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DISPOSAL ALTERNATIVES FOR PCB-CONTAMINATED SEDIMENTS FROM INDIANA HARBOR, INDIANA

Volume II

by

Environmental Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Indiana Harbor and Canal are part of a small, highly industrialized watershed in northwestern Indiana. The Grand Calumet River discharges into Lake Michigan via the Indiana Harbor and Canal. These waterways have a history of water quality problems and have been identified by the International Joint Commission on the Great Lakes as a major area of concern. The Corps of Engineers is authorized to maintain a deep-draft navigation project at Indiana Harbor and Canal. Two reaches of the navigation channel contain sediments with concentrations of polychlorinated biphenyls (PCBs) above 50 ppm. In addition, the sediments contain elevated concentrations of metals and other organic contaminants.

The purpose of this study was to evaluate alternative methods for dredging and disposing of the PCB-contaminated sediments from Indiana Harbor using appropriate testing protocols. The US Army Engineer Waterways Experiment Station has developed a management strategy for disposal of dredged material which describes a logical sequence for testing and

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Contaminants
Control measures
Disposal alternatives
Dredged material disposal
Dredging
Indiana Harbor
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19. ABSTRACT (Continued).

evaluation of disposal alternatives and a decisionmaking framework for logical application of the management strategy. These served as the basis for the testing and decisionmaking described in this study.

Three disposal alternatives (contained aquatic disposal (CAD) and two confined disposal alternatives) were identified for the PCB-contaminated sediments and evaluated to determine technical feasibility and control measures required for implementation. The magnitude and possible impacts of specific dredging and disposal problems were evaluated using appropriate testing protocols. These protocols included those for effluent quality, surface runoff quality, leachate quality, and direct uptake by plants or animals. Since there was no routinely applied laboratory testing protocol to predict leachate quality from dredged material confined disposal facilities (CDFs), research was conducted to develop a leaching test protocol. Additional research was performed to simplify and significantly reduce the costs of testing for evaluating surface runoff water quality in CDFs. Tests were conducted for use in evaluating the thickness of cap required to isolate contaminated sediments from the overlying water column and from aquatic and benthic biota. Innovative disposal alternatives and management techniques that were evaluated included confined disposal with appropriate restrictions and capping of contaminated sediments after controlled placement in the aquatic environment.

The feasible disposal alternatives identified for the PCB-contaminated sediments included CAD, in-lake CDF disposal, and upland confined disposal. With appropriate dredging equipment, disposal site designs, and contaminant control measures, any of the three disposal methods could be used to provide environmentally sound disposal of the PCB-contaminated Indiana Harbor sediments.

PREFACE

The research studies described in this report were conducted to evaluate the dredging and dredged material disposal requirements for the PCB-contaminated sediments in Indiana Harbor, Indiana. The research was conducted by laboratories of the US Army Engineer Waterways Experiment Station (WES). Funding was provided by the US Army Engineer District, Chicago, under Intra-Army Order for Reimbursable Services No. NCC-IA-85-11, dated 30 October 1984. The Chicago District Project Manager for the studies was Mr. Shamel Abou-El-Seoud.

The studies were conducted by researchers of the WES Environmental Laboratory (EL), Hydraulics Laboratory (HL), and Coastal Engineering Research Center (CERC). The main text (Parts I-VI) is included in Volume I. Appendixes A-J are presented in this volume. Appendixes A, B, and C were written by Dr. Paul R. Schroeder, EL. Appendix D was written by Drs. Bobby L. Folsom, Jr., John W. Simmers, Stratford H. Kay, and Messrs. Richard G. Rhett and Don K. Crawley, EL. Appendix E was written by Mr. John G. Skogerboe, EL. Appendix F was written by Drs. Douglas L. Gunnison, James M. Brannon, and Messrs. Thomas G. Sturgis and Issac Smith, Jr., EL. Appendix G was written by Drs. Brannon, Dixie M. Griffin, Jr., and Mr. Tommy E. Myers, EL. Appendix H was written by Mr. Myers and MAJ James M. Betteker, EL. Appendix I was written by Messrs. Walter E. Pankow and Michael J. Trawle, HL. Appendix J was written by Mr. James E. Clausner and Dr. Charles E. Abel, CERC.

The WES Study Manager was Dr. Raymond L. Montgomery, Chief, Environmental Engineering Division, EL. This work was coordinated with other dredging studies by Dr. Robert M. Engler, Manager, Environmental Effects of Dredging Programs, EL.

The work was conducted under the general supervision of Dr. John Harrison, Chief, EL.

COL Dwayne G. Lee, CE, was Commander and Director of WES, and Dr. Robert W. Whalin was Technical Director.

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CONTENTS

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:

Multiply	By	To Obtain
acres	4,046.873	square metres
acre-feet	1,233.489	cubic metres
cubic feet	0.02831685	cubic metres
cubic feet per second per foot	0.093	cubic metres per second per metre
cubic yards	0.7645549	cubic metres
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*
feet	0.3048	metres
gallons	3.785412	cubic decimetres
horsepower (550 foot-pounds (force) per second)	745.6999	watts
inches	2.54	centimetres
knots (international)	0.5144444	metres per second
miles (US statute)	1.609347	kilometres
pounds (force) per square inch	6.894757	kilopascals
pounds (mass)	0.4535924	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic metre
pounds (mass) per square foot	4.882428	kilograms per square metre
square inches	6.4516	square centimetres
yards	0.9144	metres

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* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9)(F - 32)$. To obtain Kelvin (K) readings, use $K = (5/9)(F - 32) + 273.15$.

DISPOSAL ALTERNATIVES FOR PCB-CONTAMINATED SEDIMENTS FROM INDIANA HARBOR, INDIANA

APPENDIX A: SEDIMENTATION AND FILTRATION

Settling Test Results

1. A flocculent settling test and a 15-day initial storage test were performed on a 100-g/ℓ suspension of the composited Indiana Harbor sediment. The suspension was not sieved or hydraulically separated to remove the sand prior to the tests. The sediment was about 35 percent sand as shown in Figure A-1.

2. The procedure used in the flocculent test was to dilute the composited sediment having an initial solids concentration of about 740 g/ℓ with tap water to a concentration of 100 g/ℓ. The resulting slurry was mixed well in a barrel and then pumped into a 7-ft tall, 8-in.-diam acrylic column to a depth of about 6 ft while mixing the slurry in the barrel and bubbling air through the slurry in the column to keep the solids in suspension. Samples were then taken periodically from the slurry in the column at various depths. The solids concentrations of these samples were measured and are reported in Table A1 and plotted in Figure A2.

3. The 15-day initial storage test, also known as the compression settling test, was performed in conjunction with the flocculent settling as a continuation of that test. In this test the height of the interface after forming between material that had settled from the slurry and the supernatant that formed during the test was measured as a function of the time that elapsed since the start of the test. These data are reported in Table A2. Using the ratio of the initial slurry depth in the column to the height of the interface, the average solids concentration of the settled material below the interface was determined and also reported in Table A2. These concentrations were plotted in Figure A3 as a logarithmic function of the elapsed time when the interface height was measured.

Sedimentation Analysis

4. The following evaluation of sedimentation design was made using procedures given in Palermo, Montgomery, Poindexter (1978) and Palermo

Table A1

Solids Concentrations* During Flocculent Settling Test

Time hr	Surface Height, ft	Sample Locations: Height Above Bottom of Settling Column, ft									
		6.0	5.65	5.35	4.65	4.0	3.35	2.65	2.0	1.5	1.0
0.0	6.255	Initial Solids Concentration = 100 g/ℓ									
1.0	6.220	14.70	-	67.4	78.00	78.50	88.00	94.20	96.10	106.0	110.3
2.0	6.185	10.60	-	10.70	70.40	80.90	84.80	91.30	96.8	100.9	113.6
4.0	6.150	7.10	-	7.50	7.20	7.30	78.40	92.70	111.9	140.7	187.6
12.0	6.110	4.40	-	4.30	4.20	4.20	4.80	4.30	197.3	216.5	231.4
24.0	6.070	4.60	-	3.30	3.30	3.30	3.40	3.40	190.0	231.9	-
48.2	6.010	1.60	-	2.50	2.50	2.50	2.50	2.50	22.90	249.0	-
96.0	5.930	-	1.70	1.80	1.90	1.80	2.00	1.90	1.90	254.7	-
167.5	5.856	-	1.20	1.40	1.50	1.50	1.60	1.60	1.60	47.7	-
263.5	5.730	-	0.82	1.10	1.30	1.40	1.40	1.40	1.40	6.80	-
335.0	5.648	-	-	0.91	1.20	1.30	1.30	1.30	1.30	1.50	-

---

* In grams per litre.

Table A2

15-Day Compression Settling Test Results*

Elapsed Time, hr	Interface Height, ft	Solids Concentration Below Interface g/ℓ
0.0	-	-
1.0	-	-
2.0	-	-
2.5	-	-
3.0	-	-
4.0	3.79	163
5.0	3.32	185
5.5	3.05	202
6.3	2.80	220
12.0	2.40	255
24.0	2.242	271
26.0	2.203	276
27.5	2.192	277
29.0	2.180	278
48.2	2.070	290
72.0	1.965	306
96.0	1.910	310
119.5	1.830	324
144.2	1.790	331
167.5	1.765	336
191.0	1.710	347
263.5	1.655	358
287.0	1.640	362
311.5	1.630	364
335.0	1.618	366
359.0	1.605	369

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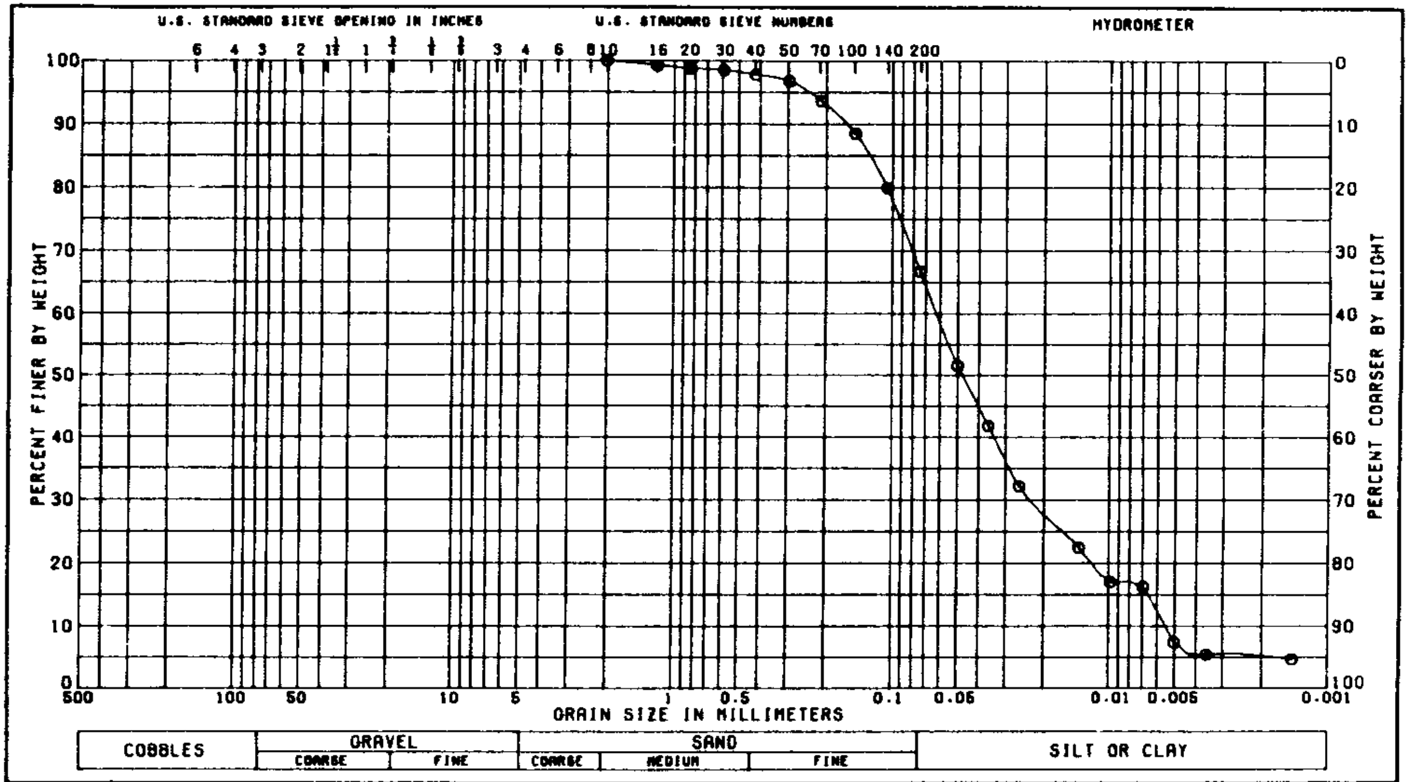
* Initial height of slurry = 6.255 ft. Initial solids concentration = 100 g/ℓ.



