not mixing with lower level waters. Such restricted mixing is induced by warmer canal waters flowing towards the lake, thereby inducing a density-driven lake underflow into the harbor (HydroQual 1984).

10. Despite the complexities of the system, such as surface water stratification and contaminant inputs from unmonitored sources, it is clear that water quality, at least for some parameters, has been improving in the Indiana Harbor Canal and the east branch of the Grand Calumet River. This trend is not so clear for the west branch of the Grand Calumet River which has shown little improvement (USEPA 1985). However, improvement in water quality in the east branch of the Grand Calumet River and the Indiana Harbor Canal has been shown only for traditional water quality parameters such as dissolved oxygen and those parameters monitored in the industrial and municipal outfalls. Waters in the Indiana Harbor Canal and Grand Calumet River have not been routinely monitored for more exotic contaminants such as polychlorinated biphenyls (PCBs) or polyaromatic hydrocarbons (PAHs). Heavy metals such as lead, chromium, zinc, cadmium, copper, nickel, and mercury in addition to PCBs have been determined (HydroQual 1984) for a limited number of water samples in the GCR/IHC. Some heavy metals have also been determined in water samples at several stations in the GCR/IHC (Indiana State Board of Health's monthly stream samples).

Sediment Quality

11. Polls et al. (1983) analyzed historical sediment data collected in the Indiana Harbor Canal and Grand Calumet River and concluded that the quality of surface sediments had shown marked improvement from the 1967-1968 sampling program to the 1982 sampling program in the Indiana Harbor Canal and Indiana Harbor. Polls et al. (1983) also conducted sediment sampling in the Indiana Harbor Canal and the Grand Calumet River and compared these results with data obtained in a 1973 sampling program. They found that sediment chemical constituent data were variable between 1973 and 1982 (different stations showed different trends), but the overall trend appeared to be an improvement in sediment quality. Sediment samples in the study of Polls et al. (1983) were only analyzed for total solids, total volatile solids, chemical oxygen demand, fats, oils and greases, phenols, and total iron. Polls et al. (1983) also reported that the overall trend in the Indiana Harbor Canal is for sediment chemical constituent concentrations to decrease with increasing distance down the Indiana Harbor Canal towards Indiana Harbor. USEPA (1985) reported that the only substantial reduction in sediment metal levels that may have occurred from 1980 to 1984 in the Grand Calumet River is lead and zinc. Sediment sampling and analysis for toxicants by the US Army Corps of Engineers has indicated, however, that high concentrations of lead, zinc, arsenic, chromium, and PCBs are present in Indiana Harbor Canal sediments (US Army Engineer District, Chicago 1979, 1984a). Core samples taken in the Indiana Harbor Canal (US Army Engineer District, Chicago 1979) show that at some sites, up to 12 ft of the sediment column contains high concentrations of chemical contaminants. These sediments therefore have surface contamination as well as contamination that has been buried by sediment accretion, which indicates that contaminant input to the Indiana Harbor Canal has occurred for an extended period. Moreover, examination of core contaminant data reveals that sediment exposed when dredging to project depth will generally remain highly contaminated. The source of fresh sediment that will eventually deposit in the dredged area is therefore highly important.

12. Surface sediments in the Grand Calumet River have been analyzed for PCBs, metals, and other chemical contaminants (Polls et al. 1983; USEPA 1977, 1985). Core data are not available for the Grand Calumet River, and fewer

chemical analyses have been conducted because it is not a navigational channel subject to dredging.

13. The sediment chemical data currently available for the GCR/IHC system consist of total chemical concentrations in sediment, elutriate and modified elutriate test results, and leachate testing to determine leachate quality in confined nearshore or upland disposal facilities. None of these tests provides the type of information needed to assess the mobility of contaminants resuspended in the water column under natural conditions (nondredging situations). Extensive adsorption/desorption tests using sediment:water ratios typical of storm events and ship traffic-induced resuspension would be needed to provide this type information. Such test procedures are currently available. The elutriate test provides information on sediment-water interactions under environmental conditions similar to those encountered during hydraulic dredging and open-water disposal. Leaching tests are designed to permit planning-level assessments of leachate quality following disposal; therefore, high sediment:water ratios are used during testing, the opposite of what is needed to assess adsorption/desorption at extremely low sediment:water ratios. Because of the effect of solids concentration on contaminant partitioning coefficients (Voice, Rice, and Webber 1983), results of leaching data at high sediment:water ratios cannot be used to provide information on adsorption/desorption at low sediment:water ratios.

Benthic Organisms

14. Numbers and diversity of aquatic organisms have been investigated in the GCR/IHC system (USEPA 1977; Potos 1981; Polls et al. 1983; US Army Engineer District, Chicago 1984b). Benthic fauna were dominated by pollution-tolerant species (oligochaetes) in all samples. The densities of benthic macroinvertebrates (94 to 100 percent oligochaete worms) were found to be greater in the Indiana Harbor Canal (average 73,366 organisms/m²) than in Indiana Harbor (30,183 organisms/m²) and nearshore Lake Michigan (13,192 organisms/m²) (US Army Engineer District, Chicago 1984b). The total numbers of groups of benthic organisms (taxa) in the GCR/IHC did show an increase in 1982 compared with 1973 (Polls et al. 1983). Comparisons between recent and historical benthic data show a slight improvement in diversity and large increases in density of pollution-tolerant species.

15. Historical surveys of fish populations in the GCR/IHC are lacking. Recent surveys of the Harbor and Canal (US Army Engineer District, Chicago 1984b) produced mainly pollution-tolerant species (carp, goldfish, and carp-goldfish hybrids). Less pollution-tolerant fish (alewife, gizzard shad, pumpkinseed, perch, etc.) were found throughout the Indiana Harbor Canal and Harbor in lower densities by weight. The extremely high densities of carp collected during the recent survey (US Army Engineer District, Chicago 1984b) may be a seasonal artifact because sampling was conducted in November and December.

Environmental Status of the GCR/IHC

16. Polls et al. (1983) concluded that the chemical content of the water and sediment and total number of benthic taxa were in agreement and indicated improving water and sediment quality in the GCR/IHC. Others have also examined the available data and concluded that water quality conditions in the Grand Calumet River have improved dramatically over the past 5 to 10 years (USEPA 1985). USEPA (1985) also recognized that chronic water quality problems remain in the Grand Calumet River despite the progress in cleaning up point sources. The apparent improvements in water quality in the GCR/IHC have focused renewed attention on toxic contaminants. In the opinion of many, toxic contaminants are now seen to be a more important factor limiting biological productivity than more conventional contaminants such as materials causing dissolved oxygen depletion in the GCR/IHC because of the improvement in the other aspects of water quality (USEPA 1985).

17. Sediments possess a great affinity for most contaminants and therefore, when exposed to pollution, generally act as a sink for contaminants. This affinity is true of sediments in the GCR/IHC which are highly contaminated as a result of long-term discharge of contaminants (USEPA 1985). Sediments on the bottom of the GCR/IHC system therefore pose a continuing hazard to water quality and aquatic organisms (USEPA 1985).

PART III: WASTEWATER SOURCES AND LOADS

18. This section identifies pollution sources to the Grand Calumet River, Indiana Harbor Canal, and Indiana Harbor; discusses the nature of these sources; and assesses the adequacy of existing data for predicting pollutant loads from these sources. Knowledge of pollutant loads from active sources, if adequate, allows comparison of water quality impacts contributed by sediment contamination versus pollutants contributed by other sources.

19. Information extracted from available reports and data related to pollution sources are contained in this section. Actual data summaries are not presented in detail because of the large volume of data available for this river system and the preliminary nature of this investigation. Two recent reports, "Master Plan for Improving Water Quality in the Grand Calumet River/Indiana Harbor Canal" (USEPA 1985) and "Grand Calumet River Wasteload Allocation Study" (HydroQual 1984), discuss and summarize available data for point sources of pollution. This discussion relies heavily on information presented in these two references and assesses how this information can be used in evaluating the impact of existing contaminated sediment on water quality in the GCR/IHC.

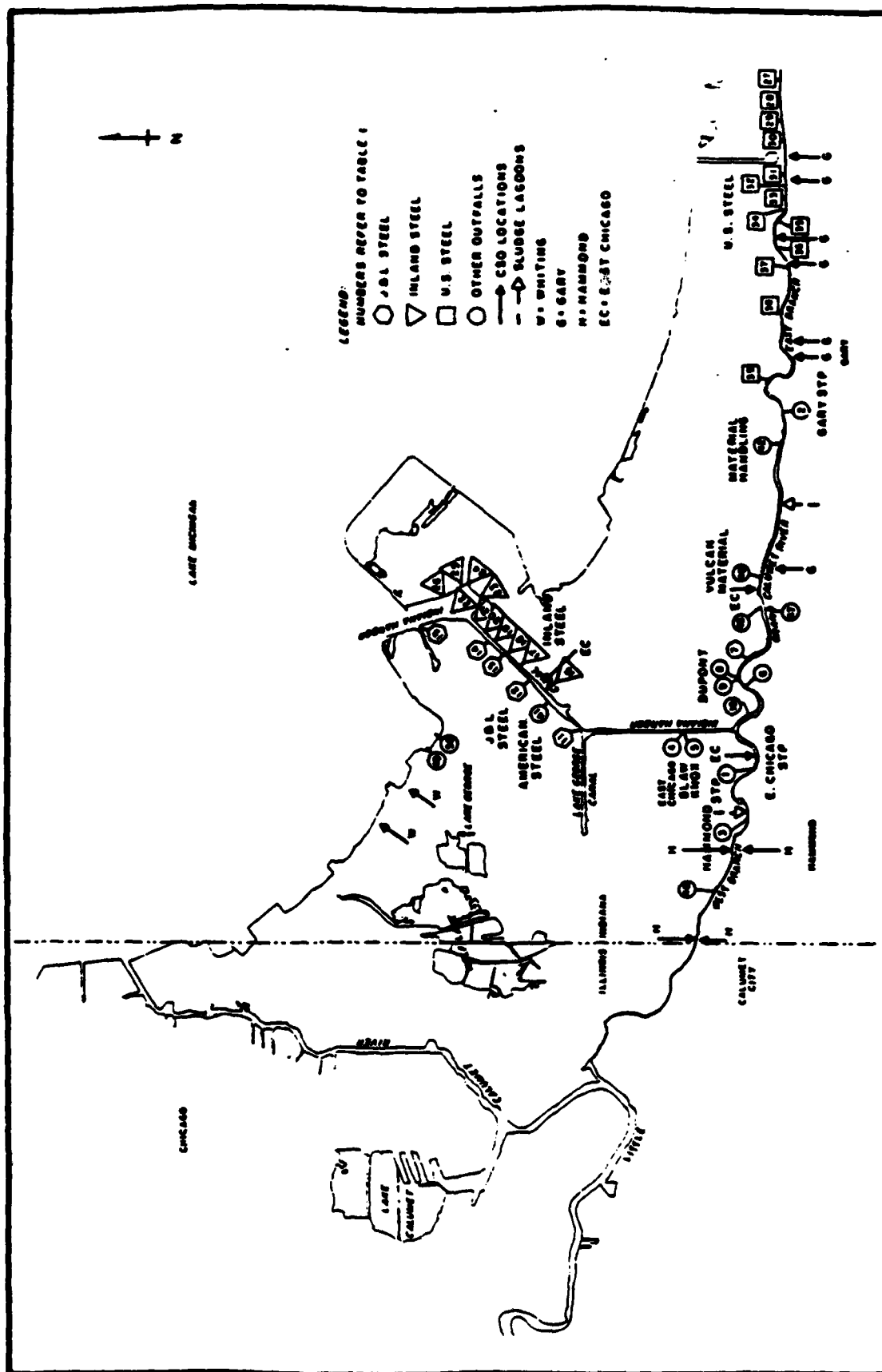
Pollution Sources

20. Recent studies showed that point pollution sources account for more than 90 percent of the base flow in GCR/IHC.* In addition to point pollution sources, nonpoint pollution sources affect GCR/IHC water quality, although less is known about the significance of these sources to GCR/IHC water quality.

Industrial point sources

21. HydroQual (1984) identified 39 industrial outfalls into the GCR/IHC from 10 industries. Figure 1 illustrates the locations of these discharges and Table 1 provides a brief description of each discharge. Most discharges are noncontact cooling waters from various industrial processes; however, process wastewater streams and treated sanitary wastes are also included. The three major steel mills, U.S. Steel, Inland Steel, and Jones and Laughlin

* USGS, 1985, Grand Calumet River survey, unpublished data.



(J & L) Steel, account for 28 of the 39 outfalls and more than 95 percent of the industrial effluent volume (HydroQual 1984). U.S. Steel is located near the upper end of the East Branch of the Grand Calumet River, while J & L Steel and Inland Steel are located on the Indiana Harbor or the Indiana Harbor Canal.

22. Each industrial discharge is subject to effluent limits prescribed in a National Pollutant Discharge Elimination System (NPDES) permit issued by the State of Indiana. In addition to the three major steel companies, the following industries also have NPDES permits for this stream: Citgo Petrochemical Corporation, E.I. duPont de Nemours and Co., U.S.S. Lead Refinery, Inc., Vulcan Materials, American Steel Foundries, Blaw Knox Foundry, Industrial Disposal, and Explorer Pipeline Co. (USEPA 1985).

23. The industrial discharges release an assortment of pollutants to the GCR/IHC. NPDES permits reflect the pollutants likely to be present in the discharge based on national technology-based guidelines for the particular industrial category or based on wastewater characterization data for each individual discharge. Table 2 lists the pollutants and associated effluent limits or monitoring requirements specified by the NPDES permits for six of the major industries (USEPA 1985). All these industries must address some of the conventional pollutants, i.e., substances having a biochemical oxygen demand (BOD), total suspended solids (TSS), pH, indicator bacteria (fecal coliform), and oil and grease. Cyanide, phenols, arsenic, chromium, copper, lead, mercury, nickel, and zinc are toxic pollutants covered by selected NPDES permits. Other nonconventional pollutants on the list include dissolved solids, ammonia, phosphorus, chloride, fluoride, sulfate, chlorine residual, iron, and tin. Temperature limits are also included in many permits.

24. U.S. Steel is currently the only industry whose permit addresses toxic organics (USEPA 1985), and the permit currently only requires monitoring. If the monitoring data expose the presence of toxic organics, then the permit may be revised establishing maximum loads for the pollutants detected. Other industrial NPDES permits which expire in the future will likely require monitoring and/or limit the discharge of toxic organics upon issuance of an updated permit. Best available treatment technology standards for the iron and steel manufacturing point source category specify maximum effluent loads for benzene, naphthalene, benzo(a)pyrene, and tetrachloroethylene, which are all on USEPA's list of toxic pollutants. Establishment of these standards

indicates that these organic compounds have been identified in effluents from iron and steel plants. However, this has not been documented specifically for the GCR/IHC.

25. Monitoring requirements for NPDES permits are established on a case-by-case basis. Permits require most major dischargers to measure flow on a continuous basis and collect samples for analysis of limited pollutants on a regular basis. A typical permit for duPont's discharge to the Grand Calumet River requires analysis of ten 24-hr composite samples collected on a random schedule each month. Assuming that other NPDES permits prescribe similar monitoring requirements, an abundance of data is available for industrial sources of many conventional pollutants to the GCR/IHC. Permittees report these data to the Indiana State Board of Health (ISBH) on a monthly or quarterly basis. Since toxic organics have not in the past been limited by NPDES permits, there is a paucity of this kind of information. The detection of these materials in sediment samples indicates that these materials have been released in the past. Whether or not toxic organics are now being discharged in harmful amounts cannot be determined based on existing data.

26. Another problem with NPDES data is that high volume discharges are not monitored for all pollutants because many pollutants are often present, but in very low concentrations. Yet on a mass loading basis, a discharge of 50 mgd with very low concentration may be more significant to water quality than a 1-mgd discharge with a higher concentration.

27. Because NPDES self-monitoring is somewhat like the honor system, there is a temptation to doubt the reliability or accuracy of NPDES data. However, the regulatory agency conducts periodic compliance monitoring for each discharge to encourage unbiased data reporting. Because of the penalties and liabilities possible for violating the permit requirements, most NPDES data should be acceptable for analyzing industrial effects on water quality.

28. Industrial dischargers have made substantial progress in cleaning up their effluents since the early 1970s. Polls et al. (1983) reported that the three major steel mills discharging into the GCR/IHC were substantially in compliance with court-ordered effluent limits. They also noted that these reductions were demonstrated by measurable improvements in concentrations of suspended solids and cyanide detected in samples from GCR/IHC. USEPA (1985) reported that most of the major industrial dischargers were in compliance with their NPDES permit during the third quarter of 1984. USEPA (1985) also

summarized the pollutant loads from the major industrial discharges as shown in Table 3. These data were based on samples collected for the ISBH wasteload allocation study (HydroQual 1984). Note that the three steel mills overshadow contributions from the other industries for most pollutants.

Publicly owned treatment works (POTWs)

29. The three POTWs in the GCR/IHC watershed are East Chicago, Hammond, and Gary. The first two discharge into the West Branch Grand Calumet River, while Gary discharges into the upper end of the East Branch (see Figure 1). These municipal dischargers are also subject to NPDES permits, but generally have poorer records of compliance than the industrial dischargers.

30. East Chicago's POTW consists of a 20-mgd conventional activated sludge system with alum addition for phosphorus removal. Hammond employs the Kraus modification of the activated sludge process along with mixed media filters for suspended solids removal. The plant is designed for 48-mgd average flow. Gary has a 60-mgd advanced wastewater treatment plant that includes two-stage activated sludge for BOD removal and nitrification, ferrous sulfate addition for phosphorus removal, and sand filtration (USEPA 1985).

31. NPDES permits for these POTWs include limits for ammonia, BOD, chlorides, fluoride, cyanide, oil and grease, phenol, phosphorus, suspended solids, pH, sulfate, fecal coliform, and flow rate. Therefore, monitoring data are available for these parameters. Many nonconventional pollutants would not normally be applied to a POTW, if it were not for the industrial discharges to the POTWs. Priority pollutant data collected on one or two occasions are reported by USEPA (1985). These data exhibit the presence of heavy metals and certain toxic organics in the POTW discharges.

32. East Chicago has experienced chronic violations of its NPDES permit. Table 4 illustrates that from 1968 to 1982 only a slight decrease in BOD load was achieved and the TSS load actually increased. A court order issued in 1982 requires improved operation of the East Chicago facility. Effluent quality has improved since 1982, but the plant still has problems meeting its limits for BOD, TSS, ammonia, phenol, cyanide, fluoride, chloride, sulfate, and oil and grease. USEPA conducted a static bioassay for this discharge in 1980 and found it to be highly toxic to fish and to contain mutagenic compounds (USEPA 1985).

33. Gary and Hammond have had some problems complying with their permits, but Table 4 shows that they generally produce an effluent with low BOD

and TSS concentrations. Gary's deficiencies are blamed on improper operation and maintenance. Hammond has been hampered by CSOs and inadequate sludge handling facilities (USEPA 1985).

34. Expiration dates for the POTWs' NPDES permits have passed. Requirements in effect are based on the expired NPDES permits or court decisions. New permits will be issued when the ISBH wasteload allocation study is completed.

35. As shown below, all three POTWs receive significant contributions from industrial sources (USEPA 1985):

<u>POTW</u>	<u>No. of Industries</u>	<u>Industrial Flow as % of Total Inflow</u>
Gary	19	14
Hammond	21	10
East Chicago	51	24

In addition to conventional pollutants, the industrial discharges may contain toxic materials, including both metals and organics. Many of these pollutants are minimally affected by the POTW processes but may have negative impacts on the POTW itself. Discharge of toxic materials into sewer systems is a common problem in many cities throughout the United States (Environmental Reporter 1985). POTW pass-through of such toxic materials is thought to be a principal source of pollutants in the GCR/IHC. The magnitude of this contribution is currently unknown. However, regulatory agencies have increased the emphasis on industrial waste pretreatment programs, and the POTWs will be required to assess the problem more intensely by collecting more priority pollutant data and tightening industrial pretreatment criteria to limit industrial input of pass-through pollutants.

Waste fills

36. Waste fills have the potential for being major active sources of certain toxic pollutants. USEPA (1985) identifies 38 waste fills in the GCR/IHC drainage area (Figure 2). The 11 sites listed on Table 5 are suspected to be of such character and proximity to the stream (less than 0.25 mile) to justify further investigation or regulatory action. Pollutant concentrations and discharge volumes from these sites are for the most part undocumented. USEPA is conducting a study to identify and quantify the leachate contribution from these sources to the river.

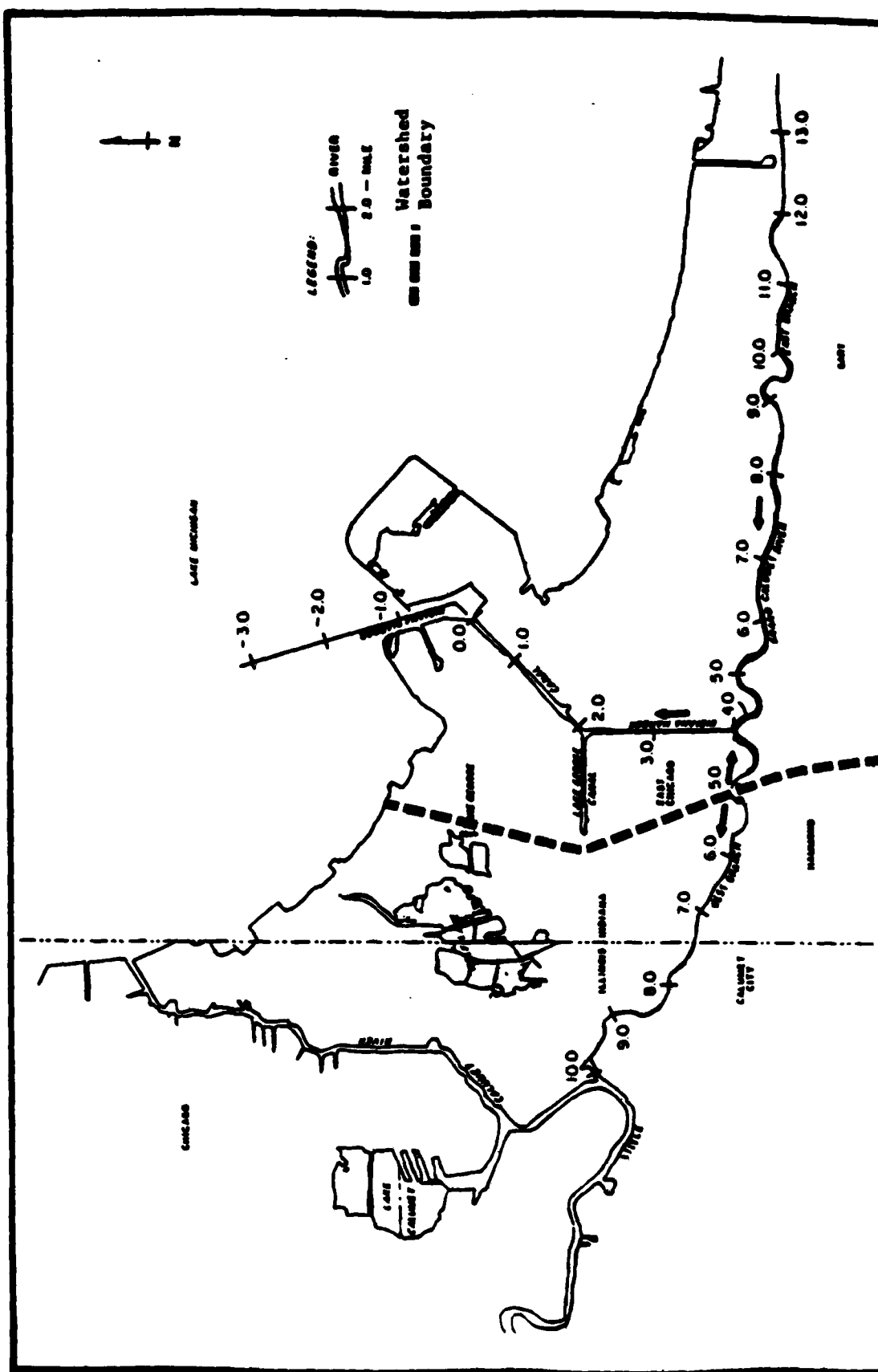


Figure 2. GCR/IHC drainage area (USEPA 1985)

Nonpoint sources

37. Runoff from a predominantly urban and industrial area such as GCR/IHC is likely to contain heavy metals, oil and grease, suspended solids, and other conventional and nonconventional pollutants. This runoff is for the most part uncontrolled. Nationally, it is frequently reported that, since implementation of Public Law 92-500, point sources of pollution have made much progress toward protecting water quality, and that further improvement in water quality can be realized only by reducing the water quality impact of nonpoint sources. Most of the point sources in the GCR/IHC basin have certainly made progress toward pollution abatement in recent years. Identification and cleanup of GCR/IHC nonpoint sources have received less attention but have not been ignored.