LL	PL	PI	GS 2.71	NAT W.%	

CLASSIFICATION

GRADATION CURVE

PROJECT INDIANA HARBOR SEDIMENTS

BORING NO. -
SAMPLE NO. 1
DEPTH/ELEV -
DATE 26 JUN 85

Figure A1. Engineering properties of sediment

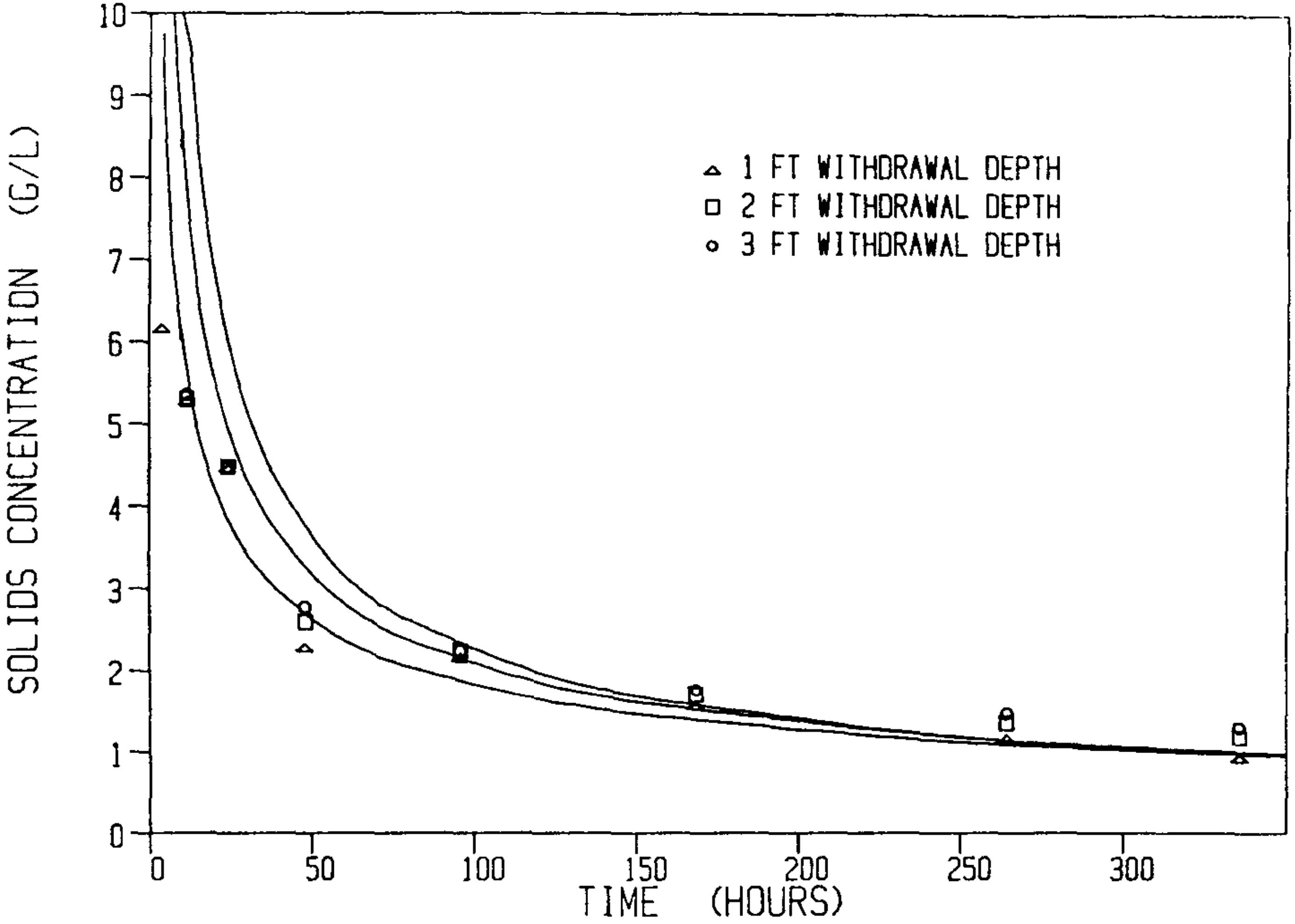


Figure A2. Flocculent settling test results

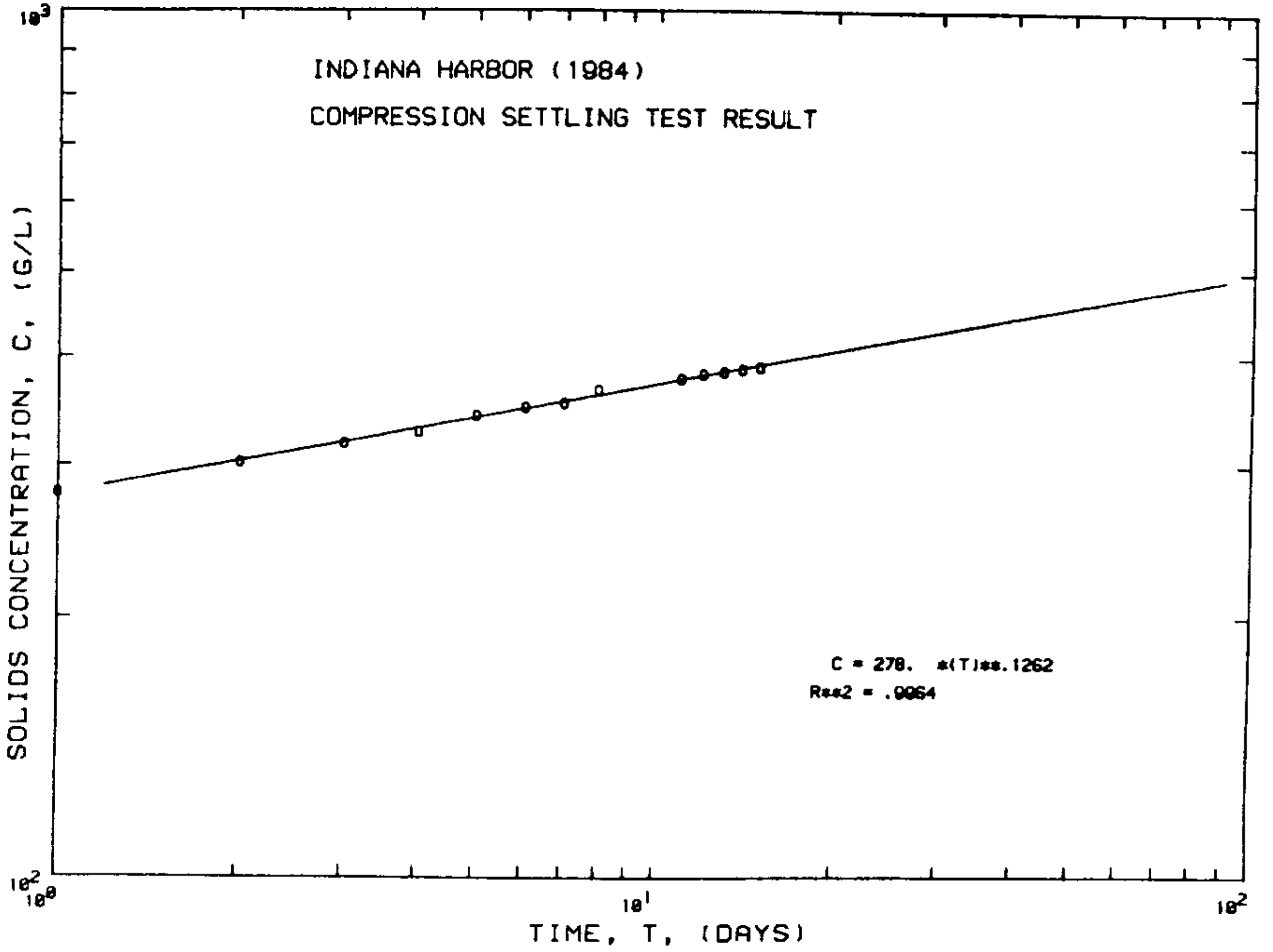


Figure A3. Compression settling test results

(1985).* This analysis will be used to determine the settling requirements for the disposal of the PCB-contaminated sediments to an in-lake CDF of a design as originally proposed for moderately and heavily polluted sediments from Indiana Harbor.

Flow rate

5. For the disposal of mechanically dredged materials, the flow rate will be roughly equal to the production rate, which is assumed for this analysis to be 200,000 cu yd per 2 month project duration (U.S. Army Engineer District, Chicago 1986). This corresponds to 3,700 cu ft/hr or approximately 1.0 cfs. For hydraulic dredging the flow rate will be from four to six times as great but probably not more than 5 cfs on the average with a matchbox dredge.

In situ concentration

6. The in situ void ratio is:

$$e_i = \frac{wG_s}{S_D}$$

$$= \frac{(88\%)(2.69)}{100\%} \qquad (A1)$$

$$= 2.37$$

where

e_i = in-situ void ratio of sediment
w = water content of sediment, percent
G_s = specific gravity of sediment solids
S_D = degree of saturation, percent

The corresponding suspended solids concentration for this void ratio is

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* See References at the end of the main text (Vol I).

$$C_i = \frac{G_s \gamma_w}{e_i + 1} = \frac{(2.69)(1{,}000\ g/\ell)}{2.37 + 1} = 798\ g/\ell \qquad \text{(A2)}$$

where

C_i = in-situ suspended solids concentration

γ_w = specific weight of water, g/ℓ

Settling results

7. If the dredged material is hydraulically transported from the scows by slurrying with water from the confined disposal facility CDF, it is assumed in this evaluation the sediment will be diluted to an influent suspended solids concentration, of less than 100 g/ℓ. At this concentration, flocculent settling controlled the sedimentation of the slurry mass. The results of the settling tests are shown in Figures A2 and A3.

8. The slurry concentration resulting from hydraulic dredging by a matchbox dredge is expected to be 100 g/ℓ based on the results of the matchbox dredge demonstration in Calumet Harbor which produced an average of 98 g/ℓ. For this evaluation, the slurry concentration will be assumed to be equal to the results of the demonstration. The settling should be very similar to the results given above for hydraulic transfer from scows. The concentration of suspended material following hydraulic disposal can be reduced by carefully placing the material on the bottom using a submerged diffuser. This concentration may be as low as 2 to 7 g/ℓ based on the results of the demonstration of the matchbox dredge and submerged diffuser.

9. A minimum ponding depth of 1 ft is assumed during the end of the disposal operation. This condition represents the worst case for settling, producing an acceptable effluent quality and stressing the filter system.

10. Mechanical transfer of mechanically dredged material from scows to the CDF would yield a drastically different supernatant and deposited material in the CDF as compared with hydraulic transfer or dredging. The resuspension of dredged material and contaminants and dilution of the deposited material would be reduced very significantly. The concentration of deposited material will

probably be greater than 600 g/ℓ and the concentration of suspended solids in the supernatant near the influent may be less than 50 mg/ℓ if a sluice is used to deposit the material. The conditions resulting from mechanical placement are very favorable to producing a good effluent and the effluent quality would be very significantly better than the following estimates for hydraulic disposal. Settling tests and tests to predict effluent quality for mechanical dredging have not been developed, but it is apparent from observations made at the Calumet Harbor disposal operation that significantly less resuspension and contaminant release would occur.

Initial storage requirements

11. The design concentration for storage of hydraulically disposed material obtained from the 15-day settling test using a design time of 30 days (one half of the project duration of 2 months) is 380 g/ℓ based on the settling test conducted on the homogenized sample during December 1984.

12. The homogenized sample was 33-percent sand and 67-percent fine-grained material. At the end of each disposal operation for 200,000 cu yd of sediment, the volume of the resulting lift will be

$$
\begin{aligned}
V_f &= V_i\ (C_i/C_f) + V_{sd} \\
&= (0.67)\ (200{,}000 \text{ cu yd})\ (798 \text{ g/ℓ} \ / \ 380 \text{ g/ℓ}) \qquad \text{(A3)} \\
&\quad + (0.33)\ (200{,}000 \text{ cu yd}) \\
&= 347{,}000 \text{ cu yd or } 215 \text{ acre-ft}
\end{aligned}
$$

where

V_f = volume of new lift at end of each disposal operation, cu yd

V_i = volume of in-situ sediment to be dredged, cu yd

C_f = concentration of newly settled material at end of each disposal operation, g/ℓ

V_{sd} = volume of newly settled sand at end of each disposal operation, cu yd

13. The average dike height above lake bottom of the proposed in-lake CDF will be about 35 ft (US Army Engineer District, Chicago 1986). The height of settled material in the CDF prior to placement of the final lift is unknown and dependent on the area of the CDF. Therefore, the minimum surface area

based on storage cannot be determined. If the previously deposited material consolidated to the in-situ concentration, the minimum volume required for storage would be the sum of the volume of sediment previously dredged (1,200,000 cu yd) and the volume for new storage (347,000 cu yd), totaling 1,550,000 cu yd or 965 acre-ft. Allowing a minimum of 3 ft of freeboard and 2 ft of ponding, the maximum height for storage is about 30 ft. Therefore, the minimum area required for storage is 32 acres (965 acre-ft/30 ft). Additional area would be required for the dikes and if less consolidation occurs.

14. The volume required for storage of mechanically disposed material would be approximately equal to the volume placed in the CDF. If it is assumed that the concentration of disposed material is 600 g/ℓ, the initial storage volume required for new lift of 200,000 cu yd of sediment would be

$$\begin{aligned} V_f &= V_i\ (C_i/C_f) \\ &= (200{,}000 \text{ cu yd})\ (798 \text{ g/}\ell/600 \text{ g/}\ell) \qquad \text{(A4)} \\ &= 266{,}000 \text{ cu yd or } 165 \text{ acre-ft} \end{aligned}$$

The resulting area required for storage would be only about 1.5 acres smaller than for hydraulic disposal.

Required area for effective zone settling

15. The minimum surface area required for effective zone settling following hydraulic disposal is determined from the results of the settling tests performed in 1980 (US Army Engineer Waterways Experiment Station 1980). This evaluation is not necessary for mechanical disposal. The maximum solids loading rate corresponds to the influent solids loading rate:

$$\begin{aligned} S_{d(max)} &= C_i V_{si} \\ &= (9.36 \text{ lb/cu ft})\ (0.30 \text{ ft/hr}) \qquad \text{(A5)} \\ &= 2.8 \text{ lb/sq ft-hr} \end{aligned}$$

where

$S_{d(max)}$ = maximum solids loading rate
V_{si} = zone settling velocity at the influent concentration, C_i

The solids loading rate determined graphically using the solids loading curve and the design concentration of 470 g/ℓ is 3.8 lb/sq ft-hr. Since this is greater than $S_{d(max)}$, the design loading rate is 2.8 lb/sq ft-hr. Therefore, the required surface area for zone settling is

$$A = \frac{Q_i\ C_i}{S_d}$$

$$= \frac{(3690\ \text{cu ft/hr})\ (9.36\ \text{lb/cu ft})\ (800\ \text{g/}\ell)}{2.8\ \text{lb/sq ft-hr} \qquad (150\ \text{g/}\ell)} \qquad \text{(A6)}$$

$$= 6{,}5800\ \text{sq ft or } 1.5\ \text{acres}$$

where

A = surface area

Q_i = discharge rate

C_i = influent concentration

S_d = design solids loading rate

Considering inefficiencies in basin hydraulics, the required area would be

$$A_d = (\text{HEF})(A)$$

$$= 2.25\ (1.5\ \text{acres}) \qquad \text{(A7)}$$

$$= 3.4\ \text{acres}$$

where

A_d = design surface area for zone settling

HEF = hydraulic efficiency correction factor

Required area and detention for flocculent settling

16. The slurry mass settles by flocculent settling at concentrations of fine-grained material below about 70 g/ℓ (US Army Engineer Waterways Experiment Station 1980). A flocculent settling test was performed on a 63-g/ℓ slurry of fines in 1980 (US Army Engineer Waterways Experiment Station 1980) and on a 100-g/ℓ slurry that was about 35-percent sand in December 1984. In the first test a 6-hr detention resulted in an effluent having 250 mg/ℓ

suspended solids, an overall removal of 99.6-percent of the influent solids. In the latter test a 96-hr detention was required to reduce the suspended solids to less than 2 g/ℓ and after 336 hr 1.2 g/ℓ of solids still remained suspended. The two tests show significantly different results, illustrating the variability of the sediments. To be conservative in this evaluation, the latter test results will be used in this sedimentation analysis and the filter design evaluation for the alternatives using hydraulic disposal. The results of this analysis apply only to hydraulic disposal.

17. A minimum detention of 96 hr is indicated as necessary from the flocculent settling test. Since basins are not perfectly hydraulically efficient, the design theoretical detention time is computed as follows:

$$\begin{aligned} T &= (\mathrm{HEF})T_d \\ &= (2.25)(96\ \mathrm{hr}) \qquad \text{(A8)} \\ &= 216\ \mathrm{hr\ or\ 9\ days} \end{aligned}$$

where

T = design theoretical detention time

HEF = hydraulic efficiency correction factor

T_d = laboratory detention time or field mean detention time

This detention time should be sufficient to achieve a supernatant having 2 g/ℓ suspended solids.

The volume of ponding required for flocculent settling is

$$\begin{aligned} V_{pd} &= Q_i T \\ &= (3690\ \mathrm{cu\ ft/hr})\ (216\ \mathrm{hr})\ (800\ \mathrm{g/\ell})/(150\ \mathrm{g/\ell}) \qquad \text{(A9)} \\ &= 4{,}250{,}000\ \mathrm{cu\ ft\ or\ 97.6\ acre\text{-}ft} \end{aligned}$$

where

V_{pd} = volume of ponded supernatant

Q_i = influent flow rate

Assuming a minimum ponded depth of 2 ft, the maximum ponded surface area required for flocculent settling is

$$
\begin{aligned}
A_{pd} &= V_{pd}/H_{pd} \\
&= (97.6 \text{ acre-ft})/(2 \text{ ft}) \qquad \text{(A10)} \\
&= 48.8 \text{ acres}
\end{aligned}
$$

where

A_{pd} = ponded surface area
H_{pd} = ponded depth

Based on this analysis, clarification controls the required surface area if flocculent settling occurs; storage requirements control the required surface area if zone settling occurs.

Supernatant suspended solids concentration

18. Comparisons of the areas required for storage, zone settling and flocculent settling show that storage controls the size of the minimum surface area for all three alternatives if zone settling occurs as expected. Therefore, the required surface area should be about 35 to 40 acres assuming a dike height of 35 ft and effective consolidation. Consequently, the ponded volume will be greater than the volume required to achieve a supernatant having 2 g/ℓ of suspended solids following hydraulic disposal from scows. The ponded volume will be about 80 acre-ft (40 acres × 2 ft of ponding). The detention time will be about 708 hr (80 acre-ft × 4,3560 sq ft/acre × 600 g/ℓ/800 g/ℓ/ 3690 cu ft/hr) for mechanical dredging and about 177 hr for hydraulic dredging. The field mean detention time will be about 315 hr (708 hr/2.25) and 79 hr, respectively. The supernatant following settling for this detention time will contain about 1.3 g/ℓ of suspended solids for hydraulic transfer from scows and about 2.1 g/ℓ for hydraulic dredging. If zone settling occurs, the supernatant will contain only about 400 mg/ℓ of suspended solids. Laboratory tests were not performed specifically for the prediction of suspended solids concentration of the supernatant following settling for the mechanical disposal. The supernatant quality for this alternative can only be estimated using the flocculent settling tests results and field measurements as a guide. Based on those results and the expected resuspension

by this disposal method, the estimate of the suspended solids concentration of the supernatant for mechanical disposal is 20 mg/ℓ.

19. To prevent resuspension at the weir between the primary and secondary areas, the weir should be designed for a weir loading rate of 0.08 cfs/ft. Therefore, weir lengths of 13 ft (1.03 cfs/0.08 cfs/ft) and 35 ft are required for mechanical dredging and hydraulic dredging, respectively. The 35-ft weir should be specified for both cases to provide for flexibility in future disposal operations.

Sedimentation Summary

20. The proposed in-lake CDF is sufficient to store the volume of dredged material to be disposed. The effluent quality of the supernatant and the loading on the filter dikes are highly dependent on the dredging and disposal methods. The suspended solids loading on the filter dikes can be as high as 2.1 g/ℓ for hydraulic dredging, 1.3 g/ℓ for hydraulic transfer of mechanically dredged sediments, and 20 mg/ℓ for mechanical disposal. The loadings for hydraulic disposal may be much lower if the influent concentration is kept high and the settling is controlled by zone settling instead of flocculent settling. Under this condition, the loadings for hydraulic transfer and hydraulic dredging would be about 250 and 400 mg/ℓ, respectively.

Filtration Analysis

Background

21. The filter system consists of a pervious dike enclosing the complete CDF and a pervious cross dike separating the primary and secondary settling areas. The cross-section of the dike is shown in Figure 30 (Volume I). The sand filter media is 10 ft thick and the prepared limestone ranges from 0 ft at the top of the dike to over 100 ft at the base. The sand filter is to be constructed of lake sand from the CDF site. The laboratory-measured coefficient of permeability of the sand ranges from 1.5×10^{-5} cm/sec to 13.6×10^{-5} cm/sec. The effective particle size D_{10} of the sand deposits is about 0.08 mm. The clays and silts of the lake bottom have effective particle sizes as low as 0.001 mm.

Filter coefficients

22. Krizek et al. (1976) developed the following relationship to estimate the filter coefficient for sands and gravels:

$$\gamma = 0.40\ D_{10}^{-1.84} \tag{A11}$$

where

γ = filter coefficient, m^{-1}

D_{10} = effective particle size, mm

For the lake sands the filter coefficient would be

$$\begin{aligned}\gamma &= (0.40)\ (0.20)^{-1.84} \\ &= 7.7\ m^{-1} \text{ or } 2.4\ ft^{-1}\end{aligned} \tag{A12}$$

Filter tests (US Army Engineer Waterways Experiment Station 1980) conducted on supernatants having 1.49 g/ℓ suspended solids, using sands having a effective size of 0.5 mm, yielded a filter coefficient of:

$$\begin{aligned}\gamma &= \frac{\ell n\ (C_o/C)}{L} \\ &= \frac{\ell n\ (1.49/0.04)}{1.2\ m} \\ &= 3.0\ m^{-1} \text{ or } 0.92\ ft^{-1}\end{aligned} \tag{A13}$$

where

C_o = suspended solids concentration of the supernatant

C = suspended solids concentration of the filtrate

L = thickness of sand filter

Krizek's relationship would have estimated the filter coefficient to be:

$$\gamma = (0.40)\ (0.5)^{-1.84} = 1.4\ \text{m}^{-1} \text{ or } 0.44\ \text{ft}^{-1} \qquad \text{(A14)}$$

The removals were probably larger in the tests because an oily sludge from the supernatant coated and clogged the sand.

Clogging potential

23. In the laboratory test simulating hydraulic disposal from scows the volume of throughput per volume of sand for clogging to occur was about 4. The volume of throughput per surface area of sand was about 500 cm or 5 m. If, as believed, clogging was caused by coating the surface and not by filling pores throughout the depth of the sand, filtrate from a supernatant having a suspended solids concentration of 1.49 g/ℓ would penetrate about 8 m or 26 ft through the sand and dike prior to clogging. The volume of throughput under these conditions would be very small and, if lake sand were used, the volume of throughput would be even smaller. The total volume of throughput before clogging for hydraulic disposal from scows would probably be less than

$$\begin{aligned} V &= \frac{(5.0\ \text{m})\ (\text{Surface area of sand})\ (\text{Test Solids})}{(\text{Supernatant solids})} \\ &= \frac{(5.0\ \text{m})\ (250{,}000\ \text{sq ft})\ (3.28\ \text{ft/m})\ (1.49\ \text{g}/\ell)}{1.3\ \text{g}/\ell} \qquad \text{(A15)} \\ &= 4{,}700{,}000 \text{ cu ft or } 174{,}000 \text{ cu yd} \end{aligned}$$

or about 12 percent of the in situ sediment volume. If based on volume of sand instead of surface area, the throughput volume would be less than

$$\begin{aligned} V &= 4\ (\text{Volume of sand})\ (\text{Test Solids})/(\text{Supernatant Solids}) \\ &= 4\ (250{,}000\ \text{sq ft})\ (10\ \text{ft})\ (1.49\ \text{g}/\ell)/(1.3\ \text{g}/\ell) \qquad \text{(A16)} \\ &= 11{,}500{,}000 \text{ cu ft or } 425{,}000 \text{ cu yd} \end{aligned}$$

or about 30 percent of the total production volume.