38. USEPA (1985) suggested that nonpoint sources in the GCR/IHC include leaching and dispersal from sediments, highway runoff, spills, surface runoff from industrial land, seepage from waste fills, rain scour, dust fall, and illegal dumping. This discussion will also include CSOs as a nonpoint source although it is sometimes defined as a point source. The only data available to characterize nonpoint pollution in GCR/IHC are related to the CSO program. USEPA (1985) reported that there are 14 CSOs discharging an estimated 11 billion gal/year into GCR/IHC from the cities of Gary, Hammond, and East Chicago. Locations of these CSOs are shown in Figure 2. Combined sewers convey industrial and domestic wastewater to POTWs during dry weather, and convey storm runoff when it rains. The sewers and the treatment facilities are not designed to convey or treat all of the storm flow, and the excess is released to the surface drainage system. The overflow is a mixture of stormwater and diluted, but untreated, wastewater. Sullivan et al. (1977) compared urban runoff for separate sewers with CSO discharges for a number of cities and concluded that the pollutant loading from combined sewers was four times the loading from separate sewers treating urban runoff.

39. Several studies have been conducted to assess the impact of CSO on GCR/IHC. Each of the three municipalities of Gary, Hammond, and East Chicago has evaluated the feasibility of reducing their CSO impact by either separating the storm and sanitary sewers or by providing treatment to the CSO. Tenech, Inc. (1982), used the stormwater management model SWMM to evaluate CSOs in the GCR/IHC area and concluded that CSOs were major contributors to water quality problems near Hammond, but that CSO impacts for East Chicago

were overshadowed by poor performance of the wastewater treatment facility. CSOs from Gary were not thought to create significant water quality problems. Tenech, Inc., also concluded that control measures for CSO discharges would not result in significant lowering of pollutant loads to Lake Michigan because of the prevalence of point source impacts. USEPA has another study in progress that will statistically evaluate the impact of CSO loads from the GCR/IHC on Lake Michigan.

40. Estimation of pollutant loads for the GCR/IHC must include nonpoint sources. For this study it is particularly important to know the active sources of sediment in the basin so that if contaminated sediment is removed, there will be some assurance that sediment deposited after the project will be an improvement over the existing sediment. Current data available are inadequate to accurately calculate nonpoint sediment loads. However, data from literature can be used to provide an order of magnitude comparison of nonpoint source sediment loads to point source sediment loads. Additional data regarding the quality of the sediment from nonpoint source loads will have to be collected to determine if nonpoint source sediment loads require controls to avoid future deposits of contaminated sediment in GCR/IHC.

41. USEPA (1983c) evaluated water quality of urban runoff from 19 cities in its National Urban Runoff Program (NURP). Important findings of this study in regard to urban runoff characteristics include the following:

- a. Total suspended solids concentrations in urban runoff are fairly high in comparison with treatment plant discharges. Urban runoff control is strongly indicated where water quality problems associated with TSS, including buildup of contaminated sediments, exist.
- b. Heavy metals (especially copper, lead, and zinc) are by far the most prevalent priority pollutant constituents found in urban runoff.
- c. Of a possible 106 organic priority pollutants, 63 were detected in urban runoff samples. PCBs were found in less than 1 percent of the samples.
- d. For planning level purposes, where onsite data are not available, it was recommended that event mean concentration values developed by NURP be used for estimating pollutant discharges from urban runoff.

42. Another USEPA-sponsored study (E. C. Jordan Co. 1984) characterized CSO discharges from eight US cities. This study reported TSS and BOD5 concentrations in CSO greater than those concentrations reported by the NURP.

Also, 46 priority pollutants, including metals and organics, were detected. Priority pollutant concentrations were very site specific and varied from one city to another.

43. Table 6 compares the NURP results for a median urban site and the median CSO results (E. C. Jordan Co. 1984) to average stream concentrations at the mouth of the Indiana Harbor Ship Canal as reported by ISBH in 1983. It was assumed that the stream concentrations were representative of base flow conditions and pollution from point sources. One fallacy of this assumption is that some of the stream samples include contributions from storm runoff and CSO. Mass load calculations for storm runoff, CSO, and stream base flow require an estimate of discharge. Annual storm runoff was calculated based on an average rainfall of 35 in./year on 68 square miles of drainage area with the ratio of runoff to rainfall estimated on the high side as 0.8. USEPA's (1985) estimate of 11 billion gal/year was used for CSO discharge. Discharge at base stream flow was selected as 1,250 mgd (HydroQual 1984).

44. Comparison of the concentration values in Table 6 shows that urban runoff and CSO have significantly greater concentrations for all the parameters listed than GCR/IHC stream concentrations. USEPA (1983c) noted that the NURP concentrations for urban runoff did not include any strictly industrial sites such as GCR/IHC, and that industrial sites would likely have greater pollutant concentrations than median urban runoff. The industrial nature of the GCR/IHC drainage area and the industrial discharge to POTWs would likely yield greater concentrations of industrial pollutants than a median site. Comparison of mass loads in Table 6 shows that nonpoint source contributions projected for urban runoff and CSOs are the same order of magnitude as pollutant loads estimated for point sources based on average stream concentrations.

45. It is interesting to note that average instream solids loading shown in Table 6, calculated from base flow (1,250 mgd) and field TSS data (14 mg/l), yields a mass load of 50×10^6 lb/year at the mouth of the Indiana Harbor Canal. This is very close to total solids loading to the waterway from individual point sources summarized in the HydroQual (1984) wasteload allocation study (56×10^6 lb/year). This would seem to support the concept that the GCR/IHC is in a state of sediment equilibrium for event base flow conditions, and that the majority of solids loading is passing to the lake.

46. Additional data are needed to more confidently estimate the sediment load from nonpoint sources. Original data collection will be required to determine the loading of toxic materials in storm runoff and CSOs in the GCR/IHC basin.

Spills

47. No documentation was reviewed to indicate the frequency or severity of industrial spills in the area. The industrialized nature of the area and the use of ship/barge transportation for materials provide ample opportunity for spill hazard.

Assessment of Available Data

NPDES self-monitoring data

48. As discussed above, data collected for compliance with NPDES monitoring requirements represent the most extensive source of information for calculating pollutant loads to the GCR/IHC. Analyses for conventional and nonconventional pollutants, including metals, are available for discharges suspected to contain these pollutants.

49. NPDES data have not in the past included toxic organics; however, some permits to be reissued in the near future will include toxic organics monitoring in an effort to improve the database and to determine if additional point source controls are necessary. Some of the data for heavy metals may be of less value because detection limits are above today's established toxic levels. To tie NPDES data to stream quality on a specific day is not always possible because the timing of sample collection differs for the various discharges.

Intensive base flow studies

50. HydroQual, Inc., performed two intensive stream and discharge surveys for calibration and verification of the wasteload allocation study sponsored by the ISBH (HydroQual 1984). These surveys, conducted in September and October 1983, involved collecting water and sediment samples and flow data from point source discharges and stations along the GCR/IHC over a 24-hr period. The complete list of constituents considered by the study was not analyzed for every sample point.

51. In October 1984, USGS performed an intensive 24-hr water quality survey. The same constituents analyzed in the HydroQual study were measured

at every station, and more care was taken in measuring stream flow than the ISBH study. A limitation of this study is that it concentrated on the East and West Branches of the Grand Calumet River and evaluated only one station in the Indiana Harbor Canal. The USGS did not sample for toxic organics. A report on the USGS data is scheduled for release in 1987. ISBH used the USGS data to enhance their wasteload allocation model (HydroQual 1985).

52. The types of discharge data collected and the loads of selected pollutants as presented in the HydroQual and USGS studies are presented in Table 7. This table shows that there are sometimes significant differences between the HydroQual and USGS numbers. However, variations from day to day are expected and long-term pollutant loadings from point sources could be estimated more reliably from NPDES data.

Routine stream monitoring data

53. The ISBH collected monthly samples at several stations along the GCR/IHC. The data, collected from the ISBH sampling network since the early 1970s, include both conventional and nonconventional pollutants. The data show that there have been noted improvements in water quality since 1977. However, HydroQual (1984) reported that in 1983 concentrations of ammonia, fecal coliform bacteria, iron, mercury, chlorides, and sulfates still violated water quality standards. For the four stations along the Indiana Harbor Canal, the minimum 1983 dissolved oxygen concentration was 4.4 mg/l, which is above the Indiana water quality standard of 4.0 mg/l set for this stream.

54. The 1983 stream data did not include any toxic organics. A STORET summary of water quality data from this system shows that PCBs were checked during the 1973-1976 time period and averaged 0.014 to 0.24 µg/l at four stations. These values exceed the water quality standard of 0.001 µg/l.

55. The stream monitoring data allow review of pollutant concentration trends. A limitation of the GCR/IHC stream data is the lack of flow measurements, which are necessary to calculate loads in the system and which would help assess conditions existing when the samples were collected. ISBH plans to install three flow-measuring stations along the GCR/IHC in the near future to alleviate this problem.*

* Personal Communication, T. P. Chang, 1984, Indiana State Board of Health, Indianapolis, Ind.

PART IV: EVALUATION OF INDIANA STATE BOARD OF HEALTH'S
GRAND CALUMET RIVER WASTELOAD ALLOCATION STUDY

Introduction

56. The Grand Calumet River Wasteload Allocation Study (HydroQual 1984) was performed to update a 1974 wasteload allocation study (Combinatorics, Inc. 1974) and to establish new wasteload allocations for municipal and industrial discharges. The 1974 study has become outdated due to changes in treatment levels, outfall flow rates, and revised water quality standards. Principal author of the 1984 report was HydroQual, Inc., a New Jersey based consultant. The ISBH published the report, and ISBH and USEPA Region 5 participated technically, as well as financially, in the study. Although primarily aimed at wasteload allocations to meet dissolved oxygen standards, the study also addressed nitrogen, phosphorus, chlorides, TDS, sulfates, fluorides, cyanides, phenols, and selected heavy metals.

57. This section reviews and critiques the 1984 study, evaluates if and how the study's wasteload allocation (WLA) model can be used to assess contaminant inputs from in-place sediments, and discusses how the WLA model can be improved to better address such concerns.

Background and Review of Previous Studies

58. The WLA report presents background information for the study area, including stream characteristics and thorough coverage of the types of discharges from municipalities and industries. It is probably the best single source of information for outfall descriptions and point source wasteloads.

59. The report contains a discussion of stream and lake water quality for current conditons (1984) and the previous 10 years. Data presented illustrate that water quality for most parameters has definitely improved since the early to mid seventies. Water quality standards are reviewed and compared with the stream water quality data. This comparison shows that existing water quality standards continue to be violated for several parameters.

60. The background information presented in the HydroQual (1984) report also briefly discusses the 1974 study. The 1974 study used the model MUTIQUAL

to simulate water quality and to establish WLAs. Many existing NPDES permits are based on the results of the 1974 WLA effort. Since 1974, modeling techniques have improved, and the 1984 study included more field data collection and better definition of hydraulic characteristics in the harbor. Other studies reviewed by the HydroQual report were CSO studies and Lake Michigan water quality evaluations.

Field Sampling Program

Procedures

61. The principal product of the HydroQual WLA study was a mathematical WLA model of the GCR/IHC system. To collect data necessary for calibration and validation of this model, an appropriately designed field sampling program was necessary. The program consisted of two intensive 24-hr sampling series conducted under base flow (dry weather) conditions in September and October 1983. Components of the field sampling program included the following:

- a. Stream/lake water quality sampling (24-hr composites).
- b. Municipal and industrial outfall sampling (24-hr composites).
- c. Sediment oxygen demand (field and laboratory determinations).
- d. Reaeration measurement in the East Branch.
- e. Time of travel studies.
- f. Measurement of flow, depth, and width.
- g. Stratification sampling.
- h. Sediment sampling for priority pollutants.

62. Samples for water quality analyses were taken at 24 stations at 0.5- to 1.5-mile intervals (Figure 2) along the East and West Branches of the Grand Calumet River, the Indiana Harbor Canal, the Indiana Harbor, and Lake Michigan. Each station was visited four times during the 24-hr period. Dissolved oxygen, temperature, and pH were measured during each visit, whereas composites of the four visits were prepared for analysis of other constituents. During the same time period 24-hr composite samples and flow measurements were taken from the 42 known municipal and industrial outfalls in the system.

63. Stream samples were analyzed for the parameters listed in Table 8. Because of cost considerations, point sources were not analyzed for all the

parameters in Table 8. An attempt was made to select analyses that would account for the majority of pollutant mass discharged to the system. For some parameters, especially those present in small concentrations but in large discharges, this resulted in unaccounted for pollutant loads in the system. In view of the time and effort required to collect the samples, an additional investment in analytical services may have been justified to provide a more accurate accounting of pollutant loads. Analyses for toxic organics were limited to selected point discharges and were not performed for stream (water) samples.

Results

64. Section 3.2 of HydroQual (1984) summarized results of the field study, graphically illustrated parameter concentrations spatially along the stream, and compared the water quality data with water quality standards. Violations of water quality standards occurred most frequently in the West Branch near the Hammond and East Chicago POTWs. The dissolved oxygen (DO) profile for the East Branch and the canal showed the minimum DO concentration to occur in the canal between miles 1 and 2 (see Figure 2). Once canal waters entered the harbor, the DO concentration rapidly recovered and met the Harbor's 7-mg/l DO standard.

65. The DO concentrations did not fluctuate during the 24-hr period by more than 1 to 2 mg/l and were not representative of typical diurnal DO changes. As a result, photosynthesis and respiration effects were not considered for the DO model.

66. Beginning at mile 2 and continuing downstream to the Lake Michigan stations, samples were collected 1 m below the surface and 1 m above the bottom of the channel. Measurable differences between top and bottom samples were observed for DO, temperature, total dissolved solids (TDS), and chlorides. The top samples were warmer, lower in DO, and higher in dissolved solids and chlorides than the bottom samples. This type of stratification is a typical phenomenon for harbors along the Great Lakes where warmer, less dense, polluted waters flow across the surface of cooler, cleaner lake waters. Lake waters are forced inward by wind-generated currents. These flow patterns and stratification in mathematical modeling suggest a two-dimensional model. The fact that water quality in the canal's and harbor's bottom layers are better quality than the top does not necessarily mean that bottom sediments are not exerting an adverse impact on water quality.

67. Data collected for ultimate carbonaceous biochemical oxygen demand (CBOD_u) show the greatest stream concentrations to be in the upper end of the east branch near mile 12. A CBOD_u concentration of 10 to 15 mg/l was detected at this point near U.S. Steel outfalls. The mass present in the stream (stream flow × concentration) was much greater than the summation of the CBOD_u mass loads from the monitored discharges. The same situation occurred in the West Branch in the vicinity of the Hammond POTW (miles 5.75 and 7.75). Unmonitored versus monitored loads for the whole system are compared below:

<u>CBOD_u</u>	<u>September 83</u>	<u>October 83</u>
Monitored, lb/day	56,156	33,350
Unmonitored, lb/day	<u>22,400</u>	<u>21,400</u>
Total, lb/day	78,556	56,750

The unmonitored loads represent 28 to 38 percent of the total CBOD_u load to the system. Sources of these unmonitored loads are believed to be combined or separate sewer overflows, leakage from lagoons, drainage from landfills, and nonpermitted or unmonitored outfalls. The USGS (1985 unpublished) data better accounted for in-stream BOD loads, and the HydroQual (1985) analysis of the USGS data reduced the unmonitored CBOD_u estimate to 5,700 lb/day.

68. Stream flows were estimated to be equal to the sum of point source discharges. For the unmonitored loads of the magnitude presented, significant flows on the order of 1 to 100 mgd as well as relatively high CBOD_u concentrations may be involved. New studies are being conducted by regulatory agencies to identify these sources. Since these loads are plugged into the WLA model at the upstream segments of the system, their actual origination should not adversely affect calibration of the model. They do however definitely impact WLA for point sources. From the standpoint of this study, they also have minor impacts because the loads are several miles upstream of the Corps projects.

Model Development

69. The model used for the HydroQual study was a two-dimensional, steady-state mathematical WLA model. It employs a steady-state mass balance approximation of the mass transport equation around individual, interconnected segments of the water body for each chemical constituent. A computer program solves the mass transport equation by using a simplified finite difference

scheme and by reducing it to a matrix of simultaneous linear equations. Called SPAM for sparse matrix, the model was developed by HydroQual.

70. SPAM is an appropriate model for the Grand Calumet River System. As discussed earlier the stratified condition and inward lake flow in the harbor dictate consideration of a two-dimensional model for the lake, harbor, and 1 to 2 miles of the canal. It allows for horizontal and vertical advection and dispersion. Were it not necessary to model these areas, a simpler one-dimensional model could have been considered. Most WLA models assume steady-state conditions. However, hydrodynamics in the GCR/IHC system are affected by industrial and municipal discharges and by Lake Michigan, and can vary by as much as 100 percent over a period of a few hours (USGS 1985 unpublished data). Data describing hydrodynamics of this system are insufficient for application of a dynamic model.

71. The WLA model focuses on DO. Sources and sinks of DO considered by the model include outfall loads, reaeration, CBOD oxidation, nitrification, photosynthesis, respiration, and benthic (sediment oxygen) demand. Sediment oxygen demand (SOD) is discussed in detail in another section of this report. Other pollutants were evaluated by the WLA study by application of the transport equation to outfall or stream loads, but the pollutants are considered to be conservative.

72. The procedure used to calibrate the WLA model is outlined as follows:

- a. Subdivide the stream into segments based on stream characteristics and numerical solution considerations (144 segments for this study).
- b. Define geometry of each segment (use a variety of data).
- c. Route freshwater flow through the system (assume flow in stream to be summation of point source outfalls).
- d. Determine dispersion coefficients (use lithium tracer study and literature values).
- e. Determine point and nonpoint loads (from field study).
- f. Determine reaeration rates (literature and field data).
- g. Execute model and adjust coefficients.

73. The model framework is adequate and addressed variables pertinent to a WLA model for this system. Assumptions and techniques employed to estimate model input parameters resulted in close correlation of model output to field data. Four areas of the field testing and model calibration program

that can be improved are identification of nonpoint source and unmonitored loads, quantification of stream flow rates in the Grand Calumet River, description of hydrodynamics of the canal and harbor, and measurement of SOD.

74. Unmonitored loads are discussed above. The unusually low SOD values are discussed in another section of this report. Flow rates in the river and canal were assumed to equal the sum of the point source discharges. A later USGS (1985 unpublished data) study confirmed that this is a valid assumption for most stations. However, because flow measurements for point sources are not always accurate and because all point sources may not be accounted for, a more comfortable analysis could be made if actual stream flow rates are known. Flow rate and velocity not only affect mass transport, but also are variables in many empirical formulas used to calculate kinetic coefficients.

75. Flow patterns in the lake, harbor, and lower end of the canal were based on pollutant stratification and relationships developed during the 1974 WLA study. No direct field measurements were made of surface or bottom velocities in the harbor. Bottom currents were calculated using wind speed. The DO sag point is very near the point where stratification begins. Therefore, it would seem that better definition of the currents in this area would be important for accurate model predictions in the harbor.

Model Calibration

76. Despite weaknesses suggested above, the calibrated model appears to adequately represent the field data. In addition to DO, the model was calibrated for chlorides, TDS, fluorides, sulfates, total phosphorus, ammonia, phenols, and cyanides. All these substances were assumed to be conservative, but the report acknowledges that this may be an oversimplification. Good reproduction of in-stream values was achieved except for phenols and cyanides, the analysis of which was hampered by measured concentrations below detection limits for many loads and stream conditions. The study suggested exercising caution in using the model for metals since there was an imbalance in the pollutant mass for the discharges versus that measured in the stream. The discrepancies resulted because not all point discharges were monitored for metals and because many analyses reported were below detectable limits.

77. The allocation conditions and sensitivity analyses point out some interesting factors affecting the calibrated model and water quality conditions. First, the study concluded that if unmonitored loads were eliminated, CBOD decay rates could be reduced, and water quality standards for DO could be maintained in the system without additional treatment technology being provided for known industrial or municipal outfalls. The unmonitored loads, therefore, play a key role in revising the WLAs. Secondly, a component analysis showed that at the critical mile point (1.7) for the DO sag curve, the major contributors of oxygen-depleting materials are the Gary POTW, U.S. Steel, and SOD. Since the Gary POTW already employs advanced wastewater treatment and significant BOD reduction for U.S. Steel may not be technologically feasible, reduction in SOD may be the best opportunity for improvement. Finally, the sensitivity analysis considered a 50-percent increase in SOD and concluded that the model is insensitive to a change of this magnitude. In view of the low SOD values measured, this may not be a fair assessment of SOD effects.

PART V: MECHANISMS BY WHICH SEDIMENTS AFFECT WATER QUALITY

78. Despite the improvements in water quality noted in the GCR/IHC, these water systems remain highly contaminated. Historical water quality monitoring for NPDES permits and surveys of water quality in the GCR/IHC have not focused on toxics, but rather on more conventional contaminants such as materials causing biochemical oxygen demand and suspended solids. There are also many sources of pollution to these water bodies that have never been analyzed (nonpoint sources). These uncharacterized sources pose a problem when attempting to evaluate the impacts that a contaminated in-place sediment has on water quality because of the difficulty in separating contaminant inputs from the sediment from those of other sources.

79. There can be little doubt that wastewater discharge has a pronounced impact on water quality in the GCR/IHC (HydroQual 1984, LMF 1984). Many of the NPDES permits issued in the past have had as their major focus the reduction of oxygen-demanding substances in discharges. This objective, in addition to new emphasis on reducing the inputs of toxic chemical contaminants into the system, remains one of the major goals of discharge restrictions. Any study that examines the contribution of sediments to contamination of the GCR/IHC system must examine in detail the contribution that wastewater discharges have on the system. This analysis must include a consideration of how the data generated in these efforts can be used to quantify the impact of contaminated sediments. Wastewater discharge allocation models (HydroQual 1984) may be particularly useful in quantitating the effects of contaminated sediments on the oxygen demand of the river system.

80. Once a sediment has been deposited there are a relatively limited number of ways in which contaminants associated with that sediment can become remobilized. These mechanisms include diffusion of soluble contaminants in the sediment interstitial water into the overlying water, resuspension of bottom sediments by storm events and ship traffic, and desorption of contaminants from resuspended sediments. Sediments, however, do not necessarily need to be resuspended to exert adverse impacts on water quality and biota. For example, if a sediment is not resuspended and does not contribute large amounts of contaminants to the water column by diffusion, the sediment contaminants can still degrade the environment by impacts on bottom-feeding fish and other

benthic organisms; these may change the community structure of benthic organisms.

81. The major mechanism for transport of sediment-bound contaminants is via suspended sediments. Numerous studies have shown that contaminants added to water containing suspended sediments will rapidly become associated with the sediment (Steen, Paris, and Baughman 1978; Collins 1973; Suzuki et al. 1979; Voice, Rice, and Webber 1983). Studies that have examined the transport of contaminants in rivers have found little of the contaminant to be transported in the soluble phase as a result of this contaminant preference for sediment; rather the contaminant was associated with particulates in the water column (Shuman, Haynie, and Smock 1978). Salim (1983) has shown that the amount of lead adsorbed on the suspended particles of river water is proportional to the surface area of the particulates, roughly proportional to the weight of these particles, and independent of particle-size distribution.

82. In addition to contaminants released from sediment, any number of other sources can contribute dissolved contaminants to the water column in the GCR/IHC system. These sources include soluble contaminants introduced directly into the river from sewage treatment plants, combined sewer outfalls, and industrial discharges. The amount of soluble contaminants introduced into the water through regulated sources, which include sewage treatment plants and industrial discharges, has probably been decreasing in conjunction with the improvement in water quality noted in the GCR/IHC system.