24. Krizek et al. (1976) reported that sands having effective particle size below 2 mm tended to clog rapidly by trapping solids at the surface of

sand instead of uniformly throughout the bed. This appears to have happened in the lab tests due to the oil content of the sediment when using sands of 0.5 mm effective size. Lake sands having effective sizes of 0.2 mm or less would certainly clog at the surface, also. Krizek et al. (1976) recommended the use of sand having an effective size of 2 to 3 mm.

25. The potential for clogging from mechanical disposal operations would be considerably less than from hydraulic transfer operations since the quantity of oil released would be much smaller. Assuming that the oil release and clogging potential is proportional to the expected suspended solids concentration of the supernatant following settling, the total volume of throughput before surface clogging for mechanical disposal would probably be about

V = (5.0 m) (Surface area of sand)
(Test solids)/(Supernatant solids)

= (5.0 m) (250,000 sq ft) (3.28 ft/m) (1.49 g/ℓ)/(0.020 g/ℓ)

= 310,000,000 cu ft or 11,000,000 cu yd or about 810 percent of the in situ sediment volume

26. For hydraulic dredging with flocculent settling the total volume of throughput before surface clogging would probably be about

V = (5.0 m) (250,000 sq ft) (3.28 ft/m) (1.49 g/ℓ) / (2.1 g/ℓ)

= 2,900,000 cu ft or 108,000 cu yd

or about 8 percent of the total in-situ sediment volume or about 2 percent of the total inflow. If zone settling occurs as seen in the laboratory at influent concentrations above 100 g/ℓ, the total volume of throughput before surface clogging would probably be about

V = (5.0 m) (Surface area of sand)
(Test solids) / (Supernatant solids)

= (5.0 m) (250,000 sq ft) (3.28 ft/m) (1.49 g/ℓ) / (0.4 g/ℓ)

$$= 15{,}000{,}000 \text{ cu ft or } 570{,}000 \text{ cu yd}$$

or about 41 percent of the total in situ sediment volume or about 15 percent of the total inflow.

27. Provisions should be made to skim the oil release around the inlet to minimize the clogging potential. Mechanical placement of material along the dike will also seal the dike and reduce the area for filtering. A settling and filtering aid will probably be required to dispose and filter the entire volume to be dredged. Chemical clarification of mechanically disposed dredged material with oil control appears to be a viable method to ensure adequate protection from clogging. Both hydraulic disposal methods appear to have the potential for clogging early in the disposal life of the CDF.

Effluent concentration

28. The effluent suspended solids can be computed using the following removal efficiency relationship:

$$\begin{aligned} C &= (C_o)\ e^{-\gamma L} \\ &= (1100 \text{ mg}/\ell)\ e^{-(2.4)\ (10)} \qquad \text{(A17)} \\ &= 0 \text{ mg}/\ell \end{aligned}$$

Sands having an effective size less than 0.4 mm would, in effect, capture all of the suspended solids using this described filter design.

Maximum discharge rate

29. The laboratory permeability of the lake sand ranges from 1.5×10^{-5} to 13.6×10^{-5} cm/sec but, as discussed previously, the field permeability would probably range from 3×10^{-4} to 5×10^{-3} cm/sec. Using an average permeability of 1×10^{-3} cm/sec for the sand, the initial maximum seepage rate without clogging would be

$$\begin{aligned} Q &= \frac{KA\Delta h}{L} \\ &= \frac{(1 \times 10^{-3} \text{ cm/sec})(250{,}000 \text{ sq ft})(8 \text{ ft})}{(30.48 \text{ cm/ft})(10 \text{ ft})} \qquad \text{(A18)} \\ &= 7 \text{ cfs} \end{aligned}$$

where

Q = rate of seepage

K = coefficient of permeability

A = surface area of sand filter

Δh = height of ponded water in CDF above the lake water level

L = thickness of sand filter

The surface area of the sand will decrease to about 60,000 sq ft at the end of the disposal operation. The permeability will also decrease as clogging occurs, falling to as low as 1×10^{-7} cm/sec. Consequently, the seepage rate is sufficient to discharge the inflow, providing that the field permeability is, as expected, significantly greater than the laboratory measured value and that clogging can be prevented. Even without clogging, the seepage rate at the end of the disposal life of the CDF when the filter area is small may be too low to permit hydraulic dredging.

APPENDIX B: EFFLUENT QUALITY

1. A modified elutriate test was performed on a 100-g/ℓ suspension of the composited Indiana Harbor sediment. The procedures used in the test are fully described in the Environmental Effects of Dredging Technical Note EEDP-04-2, "Interim Guidance for Predicting Quality of Effluent Discharged from Confined Dredged Material Disposal Area--Test Procedures." In addition to the test, contaminant analyses were performed on the site water and the bulk sediment. The results of these analyses are presented in Table B1. The site water was collected on December 10, 1984 in the Indiana Harbor Canal near the northwest corner of the railroad bridge at Canal Street. This water was used in the modified elutriate test. The results of the modified elutriate test are listed in Table B2. The water quality standards for Lake Michigan and Indiana Harbor are given in Table B3.

2. The effluent quality is a function of the disposal alternative used. The prediction of the effluent requires interpretation and analysis using the modified elutriate test results, the leaching test results, settling test results and design information. The effluent quality predictions are presented in Table B4. These estimates assume that the water in the in-lake CDF prior to disposal has no contaminants, the quantity of water available for dilution is the minimum to maintain one foot of ponding, the effluent following filtration contains 0.5 mg/ℓ suspended solids, and the concentration of dissolved contaminants does not change while passing through the filter dikes. Significant adsorption of hydrophobic contaminants such as Polychlorinated biphenyls (PCBs) onto the filter material is expected and, therefore, the estimates are conservative, and are very conservative for several of the contaminants. Furthermore, depending on the sequencing of the disposal projects, the volume of water available for dilution may be as much as four times as large as assumed in calculating the effluent quality in the following sections.

Hydraulic Transfer from Scows

3. The sediment in the modified elutriate test was diluted to 100 g/ℓ since the sediment is expected to be diluted to 100 g/ℓ during the transfer from scows. During the disposal operation, water is to be taken from the in-lake CDF to slurry the sediment. This water may be used for dilution

several times and, unlike the clean water used for dilution in the modified elutriate test, the CDF dilution water may accumulate contaminants each time that it is used for dilution. The behavior of each contaminant in response to reuse of dilution water is unknown. If the dissolved contaminant concentration of the water is in equilibrium with the sediment solid phase concentration, then additional contaminants may not partition into the water, and the concentration would not increase. Contaminants that are released by mechanical means or are present in the water at concentrations well below their solubility may be released to the supernatant water during each use of the water for dilution. Since the response of each contaminant is unknown, the dissolved contaminant concentrations predicted by the modified elutriate test will be multiplied by the number of uses as dilution water to generate a conservative estimate of the effluent quality. Many of the values in the following analysis are taken from Appendix A.

Total Volume of Sediment = 200,000 cu yd $(e_o/(1 + e_o)$

Total Volume of In Situ Pore Water = (2.37/3.37) 200,000 cu yd
= 141,000 cu yd

Total Volume of In Situ Solids = 200,000 - 141,000 = 59,000 cu yd

Total Volume of Available Dilution Water (assuming 1 ft of ponding at end of disposal) = 347,000 cu yd (initial storage volume)
+ 56,000 cu yd (ponded volume)
= 403,000 cu yd

Total Volume of Influent = (800 g/ℓ)/(100 g/ℓ) 200,000 cu yd
= 1,600,000 cu yd

Required Dilution Water = 1,600,000 - 200,000 = 1,400,000 cu yd

Ratio of Dilution Water to Pore Water in Modified Elutriate Test = 1,400,000/141,000 = 9.93

Ratio of Dilution Water to Pore Water in Field = 403,000/141,000 = 2.86

Therefore, the dilution water will be used

$$\frac{9.93}{2.86} = 3.5 \text{ times}$$

Consequently, the dissolved contaminant concentrations predicted by the modified elutriate test were multiplied by 3.5 to estimate the effluent quality for hydraulic transfer from scows.

Hydraulic Disposal by Matchbox or Cutterhead Dredge

4. The modified elutriate test predicts the release of contaminants to the supernatant water following hydraulic dredging (generally by a cutterhead dredge) where the bulk of the dredged material slurry settles rapidly by flocculent or zone settling and a significant quantity of supernatant is quickly generated. The contaminants are released by a variety of mechanisms including partitioning between the solid and liquid phases by desorption and dissolution, dilution of pore water, and mechanical means. Hydraulic disposal by a matchbox dredge is expected to produce a slurry that has a solids concentration that is similar to that used in the modified elutriate test. The slurry is expected to settle by flocculent or zone settling as the slurry does in the modified elutriate test. The modified elutriate test best represents the effluent quality from an upland CDF during hydraulic disposal. The results from the modified elutriate test should also accurately represent the effluent quality from an in-lake CDF during hydraulic dredging.

Assuming an influent concentration of 150 g/ℓ,

Total Volume of Influent = (800 g/ℓ)/(150 g/ℓ) 200,000 cu yd
= 1,070,000 cu yd

Total Volume at End of Disposal = 347,000 cu yd

Total Volume of Supernatant Produced During Disposal
= 1,070,000 - 347,000 = 720,000 cu yd

Total Volume of Dilution Water in CDF = 403,000 cu yd

Available Dilution = 720,000 cu yd/(720,000 + 403,000) cu yd
= 0.64

Consequently, the dissolved contaminant concentrations predicted by the modified elutriate test should be multiplied by 0.64 to account for the dilution in the CDF.

Mechanical Dredging and Disposal

5. Dredging and disposal by mechanical methods is expected to significantly reduce the release of contaminants. The modified elutriate test is not expected to simulate the release since the mechanical release due to the mixing and turbulence of pumping, resuspension, and volume of carrier water should be much smaller. Consequently, water released from the dredged material by resuspension and compression settling may have appreciably lower concentrations of contaminants than obtained in the modified elutriate test. This difference is evident from the initial leaching data which had contaminant concentrations that were considerably lower than the results of the modified elutriate tests. The leachate quality should represent fairly well the quality of the water released by compression settling. The quality of water released by resuspension would probably be better represented by the results of the modified elutriate test than by the leachate quality. Therefore, the contaminant release will be computed to be the sum of these two parts, and this quantity will be reduced by the dilution available in the in-lake CDF.

Total Volume of Influent = (800 g/ℓ)/(600 g/ℓ) 200,000 cu yd
= 267,000 cu yd

Total Volume at End of Disposal = (800 g/ℓ)/(615 g/ℓ) 200,000 cu yd
= 260,000 cu yd

Total Volume of Water Released by Compression Settling During Disposal = 267,000 - 260,000 = 7,000 cu yd

Total Volume of Water for Resuspension (assuming 1 ft of ponding at end of disposal) = 56,000 (volume of ponding) + 260,000 cu yd

= 316,000 cu yd

Total Volume of Influent Resuspended = (316,000 cu yd)(0.1 g/ℓ)/(600 g/ℓ)

= 53 cu yd

Total Volume of Influent Water Released by Resuspension =

53 cu yd [1 - (600/2,690)] = 41 cu yd

Ratio of Water Released by Resuspension to Water Present in CDF = 41/316,000 = 0.00013

Ratio of Water Released by Compression Settling to Water Present in CDF = 7,000/316,000 = 0.022

Consequently, the dissolved contaminant concentration in the supernatant will be about 2 percent of the initial leachate quality.

Table B1

Chemical Characterization of Indiana Harbor Site Water and Bulk Sediment

Constituent	Constituent Concentration of Sample* Site Water	Bulk Sediment
Arsenic	<0.005 ppm	36.8 ppm
Cadmium	0.0007 ppm	22.2 ppm
Chromium	0.004 ppm	514 ppm
Copper	0.005 ppm	266 ppm
Lead	<0.001 ppm	933 ppm
Mercury	0.0020 ppm	0.262 ppm
Nickel	0.008 ppm	120 ppm
Zinc	<0.03 ppm	3,785 ppm
Iron	<0.03 ppm	182,000 ppm
Manganese	0.042 ppm	2,085 ppm
Total phosphorus	0.10 ppm	2,765 ppm
NH_3-N	0.607 ppm	1,100 ppm
Aldrin	0.00002 ppm	2.41 ppm
A-BHC	<0.00001 ppm	<0.02 ppm
B-BHC	<0.00001 ppm	<0.02 ppm
G-BHC	<0.00001 ppm	<0.02 ppm
D-BHC	<0.00001 ppm	<0.02 ppm
Chlordane	<0.0002 ppm	<0.02 ppm
PPDDD	<0.00001 ppm	<0.02 ppm
PPDDE	<0.00001 ppm	<0.02 ppm
PPDDT	<0.00001 ppm	<0.02 ppm
Dieldrin	<0.00001 ppm	<0.0002 ppm
A-Endosulfan	<0.00001 ppm	<0.0002 ppm
B-Endosulfan	<0.00001 ppm	<0.0002 ppm
Endosulfan sulfate	<0.00001 ppm	<0.0002 ppm
Endrin	<0.00001 ppm	<0.0002 ppm
Endrin aldehyde	<0.00001 ppm	<0.0002 ppm
Heptachlor	<0.00001 ppm	<0.02 ppm

(Continued)

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* ppm = mg/ℓ for site water sample and mg/kg for bulk sediment.