83. Release of contaminants into the water column from suspended or resuspended sediment is a greater source of contaminants than diffusion of contaminants from bed sediments into the overlying water. Diffusion from sediments requires that the contaminant desorb from the sediment into the pore water, then slowly diffuse through the pore spaces into the overlying water (Lerman 1979, Berner 1971). By contrast, contaminants from resuspended sediments or suspended sediment from point/nonpoint sources can move directly into the overlying water without recourse to diffusion through sediment pore spaces. In an area where sediment resuspension occurs in appreciable quantities, such as the Indiana Harbor Canal, contaminant movement into the overlying water via release from suspended sediment would be expected to be much higher than that originating from a deposited sediment via diffusion. This follows in light of the great increase in surface area available for desorption of contaminants compared with the tortuous route that a contaminant

must follow to diffuse from sediment interstitial water into the overlying water. The relative importance of mechanisms controlling the movement of contaminants associated with sediments in the GCR/IHC system is therefore contaminant associated with suspended particulates > soluble contaminants desorbed from suspended particulates > soluble contaminants contributed by diffusional processes from deposited sediments. Sediment oxygen demand, while not a contaminant per se, is introduced into the water column by all the mechanisms previously mentioned. However, it is generally sufficient to treat sediment oxygen demand as an entity that encompasses all the transfer mechanisms.

84. An evaluation of the various contaminant transfer mechanisms in the GCR/IHC system based on existing data will be discussed in detail in succeeding sections of this report. This will be followed by a discussion of research needed to quantitate the impact of these various contaminant movement mechanisms on the system.

PART VI: SEDIMENT OXYGEN DEMAND

Introduction

85. Sediment oxygen demand is a critical factor in the relationship between sediment and the quality of the overlying water. Development of anoxic conditions in water as a result of respiration in the water column and oxygen demand by sediment can have severe consequences, especially if reduced chemical species are released (Gunnison, Chen, and Brannon 1983). Consideration of SOD is particularly relevant to the development of a comprehensive picture of the benefits of removing sediment from an area with a long history of intensive pollution, as is the case for the GCR/IHC system.

86. The objective of this section is to assess the role of SOD in polluted bottom sediment on water quality in the GCR/IHC system. An evaluation is also made on the role of SOD in regulating the release of contaminants from sediment to the water column.

The Nature of SOD

87. Sediment oxygen demand has two components: oxygen demand exerted by biological activity in sediment, and oxygen consumption occurring as a result of the chemical oxidation of reduced chemical species present in sediment (Wang 1981). The latter component includes dissolved and solid forms of manganese, iron, and sulfur. The relative importance of each of these components depends on whether internal sediment or sediment-water interactions dominate.

88. The influence of biological activity on SOD was studied in the bottom sediment of eutrophic Lake Esrom by Hargrave (1972). He found that inhibition of the sediment biota by formalin poisoning vastly decreased oxygen uptake at the sediment surface. By contrast, all oxygen consumption below the first centimetre of sediment appeared to result from chemical oxidation activity, although biological respiration at the sediment surface may be strongly dependent on reduced substances diffusing upwards (Hargrave 1972). Others have also validated the importance of biological processes in oxygen removal at the sediment surface (Brewer, Abernathy, and Paynter 1977; Butts

and Evans 1978). However, these authors generally did not examine streams where pollution had eliminated most of the biota.

Sediment Reduction Process

89. When the compounds in the pore water between sediment particles are being reduced, the sediment itself undergoes reduction as oxygen and nitrate disappear and reduced products are accumulated. This reduction is a result of sediment interaction with the soluble components of the interstitial water and with precipitated components that become part of the sediment. Factors active in the reduction process are more evident if sediments under emergent and submergent conditions are compared.

90. An emergent sediment or flooded soil exhibits a high redox potential, has a mineral fraction that is generally well oxidized and light colored, and has an organic fraction composed of materials in various stages of aerobic decomposition (Ponnamperuma 1972). Primary agents of decomposition under emergent conditions are bacteria and fungi. The pore space in the emergent sediment or flooded soil occupies nearly half the volume of the sediment and is composed of both air and water.

91. A submerged sediment or flooded soil is considerably different from its emergent counterpart (Ponnamperuma 1972). Air in the pore space has been displaced by water. All oxygen disappears within 1 to 3 days after submergence, and carbon dioxide is accumulated. Microorganisms, lacking DO, shift their activities to fermentation and the use of alternate electron acceptors. Nitrous oxide, nitric oxide, nitrogen gas, and ammonium are produced, with ammonium accumulating in the water. Organic fermentation products appear in the interstitial water. Reduced forms of manganese, iron, and sulfur are released; iron sulfide forms as a precipitate; and the iron sulfide accumulates in the sediment. The submerged sediment becomes black, gray, or greenish gray in color. Refractory organic matter accumulates, pushing the coloration towards the dark gray or black side. Methanogenesis becomes the final consumer of low molecular weight organic acids, and hydrogen and methane are the final gaseous products released. In the end, the sediment has the following properties: dark coloration; low redox potential; devoid of DO; and containing the reduced forms of nitrogen, sulfur, manganese, iron, plus methane and refractory organic matter (Ponnamperuma 1972). The reduced

sediment may or may not have a thin, light-colored oxidized layer at the surface, depending on the oxidation status of the overlying water column.

92. Several mechanisms are active in causing the movement of sediment and materials dissolved in the sediment interstitial water into the overlying water column. Bioturbation can be particularly effective at the sediment-water interface; polychaetes in a saline environment have been observed to extensively rework the top 5 cm of a sand cap overlying a contaminated dredged material (Brannon et al. 1985). Underwater currents also play a role through a complex series of actions, including: disturbing the uppermost layer of the sediment surface, causing resuspension of sediment, releasing interstitial water at the sediment surface, and occasionally exposing underlying reduced sediment layers to the water column.

93. Diffusion is one of the principal mechanisms whereby chemical substances in the bulk sediment move into the overlying water. A number of factors influence the diffusional process, including concentration gradients, sediment porosity, and the presence or absence of a sediment oxidized layer. Sediment porosity is the simplest factor to consider. The higher the sediment porosity, the easier it is for diffusion to occur in the sediment. Concentration gradients between sediment interstitial water and the overlying water are important because dissolved substances move along these gradients from areas of higher concentration to areas of lower concentration. For example, oxygen and nitrate generally diffuse into the sediment as a result of their relatively higher levels in the water column. Reduced substances tend to diffuse into the water column as a result of their higher levels in the sediment. It can therefore be seen that the quality of the overlying water has a direct bearing on diffusional processes. If chemical constituents are already present in high levels in the water column, diffusion of these materials into the overlying water will be slowed because of the decreased concentration gradient.

94. The sediment surface layer is important because of its role as an interface between the solid and liquid phases. An oxidized sediment surface serves as a barrier to reduced substances and other chemical constituents and as a focal point for microbial and chemical oxidation activities. It is in this layer that DO from the water column is consumed and, thus, barred from entry to lower layers. Simultaneously, reduced substances diffusing up from below are consumed as fuel for oxidational activities. Many workers have shown that an oxidized sediment surface layer can act as a barrier to the

transfer of chemical constituents from sediment to the overlying water (Mortimer 1941, 1942; Fillos and Molof 1972). Substances diffusing to the aerobic surface layer from the underlying anaerobic sediment are apparently immobilized by formation of new complexes or inorganic precipitates (Li, Bischoff, and Mathieu 1969; Bischoff and Ku 1971; Cline and Upchurch 1973; Duchart, Calvert, and Price 1973). However, when reduced, the sediment surface layer allows ready diffusion of reduced substances into the overlying water column and serves as an immediate sink for any DO in the water column. Whether or not reduced substances remain in the water column once released from sediment depends on the oxygen status of the water column.

95. Oxidation-reduction potential, in and of itself, does not regulate the release of contaminants from sediment. Rather, the oxidation-reduction potential is a measurement reflecting the intensity of oxidizing or reducing conditions (i.e., oxidized, slightly reduced, moderately reduced, or highly reduced) present in a sediment. The degree of reduction, in turn, is reflective of the tendency for a sediment to release contaminants. Thus, an oxidized sediment ($>+400$ mV) will take up DO, ammonium, nitrite, and nitrate from the water column, but will not release reduced forms of iron, manganese, sulfur, or carbon to the water column. Slightly reducing conditions ($<+400$ but $>+220$ mV) are indicative of active nitrate reduction; a sediment having a redox potential in this range will still take up oxygen, nitrite, and nitrate from the water column and will release nitrogen gas and ammonium, but not reduced forms of iron, manganese, sulfur, or carbon. Moderately reducing conditions ($<+220$ but $>+120$ mV) indicate active reduction of manganese with potential release of Mn^{+2} to the water column. Highly reducing conditions ($<+120$ but >-50 mV) indicate active iron reduction and the capacity to release Fe^2 . More intensely reducing conditions (<-50 mV) are required for active reduction of oxidized forms of sulfur and carbon; active release of reduced forms of these materials to the overlying water column cannot be expected until a sediment has reached this level of reduction.

96. The relationship of oxidation-reduction potential to the release of organic contaminants is not presently understood. Release or nonrelease of organic contaminants is better predicted from an understanding of the equilibrium partitioning of these substances between the sediment and water than from a knowledge of redox potential. Nonetheless, there is a relationship

between organic contaminants and redox potential. This will be explained in detail in the following section.

Effects of SOD on Contaminant Mobilization

97. For the purposes of this discussion, pollution will be defined as any activity of man that results in a degradation of the quality of an environment with respect to the intended use of that environment. Within the context of the aquatic ecosystem, pollution is usually applied to the water column rather than to the sediment, but can and does apply equally to sediment and aquatic life living on and within the sediment. Among the major concerns of pollution with respect to sediment are disease production, organic pollutants, mineral pollutants, recalcitrant molecules, and thermal alterations. This section of the report will address the relationship between SOD and contaminant mobilization from sediment, with the exception of thermal alterations. The majority of the information presented in this section is summarized from Dugin (1972). Specific compounds are not addressed due to the continuing paucity of pertinent information.

Disease production

98. Disease production has no direct bearing on SOD and, therefore, will not be considered at length here. However, transmission of disease by water is not merely an indication of the contamination of this medium by pathogenic bacteria, protozoans, and viruses; it also suggests contamination with human fecal material. In large amounts, human waste material can make a significant contribution to SOD because it is in a form readily available for use by microorganisms. Sludges and large pieces of untreated fecal material easily settle to the sediment surface where they can accumulate and contribute to SOD.

Organic pollutants

99. Organic pollutants are of vital importance in terms of their contribution to oxygen consumption. Modern sanitary practices tend to control waterborne disease transmission through the use of chlorine as a disinfectant. However, as pointed out above, many highly organic wastes contain materials that can be used as nutrients by other organisms, especially microorganisms. Microorganisms metabolize the organic compounds by way of oxidation reactions and consume DO in the process. Due to the relatively low solubility of oxygen

in water, DO is rapidly depleted during waste oxidation. As a consequence, both sediment and the overlying water become anoxic, resulting in the death of fish and other aquatic organisms, if present. The principal purpose of secondary waste treatment is the removal of oxidizable organic matter; however, regions with a history of nontreatment of sewage and/or addition of organic pollutants other than sewage have built up a considerable debt of organic matter in their sediment (Dugin 1972).

100. In addition to serving as substrates for oxygen consumption, many organic compounds are also nutrients for microorganisms and higher life forms. The result is an excessive growth of aquatic algae and/or other plants plus undesirable kinds and levels of microorganisms. Once under way, such growths can, by their rapid production of organic material, cause the rapid buildup of large levels of readily decomposable organic matter in sediment, adding to the existing oxygen debt.

101. Certain organic compounds are toxic to one or more forms of aquatic life, causing either direct or indirect killing of these organisms. Direct killing involves death of the organism on contact, either through suffocation by covering gill surfaces or through poisoning. Indirect killing results when a toxic organic compound is accumulated in the food chain, causing either infertility or the eventual death of an upper level consumer. Toxicity to upper level consumer species generally has little bearing on SOD, unless a massive die-off occurs yielding large amounts of easily degraded animal tissue. However, toxicity to microorganisms is of direct importance to SOD. Without its normal complement of microorganisms, a sediment cannot process additional organic materials as they are added to sediment; this means that as long as a toxic organic is present at levels lethal to the microflora, organic matter will continue to build up in the sediment. In this manner, a significant oxygen debt may accumulate in the affected sediment. In addition, the nature of some toxic organic compounds is such as to encourage their accumulation in sediment. For example, when phenol, benzene, and naphthalene were exposed singly to oil refinery settling pond inocula, each of these compounds was rapidly degraded. However, benzene and naphthalene were not metabolized in the presence of phenol (Meyers, Marcus, and Bergman 1984).

Mineral pollutants

102. There are several aspects of mineral pollution that relate directly to SOD. Mineral compounds such as carbon dioxide, ammonium,

phosphate, and sulfate are all products of the oxidation of organic matter, and all serve as nutrients for the growth of other organisms. Minerals are also added directly as crop fertilizers, surface water runoff, and air pollutants. All of these substrates can stimulate the growth of aquatic algae and higher plants. As pointed out above, the accumulation of plant material in sediment greatly adds to the existing sediment oxygen debt.

103. Acid mine drainage and the addition of toxic industrial waste minerals such as cyanide, cadmium, mercury, chromium, arsenic, and radioactive minerals can, through their outright toxicity, exert effects similar to those described for the toxic organics.

Recalcitrant molecules

104. Recalcitrant molecules are synthetic organic compounds that are not readily degraded by normal biological attack and thus tend to persist in the environment. These materials would normally be construed to have little relationship to SOD, except that many of them are markedly toxic to members of the aquatic biota at very low concentrations. If this toxicity extends to the sediment microflora, then normal sediment processing will also be influenced, and the opportunity to build up an oxygen debt will exist.

Relationship of Pollution to SOD

105. Pollution has several pronounced effects on SOD. Organic matter deposited in sediment causes an increase in the microbial activity of the sediment, and this can serve as the source of energy and materials needed to drive the sediment anoxic. Microbial processes thus fueled can be a source of reduced soluble nutrients and metals; the latter substances can have detrimental effects on the quality of the overlying water column. Organic matter that remains in the water column, but which is not deposited in the sediment, can still influence the sediment by increasing microbial activity and causing the water column to go anoxic; this establishes the conditions necessary for the reduction of the oxidized sediment surface layer with the resultant release of reduced chemical constituents from the sediment into the water column. An anoxic water column will also allow the buildup of organic matter in sediment. This occurs because the absence of DO in the sediment prohibits organic matter from being metabolized through the aerobic oxidative pathways used by microorganisms. The remaining anaerobic pathways are not as efficient

as their aerobic counterparts, and the unprocessed or partially processed organic matter tends to accumulate. Pollutants that kill aquatic life may also eliminate organisms that disturb (bioturbate) the sediment surface layer, causing sediments that were formerly worked over and oxidized to stagnate. Such a lack of benthic organisms is most likely near POTW outfalls where high chlorine residuals are present. Contaminants may also wipe out much of the microflora leading to dysfunction of normal sediment processes.

106. The influence of mineral pollutants on SOD may be more subtle. Addition of large amounts of metals may increase an existing sediment reservoir of these minerals which are then reduced, adding to the present SOD. Metals may also poison aquatic life. The addition of large amounts of nitrate may oxidize reduced sediments--a potentially beneficial effect that encourages the formation of an oxidized surface layer. Sulfate addition, on the other hand, stimulates the formation of sulfide, which not only interacts with reduced metals in the sediment and water column to form reduced precipitates (usually regarded as beneficial), but which also is highly toxic in trace quantities. Other minerals may serve to stimulate the growth of undesirable plants or microorganisms, as described above.

107. Recalcitrant molecules, because they resist degradation, tend to have little effect on SOD. However, these compounds may cause sediment dysfunction if the molecules have a toxic effect on the microflora.

Available SOD Data for the GCR/IHC System

108. The amount of SOD data available for the GCR/IHC system is very limited. From the literature examined, it appears that the only extensive measurements of SOD in the system are those given in HydroQual (1984). According to the appendix of this report, values were obtained for only 9 of the 14 stations cited as having been sampled for SOD. Further, both light and dark chamber values are given for only 7 of these 9 stations. Exactly which method was used to make these determinations is not evident because the text of the report does not describe the procedures used to obtain the data. It is also difficult to pinpoint exactly where the measurements were made using the area map presented in the report. From the remarks given in the report concerning the results presented in the appendix, it is difficult to assess why the authors were unable to obtain SOD values for all stations. The failure to

obtain a good chamber seal is frequently cited as a reason; however, the circumstances behind these failures are often not described. Existing methods and available data for estimating impacts of SOD on water quality are presented in Appendix A.

109. According to the main text of the HydroQual (1984) report, several generalizations were used when selecting SOD values for use in the model. The SOD values used in the model calibrations were 1.0 g/sq m/day in the East Branch and Canal and 3.5 g/sq m/day in the West Branch, based on the field data. The SOD in the West Branch was subsequently reduced by 50 percent to 1.75 g/sq m/day, based on anticipated reductions of SOD in previously untreated areas. In the East Branch and Canal, the SOD was set equal to the rate used in the calibrations (1.0 g/sq m/day) since this rate approaches the background levels in other streams in the area; the data supporting this rationale were not presented. Also, no rationale was given in the report for the authors' assumption that the SOD will eventually drop to the values used to run the model, nor does the report state the time required for this decrease to occur.

110. Data are available for area streams and rivers other than the GCR/IHC system. These waterways have the same geological history and many are subject to similar, if not the same, pollutional loadings. Examining the SOD data for these waterways permits the investigator to make an assessment of whether or not the data for the GCR/IHC system appear to be reasonable. There are two primary sources for such information, the data of Polls and Spielman (1977) and those of Butts and Evans (1978).

111. Table 9 presents representative SOD data as given by Polls and Spielman (1977) for deep draft waterways in Cook County, Illinois. The information summarized in this table was taken primarily from the downtown Chicago area and thus is particularly appropriate for comparison with the data given in the HydroQual (1984) report. The comparison of SOD values of IHC/GCR to Chicago waterways sampled by Polls and Spielman (1977) is especially valid since there are many similarities in these waterways, including the fact that both are relatively sluggish with a base flow composed largely of treated wastewater and both receive combined sewer overflows. While Table 9 does not contain all of the data given by Polls and Spielman (1977), the information is representative of the data and also contains the lower and uppermost values obtained by these investigators, 1.28 and 23.32 g/sq m/day, respectively.

Comparison of the data in Table 9 with the HydroQual data suggests that use of SOD values in the range of 1.0 to 3.0 g/sq m/day may be inappropriate for polluted streams in the Chicago area. Values of 5 to 10 g/sq m/day in general, and 7 to 8 g/sq m/day in particular, appear to be more representative of streams in this area.

112. Table 10 presents representative SOD data for northeastern Illinois streams as measured by Butts and Evans (1978). Although the data shown in Table 10 were generally selected because they were taken from streams in or close to Chicago, these data are not as representative of the downtown area as those of Polls and Spielman (1977) and generally have lower values than those of these authors; whether or not this results from the fact that Butts and Evans did their sampling in areas that are generally less urbanized than downtown Chicago cannot be ascertained at present. The information contained in the body of the Butts and Evans report indicated a range from a low of 0.38 g/sq m/day to a high of 9.32 g/sq m/day, with the remaining values well distributed between the two extremes (Butts and Evans 1978). Comparison of the data in Table 10 with the HydroQual data suggests that use of SOD values in the range of 1.0 to 3.0 g/sq m/day may be inappropriate, even for streams that are not in the immediate downtown Chicago area and that are not necessarily heavily polluted. Values of 2.5 to 5.5 g/sq m/day in general, and 3.0 to 4.0 g/sq m/day in particular, appear to be more representative of streams in this area. The Chicago District has recently completed analysis of the water quality impacts of the Tunnel and Reservoir Project (TARP/CUP) on Chicago waterways. This analysis included the use of a simulation model (HYDROCOMP) to examine impacts of the reduction/elimination of CSOs. The analysis concluded that reductions to SOD following elimination of CSOs would produce highly significant increases to mean instream levels of dissolved oxygen (raising the mean from 4-5 mg/l to 6-7 mg/l in many reaches).

113. The following evaluation is based on the information given above. There is a large body of information on SOD in fresh waters, and some of this is appropriate for the Chicago area. However, the information available for the GCR/IHC is limited to that given in the HydroQual (1984) report. This lack of data is particularly unfortunate in light of the intense pollution that has occurred in the GCR/IHC system since the early part of this century. The SOD values given in the HydroQual report appear to be low when compared with those of Butts and Evans (1978) and seem extremely low when compared with

those of Polls and Spielman (1977). However, the latter two sources present data for streams other than the GCR/IHC system. Based on the data from Polls and Spielman (1977) taken from streams having pollutional loadings and macroinvertebrate benthic populations that are similar to the GCR/IHC system, SOD values in the range of 5 to 10 g/sq m/day appear to be realistic. More accurate values can be obtained only by a thorough resurvey of the system. Such a survey appears to be very desirable when considering possible means to demonstrate the potential beneficial effects of dredging.

Sediment Oxygen Demand in the GCR/IHC System

114. SOD is an important oxygen-consumption process and is also instrumental in turning on and off the sediment surface layer as a "valve" for oxidized materials in the water column and reduced materials in reduced sediment layers. These functions were described previously. SOD is also an important parameter to include in any water quality model involving DO utilization and balance (Butts and Evans 1978). Past failures to use SOD in models may well have produced invalid results, depending on the nature and condition of the stream bottom and the biota living on it (Butts and Evans 1978). Oxygen balances cannot be accurately measured for streams with large and well-distributed macroinvertebrate populations by merely determining the BOD and then balancing DO consumption and reaeration with the Streeter-Phelps equation (Butts and Evans 1978). A similar statement can be made for changes in SOD that result from pollution, whether the changes are local or distributed over broad reaches.

115. From the data available for waterways in the Chicago area, it appears that SOD is frequently found to be quite high; this is not unexpected in streams that are either polluted or semipolluted. It is not possible to state, with any degree of certainty, the existing SOD value for the GCR/IHC system. It may be within the 1.0- to 3.5-g/sq-m/day range indicated by the HydroQual (1984) report; however, in view of the existing data for other area streams, this estimate is probably too low.

116. There are no historical data for SOD in the GCR/IHC system. Comparisons therefore cannot be made of existing SOD values with values obtained prior to the initiation of efforts to clean up the system, starting

after 1974. Thus, it is not possible to say whether SOD values have decreased or remained the same in response to treatment measures.

117. It is not known whether sediment in the GCR/IHC system has an oxidized or reduced surface layer. Although there are data for DO levels in bottom waters, DO requirements in the water column necessary to maintain an oxidized sediment surface layer are unknown. Recent research by Jorgensen and Revsbech (1985) has demonstrated that, in marine environments, the diffusive boundary between sediment and the water column constitutes a transfer resistance for oxygen flux across the solid-water interface; this limits oxygen flux at high uptake rates. In this case, sediment or detritus exposed to aerated water could be almost anoxic at the surface, provided these materials have sufficiently high rates of oxygen uptake.

118. For the GCR/IHC there are no data for determining which materials are available to be released from the sediment. Further, it is not possible to determine at what rates and amounts these releases would occur, should the sediment surface layer go anoxic. Based on the existing analyses of system sediments, there are a considerable number of metals available for release under anoxic conditions. Present knowledge of the behavior of these metals in other systems allows some attempts at making predictions for this system. However, without a detailed sediment-water interaction study, no accurate assessments are possible.

119. There is, at present, no basis for predicting how much time is needed for SOD in sediments to decline from high levels to lower levels once the supply of oxygen-demanding materials to the sediment is shut off. It is known from work on the "transition phase" in reservoirs that a newly flooded soil and the overlying water column require some 6 to 10 years to stabilize, once filling has been completed and assuming no new input of organic matter or other pollutants occurs. Whether a similar period is necessary for SOD in the GCR/IHC system to return to "normal values" cannot be said for certain. There is also no understanding of "normal" in this context since there are no values on which to establish a prepollutional baseline for SOD.

120. There is no basis for comparing the effects dredging will have on the SOD values for the GCR/IHC system with the existing regime. Since there is a long local history of pollution, the affected sediment may be quite deep. According to a Lake Michigan Federation report on the Grand Calumet River (LMF 1984), this sediment may be 10 to 20 ft deep in some places. Maintenance

dredging of the navigation channel will not remove all polluted sediment. If contaminated sediment is exposed following dredging, it is anticipated that the newly exposed anoxic surfaces may well have more severe oxygen demands than the existing sediment surfaces. Because it will be anoxic upon exposure, sediment exposed by dredging may initially release many contaminants into the water column before oxidation of the newly exposed surfaces can occur. Presently available data are inadequate to allow accurate prediction of the rate at which these newly exposed surfaces will be covered by sedimentation processes. It may be that the rate of covering by sedimentation will exceed the rate of oxidation. Past bathymetric data from the navigation channel suggest that sedimentation of dredged areas will cover newly exposed sediments at rapid initial rates. This rate should decrease in subsequent years. By contrast, if all polluted sediment is removed, exposing the underlying native material, an improvement in SOD can be expected.

121. Because of the uncertain nature of existing SOD data for the GCR/IHC system and the lack of adequate sediment-water interaction information, the area to be dredged should be thoroughly resurveyed for SOD. Sediment cores should be taken in the proposed dredging areas and returned to the laboratory for a determination of change in SOD with depth. This information can be used to determine where SOD values can be expected to approach reasonable values, based on SOD values for less polluted streams in the area. Finally, a sediment-water interaction study of sediments in proposed dredging areas may be necessary to quantify the nature and magnitude of potential releases from exposed sediment.

PART VII: EQUILIBRIUM PARTITIONING EVALUATION

Definition

122. As described in Part II, water quality in the GCR/IHC ecosystem is improving. However, existing sediment data are inadequate to gauge the impact of the contaminated sediment on water quality and biota. Equilibrium partitioning, although limited, can help in examining the impact that contaminated sediment can exert on water quality and biota in the absence of other contaminant sources. Equilibrium partitioning, as suggested by the name, is the theoretical distribution of a contaminant between sediment and water or sediment and biota that reaches equilibrium over a certain time period. A further discussion of the theory of equilibrium partitioning and the equations used in the application of equilibrium partitioning concepts are presented in Appendix B.

Application of the Equilibrium Partitioning Concept to the GCR/IHC System

123. Hydrophobic organic contaminants adsorbed on sediment particles may be released to the overlying water, degrading water quality and inhibiting biological recolonization in the GCR/IHC system. Levels of several organic contaminants in the GCR/IHC sediment measured previously by the USEPA and levels in this study are presented in Table 11. With the exception of the large quantities of naphthalene and indeno(1,2,3-cd)pyrene observed in this investigation of the GCR/IHC sediment, concentrations of specific organic compounds detected in the sediment were similar. Concentrations of organic compounds in interstitial water were calculated based on 7.4-percent sediment organic carbon content and are presented in Table 11. Concentrations of PCBs exceed water quality criteria (USEPA 1979). However, water criteria for other organic compounds listed in Table 11 are not available.

124. The equilibrium bioaccumulation potential for hydrophobic organic chemicals was estimated based on surface sediment organic carbon concentrations of 7.4 percent in the GCR/IHC. This value for organic carbon concentration was obtained by analyses conducted at the US Army Engineer Waterways Experiment Station (WES) on the Indiana Harbor Canal sediment samples provided

by the Chicago District. The concentration of organic carbon reported here is the carbon content in sediment organic matter excluding oil and grease contaminants in the sediment. This organic carbon value was reported to be correlated with sorption coefficients between organic contaminants and sediment particles (Lambert 1968). Relationships developed between the organic partitioning coefficient (Koc) and the octanol-water partitioning coefficient (Kow) were for sediments free of large amounts of oil and grease. Based on the relationship between Koc and Kow in Equation B3, Koc is lower than Kow. Therefore, in sediments such as Indiana Harbor which contain appreciable amounts of oil, organic contaminants such as PCBs will concentrate in the less available oil and grease fraction instead of in sediment organic matter. However, partitioning values are not available for PCBs in oil and grease. Therefore, Koc values for PCBs in the absence of oil and grease were used as a conservative estimator of equilibrium PCB concentrations in Indiana Harbor interstitial water and aquatic organisms.

125. Equilibrium concentrations of specific organic compounds in aquatic organisms having either 2- or 5-percent total extractable lipids (Table 12) were calculated using equations relating total contaminant concentration and sediment organic carbon concentration to contaminant concentrations in aquatic organisms (McFarland 1984). Lipid content in aquatic organisms is highly variable; fish generally contain higher levels of lipids while many aquatic invertebrates, such as mussels, contain low levels of lipids.* In general, lipid content in common aquatic organisms ranges between 2 and 5 percent. These lipid concentrations were selected as representative of aquatic organisms that may recolonize the GCR/IHC system.

126. Equilibrium tissue concentration results for sediment PCB concentrations measured at WES revealed that values of 35 ppm would be expected in organisms containing 5-percent lipids while values of 14 ppm would be expected in aquatic organisms containing 2-percent lipids. Recently published regulations (Federal Register 1984) have decreased the action level of PCBs in fish from 5.0 to 2.0 ppm. The predicted maximum concentration of PCBs in fish living in the GCR/IHC would therefore exceed the safety level for human consumption. Equilibrium PCB tissue concentrations in different portions of the

* Personal Communication, Victor McFarland, 1985, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Indiana Harbor Canal were also computed using sediment data from the Chicago District (US Army Engineer District, Chicago 1979). These results, presented in Table 13, indicate that fish (2-percent lipid concentration) swimming into and remaining in the Indiana Harbor and the Indiana Harbor Canal would not exceed standards for human consumption until sediments located approximately 200 ft north of the railroad bridges for the EJ&E, NYC, and B&O railroads were encountered, after which the standard would be consistently exceeded.

127. Fluxes of dissolved constituents across the sediment-water interface have been recognized to be a pathway for the release of dissolved constituents, particularly inorganic chemicals, from sediment to the overlying water. Sediment from the GCR/IHC contain high quantities of many organic compounds including PCBs. Sediment analyses performed in 1979 by the Chicago District indicated that concentrations of PCBs in the GCR/IHC sediment varied from less than detection level (<0.02 mg/kg) to 89.1 mg/kg. Up to 50 mg/kg of PCBs was detected in sediment 15 ft below the sediment-water interface at the Lake George Canal and Indiana Harbor main canal junction. These sediments may therefore serve as a source of dissolved PCBs to the overlying water.

128. Flux of PCBs from sediment to the overlying water was estimated in the GCR/IHC using known PCB concentrations in sediment (US Army Engineer District, Chicago 1979), calculation of interstitial water PCB concentrations, and calculation of diffusion rates. In obtaining the sediment PCB concentration, the values from the top 3-ft composite layer was used, with the implicit assumption that this value was the approximate concentration in the surface sediment. The theoretical concentration of PCBs in interstitial water was then calculated using the equation

$$C_w = C_s / (K_{oc} (TOC)) \quad (1)$$

where

C_w = static equilibrium concentration of chemical in water

C_s = concentration of chemical in sediment

K_{oc} = the organic partitioning coefficient

TOC = the decimal fraction of total organic carbon in sediment

which is discussed in Appendix B.

129. Fluxes of PCBs from sediment can be estimated by applying an average PCB diffusion coefficient of 100×10^{-9} cm²/day, calculated by Fisher,

Petty, and Lick (1983) from data given in Halter and Johnson (1977). A depth of 10 cm (Lee 1970) was selected as the depth of sediment that could actively contribute to diffusional processes of contaminants. The flux equation of Berner (1971) is:

$$J = D(dC/dz) \quad (2)$$

where

J = flux of contaminant across the sediment-water interface

D = the diffusion coefficient

dC = the concentration gradient

dZ = the depth of sediment contributing to the diffusional process

Using this equation, fluxes of total PCBs into the water column were calculated. Calculated values of PCB flux ranged from 0 to 22.3×10^{-5} ng/m²/day with an average flux of 6.8×10^{-5} ng/m²/day (Table 13). These calculations also show that the flux of PCBs into the water column should increase moving into the Grand Calumet River system from Indiana Harbor. Theoretical concentrations of other organic compounds in the GCR/IHC interstitial water were also estimated and are presented in Table 11. The diffusion coefficient used for the PCB calculations compensated for the high porosity of a Michigan pond sediment (containing 85 percent sand, 2.5 percent organic matter). Therefore, the actual diffusion rate of PCB in the GCR/IHC sediment, which contains higher organic carbon and higher clay-silt content than that of sediment from Michigan pond sediment (Halter and Johnson 1977), should be lower than the value the authors estimated. Lack of available diffusion coefficients for organic contaminants other than PCBs for which interstitial water concentrations were estimated (Table 11) precluded estimating the flux of these organic compounds. Also, fluxes of inorganic compounds into the water from the sediment could not be calculated because of the lack of interstitial water concentrations. Equilibrium partitioning approaches cannot be used to estimate the interstitial water concentrations of inorganic components of sediments.

130. It is recognized that diffusion of organic compounds from sediment to the overlying water is a potential problem due to the toxic effects of these compounds. However, the estimated diffusion rate of PCBs in the GCR/IHC sediments indicates that in the absence of disturbances, movement of soluble PCBs into the water column is relatively minor. On average, 1 sq m of bottom

sediment would annually contribute only 2.5×10^{-2} ng of PCBs to the overlying water. It would take 1 million square metres of sediment to contribute 25 μ g of soluble PCBs to the overlying water annually. This value would be increased in the presence of bioturbation, but would remain a fairly minor component of contaminant input into the overlying water. On the other hand, highly contaminated GCR/IHC sediment with high levels of toxic organic compounds could pose a threat to organisms that live in and around the sediment.

131. Values of Koc for organic compounds other than PCBs can be calculated using Equation B3 and values of Kow in the literature (Miller et al. 1985; Chiou 1985; Ruepert, Grinwis, and Govers 1985; Walters and Luthy 1984). Diffusion coefficients for organic contaminants other than PCBs are not readily available. However, diffusion coefficients may be estimated for these compounds using methods that have already been developed.

132. Bulk sediment diffusion coefficients (Ds) for chemicals of interest can be estimated using the value of the tracer diffusion coefficient (Dw) in a pure water system at constant temperature (Li and Gregory 1974) and the relationship

$$D_s = D_w \times \phi^2 \quad (3)$$

where ϕ is the sediment porosity, to obtain an estimate of the sediment diffusion coefficient (Lerman 1979) when information on contaminant adsorption and desorption is unavailable. Such an approach does not account for the slowing of diffusion that can occur because of contaminant adsorption to sediment particles (DiToro, Jeris, and Clarcia 1985) and is therefore a conservative coefficient that overestimates the rate of diffusion. When values of Dw are unavailable, values of Ds can be determined experimentally in the laboratory by a number of methods. Fisher, Petty, and Lick (1983) measured the mass of organic contaminant diffusing into the overlying water from a contaminated sediment. Their method assumed that PCBs, the organic contaminant studied, migrate by molecular diffusion in the interstitial waters and that an equilibrium exists between the PCBs in solution and those adsorbed on solids. DiToro, Jeris, and Clarcia (1985) determined diffusion coefficients for PCBs by following the movement of radioactive PCB compounds in sediment. Determination of the diffusion coefficients using the method developed by DiToro, Jeris, and Clarcia (1985), however, took 2 years because of the low diffusion rates of hydrophobic organic compounds such as PCBs.

PART VIII: EVALUATION OF SEDIMENT RESUSPENSION

133. The Indiana Harbor Canal is a complex, interconnected collection of Federal and non-Federal channels. The Federal channels were last dredged to project dimensions in 1972. Periodic surveys (bathymetric) have been conducted over much of the Federal channels on about a yearly interval. Examination of data from bathymetric surveys for the years 1972, 1976, 1980, and 1984 indicate that the Indiana Harbor Canal has reached shoaled equilibrium with the channel thalweg probably maintained by passage of boat traffic. A sharp decrease in the channel depths was found between the years 1972 and 1976 with progressively smaller depth changes since 1976. The 1984 survey shows only a small overall change from the 1980 survey--an indication that the total amount of shoal material has not changed, but may only be redistributed through undocumented mechanisms (Lake Michigan seiches, local storm action, ship movement, docking, towing, etc.).

134. The small amount of hydrodynamic data available show that the nonstorm-event-related currents through the Federal channels are very small (on the order of 1 fps or less), and that the current directions vary quickly over time. It was observed in recent (August and November 1985) field exercises that the water surface elevations are highly variable and can change rapidly for undocumented reasons.

135. The effects of storm events on the transport and supply of suspended solids and sediment materials in the Indiana Harbor Canal can only be roughly estimated at present (US Army Engineer District, Chicago 1986). The location of highly contaminated sediment material has, however, remained fixed for several years, implying that currents available to resuspend and transport the material are not a common occurrence.

136. The limited existing data allow only crude estimates of sediment loading and yields in the Indiana Harbor Canal and of the time frame and quality of sediments that would settle in the Indiana Harbor Canal following dredging to project depth. The following paragraphs summarize the information needed before an assessment of the hydrodynamics and sediment transport in the Indiana Harbor Canal system can be more accurately determined.

137. The field measurements necessary to best understand the complex transport processes occurring within the Indiana Harbor Canal channels include short- and long-term temporal data sets. Short-term (on the order of a day)

data sets should consist of simultaneous measurements of water surface fluctuations located at four control points, with a sampling rate of about 3 min; control point velocity measurements at surface, middepth, and bottom to determine instantaneous discharges through the system; and total suspended material measurements at the velocity sampling points. Short-term data sets should be collected seasonally through the ice-free periods of the waterway.

138. Long-term (on the order of 4 to 6 days) data sets should encompass frontal passage (storm) events, and include the same resolution and measurements of the short-term data set, with the addition of a continuous dye (rhodamine WT) release at the upstream limit of the Federal navigation channel. These data sets should be collected seasonally. Water samples should be collected hourly at the four previously established control points, throughout the episodic event, using automatic sampling equipment and recorders. Samples should be analyzed for dye concentrations, as well as sediment concentrations, and combined with the concurrent velocity measurements. The resulting data set can then be used to assist in the determination of net flows and circulations in the Indiana Harbor Canal system.

PART IX: SHORT-TERM IMPACTS VERSUS LONG-TERM EFFECTS
OF DREDGING ON WATER QUALITY

139. The most noticeable impact of dredging activities on water quality is the increase in turbidity. The amount of turbidity associated with a dredging operation is a function of the dredge type, dredging operation, and sediment characteristics (Huston and Huston 1976; Raymond 1984). Particulate concentrations in the vicinity of the dredge can exceed background particulate concentrations by two orders of magnitude (Tramontano and Bohlen 1984). The turbidity associated with the dredging operation, however, will last only as long as the dredging. Even during the operation, the turbidity is of limited areal extent. Huston and Huston (1976) analyzed turbidity data obtained during dredging operations and concluded that during cutterhead dredging, turbidity increased above background only in the immediate vicinity of the cutterhead. Surface water turbidity 240 ft from the dredge was at background levels (Huston and Huston 1976). Tramontano and Bohlen (1984) reported that at ebb tide, particulate concentrations returned to background levels 700 m from the dredging operation. Raymond (1984) demonstrated that in bottom waters suspended solids concentrations increase in the vicinity of the dredge, then decrease rapidly. Release of particulate matter to the water column can be further reduced by use of dredging techniques, such as a closed-bucket clamshell, that retain solids.

140. Peddicord et al. (1975) have demonstrated that many aquatic organisms are adversely affected only by concentrations in the grams-per-litre range or greater and then only when the elevated levels of suspended solids persist for several days to several weeks. In view of the pollution-tolerant fish population that exists in the Indiana Harbor Canal (Potos 1981), the turbidity generated during dredging operations should pose no ecological threat.

141. Dredging should result in no long-term increases in suspended solids concentration in the water column, and such concentrations should be lower in magnitude than naturally occurring sediment resuspension. Sly (1977) has reported that for the Great Lakes, dredging-disposal and shipping-induced turbulence are two means by which man causes suspension of waterway sediments. He indicated that these increases are small when compared with sediment resuspension caused by wind-wave action. The situation therefore exists whereby existing wave action and ship traffic can cause more long-term turbidity than

dredging. The physical effects of dredging should be limited to turbidity and should last only as long as the dredging operation.

142. Consistent release of trace metals has not been observed at dredging and disposal field sites. Consistent releases of manganese have been observed during the elutriate test (Lee et al. 1975), but in practice no increase in soluble manganese has been observed in field data collected during dredging and disposal operations. Schubel et al. (1978) found no discrete plumes of dissolved manganese during field evaluation of pipeline disposal at Morgan City, La., Corpus Christi, Tex., and Apalachicola, Fla., even though considerable quantities of manganese were released during the elutriate test. Lee et al. (1978) reported that the general trend for water quality data obtained within the turbid plume at a number of dredged material disposal sites showed no release of cadmium, chromium, nickel, lead, copper, mercury, arsenic, or zinc. Tramontana and Bohlen (1984) did observe release of manganese and copper into the water column during dredging operations in the lower Thames River estuary near New London, Conn. However, the concentration of dissolved materials downstream of the dredge decreased at a first-order exponential rate, returning to background levels within 180 m of the dredge. Short-term releases of trace metals, although unlikely during dredging, can occur but should be of limited impact on water quality.

143. The effect of organic contaminants on water quality during dredging and disposal operations has been documented in a number of studies. Lee et al. (1978) demonstrated that the behavior of chlorinated hydrocarbon pesticides and PCBs during aquatic disposal by hopper dredge or barge is similar to their behavior during the elutriate test. Very small amounts of either chlorinated hydrocarbon pesticides or PCBs are released from the sediment into the water during the elutriate test (Lee et al. 1978). Wright (1978) summarized the results of four major field studies on dredged material disposal. He reported that PCBs were released into the water column at the Duwamish disposal site, but actual increases over background values were quite small and did not appear to be of particular biological significance. Such results are not surprising because of the affinity of PCBs for sediments, especially those high in oil and grease content (Jones and Lee 1978). Indiana Harbor sediments are very high in oil and grease; little release of PCBs to the water column during dredging would therefore be expected.

144. No significant long-term elevations of organic contaminant concentrations have been observed in disposal site waters following disposal of dredged material (Wright 1978). The same situation could be expected to prevail at an Indiana Harbor dredging site, especially since the contaminated sediments are being removed.

145. This brief discussion has demonstrated that water quality impacts at a dredging site are of brief duration and have limited impact on the environment. The limited impact of the dredging operation also lasts only as long as the dredging operation itself. The impacts of dredge-induced concentration elevations of dissolved and particulate materials have been shown to be primarily a near-field phenomenon, producing relatively minor variations as compared with those caused by naturally occurring storm events (Tramontano and Bohlen 1984). These findings have been verified in a demonstration of innovative dredging equipment conducted recently in Calumet Harbor (Hayes, McLellan, and Truitt, in preparation). Based on testing conducted for the 1986 draft environmental impact statement for an Indiana Harbor CDF, releases of nutrients, especially ammonium-nitrogen, along with oxygen depletion and oil in the area of the dredge may be short-term problems during the dredging operation.

146. Postdredging impacts have not been an area of detailed study. However, postdredging impacts can be examined in both the near and far fields. Near-field impacts can include effects of sediment exposed during the dredging operation on the water column and biota, changes in sediment resuspension patterns caused by prop-wash and other modes of sediment resuspension, and the impacts of sedimentation of fresh material on the water column and biota. Far-field impacts of the dredging operation can include factors such as the reduction of sediment input to the outer harbor and the impact this reduction has on lake water quality and benthic habitats in the area. Following deepening by dredging, current velocities in the deepened section of the canal should decrease, causing increased sedimentation. This can result in formation of a sediment trap that retains contaminated sediment in the Indiana Harbor Canal that would otherwise enter the Lake Michigan ecosystem. Contaminated sediment entering the lake may possibly limit diversity of biological life and result in higher levels of contaminants in biota through bioaccumulation. The ability of the Indiana Harbor Canal to act as a sediment trap is illustrated by the annual removal of an average of 100,000 cu yd of dredged material from the Indiana Harbor Canal between 1955 and 1972 (US Army Engineer

District, Chicago 1986). This represents approximately 60 percent of the estimated annual suspended solids loading to the GCR/IHC in 1974 (US Army Engineer District, Chicago 1986).

PART X: EVALUATION OF WASTELOAD ALLOCATION MODELS

147. This section of the report reviews existing WLA models for applicability to the GCR/IHC system. This discussion does not represent an exhaustive review of the myriad of available water quality models, but focuses on models commonly used for WLA that may be appropriate for the study area. Generally, the purpose of a WLA model is to determine the maximum amount of pollutant that can be discharged to a water body while ensuring that water quality standards are met. This section deals primarily with means of estimating contaminant loading effects on DO concentration. An evaluation of models of toxic materials is provided elsewhere in this report.

Model Requirements

148. In order to select WLA models for consideration one must first decide what capabilities and features are necessary to model the study area and, in this case, meet the objective of the no action alternative study. For the no action alternative study, it may only be necessary to demonstrate the relative impact of sediments in relation to other loadings and benefits, if any, of their removal. Important considerations in selecting a WLA model are: number of dimensions; time scale; constituents to be modeled; loads, sources, and sinks; spatial extent; transport systems; and discretization. Each of these considerations is discussed below for the GCR/IHC system.

Number of dimensions

149. Most WLA models used by the USEPA and state regulatory agencies to establish effluent limitations for oxygen-demanding materials are one-dimensional (longitudinal). The changes in stream oxygen concentration in the longitudinal or downstream direction usually are much more pronounced than changes in the vertical or lateral direction. Water quality data for the GCR/IHC follow this pattern for much of the GCR/IHC's length (HydroQual 1984). The ISBH WLA study (HydroQual 1984) did not detect significant vertical differences in water quality except for the harbor and nearshore lake areas of the system. Stream profiles taken from the HydroQual report (1984) for DO, temperature, pH, chlorides, fluorides, and TDS are illustrated in Figures 3 and 4. Samples were collected at two separate depths (1 m below the surface and 1 m above the bottom) at eight sample points downstream of milepoint 2.6.