Table B1 (Concluded)

Constituent	Constituent Concentration of Sample	
	Site Water	Bulk Sediment
Heptachlor epoxide	<0.00001 ppm	<0.0002 ppm
PCB-1016	<0.0002 ppm	<0.2 ppm
PCB-1221	<0.0002 ppm	<0.2 ppm
PCB-1232	<0.0002 ppm	<0.2 ppm
PCB-1242	<0.0002 ppm	<0.2 ppm
PCB-1248	0.0003 ppm	29.4 ppm
PCB-1254	<0.0002 ppm	<0.2 ppm
PCB-1260	<0.0002 ppm	<0.2 ppm
Toxaphene	<0.0002 ppm	<0.2 ppm
Naphthalene	<0.01 ppm	2050 ppm
Acenaphthylene	<0.01 ppm	22 ppm
Acenaphthene	<0.01 ppm	110 ppm
Fluorene	<0.01 ppm	83 ppm
Phenanthrene	<0.01 ppm	210 ppm
Anthracene	<0.01 ppm	64 ppm
Fluoranthene	<0.01 ppm	175 ppm
Pyrene	<0.01 ppm	145 ppm
Chrysene	<0.01 ppm	98 ppm
Benzo(a)anthracene	<0.01 ppm	110 ppm
Benzo(b)fluoranthene	<0.01 ppm	165 ppm
Benzo(k)fluoranthene	<0.01 ppm	165 ppm
Benzo(a)pyrene	<0.01 ppm	115 ppm
Indeno(1 2 3-c d)pyrene	<0.025 ppm	60 ppm
Dibenzo(a h)anthracene	<0.025 ppm	<10 ppm
Benzo(g h i)perylene	<0.025 ppm	42 ppm
Total organic carbon	4.6 ppm	48,258 ppm
Phenol	<0.01 ppm	4.02 ppm
Dissolved solids	342 ppm	
Suspended solids	<4 ppm	

Table B2

Results of Modified Elutriate Test

Constituent	Constituent Concentration of Modified Elutriate Test Samples	
	Unfiltered Water	Filtered Water
Arsenic	0.148 ± 0.050 ppm	0.004 ± 0.003 ppm
Cadmium	0.0026 ± 0.0008 ppm	0.0023 ± 0.0005 ppm
Chromium	0.182 ± 0.088 ppm	0.035 ± 0.005 ppm
Copper	0.077 ± 0.024 ppm	0.035 ± 0.008 ppm
Lead	0.211 ± 0.066 ppm	0.064 ± 0.031 ppm
Mercury	0.0176 ± 0.0005 ppm	<0.0008 ppm
Nickel	0.058 ± 0.010 ppm	0.032 ± 0.000 ppm
Zinc	1.151 ± 0.175 ppm	0.430 ± 0.046 ppm
Iron	7.94 ± 3.16 ppm	0.686 ± 0.104 ppm
Manganese	0.246 ± 0.154 ppm	0.039 ± 0.007 ppm
Total phosphorus	42.6 ± 17.0 ppm	0.38 ± 0.10 ppm
NH3-N	40.4 ± 18.0 ppm	44.2 ± 0.5 ppm
Aldrin	<0.00001 ppm	0.00011 ± 0.00003 ppm
A-BHC	<0.00001 ppm	<0.00001 ppm
B-BHC	<0.00001 ppm	<0.00001 ppm
G-BHC	0.00012 ± 0.00021 ppm	<0.00001 ppm
D-BHC	<0.00001 ppm	<0.00001 ppm
Chlordane	<0.0002 ppm	<0.0002 ppm
PPDDD	<0.00001 ppm	<0.00001 ppm
PPDDE	<0.00001 ppm	<0.00001 ppm
PPDDT	<0.00001 ppm	<0.00001 ppm
Dieldrin	<0.00001 ppm	<0.00001 ppm
A-Endosulfan	<0.00001 ppm	<0.00001 ppm
B-Endosulfan	<0.00001 ppm	<0.00001 ppm
Endosulfan sulfate	<0.00001 ppm	<0.00001 ppm
Endrin	<0.00001 ppm	<0.00001 ppm
Endrin aldehyde	<0.00001 ppm	<0.00001 ppm
Heptachlor	<0.00001 ppm	<0.00001 ppm
Heptachlor epoxide	0.00026 ± 0.00004 ppm	0.00004 ± 0.00006 ppm

(Continued)

(Sheet 1 of 3)

Table B2 (Continued)

Constituent	Constituent Concentration of Modified Elutriate Test Samples Unfiltered Water	Filtered Water
PCB-1016	<0.0002 ppm	<0.0002 ppm
PCB-1221	<0.0002 ppm	<0.0002 ppm
PCB-1232	<0.0002 ppm	<0.0002 ppm
PCB-1242	<0.0002 ppm	<0.0002 ppm
PCB-1248	31.5 ± 16.4 ppm	0.0034 ± 0.0017 ppm
PCB-1254	<0.0002 ppm	<0.0002 ppm
PCB-1260	<0.0002 ppm	<0.0002 ppm
Toxaphene	<0.0002 ppm	<0.0002 ppm
Naphthalene	4.2 ± 1.4 ppm	<0.01 ppm
Acenaphthylene	0.086 ± 0.047 ppm	<0.01 ppm
Acenaphthene	0.39 ± 0.22 ppm	<0.01 ppm
Fluorene	0.30 ± 0.17 ppm	<0.01 ppm
Phenanthrene	0.77 ± 0.46 ppm	<0.01 ppm
Anthracene	0.20 ± 0.12 ppm	<0.01 ppm
Fluoranthene	0.59 ± 0.35 ppm	<0.01 ppm
Pyrene	0.54 ± 0.30 ppm	<0.01 ppm
Chrysene	0.34 ± 0.20 ppm	<0.01 ppm
Benzo(a)anthracene	0.24 ± 0.17 ppm	<0.01 ppm
Benzo(b)fluoranthene	0.43 ± 0.28 ppm	<0.01 ppm
Benzo(k)fluoranthene	0.43 ± 0.28 ppm	<0.01 ppm
Benzo(a)pyrene	0.26 ± 0.19 ppm	<0.01 ppm
Indeno(1 2 3-c d)pyrene	0.09 ± 0.16 ppm	<0.01 ppm
Dibenzo(a h)anthracene	<0.10 ppm	<0.025 ppm
Benzo(g h i)perylene	0.08 ± 0.14 ppm	<0.025 ppm
Total organic carbon	1073 ± 607 ppm	44.5 ± 3.7 ppm
Phenol	0.070 ± 0.015 ppm	0.037 ± 0.004 ppm
Dissolved solids	154 ± 6 ppm	
Suspended solids	5392 ± 299 ppm	
Conductivity	<5 mmhos	

(Continued)

(Sheet 2 of 3)

Table B2 (Concluded)

Constituent	Constituent Concentration of Modified Elutriate Test Samples	
	Unfiltered Water	Filtered Water
pH	7.59	
Dissolved oxygen	1.3 ± 0.1 ppm	

(Sheet 3 of 3)

Table B3

Summary of Water Quality Standards

Constituent	Constituent Concentrations, ppm Drinking Water Standards	USEPA Maximum Criteria	Indiana Harbor WQ Standard	Lake Michigan WQ Standard
Arsenic	0.05	0.44	-	0.050
Cadmium	0.01	0.0015-0.0024	-	0.010
Chromium	0.05	2.2-9.9	-	0.050
Copper	1.0	0.012-0.043	-	-
Lead	0.05	0.074-0.400	-	0.050
Mercury	0.002	0.0017	0.0005	0.00005
Nickel	-	1.1-3.1	-	-
Zinc	5.0	0.18-0.57	-	-
Iron	0.3	-	0.300	0.150
Manganese	0.05	-	-	-
Total phosphorus	-	-	0.1	0.03
NH3-N	-	-	1.5	-
Aldrin	-	-	-	-
A-BHC	-	-	-	-
B-BHC	-	-	-	-
G-BHC	-	-	-	-
D-BHC	-	-	-	-
Chlordane	-	-	-	-
PPDDD	-	-	-	-
PPDDE	-	-	-	-
PPDDT	-	-	-	-
Dieldrin	-	-	-	-
A-Endosulfan	-	-	-	-
B-Endosulfan	-	-	-	-
Endosulfan sulfate	-	-	-	-
Endrin	-	-	-	-
Endrin aldehyde	-	-	-	-
Heptachlor	-	-	-	-
Heptachlor epoxide	-	-	-	-

(Continued)

Table B3 (Concluded)

	Constituent Concentrations, ppm			
Constituent	Drinking Water Standards	USEPA Maximum Criteria	Indiana Harbor WQ Standard	Lake Michigan WQ Standard
PCB-1016	-	-	-	-
PCB-1221	-	-	-	-
PCB-1232	-	-	-	-
PCB-1242	-	-	-	-
PCB-1248	-	0.014	0.000001	0.000001
PCB-1254	-	-	-	-
PCB-1260	-	-	-	-
Toxaphene	-	-	-	-
Naphthalene	-	-	-	-
Acenaphthylene	-	-	-	-
Acenaphthene	-	-	-	-
Fluorene	-	-	-	-
Phenanthrene	-	-	-	-
Anthracene	-	-	-	-
Fluoranthene	-	-	-	-
Pyrene	-	-	-	-
Chrysene	-	-	-	-
Benzo(a)anthracene	-	-	-	-
Benzo(b)fluoranthene	-	-	-	-
Benzo(k)fluoranthene	-	-	-	-
Benzo(a)pyrene	-	-	-	-
Indeno(1 2 3-c d)pyrene	-	-	-	-
Dibenzo(a h)anthracene	-	-	-	-
Benzo(g h i)perylene	-	-	-	-
Total organic carbon	-	-	-	-
Phenol	-	-	0.01	0.001
Dissolved solids	-	-	500	172
Suspended solids	-	-	-	-

Table B4

Summary of Estimated Effluent Water Quality from In-Lake CDF under Alternative Disposal Methods

Constituent	Estimated Constituent Concentrations, ppm* Hydraulic Transfer	Matchbox Dredge	Mechanical Disposal
Arsenic	0.014	0.003	0.0003
Cadmium	0.0080	0.0015	0.00005
Chromium	0.122	0.022	0.0013
Copper	0.122	0.022	0.001
Lead	0.224	0.041	0.052
Mercury	<0.0028	<0.0005	<0.0001
Nickel	0.112	0.020	0.0007
Zinc	1.505	0.275	0.066
Iron	2.402	0.440	0.066
Manganese	0.136	0.025	0.0009
Total phosphorus	1.33	0.25	0.008
NH3-N	154.7	28.3	1.0
Aldrin	0.00039	0.00007	0.000002
A-BHC	<0.00004	<0.000006	<0.000001
B-BHC	<0.00004	<0.000006	<0.000001
G-BHC	<0.00004	<0.000006	<0.000001
D-BHC	<0.00004	<0.000006	<0.000001
Chlordane	<0.0007	<0.00013	<0.00001
PPDDD	<0.00004	<0.000006	<0.000001
PPDDE	<0.00004	<0.000006	<0.000001
PPDDT	<0.00004	<0.000006	<0.000001
Dieldrin	<0.00004	<0.000006	<0.000001
A-endosulfan	<0.00004	<0.000006	<0.000001
B-endosulfan	<0.00004	<0.000006	<0.000001
Endosulfan sulfate	<0.00004	<0.000006	<0.000001

(Continued)

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* Assuming that the water in the CDF has no contaminants prior to disposal, that the water available for dilution is the volume for initial storage for the new lift of material plus the ponded volume for a 1-ft ponding depth, that the effluent following filtration contains 0.5 mg/ℓ suspended solids, and that the concentration of dissolved contaminants does not change while passing through the filter dikes.