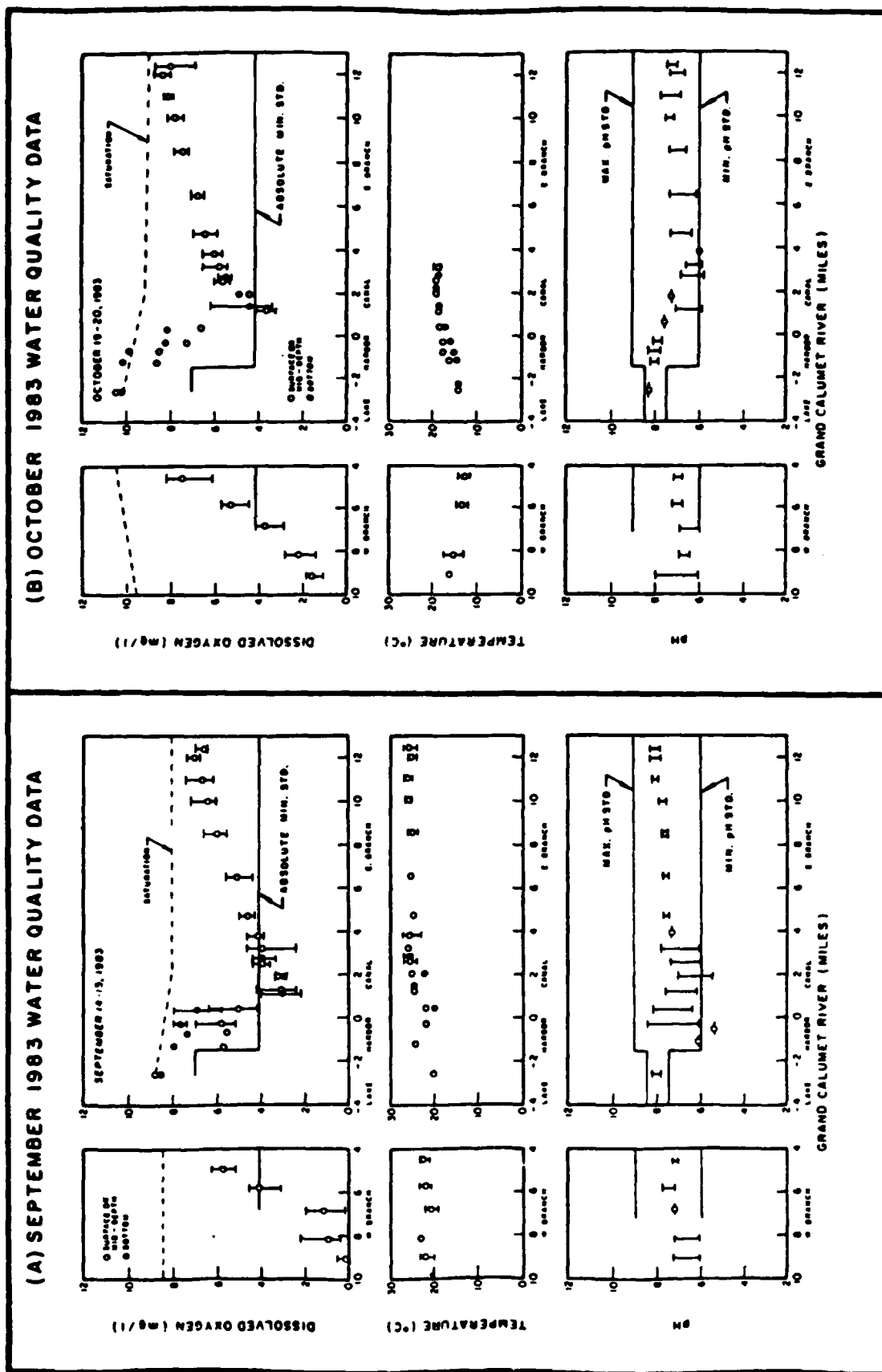


Figure 3. Dissolved oxygen, temperature, and pH data (HydroQual 1984)

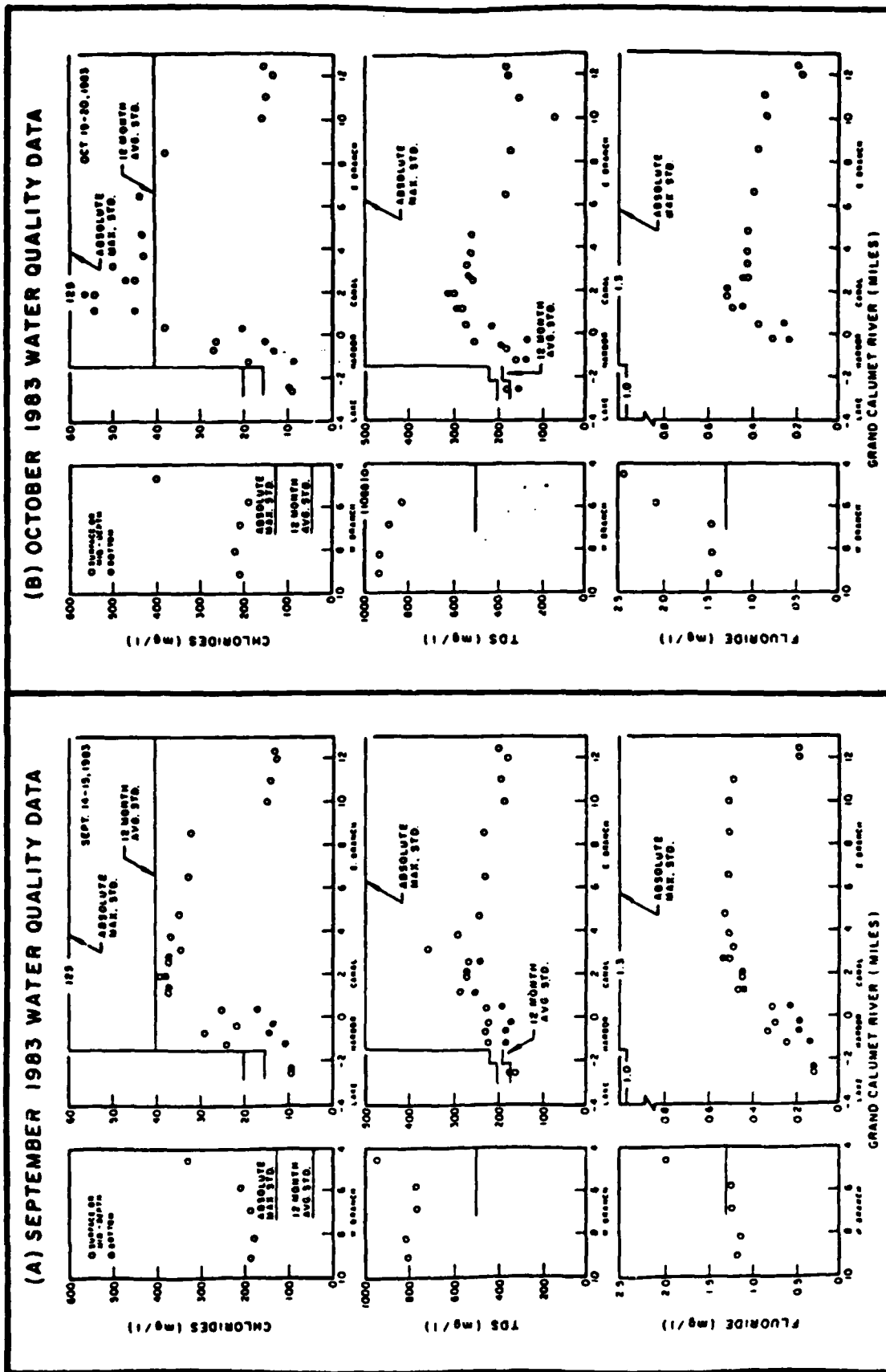


Figure 4. Chloride, TDS, and fluoride data (HydroQual 1984)

The profiles show that vertical differences in constituent concentration occurred primarily in the harbor and nearshore Lake Michigan and that vertical differences were larger than the longitudinal differences between the stations selected. Vertical constituent profiles for the harbor area show a transition zone between 10 and 20 ft deep for the 35- to 40-ft-deep harbor.

150. A one-dimensional analysis is suitable for the canal and river upstream of the harbor. HydroQual's DO data for the East Branch, canal, and harbor show that the minimum concentration occurs just upstream of the canal's mouth into the harbor (mile 1.0). Dissolved oxygen concentration then increased abruptly at the first sampling station in the harbor. Because the sag point is so near the vertically stratified part of the system, it is difficult to decide if two-dimensional (longitudinal-vertical) modeling is worthwhile to define upstream controls and treatment. There are a number of large discharges into the harbor itself. Effects of these discharges would be impacted by the harbor's stratified condition, and modeling the harbor and nearshore lake in two dimensions would provide a more accurate representation of the system.

151. In a situation similar to the GCR/IHC, Delos (1976) applied a one-dimensional, steady-state, finite section estuary model to Ohio's Black River, which drains into Lake Erie. Industrial effluents, including steel mills, and municipal effluents have degraded the water quality of the Black River. The river flows through a harbor just before entering Lake Erie. Cooler, cleaner Lake Erie waters flow landward underneath the warmer, more polluted, lakeward flowing river waters. Delos judged DO concentration gradients of 1 mg/l to be small enough to allow choosing a one-dimensional model. The model used was AUTO-SS, which can be used for rivers or estuaries (Scholl and Wycoff 1981). A sensitivity analysis of the verified model showed it to be most sensitive to changes in the reaeration rate and the longitudinal dispersion coefficients. Delos concluded that transport in the harbor area is influenced much more by dispersion than by advection.

152. Consideration of alternate models for the GCR/IHC could include one- or two-dimensional models. Two-dimensional models would provide a better picture of what is happening in the harbor, but they will require a better understanding of vertical and longitudinal advection and dispersion in the harbor. However, a one-dimensional model may prove of equal utility in defining WLAs upstream of the harbor.

Time scale

153. Wasteload allocations for point source discharges usually require analysis at low flows and warm temperatures. Historical data for GCR/IHC indicate that DO concentrations dip to their lowest point during the summer months (HydroQual 1984). However, 1983 stream monitoring data show that low DO values for that year also occurred during November and February (HydroQual 1983). Suspended solids and pollutants associated with storm runoff often exhibit higher concentrations during the winter and spring. Stream flow data are not included in the water quality monitoring for the GCR/IHC system, making it difficult to compare poor water quality conditions with stream flows. Because flow in the GCR/IHC is so dependent on point sources, and higher flows would dilute pollutant concentrations, low flow periods are generally assumed to be the more critical for WLA modeling. However, since point sources have made substantial progress toward reducing their pollutant loads, sediment and pollutants delivered by or agitated by stormwater flows may have the greater impact on water quality.

154. The other time scale consideration is the analysis of how water quality varies within the selected critical time period. Wasteload allocation models are available for steady-state analysis, quasi-steady-state, or dynamic (fully time-variable). Although wasteloads from point sources often vary from hour to hour and day to day, these variations are difficult to quantify and relate to a particular cycle or pattern, particularly where a number of discharges are involved. Wasteload allocations for point sources are usually modeled using the less complex steady-state analysis and time-averaged concentrations to predict a spatial concentration profile.

155. HydroQual (1984) found GCR/IHC DO concentrations to vary less than 1 to 2 mg/l during a 24-hr time period and stated the fluctuations were not typical of freshwater diurnal DO changes. Averages of flow-weighted, 24-hr composite samples were used to calibrate the HydroQual steady-state model. USGS (1985 unpublished data) reported the following constituent ranges at mile 3.8 on the Indiana Harbor Canal during 3-4 October 1984:

DO, mg/l	4.8 - 6.2
Temperature, °C	17.3 - 20.2
Specific Conductance, umhos/cm	465 - 579
pH	7.3 - 7.5
Flow, cfs	275 - 593

This shows relatively small concentration differences but more than 100-percent variation in the flow. Fluctuations for other constituents are unknown. Some quasi-steady-state models can handle variable stream flow if the loads remain constant. For point source loads in the GCR/IHC, steady-state or quasi-steady-state models are reasonable selections for WLAs.

156. Stormwater flows and nonpoint source impacts require a quasi-steady-state or dynamic analysis. HydroQual (1984) reviewed several studies that evaluated CSOs resulting from stormwater runoff. These studies were concerned primarily with conventional pollutants and the need for separation of sanitary and storm sewers. In one of the studies (Tenech, Inc. 1982) the stormwater management model (SWMM) was used to estimate pollutant loadings during storm events. Based on the model results and field sampling in the East Chicago area, this study concluded that stormwater runoff has only slight impacts on Grand Calumet River water quality. Without additional water quality data during stormwater flows to indicate loading for nonconventional, as well as conventional, pollutants, and without hydrodynamic data for the system, dynamic modeling of the GCR/IHC would be difficult. However, stormwater runoff and sediment resuspension may be major sources of pollutant loads and may exhibit critical short-term effects on water quality. As a minimum, "averaged out," short-term stormwater loads should be determined for analysis by steady-state models.

Constituents to be modeled

157. Because of the importance of DO for water quality and aquatic organisms and because oxygen-demanding organic material is a common pollutant for all municipal discharges and for many industrial discharges, the purpose of most WLA models is to determine the effect of wasteloads on stream DO levels. The ISBH's recent modeling effort included other constituents, such as cyanide, chlorides, metals, and ammonia, but considered DO in the most detail.

158. Any assessment of the impact of contaminated sediments should consider DO, but a more environmentally significant effect of contaminated sediments is a long-term source of heavy metals and toxic organics. Wasteload allocation modeling for toxic materials is a developing technique. Personnel of the USEPA Center for Water Quality Modeling noted that although modeling technology for toxic materials is available, it has not been used as a matter

of practice for establishing effluent limitations from point sources.* USEPA (1985) in their master plan for the GCR/IHC recommended the development of a toxic wasteload allocation for the GCR/IHC and suggested that it be used to complement the ISBH's WLA model and a soon-to-be-completed model study of CSO impact on water quality in nearshore Lake Michigan. USEPA's time table for this effort is 1985-1987. USEPA's Region 5 Office stated that this proposal is in the early stage of development.** Any examination of the impact of contaminated sediment should be closely coordinated with USEPA and ISBH to ensure compatible approaches in gathering data for modeling toxic substances in the GCR/IHC.

159. Constituents to be considered when selecting WLA models for potential use are oxygen demand and suspended solids, heavy metals, and toxic organics. Previous modeling studies have not indicated that nutrients are a serious problem in the GCR/IHC. Indicator bacteria are important to Lake Michigan's water quality and could be affected by contaminated sediments, as well as point and nonpoint discharges. Modeling of indicator bacteria is of lower priority than identification and elimination of sources. The level of oil and grease is a notable problem in the waterway, but trying to model this pollutant would add another dimension to the study.

Loads, sources, and sinks

160. The loads, sources, and sinks to be considered in selecting a WLA model depend on the particular constituent being modeled. (Pollutant loads are discussed in another section of this report.) HydroQual (1984) evaluated the following sources and sinks of DO within the stream: oxidation of carbonaceous BOD, nitrification, algal photosynthesis and respiration, oxygen transfer from the atmosphere, sediment oxygen demand, and oxygen deficits in point source discharges. Based on stream data, it was concluded that nitrification and photosynthesis/respiration were not significant factors for the oxygen model. Other parameters modeled, including heavy metals, phenols, and inorganic materials, were assumed to be conservative. The only sources of

* Personal Communication, T. Barnwell, 1985, Center for Water Quality Modeling, US Environmental Protection Agency, Athens, Ga.

** Personal Communication, Howard Zar, 1985, Region 5, US Environmental Protection Agency, Chicago, Ill.

conservative constituents considered were point source discharges, and no sinks were addressed.

161. Modeling of toxic pollutants will require extensive data for sources, sinks, and kinetic coefficients for the toxic constituents selected for modeling. Also, as noted in Part III of this report, toxic pollutant loads are inadequately characterized and additional field data will need to be collected. Sources and sinks include exchange of pollutants between suspended sediment and water and between sediment and water, chemical and biological degradation of pollutants, and exchange with the atmosphere. These types of data are not specifically available for the GCR/IHC. Some relationships will have to be developed for this site; however, much information may be derived from numerous studies of toxic pollutants in the Great Lakes. Some of this type of information is not within the current state of knowledge.

Spatial extent

162. Spatial extent of the modeling analysis should be well into the zone of recovery, i.e., where stream water quality overcomes the influence of pollution sources (USEPA 1983b). This suggests that modeling of GCR/IHC should include the harbor and nearshore Lake Michigan where water quality improves dramatically, primarily due to dilution. The drastic change in system geomorphology at this point may limit the benefits achieved by extending the model into this area. However, since Lake Michigan waters are such a priority resource for the area, future studies may need to consider Lake Michigan, even if this process requires a separate modeling analysis.

Transport systems

163. Many WLA models for rivers consider only advection as the transport mechanism for pollutants and neglect dispersion. HydroQual (1984) performed tracer studies to determine dispersion in the Grand Calumet River and calculated a longitudinal dispersion coefficient of 350 sq ft/sec. Vertical dispersion coefficients for the Grand Calumet River and vertical and horizontal dispersion coefficients for the outer harbor and Lake Michigan were based on literature values. Delos (1976) showed that longitudinal dispersion was the primary transport mechanism for another stratified Great Lakes harbor.

164. The hydrodynamics of the GCR/IHC system must be better defined for expansion of current modeling efforts. Hydrodynamic studies coupled with sediment transport studies and a "box" model for sediment and other

contaminants is one approach for modeling the GCR/IHC. This is discussed further elsewhere in this report.

Discretization

165. The number of segments or spatial grids limits, in terms of cost and time, application of some models to a system. HydroQual (1984) used 144 segments in the river, harbor, and lake to run their two-dimensional model. This included a top and bottom segment for the canal, harbor, and lake. The relatively short total length of the system, 20 miles, should not require too many segments for most models.

Model Availability and Selection

166. A number of mathematical models have been developed for simulating water quality in order to establish WLAs. Most widely applied are those models that establish BOD, ammonia and/or organic nitrogen, and DO criteria for point sources releasing wastewater to streams and rivers.

167. USEPA (1983a) presents technical guidance for performing WLAs to maintain minimum DO concentrations in streams. The following models were reviewed: DOSAG-I, SNSIM, QUAL-II, and RECEIV-II. While recognized as not being a comprehensive list of DO models, these four models represent most of the phenomena considered in stream DO models. The USEPA (1983a) manual discusses features of each of these models.

168. DOSAG-I would not be suitable for the Grand Calumet River because it neglects benthic demand. SNSIM and RECEIV-II do not account for longitudinal dispersion, an important effect in GCR/IHC. DOSAG-I, SNSIM, and QUAL-II are all one-dimensional and could not simulate the harbor's stratified condition. QUAL-II could potentially be used for the river portion of the system. Input requirements for QUAL-II could be easily extracted from ISBH's WLA study or from the literature. The model is readily available, easy to use, and well documented.

169. The ISBH model, developed, calibrated, and verified by HydroQual, Inc. (HydroQual 1984), accounts for all the model elements required with respect to DO. It is reviewed in Part IV of this report. Also, it has been sanctioned by USEPA and ISBH. The GCR/IHC model is currently being refined with additional field data already collected, and could be further improved as more field data become available. In view of its demonstrated suitability for

the GCR/IHC system, it is recommended that any additional WLA modeling for DO consider using the HydroQual model.

PART XI: EVALUATION OF CONTAMINANT MODELS

Introduction

170. This part of the report provides a summary of available contaminant models and discusses their applicability to the GCR/IHC system. This summary is not intended to be exhaustive, but rather to provide an overview of the models available, the processes they describe, and their possible uses.

171. Mathematical contaminant models can provide objective, rational aid for management decisions. However, it must be realized that while toxic substance models have often been tested for theoretical integrity and at the process level, they have not achieved the degree of rigorous validation of other water quality models. This is due to their relatively recent evolution, the complexity of contaminant interactions, and the lack of adequate databases. Thus, mathematical contaminant models should be used to supplement, rather than supplant, other aids for arriving at management decisions for the GCR/IHC system.

172. Contaminant models are currently available that may provide management and screening aids. Most available models exhibit similarities in the characterization of major processes, but sufficient differences exist to make selection of an appropriate model critical. The processes described which affect the fate of contaminants in aquatic systems include transport, transfer, and transformation. Transport and transfer processes include hydrodynamic and particle transport, ionization and complexation, sorption onto organic and inorganic surfaces, and bioaccumulation and biointeractions, such as with benthic forms. Transformation processes include oxidation, photolysis, and biological degradation. The degree to which each of these processes affect their ultimate fate varies with the contaminant, and the selection of a contaminant model must be based upon the capability of that model to describe the appropriate processes. Each process is briefly described in Appendix C.

Contaminant Models

173. Contaminant models can be generally characterized as either intended for trace metals or for trace organics. Although some models have been described as generalized, the processes affecting these two groups are

sufficiently different to require either extensive modification of a single model or the use of two separate models. The models available for metals and synthetic trace organics will be treated separately. A summary of the characteristics of a number of contaminant models is provided in Table 14.

Trace metals

174. MEXAMS. This model (Felmy et al. 1984) was developed by USEPA by coupling MINTEQ, a geochemical model, to EXAMS, an aquatic exposure assessment model. It is a steady-state model that includes speciation effects on the adsorption and precipitation of metals assuming equilibrium conditions. Adsorption is calculated using one of six models, including linear partition coefficient, Freundlich isotherm, Langmuir isotherm, constant capacitance, and triple layer models.

175. UTM-TOX. The Unified Transport Model for TOXicants (Browman, Patterson, and Sworski 1982) was developed at the Oak Ridge National Laboratory based upon their Unified Transport Model (UTM) developed during the early 1970s. It contains air, water, and terrestrial submodels. The aquatic fate submodel includes components which allow its application to trace metals as well as trace organics.

176. Other models. A variety of other models are available to describe the speciation of toxic metals in aquatic systems, including REDEQL2 (McDuff and Morel 1973), WATEQ (Truesdale and Jones 1974), MINEQL (Westall, Zachary, and Morel 1976), GEOCHEM (Sposito and Mattigod 1979), and NONEQUI (Fontaine 1984). These models generally describe species distributions given concentrations of metals and ligands based on thermodynamic constants. They are generally equilibrium models and do not allow for simulation of kinetics or transport, with the exception of NONEQUI. However, NONEQUI is limited to acidic systems ($\text{pH} < 6.5$). These models may be of utility in estimation of steady-state distributions of trace metals; however, their use in dynamic simulations is limited. Other, simplified approaches may be better suited to coupling with existing models, such as WLA models, if the simplifying assumptions on which they are based can be justified.

Trace organics

177. A variety of models are also available that are generally intended for the simulation of synthetic organic contaminants. A brief review of some of the major contaminant models with the capability of simulating toxic organics is provided below.

178. EXAMS. The EXposure Analysis Modeling System (Burns, Cline, and Lassiter 1982) was developed as a screening tool for estimating long-term fates, residual concentrations, and persistence of contaminants. A second version of the code (EXAMS2) computes the rates of transformation products and allows variation in conditions and simulation intervals permitting simulation of more dynamic conditions than EXAMS.

179. HSPF. The Hydrologic Simulation Program, FORTRAN (Johanson, Imhoff, and Davis 1980; Johanson 1983; Johanson et al. 1984), incorporates the process models of SERATRA in its aquatic section to allow modeling of organic contaminants. The chemical simulation capabilities are roughly compatible with those of the TOXIWASP and WASTOX models. HSPF is primarily suited to upland streams and one-dimensional reservoirs. It is based upon the Stanford Watershed Model (SWM), the Agriculture Runoff Management (ARM) model, and the HSP water quality model.

180. PEST. The PEST model (Park et al. 1980) contains elaborate algorithms for biological phenomena but does not provide for spatial resolution or transport. It treats the system as a single well-mixed reactor. PEST allows simulation of time-varying concentrations in as many as 16 carrier compartments, such as phytoplankton, fish, macrophytes, waterbugs, clays, and water. PEST was developed within the framework of Rensselaer Polytechnic Institutes CLEAN (Comprehensive Lake Ecosystem Analyzer) and has been applied to fishponds as well as to an Iowa reservoir.

181. SERATRA. The SEDiment-RAdionuclide TRANsport model (Onishi and Wise 1982) was originally developed to describe sediment-radionuclide transport and decay and was later expanded based upon the process models published by Stanford Research Institute (SRI). SERATRA is a two-dimensional (longitudinal-vertical), unsteady, finite element model containing detailed and mechanistic descriptions of sediment predictions (more so than other models such as TOXIWASP). Hydrodynamic conditions over time are required as input variables. A one-dimensional (TODAM) version and two-dimensional (longitudinal-lateral) estuarine version (FETRA) are also available.

182. TOXIC. The TOXIC model (Schnoor and McAvoy 1981, Schnoor et al. 1983) added fish uptake and depuration to the SRI model and was developed during the course of field studies on pesticides and herbicides in Iowa reservoirs. TOXIC was developed at the University of Iowa as an elaboration of the SRI model and is intended for use in reservoirs.

183. UTM-TOX. This model was described in the previous section under metals and contains algorithms to allow its use for either trace metals or organics.

184. TOXIWASP. The TOXIcant Water Analysis Simulation Program (Ambrose, Hill, and Mulkey 1983) was developed by USEPA by modifying, and in some cases simplifying, the kinetic structure from the EXAMS model and coupling these modifications to the transport framework of the Water Analysis Simulation Program (WASP). A second version of the model called WASTOX was developed by HydroQual with participation of the group responsible for WASP (Connolly 1982). TOXIWASP and WASTOX allow simulation of more dynamic transport and loading than the EXAMS model. They are suited to stratified lakes and reservoirs, large rivers, estuaries, and coastal waters. Transport data can be supplied through monitored data or predictions from hydrodynamic models. It does not allow simulation of ionized species. Sediment processes include bed sedimentation, erosion, and burial.

Data Requirements

185. All models are similar in requiring geometric information, initial conditions for the materials they simulate, and boundary conditions. Boundary conditions include flows and concentrations, or loadings (point and nonpoint), from all sources; they also include information on meteorological conditions which affect processes, such as interfacial exchange and photolysis. The frequency at which these boundary conditions are updated varies with the model. A steady-state model requires average conditions over the period of interest, while dynamic models require updates according to their time step. Hydrodynamic and sediment transport information can either be computed internally or supplied to the model as input data.

186. In addition, models require constants and coefficients which are used in process descriptions. Each process discussed in Appendix C requires specific information depending upon how it is described. Values of constants may be taken from the literature, while rate coefficients must often be determined for each particular application. Table 15 provides a general indication of data requirements for toxic substances models. However, the amount of data required varies considerably between models.

187. Data are also necessary for model calibration and verification. This usually requires two independent data sets to allow comparison of model predictions and field observations. Proper verification is essential, particularly if the model is to be used for wasteload allocations.

Applicability of Models and Simplified Procedures to the GCR/IHC System

188. Issues that must be addressed in the GCR/IHC system include environmental impacts of dredging, evaluation of the action/no action alternative, and ultimate or long-term fate of contaminants. These issues involve three levels of study. The first two levels involve identification of contaminant loadings from sediments prior to, during, and following dredging operations, exclusive of all other loadings and interactions. These two study levels can be completed without application of relatively expensive to apply, data intensive, contaminant models. They would require instead the use of simplified modeling procedures and process descriptions coupled with results of field and laboratory experiments. The first two study levels are intended solely to evaluate relative impacts of contaminated sediments and demonstrate potential benefits of dredging. However, these first two study levels will not allow assessment of impacts of other loadings to the system, dynamic effects over long time periods, or processes affecting the long-term fate of contaminants. Such an assessment would be required for managing overall water quality in the GCR/IHC system. The third study level involves the use of detailed contaminant models to provide management and screening aid.