Table B4 (Concluded)

Constituent	Estimated Constituent Concentrations, ppm*		
	Hydraulic Transfer	Matchbox Dredge	Mechanical Disposal
Endrin	<0.00004	<0.000006	<0.000001
Endrin aldehyde	<0.00004	<0.000006	<0.000001
Heptachlor	<0.00004	<0.000006	<0.000001
Heptachlor epoxide	0.00014	0.00003	<0.000001
PCB-1016	<0.0007	<0.00013	<0.00001
PCB-1221	<0.0007	<0.00013	<0.00001
PCB-1232	<0.0007	<0.00013	<0.00001
PCB-1242	<0.0007	<0.00013	0.00001
PCB-1248	0.0238	0.0051	<0.00001
PCB-1254	<0.0007	<0.00013	<0.00001
PCB-1260	<0.0007	<0.00013	<0.00001
Toxaphene	<0.0007	<0.00013	<0.00001
Naphthalene	<0.04	<0.007	<0.0001
Acenaphthylene	<0.04	<0.007	<0.0001
Acenaphthene	<0.04	<0.007	0.0003
Fluorene	<0.04	<0.007	0.00003
Phenanthrene	<0.04	<0.007	0.00009
Anthracene	<0.04	<0.007	<0.0001
Fluoranthene	<0.04	<0.007	0.0004
Pyrene	<0.04	<0.007	0.0004
Chrysene	<0.04	<0.007	0.0002
Benzo(a)anthracene	<0.04	<0.007	0.0002
Benzo(b)fluoranthene	<0.04	<0.007	<0.0002
Benzo(a)pyrene	<0.04	<0.007	<0.0001
Indeno(1 2 3-c d)pyrene	<0.04	<0.007	<0.0001
Dibenzo(a h)anthracene	<0.09	<0.016	<0.0005
Benzo(g h i)perylene	<0.09	<0.016	<0.0001
Total organic carbon	156	28.6	1.
Phenol	0.130	0.024	0.0008
Dissolved solids	-	-	-
Suspended solids	0.5	0.5	0.5
Discharge volume	347,000 cu yd	1,070,000 cu yd	260,000 cu yd

Conclusions

6. In general, the contaminant concentrations in the effluent from an in-lake CDF during hydraulic transfer from scows are about 5 to 6 times as high as for matchbox dredging and about 50 to 150 times as high as for mechanical disposal. Considering the discharge volume, the quantities of contaminants released by the hydraulic transfer alternative are about twice as large as by the matchbox dredge alternative and about 70 to 200 times as large as by the mechanical disposal alternative.

7. The maximum quantity of PCBs expected to be released from the proposed CDF during the disposal operation is 6.3 kg for the hydraulic transfer from scows alternative, 4.2 kg for the matchbox dredge alternative, and 0.0027 kg for the mechanical disposal alternative. The actual quantity of PCBs released through the filter dikes could actually be much less (orders of magnitude less) since PCBs are very hydrophobic and are adsorbed very easily.

8. Only the concentrations of PCBs for all three alternatives exceeds the Indiana Lake Michigan water quality standards. The concentrations of chromium, lead, iron, manganese, total phosphorus, ammonia, phenol and probably total organic carbon for the hydraulic transfer from scows alternative exceed the water quality standards. The concentrations of total phosphorus, ammonia, phenol, and possibly total organic carbon for the matchbox dredging alternative barely exceed the water quality standards without considering a mixing zone.

APPENDIX C: RESULTS FROM PREVIOUS SETTLING AND FILTERING TESTS

1. Laboratory settling and filtering tests were performed in 1980 on sediments from Indiana Harbor. Descriptions and results of these tests were reported in US Army Engineer Waterways Experiment Station (1980).* Results of those tests are excerpted from the report and presented in this appendix.

2. A flocculent settling test was run on a 63-g/ℓ suspension and the results are shown in Figure C1. Zone settling tests were run on seven slurries at concentrations ranging from 110 g/ℓ to 220 g/ℓ, and the resulting zone settling velocities are plotted as a function of solids concentration in Figure C2. A 15-day compression settling test was run on a 145-g/ℓ suspension. The results of this test are plotted in Figure C3.

3. Several filtering tests were performed on supernatant from sedimentation of 190 g/ℓ. The supernatant had a solids concentration of 1.49 g/ℓ. A summary of the tests is listed in Table C1. Results of the filtering tests are given in Tables C2-C6.

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* See References at the end of the main text (Vol 1).

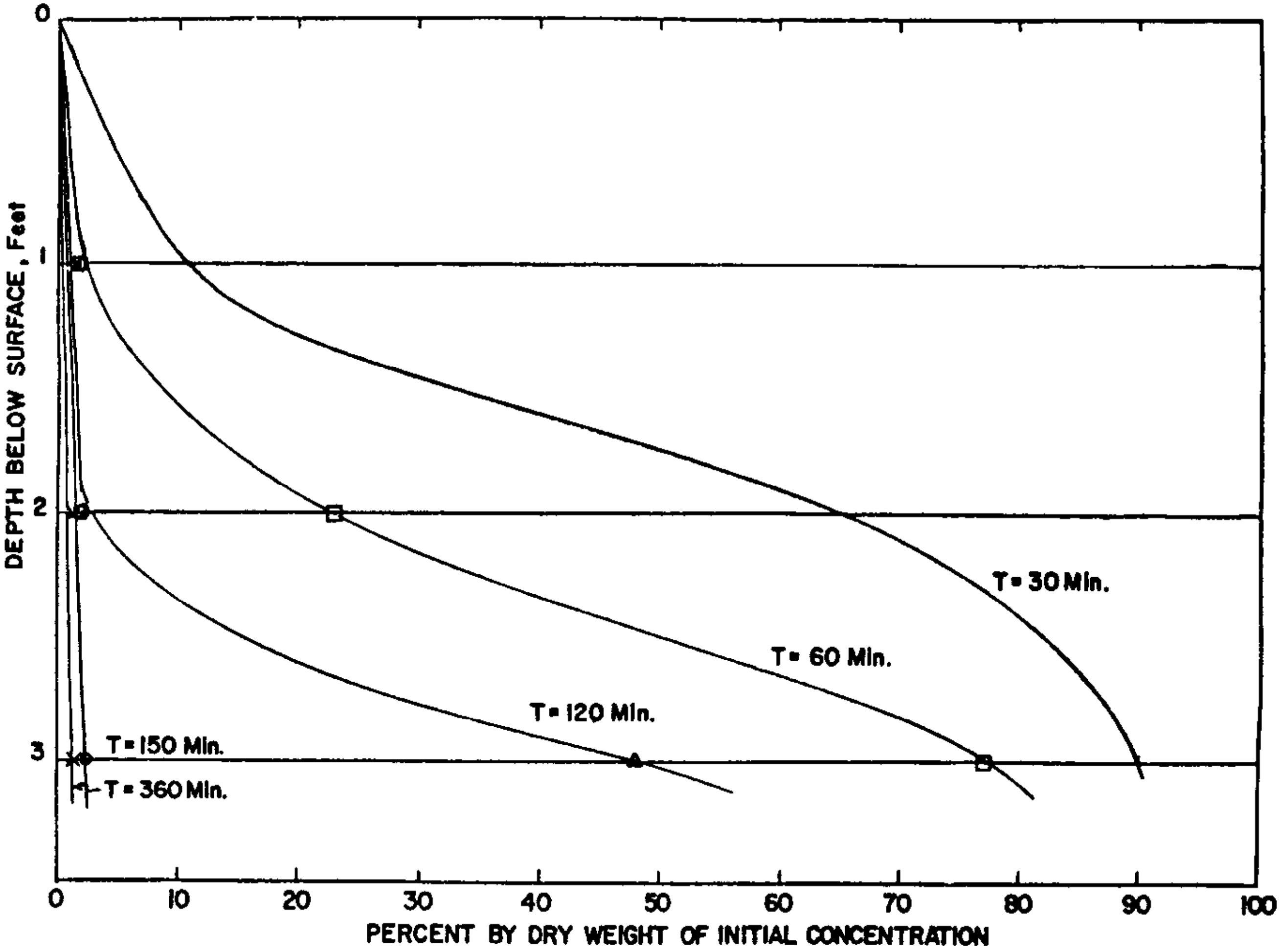

Figure C1. Solids concentration depth profile at various times during settling

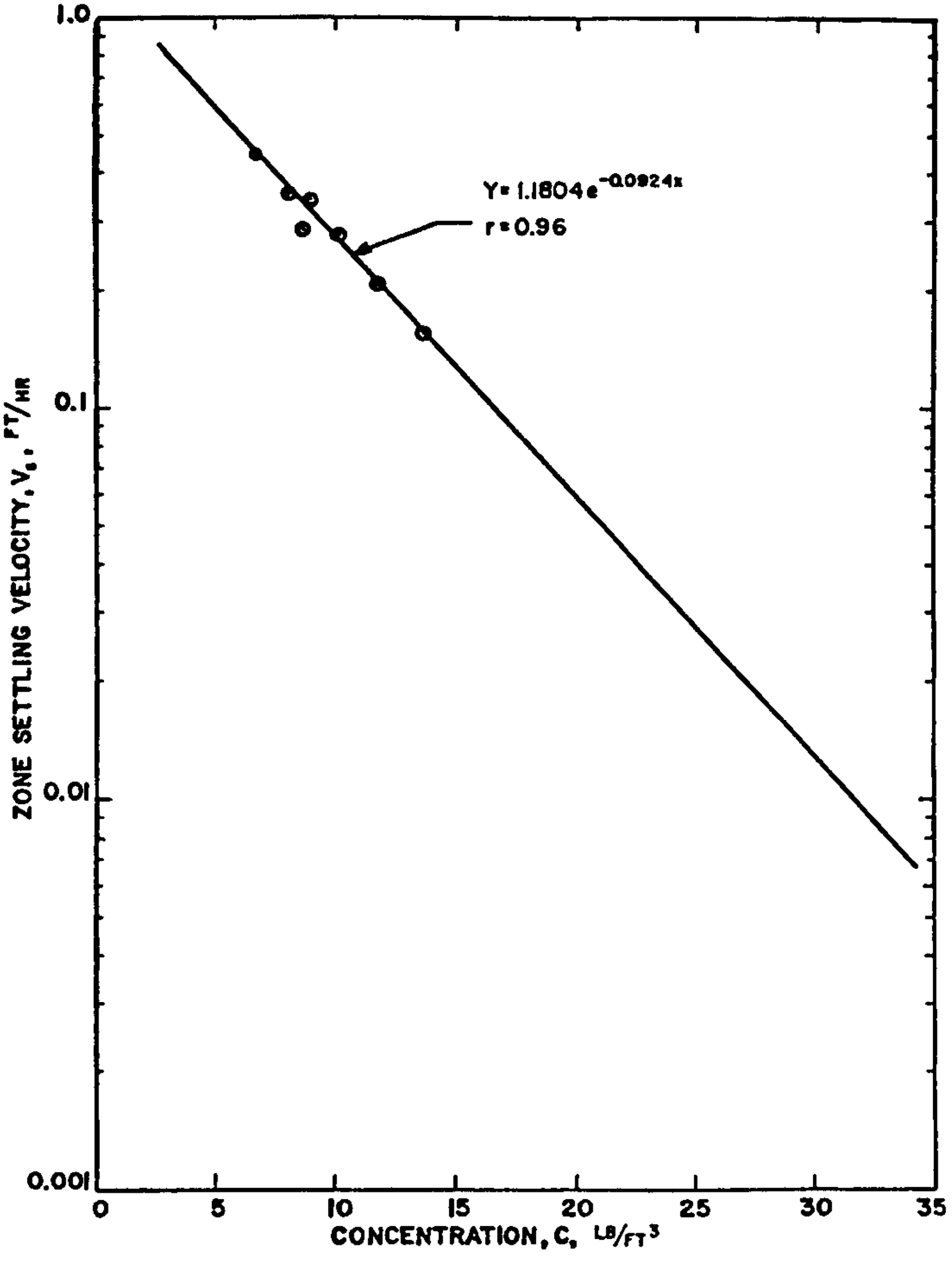

Figure C2. Zone settling velocity versus concentration

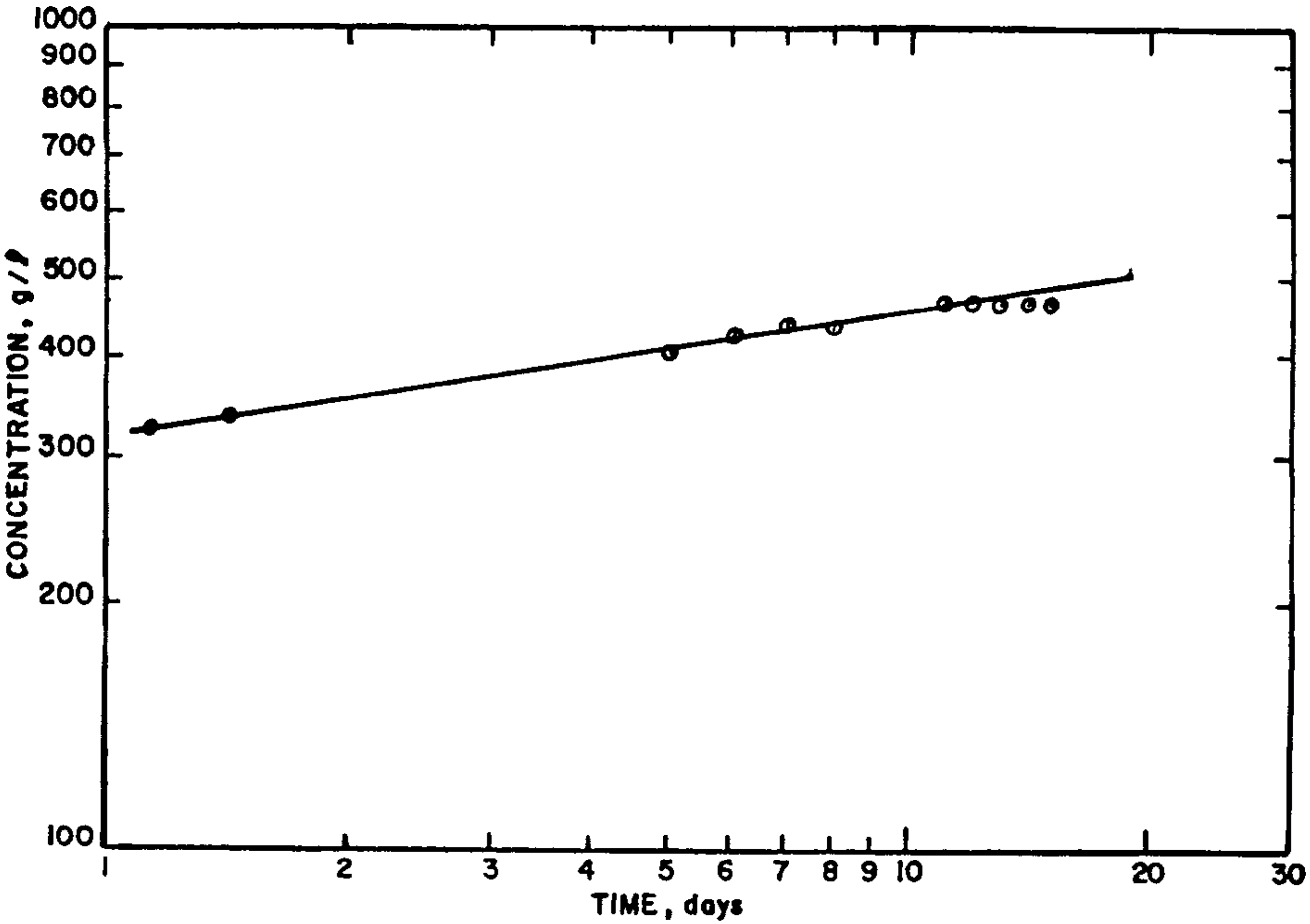

Figure C3. Solids concentration versus time

Table C1

Summary of Laboratory Filter Tests

Test Run	Filter Media	Filter Depth cm	Concentration** mg/ℓ	Head cm	Initial Discharge ℓ/min	Total Volume of Throughput ℓ	Length of Test before Plugging mins
Sand I	Fine sand	120	1490	157	0.49	45.4	75*
Sand II	Fine sand	120	1490	220	0.68	37.9	115
Carbon	Calgon Filtrasorb 400	120	1490	157	0.49	60.6	105
Sand-Carbon	Fine sand Filtrasorb 400	240	1490	179	0.42	53.0	--

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* Test was terminated at an effluent flow rate of 0.15 ℓ/min.

** Suspended solids concentration applied to filter.

Table C2

Suspended Solids Analysis of Filter Samples

Sample Identification	Sample No. 1 g/ℓ	Sample No. 2 g/ℓ	Sample No. 3 g/ℓ	Ave g/ℓ	Removal Efficiency %
Supernatant	1.510	1.473	1.490	1.491	--
Sand I	0.028	0.040	0.028	0.032	97.9
Sand II	0.047	0.038	--	0.043	97.1
Carbon	0.022	0.035	--	0.029	98.1
Sand-Carbon	0.008	0.017	0.019	0.015	99.0

Table C3

PCB* Analysis of Filter Samples

Sample Identification	Aroclor 1242 μg/ℓ	Aroclor 1248 μg/ℓ	Aroclor 1254 μg/ℓ	Aroclor 1260 μg/ℓ	Total PCB μg/ℓ	Removal Efficiency %
Supernatant	8.8**	0.03*	2.8	0.03	11	
Sand I	0.09	0.03	0.38	0.03	1.3	88.2
Sand II	0.78	0.03	0.25	0.03	1.0	90.9
Carbon	0.73	0.03	0.63	0.03	1.4	87.3
Sand-Carbon	0.50	0.03	0.03	0.03	0.50	95.5

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* PCB = Polychlorinated biphenyls.

** Typographical correction from the original report.

Table C4

Additional Chemical Analyses of Filter Samples

Sample Identification	Parameter							
	TKN mg/ℓ	Removal Efficiency %	Total Phos. mg/ℓ	Removal Efficiency %	Phenol mg/ℓ	Removal Efficiency %	Oil & Grease** mg/ℓ	Removal Efficiency %
Supernatant	46.3		5.57		0.033		15*	
Sand I	39.6	14.5	0.565	89.8	0.033	0	5,850*	99.7
Sand II	76.4	--	0.815	85.4	0.038	--	5	99.9
Carbon	35.3	23.7	0.725	87.0	0.012	63.6	29	99.5
Sand-Carbon	26.9	41.9	0.800	85.6	0.010	--	10	99.8

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* Samples apparently switched during analysis.

** O-G = Oil and grease.

Table C5

Metal Analyses of Filter Samples

Sample Identification	As mg/ℓ	Cd mg/ℓ	Cr mg/ℓ	Cu mg/ℓ	Pb mg/ℓ	Mn mg/ℓ	Ni mg/ℓ	Zn mg/ℓ	Hg mg/ℓ
Supernatant									
Total	0.19	0.0412	0.989	0.350	1.110	1.30	0.113	7.77	0.0022
Filtered	<0.010	<0.0001	0.002	0.004	<0.001	0.122	0.018	<0.050	<0.0002
Sand I									
Total	<0.010	0.0046	0.102	0.095	0.148	0.168	0.028	1.22	<0.0002
Filtered	<0.010	0.0006	0.002	0.012	<0.001	0.132	0.020	0.815	<0.0002
Sand II									
Total	<0.010	0.0100	0.155	0.210	0.262	0.185	0.042	2.44	0.0002
Filtered	<0.010	0.0002	0.002	0.010	<0.001	0.108	0.020	0.448	<0.0002
Carbon									
Total	0.017	0.0034	0.091	0.057	0.114	0.076	0.012	1.01	0.0006
Filtered	0.018	0.0002	<0.001	0.004	<0.001	0.046	0.006	0.329	<0.0002
Sand-Carbon									
Total	0.022	0.0008	0.026	0.196	0.176	0.026	0.012	0.657	<0.0002
Filtered	0.026	0.0004	<0.001	0.014	<0.001	0.016	0.006	0.232	<0.0002
Blank									
Total	<0.010	0.0006	<0.001	<0.001	<0.001	<0.001	<0.003	<0.050	
Interim Drinking Water Standard	0.05	0.01	0.05*	1.0	0.05	0.05	--	5.0	0.002

* Standard for Cr^{+6}.

Table C6

Percentage Removal Efficiencies for Total Metals

Sample Identification	As	Cd	Cr	Cu	Pb	Mn	Ni	Zn	Hg
Sand I	--	89	90	73	99	87	88	84	--
Sand II	--	76	84	40	76	86	81	69	91
Carbon	10	92	91	84	90	94	95	87	73
Sand-Carbon	--	98	97	44	84	99	95	92	--

APPENDIX D: PLANT AND ANIMAL BIOASSAY PROCEDURES AND DATA

Plant Bioassay

1. Confined disposal is one of the disposal alternatives for contaminated dredged material. A potential problem resulting from confinement of contaminated dredged material is that of plant uptake of contaminants from the dredged material and subsequent mobilization into the ecosystem. A plant bioassay was conducted on Indiana Harbor sediment to evaluate the uptake and potential mobility of contaminants through plants into the environment.

Methods and materials

2. Sediment preparation. Enough sediment for the upland portion of the plant bioassay and for chemical and physical analysis was poured into aluminum drying flats and allowed to air dry. Samples of the wet-flooded sediment were also taken as the sediment was being poured into the flats. The sediment was turned daily to facilitate drying. The air-drying process was conducted for about 4 weeks in the greenhouse to minimize airborne contamination of the sediment and to keep rainfall from rewetting the sediment. Temperature of the greenhouse was maintained at 90°F from 0600 hr to 2200 hr, and 70°F from 2200 hr to 0600 hr. The air-dried sediment was subsequently ground in a Kelly Duplex grinder (The Duplex Mill and Manufacturing Company, Springfield, Ohio) to pass a 2-mm screen. Samples of air-dried sediment were taken for both chemical and physical analyses.

3. Greenhouse procedures. The plant bioassay was conducted using the WES plant bioassay procedure. This method was reported by Folsom and Lee (1981).* A schematic diagram of the Experimental Unit (EU) is illustrated in Figure D1. The air-dried (upland) sediment (7,420 g oven-dry weight basis (ODW)) to be tested was placed into the inner container of the EU (Figure D1). A 7.6-ℓ plastic Bain Marie container rested on two 2.54-cm polyvinyl chloride (PVC) pipes inside a larger (22.7-ℓ Bain-Marie) outer container. Six 6.35-mm-diam holes were drilled in the bottom of the inner container, and a 2.54-cm

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* See References at the end of the main text (Vol I).