189. Work conducted at all three study levels will require a good knowledge of the system's hydrodynamic and sediment transport characteristics. However, application of hydrodynamic and sediment transport models is necessary to determine the quality and quantity of sediments deposited in newly dredged areas. Selection of sediment transport models should be coordinated with responsible parties involved in contaminant evaluation studies to ensure compatibility. Additionally, studies at all levels should be conducted cooperatively with all agencies involved in order to ensure that the studies result in usable products that are well integrated.

Dredging operation

190. The first study level in evaluating the impact of contaminated sediments involves quantification of the mass loadings of contaminants to

the water column during dredging and nondredging conditions. Effects of dredging include increased near-field turbidity and possibly increased contaminant levels in the water column as a result of sediment disturbance. Effects of dredging have been shown to be limited to zones near the actual operations and are generally transient. Mathematical modeling of such events requires use of near-field models. The dynamics of the near-field event are such that the mechanics are usually poorly described, often necessitating the use of empirical rather than mechanistic models (Koba 1983). However, results of a number of studies on the effects of dredging equipment on sediment resuspension are available from work done under the Improvement of Operations and Maintenance Techniques (IOMT) Program for areas other than the GCR/IHC (Hayes, McLellan, and Truitt, in preparation). Information from these studies can be applied to the problem of contaminant loadings induced by dredging, once the resuspension properties of the sediment are identified. Changes in total contaminants in the water column can be estimated from initial water concentrations, initial concentrations of contaminants adsorbed onto sediments, and changes in sediment concentrations in the water column due to dredging. The loadings to the water column can then be estimated using relationships describing contaminant partitioning. Estimates of factors such as pH and ligand concentrations affecting partitioning of ionizable contaminants, as well as experimental data on partitioning kinetics and reversibility, are also required. Comparisons of mass loadings of contaminants under dredging and nondredging conditions (as determined in the second study level) can provide information on the relative impacts of dredging operations.

191. Sediment transport studies can also aid in evaluating the impacts of dredging. If desorption can be neglected, such as may be reasonable in the case of some PCBs, sediment tagging simulations can be used to identify the extent of dredging impacts.

Action/no-action alternative

192. A second study level in evaluating the impact of contaminated sediments on the GCR/IHC system involves determination of the relative loadings from sediments prior to and following dredging operations. Benefits can often be demonstrated by comparing relative magnitudes of these loadings. Data are not presently available to conduct these evaluations.

193. A first criterion in assessing the relative benefits of dredging operations is the establishment of the expected quality of surficial sediments

following the dredging operation. The Chicago District (US Army Engineer District, Chicago 1979) reported that sediment profiles having increasing PCB concentrations with depth were found in areas with the highest PCB levels (>50 ppm). In most other areas of the harbor and canal, consistent vertical trends were not evident. Thus, the removal of overlying sediments to project depth could expose sediments of greater or equal contamination than those presently in place.

194. Demonstration of the relative impacts of contaminated sediments on water quality in the GCR/IHC requires that data be available on the present mass transport of contaminants from sediments due to diffusion and sediment transport. Data are available to estimate loadings from diffusional processes for some contaminants. Information from sediment transport studies can be applied to the problem of contaminant transport induced by sediment resuspension, once the resuspension properties of the sediment are known. Sediment transport studies can provide frequency of occurrence of resuspended sediment concentrations by particle size class due to flow variations. Estimates of frequency of contaminant loadings to the water column can then be determined from sediment and water contaminant concentrations and partitioning relationships.

195. Data are also required to estimate the relative impacts of sediments on the GCR/IHC following dredging operations. This requires establishment of the characteristics of sediment expected to be exposed. Relative impacts of the potentially exposed sediment may then be determined similarly to assessment of existing sediments.

196. The study procedures described above allow comparisons of the relative magnitude of loadings exclusively from sediments. However, the loadings from sediments in relation to other external loadings, from both point and nonpoint sources, are also of interest. Comparisons of loadings from all sources could provide an indication of the potential water quality benefits of dredging operations. For example, if the present loadings from sediments in the GCR/IHC system were found to comprise only a small fraction of the total loadings, then sediment removal would not be expected to appreciably impact water quality. The loadings to sediment from external sources are also of interest. Exposed sediments may be covered fairly rapidly by inputs of new sediment. However, the sources and quality of new sediment to the system are not known. If contaminated sediments quickly become reestablished, with

loadings from sediments returning to predredging conditions, this would affect the benefits of dredging operations conducted solely to improve water quality. To determine these potential benefits, estimates of loadings from external sources, both point and nonpoint, would be required. Much of this data is presently unavailable, necessitating additional field studies. Such data will also be required if future application of contaminant models to the system is anticipated.

Contaminant fate modeling

197. A third study level involves determination of the ultimate, long-term fate of contaminants in the GCR/IHC system. This activity requires assessment of all major processes affecting contaminants, including reaction kinetics, loadings, and mass transport, in order to establish trends and to provide aid for management decisions. Determining the fate of organic contaminants in the GCR/IHC system may be aided by the use of mathematical models. Where the primary concern is long-term trends, the use of steady-state models such as EXAMS or EXAMS2 may be appropriate. However, this approach would not allow examination of short-term processes, such as those due to sediment resuspension. As indicated previously in this report, sediment resuspension followed by contaminant desorption can contribute many more contaminants to the water column than diffusion processes. Simulating such processes requires the use of models allowing dynamic interactions. A candidate for such an effort is the SERATRA family of models. SERATRA contains mechanistic sediment transport as well as contaminant descriptions and allows coupling with hydrodynamic models. Onishi, Mayer, and Argo (1982) coupled FETRA, a modification of SERATRA, with hydrodynamic codes in simulating sediment and contaminant transport for coastal waters, estuaries, and rivers. It may be possible to couple portions of SERATRA with TABS2, a sediment transport model that may be applied to GCR/IHC, in order to avoid duplication of effort. The coupling of contaminant processes with the finite difference hydrodynamic and sediment transport code LARM-SED may also be possible.

198. The box models TOXIWASP or WASTOX may also be used to simulate contaminants in the GCR/IHC system. These models are advantageous because they can be expanded to the required number of dimensions, allowing spatial and temporal segmentation to be adapted to the particular problem. Techniques have been developed at WES for coupling hydrodynamic predictions to box models. The major advantage of coupling hydrodynamic predictions to a box

model is that long-term, dynamic simulations can be performed in a cost-effective manner. It may also be possible to incorporate sediment transport predictions into this model, rather than to recompute them.

199. Studies should be conducted to identify the primary processes affecting critical contaminants and the feasibility of coupling these processes with hydrodynamic and sediment transport models. These studies should be accomplished prior to the selection of a sediment transport model for use in the GCR/IHC system.

200. A separate modeling effort will probably be required for trace metals and synthetic organics. Of the models examined, MEXAMS appears promising, but again this model only allows for steady-state predictions. The coupling of simplified equilibrium approaches to predict metal speciation with existing WLA models may also be a viable approach. However, a variety of models are available which were not considered in this review and a final selection of the models to be used cannot be made at this time.

PART XII: SUMMARY AND CONCLUSIONS

201. The intent of this report was to assess the influence of polluted bottom sediments on the quality of water in the GCR/IHC system. This information was needed to quantify the benefits that would accrue from dredging the contaminated sediments in the Indiana Harbor Canal. The USEPA is also interested in dredging and other means of cleaning up the complex, contaminated GCR/IHC system. The following discussion summarizes what is currently known about the GCR/IHC system relevant to the objectives of this study.

Mechanisms Affecting Water Quality and Contaminant Loading

202. The scientific literature consistently identifies the movement of suspended sediment as the major mechanism for transport of sediment contaminants. Other routes of contaminant mobilization from the sediment are through release of adsorbed contaminants from resuspended sediments and diffusion of contaminants from in-place sediment. The relative importance of mechanisms controlling contaminant movement from sediment in the GCR/IHC is in the order: transport of contaminants associated with particulates > transport of contaminants desorbed from suspended particulates > transport of soluble contaminants released from deposited sediment. Another mechanism for contaminant movement is through bioaccumulation. At present, this last mechanism is of minor importance in the GCR/IHC due to the limited numbers of pollution-tolerant fish and the lower numbers of less pollution-tolerant fish species. Studies conducted at WES have shown that Indiana Harbor Canal sediment is highly toxic to less pollution-tolerant aquatic organisms. Recolonization of the GCR/IHC by less pollution-tolerant species will probably be limited as long as the contaminated sediment remains.

Wastewater Reallocation

203. In order to understand the role of sediment as a source of contaminants in the GCR/IHC, it is necessary to understand the relative importance of sediment and water from the GCR/IHC as contaminant sources to Lake Michigan. To accomplish this, the data available on sources of

pollutants to the GCR/IHC were examined, and a WLA developed for the GCR/IHC was evaluated.

204. Data from NPDES on municipal and industrial point sources are available for use in calculating loads of conventional and some nonconventional pollutants. Estimates have also been made for some conventional pollutant loadings from CSOs and urban runoff; however, pollutant loading estimates for waste fills are unavailable due to a lack of data. Further, existing information is inadequate to either predict toxic organic loading from pollution sources or to confirm the presence of toxic organics, although the presence of organics in the sediments is strong circumstantial evidence of their presence. Existing data will not allow separation of sediment contaminant inputs from point and nonpoint industrial, municipal, and urban sources.

205. Rough estimates have been made of the relative importance of point discharges, combined sewer overflows, and urban runoff to the GCR/IHC (US Army Engineer District, Chicago 1986). More detailed evaluation of the benefits of dredging the Indiana Harbor Canal system will require more data on the sources of sediment and how these sediments move through the system.

206. Evaluation of the WLA model developed for the Grand Calumet River system by the ISBH showed that the model simulates field water quality data for dissolved oxygen and conservative pollutants within a reasonable range of accuracy. At present, the model is unsuitable for nonconservative contaminants such as PCBs, PAHs, and heavy metals. Weaknesses identified by this study in the existing database included unmonitored loadings and limited flow data for the stream and harbor. Review at WES has also identified surprisingly low values of SOD in the WLAs as a potential weakness. The values appear to be low because the wasteloads for the Grand Calumet River are similar to or heavier than wasteloads in other systems that have been demonstrated to have much higher SODs. The low levels of the SOD constitute a weakness because unrealistically low values may not trigger the anaerobic releases from suspended and benthic sediment of metals that are normally released in the GCR/IHC. Finally, the WLA study did not consider toxic organics, resuspension of sediment, storm water loads, pollutant release from sediment, or oil and grease.

207. WLA models currently in use are of limited value for evaluating the transport of sediment contaminants out of the GCR/IHC system or for quantifying the impacts of contaminated sediment on water quality. Their

value resides in the evaluation of such parameters as DO, TDS, chlorides, and sulfates. These models are currently unsuitable for evaluating remobilization and transport of nonconservative chemical contaminants.

Sediment Oxygen Demand

208. SOD is an important oxygen consumption process and is also instrumental in turning on and off the sediment surface layer as a "valve" for oxidized and reduced materials. SOD is also a key parameter in any water quality model that includes DO utilization and balance. From the data available for waterways in the Chicago area, it appears that SOD is frequently found to be quite high; this is not unexpected in streams that are moderately to heavily polluted. However, it is not possible to state with any degree of certainty the existing SOD values for the GCR/IHC system. The values given in the HydroQual report are much lower than values given for similarly polluted streams in the Chicago area and thus are probably too low. In addition, the investigators who obtained the data for the HydroQual report were often unable to obtain satisfactory SOD readings within the Indiana Harbor Canal region. The reasons for this were not clear from the HydroQual report.

Equilibrium Partitioning

209. Diffusion rates of PCBs into the water column from deposited sediments were developed by estimating equilibrium partitioning values of PCBs in sediment interstitial waters and appropriate diffusion equations. The estimated diffusion rates of PCBs in the Indiana Harbor Canal sediments indicate that, in the absence of disturbances, movement of soluble PCBs is relatively minor. On the average, 1 sq m of bottom sediment would annually contribute 0.025 ng of PCBs to the overlying water. This value would be increased in the presence of bioturbation, but would remain a fairly minor component of contaminant input into the overlying water.

210. Results of equilibrium partitioning calculations made using data specific for the GCR/IHC system indicate that Food and Drug Administration limits on PCB concentrations in fish tissue for human consumption will be exceeded; this is provided that fish stay in the Indiana Harbor Canal for a

sufficient period to come to equilibrium with sediment PCBs. Fish moving into the Indiana Harbor Canal from the lake and harbor or living in the canal would not exceed PCB standards for human consumption until encountering sediments in the vicinity of the EJ&E, NYC, and B&O railroad bridges near LTV Steel Co. (US Army Engineer District, Chicago 1979); after this, tissue concentrations, predicted by equilibrium partitioning, would exceed limits. Unfortunately, equilibrium partitioning cannot be conducted on compounds other than hydrophobic organic compounds for which sediment data are available. This means that hydrophobic organic compounds known to be present in the Indiana Harbor Canal, but for which sediment data are not available, as well as nonpolar organic compounds and inorganic heavy metals, cannot be evaluated by this procedure. In addition, a major weakness of the equilibrium partitioning approach is that the time necessary to reach equilibrium between sediment contaminants and the biota is unknown. Thus, it is impossible to predict how long a fish population must remain in an area before the equilibrium concentration is reached.

Sediment Resuspension and Transport

211. Under nondredging conditions, there are two major avenues for the resuspension and transport of sediment from the GCR/IHC system--normal ship traffic and storm events. Examination of data from bathymetric surveys for the years 1972, 1976, 1980, and 1984 indicates that the Indiana Harbor Canal has reached a shoaled equilibrium with the channel thalweg provided by passage of boat traffic. Shoaled equilibrium means that incoming sediment is equal to the outgoing sediment which moves into Indiana Harbor and Lake Michigan. A sharp decrease in the channel depths was found between the years 1972 and 1976, with progressively smaller depth changes since 1976. The 1984 survey shows only a small overall change from the 1980 survey, an indication that the total amount of shoal material has not changed, but may only be redistributed through undocumented mechanisms (Lake Michigan seiches, local storm action, ship movement, docking, towing, etc.).

212. The database for the GCR/IHC has only limited data on contaminant releases during interactions between suspended sediment and water. Current velocity data and information on sediment resuspension are also very limited. To determine the mass of contaminants transported from the sediments during

dredging and nondredging conditions, it may be necessary to use mathematical models.

Contaminant Models

213. Contaminant models are currently available that can provide objective, rational aid for management decisions. However, simulation of organic and inorganic contaminants in the GCR/IHC system may require the use of two separate fate models due to differences in their speciation chemistry. Regardless of the models used, contaminant modeling/analysis can be conducted on at least three study levels. These include evaluation of contaminant loadings due to the actual dredging operation, determination of the relative loadings from sediments prior to and following dredging operations and between sediments and other loadings, and determination of the ultimate, long-term fate of contaminants in the GCR/IHC system. Additional data will be required prior to implementation of any of these three levels of study. The prior application of hydrodynamic and sediment transport models to the system will provide information necessary to the first two study levels and which may be used as input to the third study level.

214. Review of existing models revealed that application of contaminant models to the near-field problem resulting from dredging operations is not recommended. A number of studies on the effects of various types of dredging equipment on sediment resuspension are available from work done under the IOMT Program for areas other than the GCR/IHC (Raymond 1984) in addition to recent studies conducted in Calumet Harbor (Hayes, McLellan, and Truitt, in preparation). Information from these studies can be applied to the problem of contaminant transport induced by dredging once the resuspension properties of Indiana Harbor Canal sediment have been established. A rough estimate of total sediment deposition rate in the navigation channel can be approximated using dredging records and bathymetric surveys (US Army Engineer District, Chicago 1986). However, a detailed evaluation of deposition rates requires a knowledge of system hydrodynamics, loadings, and transport, as well as sediment resuspension properties that are not currently available. Such information is needed to accurately determine the extent to which the dredged area may serve as a settling basin for particulates. It appears that simplified models and/or process descriptions coupled with field and laboratory

experiments may be best suited to evaluation of the no-action alternative (the second level of complexity). For the third level of complexity, applications of long-term contaminant fate modeling should be coupled with information obtained through hydrodynamic and sediment transport modeling. Modeling requirements for contaminants should be considered in the selection of the hydrodynamic and sediment transport models (e.g. their dimensionality) to avoid duplication of effort.

215. Prediction of the ultimate fate of contaminants in the GCR/IHC system, required for evaluation of overall water quality, may be aided by the use of contaminant models, but additional field and laboratory data should be obtained prior to intensive contaminant fate modeling studies. Laboratory and field experiments should be conducted with model data requirements in mind so that the data may be utilized in future modeling efforts. In fact, preliminary application of toxic substances model(s) may be of utility in evaluating the database generated by field and laboratory studies and the relationship of such data to the processes of interest. Also, in any such study, contaminant modeling as well as field and laboratory studies should be coordinated with the USEPA and other concerned agencies.

Conclusions

216. Results of this study have shown that the data available allow only rough estimates, such as those in the Indiana Harbor Environmental Impact Statement (US Army Engineer District, Chicago 1986), of the sediment loadings, sediment yield, and benefits that would accrue from dredging the Indiana Harbor Canal. More detailed hydrodynamic and suspended sediment transport data are necessary to allow use of more sophisticated analytical techniques for evaluating sediment sources, sediment resuspension, and sediment transport. Historical dredging data strongly suggest, however, that dredging the Indiana Harbor Canal would allow it to act as a sediment trap, retaining contaminated sediment that would otherwise be transported into Lake Michigan. Additional data must also be collected before analytical techniques more sophisticated than those already conducted can be applied to the GCR/IHC system for either metals or toxic organics. Therefore, the immediate detailed application of either hydrodynamic or contaminant models is not recommended.

PART XIII: RECOMMENDATIONS

217. Assessment of the impacts of dredging contaminated sediment in the GCR/IHC system can be conducted at a number of levels of effort. For this reason, recommendations for future studies are given for three study levels to allow the Chicago District to tailor studies to meet specific objectives for maximum benefit at lowest costs. However, any level of study of the GCR/IHC requires a knowledge of the system's hydrodynamic and sediment transport characteristics. The information required for an assessment of the system's hydrodynamics and sediment transport will require both short-term (on the order of a day) and long-term (on the order of 4 to 6 days) field data sets. The short-term data sets should consist of simultaneous measurements of water surface fluctuations located at four control points, with a sampling rate of about 3 min; control point velocity measurements at surface, middepth, and bottom to determine instantaneous discharges through the system; and total suspended material measurements at the velocity sampling points. These short-term data sets should be collected seasonally. Long-term data sets should encompass frontal passage (storm) events, and include the same resolution and measurements as the short-term data set, with the addition of a continuous dye release at the upstream limit of the Federal navigation channel. These data needs are described in more detail in Part VIII of this report.

Contaminant Loadings Prior to, During, and Following Dredging Operations

218. Essentially the same information is required for the following activities: (a) evaluation of contaminant loadings due to the actual dredging operation; (b) determination of the relative loadings from sediments prior to and following dredging operations; and (c) determination of relative loadings between sediments and other loadings. The two study levels required to determine these contaminant loadings can be conducted concurrently and are, therefore, presented together. The first study level involves quantification of the mass loadings of contaminants to the water column during dredging and nondredging conditions. The second study level involves a determination of the relative loadings from sediments prior to and following dredging operations and between sediment and nonsediment loadings to the GCR/IHC. These two levels are intended solely to evaluate relative impacts of contaminated

sediment before, during, and after dredging. These assessments will require an evaluation of partition coefficients between sediment and water using surface sediments and those sediments that will be exposed following dredging. In addition, sediment transport and resuspension due to ship traffic and storm events must be understood. Also, the magnitude of loadings from other contaminant sources such as nonpoint sources must be determined to quantify the impact of sediment contaminants in the GCR/IHC system. Complex contaminant models would not be used for this portion of the study; at most, simplified steady-state analytical techniques will be needed. To determine the amounts and quality of sediment that would deposit in areas that are dredged, a sediment transport model is required. For this effort it is important that sources of sediment be identified. Selection of the sediment transport model will require coordination with hydraulic engineers if results of hydrodynamic and sediment transport studies are to be used as an input to contaminant modeling studies beyond the second level of study. Coordination with potential modelers is recommended to ensure that data collected for the first and second study levels can be applied to future modeling applications should the need arise.

219. To implement the first and second study levels, field and laboratory studies to provide the information previously discussed in this section are recommended. In case of funding limitations, priority should be given to quantifying suspended sediment loads as a function of environmental disturbance, obtaining hydrodynamic data for the system, identifying the sources of sediment to the Indiana Harbor Canal, quantifying the impact of various unmonitored contaminant sources on the system, and determining the concentration of critical contaminants such as PCBs, heavy metals, and PAHs at varying depths in the sediment.

Long-Term Fate of Contaminants in the GCR/IHC System

220. The immediate detailed application of either hydrodynamic or contaminant models is not recommended for the Indiana Harbor Canal. However, if future needs dictate more detailed information on the Indiana Harbor Canal, a third study level could be implemented. The third study level involves a determination of the long-term fate of contaminants. This study level is intended to provide information for the management of water quality in the

GCR/IHC system. In addition to the data needed to complete the first and second study levels, an additional assessment of all major processes affecting contaminants, including reaction kinetics, loadings, and mass transport will be needed. This would include information on many of the processes affecting contaminant fate that are described briefly in Appendix C.

221. Contaminated sediment transported into Indiana Harbor and the near-shore region of Lake Michigan would certainly have an impact on water quality and biota. Evaluation of the effects of this contaminated sediment, however, would require information similar to that needed for a third level study. It would also require additional hydrodynamic and sediment transport information beyond that required for the GCR/IHC system. This information is needed to determine the mass of sediment and contaminants transported into the harbor and near-shore areas and the fate of this sediment following initial deposition.

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Table 1
Industrial Discharges to Grand Calumet System
1983 Dry Weather*

<u>Industry</u>	<u>Outfall No.</u>	<u>Description</u>
U.S. Steel	002	Tube operation recycle blow down, noncontact water from coke plant
	005	Noncontact cooling water from coke plant
	007	Noncontact water from coke plant, miscellaneous
	010	Noncontact water from coke plant
	015	Noncontact water from #3 sinter plant
	018	Noncontact water from energy division
	020	Noncontact water from #1 basic oxygen process (BOP) shop
	028	Primary bar plate mills and BOP shops
	030	Primary bar plate mills and BOP shops
	032	Noncontact water from bar mills
	033	Noncontact cooling water from atmospheric gas plant and miscellaneous finishing operations
	034	Process water from terminal treatment plant and 84-in. hot strip mill recycle system blow down. Noncontact cooling from miscellaneous finishing operations
Industrial disposal	001	--
Vulcan materials	001	--
E.I. duPont	001	Process and noncontact cooling from chemical production
	002	Process and noncontact cooling from chemical production
	003	Process and noncontact cooling from chemical production
Harbison-Walker	001	--
U.S.S. Lead	001	Noncontact cooling water from blast furnace and casting mold
Blaw-Knox	001	--
	004	--
American Steel	001	Process and cooling waters from foundry
J & L Steel	001	Process and cooling from flat roll operations

(Continued)

* After HydroQual (1984).

Table 1 (Concluded)

Industry	Outfall No.	Description
J & L Steel	002	Cooling water from cold rolling and finishing
	009	Powerhouse and sinter plant cooling water
	010	Powerhouse and blast furnace cooling water
	011	Process and cooling water from steel plant operations
Inland Steel	001	Process and cooling water from electric furnace steel shop and bar mill
	002	Process water, cooling water, and noncontact water from numerous operations
	003	Process and noncontact cooling water from numerous operations
	005	Process and noncontact cooling water from bar mill
	007	Noncontact cooling from blast furnaces
	008	Noncontact condenser cooling water from powerhouse
	011	Noncontact cooling from blast furnaces, noncontact from sinter plant and powerhouse
	012	Blast furnaces blow down, cooling water from coke plant, and treated sanitary water
	014	Process water from numerous operations
	015	Noncontact water from open hearth furnace and small amount of treated sanitary water
	018	Grit water from basic oxygen furnaces, contact and noncontact basic oxygen furnace, powerhouse cooling water

Table 2
Industrial Constituents Limited or Monitored by NPDES
Permits Issued Prior to 1985 (USEPA 1985)

<u>Constituent</u>	<u>duPont</u>	<u>Inland Steel</u>	<u>J & L Steel</u>	<u>U.S.S. Lead</u>	<u>U.S. Steel</u>	<u>Vulcan Materials</u>
BOD	X	X				X
pH	X	X	X	X	X	X
Temperature			X		X	X
Suspended solids	X	X	X	X		X
Fats, oil, and grease	X	X	X		X	X
Fecal coliform		X				
TDS	X					
Ammonia	X	X	X		X	
Phosphorus	X					
Chloride	X	X	X			X
Fluoride		X	X	X	X	
Sulfate	X	X	X	X	X	
Cyanide		X	X		X	
Phenols		X	X		X	
Chlorine residual		X			X	
Arsenic				X		
Chromium		X	X		X	
Copper		X				
Iron					X	
Lead		X	X	X	X	
Mercury					X	
Nickel		X				
Tin			X			X
Zinc		X	X	X	X	
Toxic organics					X	

Table 3
Industrial Point Source Loadings, HydroQual (1984) Survey*,**

Industry	Flow mgd	BOD	Ammonia	Phosphorus	Chlorides	TDS	Sulfates	Cyanides	Iron	Phenols	Lead
Citgo	-†	-	-	-	-	-	-	-	-	-	-
duPont	4.70	157	-	0.2	1,137	52,486	33,935	-	-	-	-
Inland Steel	592	23,704	1,977	147	85,322	919,578	135,306	39	352	31	0††
J & L Steel	154	5,195	484	47	51,878	335,274	50,059	32	0	9	-
U.S.S. Lead	0.06	4	-	-	95	403	260	-	-	-	-
U.S. Steel	309	10,710	827	107	58,221	525,617	66,572	3	637	6	0
Vulcan Materials	0.12	14	-	-	950	1,661	42	-	-	-	-
Industrial disposal	1.00	127	-	3	9,365	23,567	2,977	-	-	-	-
American Steel	0.13	2	-	-	39	358	69	-	1	-	-
Blaw Knox	0.04	4	-	-	24	140	33	-	-	-	-
Explorer Pipeline	-	-	-	-	-	-	-	-	-	-	-
Totals	1,061	39,917	3,288	301	207,031	1,859,084	289,253	74	989	46	0

* USEPA (1985).

** All water quality parameters are shown in pounds per day $\left(\text{mg/l} = \text{lb/day} \times \frac{1}{8.34} \times \frac{1}{\text{Flow}} \right)$.

† - indicates parameter not measured.

†† 0 indicates parameter measured to be zero.

Table 4
POTW Improvement, 1968-1982*

<u>POTW</u>	<u>Parameter</u>	<u>1968</u>	<u>1982</u>
East Chicago	Flow, mgd	11.3	16.7
	BOD ₅ , lb/day (mg/l)	13,700(146)	10,400(73)
	TSS, lb/day (mg/l)	10,400(110)	15,000(99)
Hammond	Flow, mgd	33.4	37.9
	BOD ₅ , lb/day (mg/l)	10,800(39)	540(1.7)
	TSS, lb/day (mg/l)	9,360(37)	600(1.9)
Gary	Flow, mgd	48.5	41.4
	BOD ₅ , lb/day (mg/l)	4,590(11)	3,107(9.0)
	TSS, lb/day (mg/l)	8,480(21)	2,070(6.0)

* USEPA (1985).

Table 5
Waste Fills of Greatest Concern*

<u>Site No.</u>	<u>Miles to River Bank</u>	<u>Owner or Name</u>	<u>Potential Pollutants</u>
3A	0.1	J & L Steel	Oily wastes, heavy metal
11B	0.1	U.S. Steel	N/A
12B	0.1	Uncontrolled	N/A
17B	0.1	duPont	N/A
18B	0.1	U.S.S. Lead	Lead, arsenic
28C	0.1	Gary Sludge Lagoon	POTW sludge
29C	0.1	Gary Sludge Lagoon	POTW sludge, PCB
35D	0.1	Mobile Oil Terminal	Refinery waste
36D	0.2	GATX Corporation	Waste storage pond
37D	0.2	E. Chicago Landfill	N/A
38D	0.1	Hammond Sludge Lagoon	POTW sludge

* USEPA (1985).

Table 6
Comparison of GCR/IHC Water Quality to Typical Urban Runoff Quality
and to CSO Quality

Constituent	Concentration, mg/l			Mass Load, 10 ⁶ lb/year		
	NURP	CSO	GCR/IHC In-Stream*	Urban	CSO†	Avg.
	Median Site	Median Site		Runoff**		Stream††
TSS	100	190	14	30	20	50
BOD ₅	9	54	2.2	2	5	8
Total phosphorus	0.33	NA	0.07	0.09	NA	0.3
Total copper	0.034	0.11	0.005	0.009	0.01	0.02
Total lead	0.144	0.32	0.011	0.04	0.03	0.04
Total zinc	0.160	0.43	0.049	0.04	0.04	0.2

* Average stream concentration for nine monthly samples collected at mouth of Indiana Harbor Ship Canal (HydroQual 1984).

** Based on 35 in./year rainfall, 68-square-mile drainage area, runoff coefficient of 0.8, and NURP concentrations.

† Based on USEPA (1985) CSO flow estimate of 11 billion gal/year.

†† Based on 1,250 mgd base flow (HydroQual 1984) and average in-stream concentration.

Table 7
Point Source Pollution Loads in the East Branch, Grand Calumet River*

Dis-charge No.	Discharger (Outfall No.)	Flow, mgd			CBOD _u , lb/day**			NH ₄ -N, lb/day			Total Phenols, lb/day			TDS, lb/day		
		H-Qual 9/83	H-Qual 10/83	USGS 10/84	H-Qual 9/83	H-Qual 10/83	USGS 10/84	H-Qual 9/83	H-Qual 10/83	USGS 10/84	H-Qual 9/83	H-Qual 10/83	USGS 10/84	H-Qual 9/83	H-Qual 10/83	USGS 10/84
27	U.S. Steel (002)	36.3	27.5	28.2	5,056	344	1,529	0	46	136	BDL	BDL	BDL	61,759	38,989	43,300
28	U.S. Steel (005)	1.8	2.0	0.84	369	50	31.5			6.5	BDL	BDL	BDL	2,447	3,169	1,210
29	U.S. Steel (007)	15.5	12.8	8.00	129	320	867	719	288	113	1.2	2.2	4.3	28,181	21,350	16,900
30	U.S. Steel (010)	3.4	1.7	4.12	284	37	240	48	20	21.6	0.3	1.8	53.6	5,274	2,552	5,570
31	U.S. Steel (015)	1.8	1.6	1.85	173	28	46.3	8		1.4	BDL	0.1	BDL	2,822	2,535	2,690
32	U.S. Steel (018)	42.2	34.2	36.1	387	314	1,505	107	185	160	BDL	BDL	5.2	59,831	42,784	50,600
33	U.S. Steel (019)	46.3	39.6	37.3		495	1,244	11	30	28	BDL	3.6	BDL	63,716	49,540	44,800
34	U.S. Steel (020)	81.6	65.8	75.8		659	1,897	12	38	107	BDL	BDL	32.9	122,498	98,779	125,000
35	U.S. Steel (028)	23.4	16.4	4.97		164	536	15	93	53.9	BDL	0.1	0.04	42,349	23,251	6,920
36	U.S. Steel (030)	59.9	36.5	30.2		369	3,022			242	BDL	1.5	BDL	106,907	48,706	48,600
37	U.S. Steel (032)	2.7	2.6	2.55	14	161	64	1		1.1			BDL	4,414	4,337	3,450
38	U.S. Steel (033)	2.1	1.5	1.70	77	46	99	11		8.1			BDL	2,644	2,752	5,660
39	U.S. Steel (034)	33.4	25.9	21.8	7,187	2,268	5,636	8	13	40.0	BDL	1.1	12.2	122,565	87,082	95,100
2	Gary POTW (001)	33.5	27.3	32.7	1,118	1,434	3,818	606	706	166	BDL	BDL	0.5	130,475	126,819	131,000
42	Industrial disposal (001)	0.78	1.19		159	95					BDL	BDL		18,293	28,841	
40	Vulcan Materials (001)	0.10	0.14	0.10	22	5	3.3			0.1	BDL	BDL	BDL	2,318	1,004	315
7	E.I. duPont (001)	3.3		4.52	107	107	452			52.8			0.6	7,348	7,348	10,700
8	E.I. duPont (002)	1.09	0.48	1.14	62	62	238			12.4			BDL	3,627	1,021	11,800
9	E.I. duPont (003)	0.57	0.60	0.70	11	11	38			0.8			0.03	49,059	36,569	53,100
6	Harbison Walker (001)	0.01	0.01	0.04	0	0	1.3			0.1			0	14	8	55
10	U.S.S. Lead (001)	0.06	0.06	0.01	4	4	0.6			0.1			BDL	200	605	59
-	U.S. Steel (031)			7.05			176			7.1			BDL			13,800

(Continued)

Note: BDL indicates below detection limit for the particular analysis. Blank indicates analysis not performed for that outfall.
 * HydroQual (1984) and USGS (1985 unpublished data).
 ** CBOD_u = ultimate carbonaceous biochemical oxygen demand.

Table 7 (Concluded)

Dis- charge No.	Discharger (Outfall No.)	Cyanide, lb/day			Iron, lb/day			Mercury, lb/day			Chromium, lb/day			Lead, lb/day		
		H-Qual			H-Qual			H-Qual			H-Qual			H-Qual		
		9/83	10/83	USGS 10/84	9/83	10/83	USGS 10/84	9/83	10/83	USGS 10/84	9/83	10/83	USGS 10/84	9/83	10/83	USGS 10/84
27	U.S. Steel (002)	3	BDL	9.4			89.4			0.1			BDL			0.2
28	U.S. Steel (005)			0.1			2.2	BDL		0.005	BDL		BDL			BDL
29	U.S. Steel (007)	BDL	3.2	BDL			24			0.2			BDL			BDL
30	U.S. Steel (010)	BDL	BDL	1.7	3		14.1			0.01			0.07			BDL
31	U.S. Steel (015)	BDL	BDL	BDL			8.3			0.005			BDL	BDL		0.3
32	U.S. Steel (018)	BDL	BDL	BDL			75.3			0.2			0.09			BDL
33	U.S. Steel (019)	BDL	BDL	BDL			109			0.09			BDL			BDL
34	U.S. Steel (020)	BDL	BDL	37.9			544	BDL		0.6			BDL			2.5
35	U.S. Steel (028)	BDL		BDL	74	248	19.5			0.008			0.08			BDL
36	U.S. Steel (030)			12.6	190	490	191			0.3			0.3			0.8
37	U.S. Steel (032)			BDL	5	2	4.5			0.009			0.04			0.02
38	U.S. Steel (033)			BDL			85			0.02			0.01			0.04
39	U.S. Steel (034)	BDL	BDL	BDL	89	173	200			0.2	BDL		0.2			BDL
2	Gary POTW (001)	BDL	BDL	BDL	53	39	123	BDL	BDL	0.1	BDL	BDL	BDL	BDL		0.3
42	Industrial Disposal (001)								BDL							
40	Vulcan Materials (001)			BDL			0.2			0.001			0.002			0.004
7	E.I. duPont (001)			0.004			64			0.01			0.04			0.6
8	E.I. duPont (002)		BDL	BDL			11.4			0.002			0.08	BDL	0.01	0.1
9	E.I. duPont (003)		BDL	BDL			5.8			BDL			0.04			0.2
6	Harbison Walker (001)		BDL	BDL			0.1			0.000			0.002			0.007
10	U.S.S. Lead (001)		BDL	BDL			0.2			0.000			BDL			0.000
-	U.S. Steel (031)		BDL	BDL			28.8			0.04			0.06			0.06

Table 8
Summary of Variables Monitored During
Water Quality Surveys*

Conservative tracers	Metals
Chlorides	Copper (total)
TDS	Lead (total)
	Chromium (total)
Oxygen-related variables	Chromium, hexavalent
Temperature	Zinc (total)
DO	Nickel (total)
5-day CBOD	Iron (total)
Time series CBOD	Mercury
Time series nitrogenous BOD	
Ammonia nitrogen	Other
Total Kjeldahl nitrogen	pH
Nitrate/nitrite	Fecal coliform
Total and ortho phosphorus	Fluoride
Suspended solids	Sulfate
SOD	Total cyanide
	Phenol
Additional point source parameters	Chlorophyll (selected samples
(limited) to NPDES requirements	from ambient water column)
Benzene	PCB (selected samples from
Toluene	ambient water column)
Napthalene	
Fluoranthene	Sediments (selected canal and
Tetrachloroethylene	river sites)
Chlorobenzene	Priority pollutants, except
1,1,1 Trichloroethane	31 volatiles
PNAH	
Chloroform	
Tin (total)	

* HydroQual (1984).

Table 9
Representative SOD Values for Deep Draft Waterways in Cook County,
Illinois, During 1976 (Data of Polls and Spielman 1977)

<u>Waterway</u>	<u>Location</u>	<u>SOD*</u> <u>g/sq m/day</u>
Calumet River	Ewing Avenue Bridge	2.40
	Norfolk and Western R. R. Bridge	7.61
Little Calumet River	Indiana Avenue Bridge	7.00
	Halstead Street Bridge	7.68
Cal-Sag Channel	Route 83 Bridge	2.26
Chicago Sanitary and Ship Canal	Western Avenue Bridge	5.62
	Harlem Avenue Bridge	14.14
	16th Street Bridge	3.46
North Shore Channel	Maple Avenue Bridge	9.26
	Main Street Bridge	16.32
North Branch, Chicago River	Division Street Bridge	1.23
	Diversey Parkway Bridge	23.32

* All values given are at 20° C. Values presented were those computed from the highest sampling temperature used, if more than one temperature was sampled.

Table 10
Representative SOD Values for Northeastern Illinois
Streams (Data of Butts and Evans 1978)

<u>Stream</u>	<u>Milepoint Location</u>	<u>SOD*</u> <u>g/sq m/day</u>
North Branch, Chicago River	17.40	2.18
Little Calumet River	13.80	1.66
	17.90	3.46
	26.00	8.93
Calumet Union Canal	1.00	7.34
Thorn Creek	10.00	2.45
Deer Creek	19.50	2.35
Des Plaines River	36.10	5.65
	62.40	3.93
	83.40	1.43
	103.00	3.05
West Branch, DuPage River	28.40	2.65
	36.70	1.93
	42.60	1.50
	52.40	0.94

* All values given are at 20° C.

Table 11
Sediment Organic Concentrations in the Grand Calumet River
(USEPA 1985) and the Indiana Harbor (This Study)

Organic	Sediment Concentration, ppm		Estimated Interstitial Concentration, ppb
	This Study	USEPA (1985)	
PCBs (1248)	27	17	1.3
Naphthalene	2000	33	28.6
Acenaphthylene	22	27	0.12
Acenaphthene	96	100	0.28
Fluorene	69	98	0.22
Phenanthrene	200	201	0.2
Anthracene	62	170	0.06
Fluoranthene	150	120	5.07
Pyrene	140	65	0.04
Chrysene	92	130	0.57
Benzo(a)anthracene	86	140	0.04
Benzo(b)fluoranthene	140	200	3.38
Benzo(k)fluoranthene	140	120	3.31
Benzo(a)pyrene	87	200	0.54
Indeno(1,2,3-cd)pyrene	50	6.8	42.2
Benzo(g h i)perylene	35	38	2.91

Table 12

Prediction of Bioaccumulation Potential (TBP) and Hypothetical Maximum
Whole Organism Concentrations of Organics for Lipid Contents
of 2 and 5% Based on TBP for Sediments

Organic	Conc. in Sediment ($\mu\text{g/g}$)	TBP* (ppm)	Max Ct** for Lipid Contents of	
			2%	5%
PCBs	27	702	14	35
Naphthalene	2,000	51,975	1,040	2,599
Acenaphthylene	22	572	11	29
Acenaphthene	96	2,495	50	125
Fluorene	69	1,793	36	90
Phenanthrene	200	5,198	104	260
Anthracene	62	1,611	23	81
Fluoranthene	150	3,898	78	195
Pyrene	140	3,698	74	185
Chrysene	92	2,390	48	120
Benzo(a)anthracene	86	2,235	45	112
Benzo(b)fluoranthene	140	3,638	73	182
Benzo(k)fluoranthene	140	3,638	73	182
Benzo(a)pyrene	87	2,261	45	113
Indeno(1,2,3-cd)pyrene	50	1,299	26	65
Benzo(g h i)perylene	35	910	18	46

* $\text{TBP} = (\text{Cs}/\text{foc})/0.52$ where Cs = chemical concentration in sediment (ppm) and foc = decimal fraction organic carbon in sediment.

** Ct = Tissue concentration, fresh weight (ppm).

Table 13
Estimated Fluxes for PCBS in the GCR/IHC Ecosystem*

Location**	Sediment Concentration mg/kg	Interstitial Water Concentration µg/l	Estimated Flux† ng/m ² /day × 10 ⁻⁵	Max Conc. at 2% Lipid ppm
1	13.15	0.93	9.2	6.8
2	5.86	0.41	4.0	3.0
3	27.38	1.90	18.9	14.2
4	11.34	0.80	7.9	5.9
5	31.74	2.24	22.3	16.5
6	22.93	1.62	16.1	11.9
7	7.36	0.52	5.1	3.8
8	1.11	0.08	0.7	0.6
9	3.13	0.22	2.1	1.6
10	1.89	0.13	1.2	1.0
11	nd††	nd	nd	nd
12	0.09	0.006	0.05	0.05
13	nd	nd	nd	nd

* Hypothetical maximum whole organism concentration of PCBs in organism with lipid content of 2 percent.

** Locations are the same as those used in US Army Engineer District, Chicago (1979).

† PCB concentration in overlying water is 0.8×10^{-5} mg/l.

†† nd = less than detection level (e.g. <0.02 ppm).

Table 14

General Categorization of Contaminant Models (Delos et al. 1984)*

<u>Model</u>	<u>Aquatic System</u>	<u>Chemicals</u>	<u>Sediment Size</u>	<u>Dimensions</u>	<u>Numerical Solution</u>	<u>Time Frame</u>	<u>Availability</u>
CTAP	G	O	5	B	SS	SS	C
EXAMS	G	O	D	B	SS	SS	A
EXAMS2	G	O,D	D	B	FD	S	A
HSPF	R	O,D	3	1	FD	D	A
MEXAMS	G	M	D	B	SS	SS	A
MICRIV	R	O	1	1	SS	SS	GI
SERATRA	R	O	3	2V	FE	D	A
TODAM	R	O	3	1	FE	D	
TOXIC	G	O	1	B	FD	D	
TOXIWASP	G	O	1	B	FD	D	A
UTM-TOX	R	O,M	4	1	FD	D	
WASTOX	G	O	3	B	FD	D	A

-
- * G = generalized aquatic system; R = river.
 O = generalized pollutant; M = metal, specifically; D = daughter product.
 D = descriptive input, not simulated.
 B = box approach; 2V = two dimensions (x-z).
 FD = finite difference; FE = finite element; SS = steady-state.
 S = seasonal; D = daily.
 A = available from USEPA Center for Water Quality Modeling, Athens, Ga.
 C = available from Chemical Manufacturing Association; GI = available from USEPA, Gross Ile.

Table 15

Model Data Needs*

Variable	Symbol	Unit	Remarks/Qualifications
Channel data			
River flow	Q_1	m^3/sec	Measure or obtain from USGS gage.
Velocity	U_1	m/sec	Measure directly with time-of-passage dye study, or compute from area and flow: $U = Q/A$.
Cross-sectional area	A_1	m^2	Compute from measured width and depth, or compute from velocity and flow.
Reach length	L	m	Reaches determined by significant morphometric changes, tributaries, or point sources; measure from charts, confirm in field.
Depth of water	H_1	m	Measured directly or compute from cross-sectional area and measured width.
Loading data			
Upstream "boundary" Concentration			
Toxicant	C_u	μ/l	Direct measurement.
Suspended solids	m_1	mg/l	Direct measurement.
Point sources			
Flow	Q_w	m^3/sec	
Concentration toxicant	C_w	$\mu g/l$	
Load Toxicant	W_w	kg/day	Product of flow and concentration.
(Continued)			

* Delos et al. (1984).

Table 15. (Continued)

Variable	Symbol	Unit	Remarks/Qualifications
Loading data (cont.)			
Concentration-Sus. Solids	-	mg/l	
Load-Sus. Solids	-	kg/day	
Bed and particulate data			
Thickness of active sediment	H ₂	m	Estimate from core samples, measuring vertical distribution of organic contaminants, or use typical published values. This parameter has no effect on steady-state results unless significant decay occurs in the bed.
Solids concentration in bed	m ₂	mg/l	Measure or estimate: m ₂ = (particle density) (1 - ϕ)
Porosity	ϕ	-	
Solids type	-	-	
Size distribution	-	μ m	
Settling velocity	w _s	m/day	Estimate from particle-size distribution and stream turbulence coupled with published data or Stokes formula. Measure with sediment traps or in laboratory. Adjust by calibration.
Resuspension velocity	w _{rs}	m/day	Calibrate to m ₁ data; estimate from theory.
Partition coefficient	π	l/mg	Calibrate for dissolved and particulate data: $\pi = C_p/mC_d$. Otherwise, use literature values.
Sediment diffusion	K _L	m/day	Literature values.

(Continued)

Table 15. (Continued)

Variable	Symbol	Unit	Remarks/Qualifications
Degradation rates			
Volatilization coefficient	K_v	l/day	Calculate from theory. For volatile hydrophobic pollutants, compare with reaeration rate.
Reaeration coefficient	$K_v(O_2)$	l/day	Calculate using stream depth, velocity, and possibly slope.
Solubility	S	mg/l	Published data.
Vapor pressure	P	torr	Published data.
Photolysis rate	K_p	l/day	Use estimation method; direct measurements made using actinometer.
Chlorophyll <u>a</u>	CHL A	mg/l	Standard methods.
Diss. organic carbon	DOC	mg/l	Standard methods.
Suspended solids	SS	mg/l	Standard methods.
Solar/UV Radiation*			UV radiometer.
Near-surface rate	K_{PD}	l/day	Measured by actinometer at water surface.
Biolysis rate	K_B	l/day	Sterile vs. nonsterile dark bottle experiments.
Cell count		#/ml	
Chlorophyll <u>a</u>	-	mg/l	
Hydrolysis rate	K_H	l/day	Laboratory experiment at different pH or published data.
pH			
Ancillary data: temperature		°C	

(Continued)

* UV = ultraviolet.

Table 15. (Concluded)

Variable	Symbol	Unit	Remarks/Qualifications
Calibration/verification data			
Suspended solids	m_1	mg/l	Standard methods, usually using 0.45- μ m filter.
Toxicant concentration			In water column and bed sediment.
Total	C_T	μ g/l	Direct measurement at appropriate times and places.
Dissolved	C^d	μ g/l	Defined according to filter used; i.e., 45 μ m.
Particulate	C_p	μ g/l	Calculated: $C_p = C_T - C^d$.

APPENDIX A: EXISTING METHODS AND AVAILABLE DATA FOR ESTIMATING
IMPACTS OF SEDIMENT OXYGEN DEMAND ON WATER QUALITY

1. There are two methods for evaluating sediment oxygen demand (SOD)-- field methods and laboratory methods. Both will be discussed in this appendix.

Field Methods

2. Field methods offer several advantages. They are direct measurements made in situ; no manipulations of the sediment are made that would give erroneous results. Field methods cause little, if any, disturbance of the integrity of the sediment surface; underlying sediment layers are not brought to the surface to contribute unwanted oxygen demands resulting from the presence of reduced chemical species. Field methods often include the total assemblage of biological and abiotic components present on the sediment surface and within the sediment itself. The only large source of error usually introduced is the elimination of currents resulting from the presence of a SOD measurement device; this may or may not alter the respiration rate of the organisms present due to a lack of water exchange. Field measurements probably come as close to the real value for SOD as can presently be obtained.

3. Field methods also have several disadvantages. Much of the equipment used is cumbersome and must be hauled out to the site; this requires rigorous and comprehensive planning to avoid repeated excursions. Field methods are often inflexible. Unforeseen results cannot be further examined because the needed equipment or reagents have not been brought along. Under field situations, it is often difficult or impossible to control environmental conditions. This sometimes makes it hard to complete a study and, more often, makes it difficult to accurately predict what changes in results would occur under different environmental circumstances. Finally, the environmental impact of some procedures readily used in the laboratory may preclude their application to field work; this may be important if these procedures would otherwise enable the investigator in the field to make more rapid or more accurate determinations of various portions of the total SOD picture.

4. All of the currently available methods for field studies use some type of closed chamber respirometer that is placed over the sediment surface.

Laboratory Methods

6. Laboratory methods, like field methods, have their advantages. Many laboratory methods require only small surface areas of sediment, although large volumes can sometimes be required. Depending on the methods used, the SOD may be fractionated into biological and chemical demand components, a task that is difficult to accomplish in the field (see Gunnison, Chen, and Brannon 1983). Laboratory procedures often offer the advantage of rigorous environmental control, enabling isolation of major factors influencing oxygen consumption rates. Through the ability to isolate sediment from other factors present in the field, laboratory studies remove many opportunities that would otherwise cause disruption. Thus, interruption of measurements by passing boaters, loss of equipment through vandalism, and other problems encountered in the field have no influence on the results. In addition, many sophisticated procedures that are difficult or impossible to perform in the field, such as the use of hazardous radiotracers, can be readily applied in the laboratory.

7. Laboratory methods also have disadvantages. Much controversy exists over the validity of data obtained in the laboratory relative to data obtained in the field; i.e., are laboratory data really reflective of what is occurring in the field? To obtain sediment samples for use in the laboratory, the scientist has to disturb the sediment surface, potentially causing artifacts in the data resulting from the presence of oxygen-demanding reduced chemical species. Many investigators do not routinely take adequate precautions to preserve the anaerobic integrity of sediment during acquisition, transport, and placement into test devices; this may cause sediment to become oxidized with a resultant decrease in the SOD measured. In addition, many investigators do not allow adequate equilibration periods for sediment stabilization following placement of a sediment into a test vessel; this oversight may yield erroneous results. Unfortunately, it is not common practice to measure some simple sediment parameters, such as pH and oxidation-reduction potential, both in the field and following transport to the laboratory. A comparison of values obtained in both situations is an easy means to ensure that sediment samples have not been adversely affected by the processes of acquisition, transport, and manipulation.

8. Laboratory methods that are currently available use many varieties of test container, ranging in size from Warburg respirometer flasks to large (up to 250 l) sediment-water interaction chambers; some of the latter devices hold sediment on the bottom and use the remaining volume over the sediment surface to duplicate the function of a field respirometer. Small vessels and their allied instrumentation are often used for very specific studies, i.e., oxygen uptake, carbon dioxide release, etc. These devices can also be used to differentiate between purely chemical oxygen consumption and that resulting from microbial respiration (for a discussion of this, see Gunnison, Chen, and Brannon 1983). Larger chambers may be used solely for oxygen consumption studies, but may also be used to monitor other parameters (Gunnison, Chen, and Brannon 1983; Brannon, Chen, and Gunnison 1985). Additional information on laboratory methods and their application may be found in Brewer, Abernathy, and Paynter (1977); Laffont, Capdeville, and Roques (1979, 1981); Bowman and Delfino (1980); and Belanger (1981).

9. There are many limitations to laboratory methods, several of which were described in the preceding paragraphs. In addition, laboratory methods, to a much greater degree than field methods, suffer because of the large variation in methodologies used by different investigators; this makes any comparison of results between studies difficult or impossible (Bowman and Delfino 1980; Gunnison, Chen, and Brannon 1983). Laboratory procedures are often oriented towards the basic aspects of the SOD issue, i.e., determining the chemical and biological processes that contribute to SOD--rather than being geared towards obtaining many SOD values for a number of different locations. Other studies have been designed to produce numerical values. However, these values are often intended for some specific purpose, such as for use in mathematical water quality models; this often influences what study is done, the manner in which the study is carried out, and the final form of the data. Such data may or may not be suitable for other uses.

APPENDIX B: BACKGROUND MATERIAL ON EQUILIBRIUM PARTITIONING

Sediment-Water (Interstitial Water) Equilibrium

1. The equilibrium state for adsorption and desorption reactions is dependent on the chemical and physical natures of the adsorbing substrate and the material being adsorbed. Major adsorption mechanisms binding organics to sediment particles include Van der Waals' forces, ion exchange, hydrophobic bonding, and other electrostatic bonding. These sorption processes have been described in various models, including Henry's Law, Langmuir's Law, the Freundlich Isotherm, and multilayer adsorption (e.g. double layer adsorption). Van der Waals' interaction is weak, and its influence decreases in proportion to the intermolecular distance. Hydrophobic bonding may be the major mechanism accounting for strong adsorption between sediment and hydrocarbons or other nonpolar organic compounds. These adsorption properties can also be modified by such environmental factors as pH, redox potential, sediment particle size, temperature, salinity, nature of the saturated cation on sediment, and structure of organic compounds.

2. Organic compounds, which have hydrophobic characteristics in an aquatic environment, normally demonstrate low water solubility and high retention by nonpolar fractions of organic matter in sediment through a partitioning effect. Any increase in the size of the hydrophobic portion of organic molecules relative to polar or coulombically interacting sites promotes partitioning of organics from water to the hydrophobic sites of sediment organic matter. Although Bailey, White, and Rothberg (1968)* suggested that a positive relationship should exist between water solubility and the extent of adsorption by clay minerals, overwhelming evidence indicates that soil organic matter is the prime determinant of organic substance adsorption (Lambert 1967). This relationship has also been shown to hold for sediment (Weber et al. 1983). Sorption reactions of organic pesticides in a sediment-water system were reviewed and discussed in detail by Browman and Chesters (1977). Partitioning of inorganic and organic substances to sediment or suspended sediment is, in general, a reversible process that can be quantified in terms of an equilibrium constant or partition coefficient (Zepp 1980;

* See References at the end of the main text.

DiToro and Horzempa 1982). Differences in the kinetics of sorptions which occur in the partitioning of organics onto aquifer sorbents also show that desorption is slower than adsorption in many cases (Isaacson and Frink 1984). After surveying the distribution of organic compounds in Elliott Bay (Puget Sound), Pavlou and Dexter (1979) reported that the sediment contained about 60,000 times more polychlorinated biphenyls (PCBs) than the overlying water. Similar sorption phenomena have been commonly observed in natural aquatic ecosystems where the concentration of solute is smaller than under equilibrium conditions in a pure water system.

3. The concentration ratio between the adsorbed phase and the aqueous phase is constant when an aqueous solution of organic compounds has been equilibrated with sediment. Equilibrium will be shifted by changes in concentration of substances in either phase, temperature, or other physical conditions. When the reaction reaches the equilibrium state, the partition coefficient K_p can be expressed as:

$$K_p = C_s/C_w \quad (B1)$$

where

C_s = absorbed concentration in the sediment

C_w = water concentration of a specific substance

This simple linear relationship holds true for low solute concentrations that are typically found in most environmental phase partitioning situations (e.g. sediment-water ecosystems), but becomes nonlinear at higher solute concentrations.

4. This relationship apparently holds true for most chemical compounds absorbed on sediment particles, even though solid-liquid partitioning in an aquatic system is more complex than simple equilibrium. O'Connor and Connolly (1980) reported that partition coefficients between water and sediment change as a function of solids concentration. Partition coefficients are inversely proportional to the concentration of solids for a wide range of organic compounds and metals. In a later study on adsorption of highly hydrophobic organics to sediment, DiToro and Horzempa (1982) demonstrated that the bonding of hydrophobic organics to sediment is different from simple phase partitioning. The sediment-organic interaction apparently involves binding by sediment organic carbon because desorption has a resistant component. Voice, Rice, and

Weber (1983) investigated the sorption characteristics of hydrophobic organic compounds by sediments and suspended solids and concluded that adsorption is proportional to the octanol/water partitioning coefficient of the solute and the organic carbon content of sediment. Consideration of organic carbon in solution or microparticulates improves the correlation between K_p and the octanol/water partition coefficient K_{ow} for suspended particulates. In a recent study, Gschwend and Wu (1985) concluded that variation of the distribution coefficient K_d as a function of solid-to-solution ratio observed in other studies was probably caused by nonsettling microparticulates which are buoyant organic complexes or colloidal associations of macromolecular organic compounds in solution.

5. When results are corrected for the effects of nonsettling microparticulates, both Chiou, Peters, and Freed (1979) and Gschwend and Wu (1985) showed that the K_d between water and sediment for hydrophobic organic compounds remains constant over a wide range of solid-to-solution ratios. Sorption reactions of hydrophobic organic compounds and freshwater sediment are rapid, and equilibrium occurs within 4 hr in most cases (Weber et al. 1983). Thus, an equilibrium state would be continuously maintained under natural environmental conditions (Browman and Chesters 1977).

6. The octanol/water partition coefficient is a distribution coefficient of solute monomers between an aqueous phase and a hydrophobic organic phase. Comparing estimated and measured partition coefficient data, Karickhoff (1981) developed a predictive, linear relationship between the octanol/water partition coefficient of the solute and the organic carbon content of the sorbent as follows:

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \quad (B2)$$

$$K_{oc} = 0.411 K_{ow} \quad (B3)$$

where K_{oc} is the organic partitioning coefficient. The concept of linear partitioning is assumed to be valid only at low concentrations of solute, or when the concentration of the solute is well below the aqueous solubility (Karickhoff 1981).

7. The partitioning of hydrophobic organic compounds between water and sediment particles depends on many environmental factors, which have been

described elsewhere (Browman and Chesters 1977). Evidence indicates that the amount of organic carbon in sediment appears to be the major factor controlling the partitioning of highly insoluble hydrophobic compounds such as polyaromatic hydrocarbons (PAHs) and PCBs (Zepp 1980; Browman and Chesters 1977). DiToro and Horzempa (1983) studied the adsorption of hexachlorobiphenyl (HCBP) onto lake sediment and concluded that partitioning appeared to be correlated with sediment surface area in addition to sediment organic matter content.

8. The fate and transport of organic contaminants in a sediment/water ecosystem depend largely on the sorptive nature of the sediment, particularly those sediments with appreciable organic matter content. Humic materials in sediment can significantly affect the fate of organic contaminants. Binding of organic contaminants such as DDT to humic acids has been shown to be much stronger than binding to fulvic acids (Carter and Suffet 1982). The binding constant K_b of nonpolar organic compounds to dissolved humic materials was defined by Josephson (1983) as follows:

$$K_b = \frac{\text{weight of contaminant/g of dissolved organic carbon}}{\text{weight of contaminant/g of water}} \quad (B4)$$

There are large differences in binding constants among humic and fulvic acids from different sources. Adsorption of hydrophobic organic compounds onto clay particles is of less magnitude than adsorption onto organic matter because the adsorption mechanisms for sorption on clays are generally hydrogen binding and van der Waals' forces (Browman and Chesters 1977; Herbes 1977). The adsorption capacities (at 50-percent solubility) for PAHs onto different adsorbents were summarized by Walters and Luthy (1984). By studying the adsorptive behavior of many PAHs, Walters and Luthy (1984) suggested that adsorption at a low equilibrium concentration is governed by factors which influence partitioning, while adsorption at a high equilibrium concentration is governed by factors which influence solubility.

9. Release rates of particulate bound PCBs from contaminated sediment have been shown to be a function of sediment concentration, chlorine substitution pattern, and degree of chlorination (Fisher, Petty, and Lick 1983). Release of PCBs from the sediment to the overlying water is enhanced by sediment resuspension and bioturbation. Because of the high affinity for sediment

of PCBs and some PAHs with low water solubility, distribution of these organics in the aquatic environment is mainly dominated by wave or tidal action and depositional processes (Herrman and Heubner 1982). Distribution of other PAHs with high water solubility and low partitioning coefficients, however, is not affected by sediment transport or resuspension, but instead is affected by volatility (Readman et al. 1982).

10. Release of trace metals from sediment to the overlying water is a complex process and is also affected by many environmental variables. Redox potential and pH are two of the most important factors that affect the partitioning of trace metals between water and solids (Ponnamperuma 1972). (See Part VI for a detailed explanation.) Precise and accurate means of measuring the partitioning of metals are not currently available. Empirical distribution coefficients have been determined by measuring the distribution of trace metal concentrations between sediment and interstitial water and normalizing to the organic carbon content of the sediment (JRB Associates 1984). This approach has not been generally accepted because there are many factors in addition to organic carbon content of the sediment that can affect partitioning of trace metals into the interstitial water. These factors include such parameters as concentrations of iron and manganese oxides which have been consistently implicated as affecting the behavior of trace metals in the environment. Equilibrium partitioning of trace metals has, therefore, not been addressed in this document.

Water/Sediment/Animal Equilibrium

11. Accumulation of organic pollutants by aquatic organisms has become a matter of concern since early 1970. The bioconcentration factor of an organic compound in aquatic organisms can generally be measured in two ways:

- a. Expose a target aquatic organism to a aqueous solution containing organics in a static or flow-through system until steady-state is determined by no further change in concentration C_t of the organic compound in the aquatic organism.
- b. Expose a target organism in a static or flow-through system for a short interval during which both water and organism samples are taken at several time intervals. The organism is then depurated and K_1 , the adsorption rate constant, and K_2 , the depuration rate constant, are calculated (Banerjee, Sugatt, and O'Grady 1984). The bioaccumulation factor (BCF) can then be expressed as the ratio K_1/K_2 . A modified method which uses

time sequence sampling during the uptake phase, but which stretches out the exposure period (i.e. up to 18 to 30 days) while holding water concentration constant, is recommended to use for obtaining primary information for use in first-level evaluations (McFarland 1984). Various aquatic organisms are able to accumulate PCBs from the surrounding water; the bioaccumulation of PCBs in typical aquatic organisms ranges from a bioconcentration factor of 300 to 61,000 (Gooch and Hamdy 1983; Banerjee, Sugatt, and O'Grady 1984).

12. The sediment-biota equilibrium partitioning approach has been used recently by the US Environmental Protection Agency and US Army Corps of Engineers as a tool for assessing the bioaccumulation effects of hydrophobic or neutral organic compounds on selected aquatic organisms. By using a flow-through system to assess bioavailability of organic chemicals in sediments, McFarland (1984) recently developed semiempirical relationships and theory from molecular thermodynamics to improve the technique used in evaluating bioaccumulation potential. A thermodynamic bioaccumulation potential (TBP) can be generated by the following equation:

$$\text{TBP} = (\text{Cs}/\text{foc})/0.52 \quad (\text{B5})$$

where

TBP = the equivalent concentration of organics in an organism lipid, ppm

Cs = the chemical concentration in the sediment, ppm

foc = the decimal fraction organic carbon in the sediment

The factor of 0.52 was obtained by calculating data reported by other studies. A preference factor of 0.58 should be measured if calculated at the geometric mean log (Kow) of the two data sets rather than at y-intercept.*

13. Most organic contaminants, such as PCBs, are insoluble or slightly soluble in water, but are associated with the organic carbon matrix on sediment. For organisms that live in or on contaminated sediment, the contaminants adsorbed in the sediment may be the controlling factor with regard to bioaccumulation potential.

* Personal Communication, Victor McFarland, 1985, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.

14. The bioconcentration of PCBs is considered to be the result of competitive uptake and depuration processes which normally follow first-order kinetics (Shaw and Connell 1984). At equilibrium, the total bioconcentration should be directly related to the partition coefficient. In a study on the bioconcentration of PCBs using carbon-14 labeled PCB (Aroclor 1254), Gooch and Hamdy (1983) confirmed the statement presented by Richardson and Waid (1979) that direct uptake of PCBs from water is the major route of entry into fish. Localized distribution of PCBs and other organic compounds in fish (e.g., head, fins, and liver) after exposure to these chemicals in water was also detected (Richardson and Waide 1979; Gooch and Hamdy 1983). Bioaccumulation of PCBs and other organics involved not only partitioning between lipids in the organism and the surrounding organics, but also included surface adsorption and efficiency in passage through membranes (Shaw and Connell 1984). Bioaccumulation of organics is a complicated process that involves the movement of many individual organics such as PCB compounds (possibly up to 209 individual compounds) through an external membrane to the interior of the organism. Since great differences in the bioconcentration of closely related organic isomers (such as PCBs) by the same aquatic organism have been documented (Courtney and Denton 1976), the actual uptake process of organics by tested organisms is obviously complex. Results of recent bioconcentration studies indicated that the maturity of the fish (Gooch and Hamdy 1983), membrane permeability, and lipid content of the organisms are probably the major limiting factors for bioconcentration. These processes become more complex as they also involve many sorption processes which occur at the surface of the organisms (Woodburn, Doucette, and Andren 1984).

15. The octanol/water partitioning coefficient has been widely used to predict the extent of bioconcentration of organic pollutants. Based upon results obtained from bioassay studies, a log-log correlation between the octanol/water partitioning coefficient and the bioconcentration factor by aquatic organisms was observed (Neely, Branson, and Blau 1974; Chiou et al. 1977; Mackay 1982). Kenaga and Goring (1980) also developed regression equations to describe the relationship among sediment, overlying water, and bioaccumulation as follows:

$$\log \text{BCF} = -1.495 + 0.935 \log \text{Kow}$$

$$\log \text{Koc} = 1.377 + 0.544 \log \text{Kow} \quad (\text{B6})$$

$$\log (\text{BCF}/\text{Ksed}) = -2.872 + 0.391 \log (\text{Kow}) + \log (\% \text{ organic content})$$

where Ksed is the sediment partitioning coefficient.

16. Evaluation of the bioconcentration effects on aquatic organisms was performed by conducting a statistical analysis on the field data from Puget Sound and the New York Bight. Conner (1984) summarized the evaluation and concluded that relying on octanol/water partitioning coefficients to make accurate predictions on bioconcentration of DDT and PCBs in aquatic organisms in the field is not currently feasible. The concentration of organic contaminants in bottom fish correlates well with the sediment concentrations of these compounds. However, the degree of bioaccumulation is also affected by the retention time of contaminated water to the testing organisms and mixed-function oxygenase of the aquatic organism (Conner 1984). Based on liquid solute solubility or the corrected solid solute solubility theory from a physical-chemical viewpoint, Mackay (1982) developed a one-constant correlation equation that gave a satisfactory fit of the available hydrophobic organics data for fish.

APPENDIX C: PROCESSES AFFECTING CONTAMINANT FATE

Transport and Transfer Processes

Transport

1. The Grand Calumet River/Indiana Harbor Canal (GCR/IHC) system is extremely dynamic, as evidenced by rapid changes and reversals that occur in flow patterns. Accurate prediction of ultimate contaminant fates may depend largely upon adequately characterizing the system's hydrodynamics as the first step. A major consideration in the selection of contaminant models is the ease of utilization of hydrodynamic results (hydrodynamic simulations are discussed in Part X). Dimensionality and discretization of the models are critical. If segmentation is different, such as between box contaminant models and finite difference hydrodynamic codes or between time steps, then spatial and/or temporal averaging of hydrodynamics must be performed before their use in contaminant models. If hydrodynamic data are numerically averaged, then numerical accuracy must not be compromised. Transport to and from the sediment-water interface via advective and diffusive mechanisms must also be adequately characterized.

Particle transport

2. Toxic materials are often strongly associated with particles, and particle transport mechanisms may markedly affect the fate of a contaminant. Contaminant models vary in the detail with which they describe sediment transport, and sediment transport effects can be determined using the selected model's existing structure. However, a preferable approach may be to couple, or "piggyback," the contaminant and sediment transport models. The ease with which this coupling can be accomplished is an important consideration in the selection of contaminant models.

Ionization and complexation

3. Inorganic and many organic contaminants occur as functional groups which disassociate to yield charged species. Metal ions may also combine with inorganic and organic ligands to form stable metal-ligand complexes. The degree of toxicity that a contaminant exerts may largely depend on its speciation. For example, the free (unbound) metal species are generally considered the most toxic (Allen, Hall, and Brisbin 1980; Fontaine 1984).^{*} Depending on

^{*} See references at the end of the main text.

the species present, this may result in waters with higher contaminant concentrations being less toxic than those of lower concentrations (Florence 1980). Differences in speciation chemistry between metals and trace organics may preclude their being treated by the same contaminant model. Speciation of metals is usually determined by multiligand, multimetal equilibrium models. Under certain simplifying assumptions, single metal models may be used. However, prediction of critical factors such as pH, redox potential, and total metals concentrations, as well as concentration of sorbing materials and inorganic and organic ligands, must be obtained, either through field measurements or by water quality models. Some models primarily intended for synthetic organics, such as EXAMS, do allow for consideration of ionic species, while others consider only the unionized forms.

Sorption

4. The characterization of contaminant adsorption/desorption onto surfaces is extremely important in evaluating the impact of sediment-water interactions on water quality. Sorptive processes vary within and between various contaminant groups, and care must be exercised in selection of contaminant models to ensure that they adequately describe sorption processes and that the individual contaminants are properly characterized. For example, most contaminant models assume local equilibrium and reversibility; that is, the same sorption isotherm describes adsorption and desorption. However, various species of polychlorinated biphenyls (PCBs) are adsorbed at different strengths (DiToro and Horzempa 1982; DiToro, Horzempa, and Casey 1983). If strongly and weakly adsorbed fractions are not simulated separately, then the assumption of reversibility is not valid. The adsorption models also vary in their applicability, such as between neutral and ionic contaminants. For example, the adsorption of many neutral organics depends upon the organic carbon content of the solids requiring the use of a carbon-normalized partition coefficient.

5. Sorption processes for ionic species, such as metal cations or organic acids and bases, may depend upon competition for available surface sites. These sorption processes are often strongly affected by pH and redox potential. A pH variation of only 0.5 may often make the difference between complete adsorption and complete desorption (Florence 1980). Therefore, isotherms determined at one pH value may be drastically different from those determined at another. A variety of models have been used to describe pH and

other effects upon adsorption of inorganic cations (Anderson and Rubin 1981; Martin, Batchelor, and Chapra 1985). Competitive isotherm models using the cation exchange capacity have often been used to describe sorption of organic cations. Sorption can also vary with sediment size or mass. Toxic models vary in the number of size fractions of sediments allowed from one to five. Other models require that sediment information be provided as an input variable. Adsorption can occur onto suspended sediments or directly onto the sediment bed when contaminant concentrations are high, and desorption can occur when contaminant water concentrations are low. Sediment-water interactions are described in most models of synthetic organics.

Interactions with benthic subsystems

6. The mixing of the sediments by organisms (bioturbation) can affect particle and toxic material distributions. Physical disturbances of the sediment and irrigation of the sediments by benthic organisms are often treated as diffusional processes and require estimation of biodiffusion coefficients. Gas bubbles released from sediments may also contribute to sediment mixing.

Biosorption and bioaccumulation

7. Biosorption, the adsorption/desorption of contaminants onto a living organic surface, is often treated similarly to sorption onto inorganic surfaces or is described by a simple partition coefficient. Bioaccumulation is not explicitly described in the majority of contaminant models, and must be estimated from predicted concentrations in various compartments and partition coefficients.

Volatilization

8. Transfer of materials across the air-water interface can result in gains or losses of contaminants to the system. For example, air-water exchange can serve as the major source of PCBs to some aquatic systems. Interfacial exchange of contaminants is usually simulated using Whitman's two-film or two-resistance theory coupled with expressions to determine the transfer rate. The transfer can be controlled primarily by the gas film or the liquid film at the interface, depending upon the solubility or vapor pressure of the material. Most PCBs are liquid controlled while compounds such as dieldrin and lindane are gas controlled. Some contaminant models do not include gas film limited transfer, and care must be exercised in their use. Volatilization is primarily important in simulations of organic

contaminants; however, volatilization of mercury is included in some modeling schemes.

Transformation Processes

Photolysis and oxidation

9. Photolysis refers to the breakdown or transformation of chemicals due to the radiant energy of light. This action can be directly due to the radiant energy (direct photolysis) or may be enhanced due to sensitization of other materials in the water such as humic materials (indirect photolysis). The result of indirect photolysis is that the breakdown can occur at a greater rate in natural water than in distilled water. The description of photolysis is based upon first describing the distribution of light of various wavelengths with depth. Once this is accomplished, photolysis rates can be estimated using information upon the efficiency of reactions due to absorption of light or reaction quantum yields, the specific light absorption rate, and the contaminant concentration integrated over a given depth. Chemical oxidation of organic toxicants results from interactions with free radicals such as alkylperoxy radicals, hydroxyl radicals, and oxygen. Free radicals may often be formed as a result of photolysis. Chemical oxidation is often modeled as a second-order process, requiring a rate constant and the concentration of the free radicals, as well as the toxic organic.

Biodegradation

10. Biodegradation of aquatic toxicants encompasses a variety of processes and can result in eliminating or actually enhancing the toxicity of the material. However, only microbial degradation is considered in most modeling schemes. Biotransformation by higher organisms is described in relatively few models.