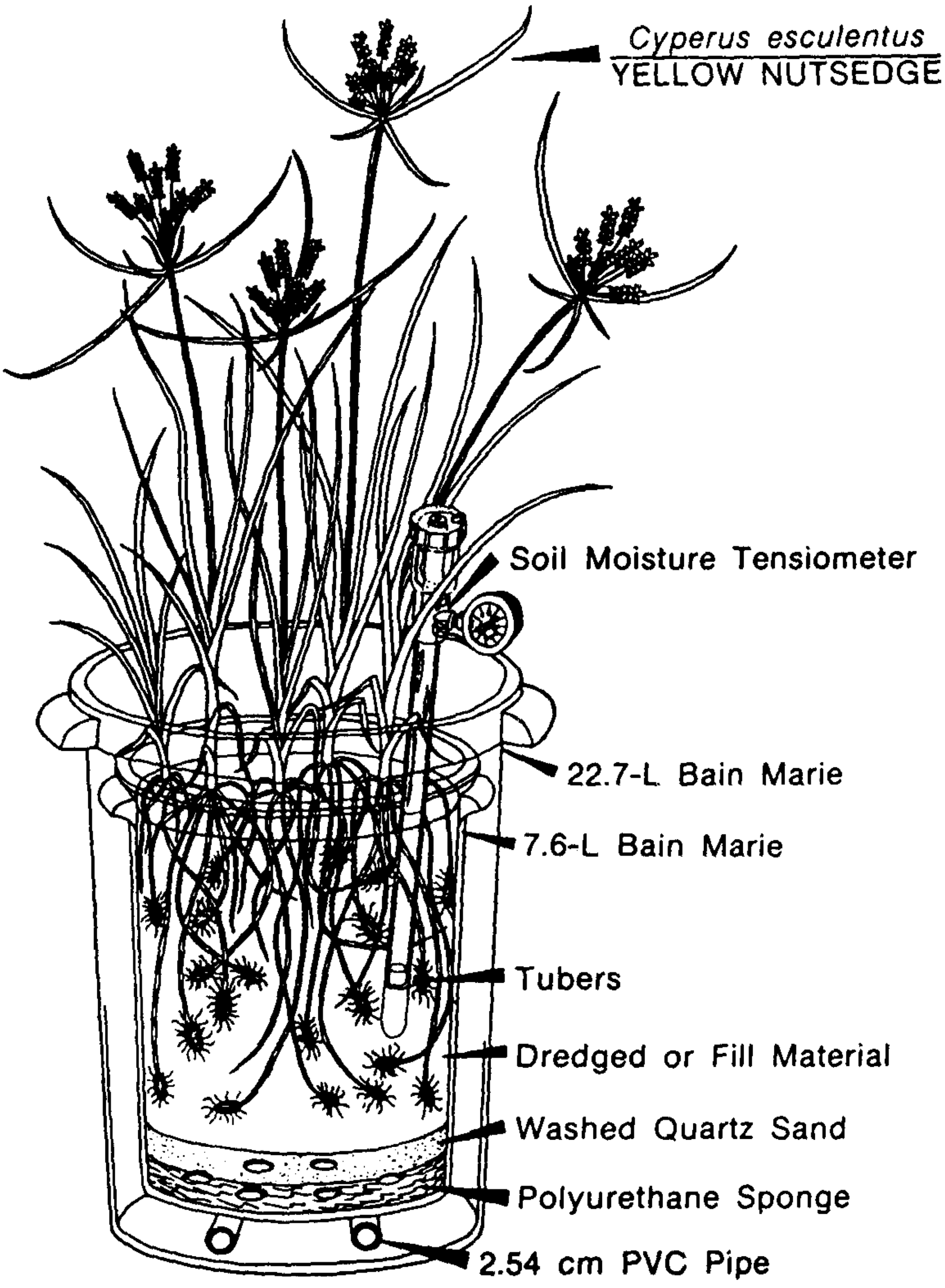

Figure D1. Plant bioassay experimental unit polyurethane sponge overlaid with a 2.54-cm layer of washed quartz sand was placed on the sponge. The sand and sponge acted as a filter to keep the sediment from draining out the bottom of the inner container through the small holes. The holes in the inner container also allowed water movement into and out of the sediment. After the sediment had been placed into the container, a soil-moisture tensiometer was placed into each EU to measure sediment moisture. Sediment moisture of all the upland treatments was maintained at between 0.03 and 0.05 Megapascal (MPa) (a reading between 30 and 50 percent on the dial of the tensiometer). The source of water used was deionized water obtained from a Continental Model 3230 Reverse Osmosis (RO) water system. The sediment was not allowed to drain or dry out for the flooded treatment. At least a 5-cm depth of water was maintained over the surface of the sediment by addition of RO water as needed. An EU containing reference soil fertilized for adequate plant growth was included with the test to ensure an adequate greenhouse environment was maintained during the course of the experiment. Plant growth and yield were the only parameters of the WES EU used for comparative purposes.

4. Three sprouted *Cyperus esculentus* tubers were planted in four replicates of the flooded sediment and four replicates of the air-dried sediment (to reflect submerged and upland conditions, respectively) and allowed to grow for 45 days before harvest. Plants were watered when the reading on the tensiometer was greater than 0.050 MPa, deionized RO water was used to fill the outer container up to the level of the sediment sample in the inner container. When the tensiometer reading was less than 0.03 MPa, the water was siphoned out of the outer container. The tensiometers were monitored daily and all EU were maintained between 0.03 and 0.05 MPa.

5. After 45 days, the plants were cut 5 cm above the sediment surface with stainless steel scissors and placed in a plastic tray containing RO water. The plant leaves were swirled about in the water to remove any leaf surface adsorbed particulates. The leaves were placed in a second plastic tray filled with RO water and rinsed again. The leaves were removed from the water and blotted dry. One half of the leaf tissue was put into a labeled acid rinsed glass jar. The other half was placed into a paper bag and oven dried at 70°C until constant weight. This procedure was repeated for each treatment. The upland treatment did not have sufficient plant growth in each replicate to

allow chemical analysis for either metals or organics. Therefore, a composite sample was made by combining the plant tissue from all four replicates to give enough tissue for subsequent analyses.

6. Laboratory procedures. Ten grams of sediment (ODW basis) was weighed into a 50-ml Pyrex glass beaker. Twenty millilitres of RO water was added, and the mixture stirred with a polyethylene rod until all dry particles had become wet. The suspension was stirred for 1 min. every 15 min. for 45 min. with a magnetic stirrer. After 45 min., the pH of the suspension was determined using a glass and reference calomel electrode on a Beckman Model SS-3 pH meter (Beckman Instrument Co., Inc., Irving, California). Calcium carbonate equivalent (i.e. lime requirement) was determined on the sediments using the method of Allison and Moodie (1965). Particle size was determined on air-dried sediments using the method of Day (1956) as modified by Patrick (1958). The CEC was determined using the ammonium saturation method of Schollenberger and Simon (1945). The EC was determined on extracts of saturated pastes from sediments using the method of Rhoades (1982). The conductivity meter used was a Model Number 31 YSI (Yellow Springs Instrument Company, Yellow Springs, Ohio). Total and DTPA-extractable metals were determined on both the flooded and air-dried sediments using the procedures of Folsom, Lee, and Bates (1981). Sediments were also analyzed for PCB, PAH, and pesticides using standard EPA procedures (USEPA 1982).

7. The plant tissue digestion was accomplished by the following procedure. Two grams of oven-dried plant tissue was placed into a 100-ml micro-Kjeldahl flask. Fifteen millilitres of concentrated nitric acid was added; the mixture was placed on a digestion rack, and the mixture was heated until almost dry. Five millilitres of red fuming nitric acid was added, and then the solution was again heated until almost dry. The mixture was allowed to cool to room temperature and diluted with 30 ml of 1.2 N hydrochloric acid (HCl). The solution was quantitatively transferred with 1.2 N HCl and filtered through Whatman No. 42 paper in a long-stem funnel into a 50-ml volumetric flask. The filtered solution was diluted to volume with 1.2 N HCl and analyzed for the metals zinc, cadmium, copper, iron, manganese, arsenic, mercury, nickel, chromium, and lead. Plant tissue analysis for PCB, PAH, and pesticides was performed according to USEPA (1982).

Results and discussion

8. Selected physical and chemical parameters of the Indiana Harbor sediment are listed in Table D1. The data presented in Table D1 indicate that the Indiana Harbor sediments were neutral to slightly alkaline, organic, sandy silts. The EC of both the flooded and upland sediments was in the range where plant growth is adversely affected. Oxidation of organic matter as the air drying process occurred was evident from the reduced level of organic matter in the air-dried sediment compared with the original flooded sediment (56.7 percent compared to 18.7 percent, respectively) and could explain the decrease in percent clay size particles. An increase in both inorganic and organic anions and cations could result from the decomposition of organic matter. Organic contaminants found in the Indiana Harbor sediments are listed in Table D2.

Table D1

Selected Chemical and Physical Characteristics of Indiana Harbor Sediments Placed Under Two Different Environmental Conditions, Original-Flooded (Reduced) and Air-Dried Upland (Oxidized)

Characteristics	Sediment Flooded	 Upland
Percent sand	72.5a*	75.0a
Percent silt	20.0a	22.5a
Percent clay	7.5a	2.5b
CEC, meq/100g	3.08b	8.78a
pH	7.40a	7.50a
Electrical conductivity, S/m**	0.367a	0.390a
Percent organic matter	56.7b	18.7a

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* Mean of four replicates. Means followed by the same letter are not significantly different between environments at P = 0.05 level of probability using Duncan's New Multiple Range Test.

** S/m = Siemans per metre = 0.1 χ mmhos per centimetre.

Table D2

Concentration of Organic Contaminants in Indiana Harbor Sediment

Compound	Concentration, μg/g (ODW)*	
	Flooded	Upland
Aldrin	4.800a	4.600a
A-BHC	<0.155a	<0.200a
B-BHC	<0.155a	<0.200a
G-BHC	<0.155a	<0.200a
D-BHC	<0.155a	<0.200a
CHLORDANE	<0.155a	<0.200a
PPDDD	<0.155a	<0.200a
PPDDE	<0.155a	<0.200a
PPDDT	<0.155a	<0.200a
Dieldrin	<0.02a	<0.02a
A-endosulfan	<0.02a	<0.02a
B-endosulfan	<0.02a	<0.02a
Endosulfan sulfate	<0.02a	<0.02a
Endrin	<0.02a	<0.02a
Endrin aldehyde	<0.02a	<0.02a
Heptachlor	<0.02a	<0.02a
Heptachlor epoxide	<0.02a	<0.02a
PCB-1016	<1.55a	<2.00a
PCB-1221	<1.55a	<2.00a
PCB-1232	<1.55a	<2.00a
PCB-1242	<1.55a	<2.00a
PCB-1248	62.3a	66.3a
PCB-1254	<1.50a	<2.00a
PCB-1260	<1.55a	<2.00a
Toxaphene	<1.50a	<2.00a
Naphthalene	693a	123a
Acenaphthylene	13.9a	5.00b
Acenaphthylene	81.5a	39.3b
Fluorene	72.5a	42.8b
Phenanthrene	225a	188a
Anthracene	62.8a	38.0a
Fluoranthene	175a	143a
Pyrene	150a	120a
Chrysene	99.3a	76.5a
Benzo(a)anthracene	121a	94.0a
Benzo(b)fluoranthene	143a	118a
Benzo(k)fluoranthene	137a	111a
Indeno-1,2,3-C D)pyrene	79.5a	71.0a
Dibenzo(a h)anthracene	21.3a	25.0a
Benzo(a) pyrene	136a	111a
Benzo(g h i)perylene	45.3a	41.0a

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* Mean of four replicates. Means followed by the same letter in a row are not significantly different at P = 0.05 level of probability using Duncan's New Multiple Range Test.

9. The compounds aldrin through heptachlor epoxide are pesticides. PCB-1016 through PCB-1260 are PCBs, and toxaphene through Benzo(g h i)perylene are PAHs.

10. There were measurable quantities of aldrin; PCB-1248, and all of the PAHs except toxaphene in both the flooded and upland sediments. PCB-1248 concentration was above 60 µg/g in both the flooded and upland sediments. Drying had no effect on PCB-1248 concentration in the sediment. Statistically significant differences existed between the flooded and upland conditions for acenaphthylene, acenaphthene, and fluorene. Although not statistically significant, the other PAHs also appeared to be lower in the upland sediment. The reductions of PAH compounds were most probably the result of volatilization and oxidation or photolysis (see discussion of volatilization, Appendix G). There were no significant reductions of aldrin or PCB in the dried sediments.

11. Total and DTPA extractable heavy metals are listed in Tables D3 and Table D4, respectively. Total quantities of some of the metals are quite

Table D3

Total Heavy Metal Content of Sediment from Indiana Harbor

Metal	Concentration, µg/g	
	Flooded	Upland
Zn	4550a*	4270a
Cd	28.1a	27.2a
Cu	322a	316a
Fe**	135a	134a
Mn	2219a	2288a
As	22.9a	23.7a
Hg	0.505a	0.500a
Ni	137a	139a
Cr	650a	623a
Pb	197a	301a

* Mean of four replicates. Means followed by the same letter in a row are not significantly different at P = 0.05 level of probability using Duncan's New Multiple Range Test.

** Fe concentration is milligrams per gram.

Table D4

Heavy Metal Concentrations in DTPA Extracts of Indiana Harbor Sediment

Metal	Concentration, μg/g	
	Flooded	Upland
Zn	270a	1300a
Cd	0.245a	8.86b
Cu	<0.005a	0.154a
Fe	259a	442a
Mn	18.3a	41.9a
As	0.083a	0.091a
Hg	<0.001a	<0.001a
Ni	19.0a	19.1a
Cr	0.118a	0.314b
Pb	3.14a	26.9b

* Mean of four replicates. Means followed by the same letter in a row are not significantly different at P = 0.05 level of probability using Duncan's New Multiple Range Test.

high, but would not represent a potential problem unless they were in an available form. Cadmium and lead are the major metals that would be mobilized into the environment upon air-drying of the sediment; chromium and zinc would be mobilized to some extent.

12. Plant growth (Figure D2) on the flooded Indiana Harbor sediments was greater than that on the upland sediment. This difference is also reflected in a greater yield on the flooded IN sediments compared to that of the upland sediments (Table D5).

Table D5

Yield (g, ODW) of C. esculentus Grown in Sediments from Indiana Harbor and the WES Reference Soil

Indiana Harbor		WES Reference	
Flooded	Upland	Flooded	Upland
1.82b*	0.034a	5.38d	3.74c

* Mean of four replicates. Means followed by the same letter in a row are not significantly different at P = 0.05 level of probability using Duncan's New Multiple Range Test.

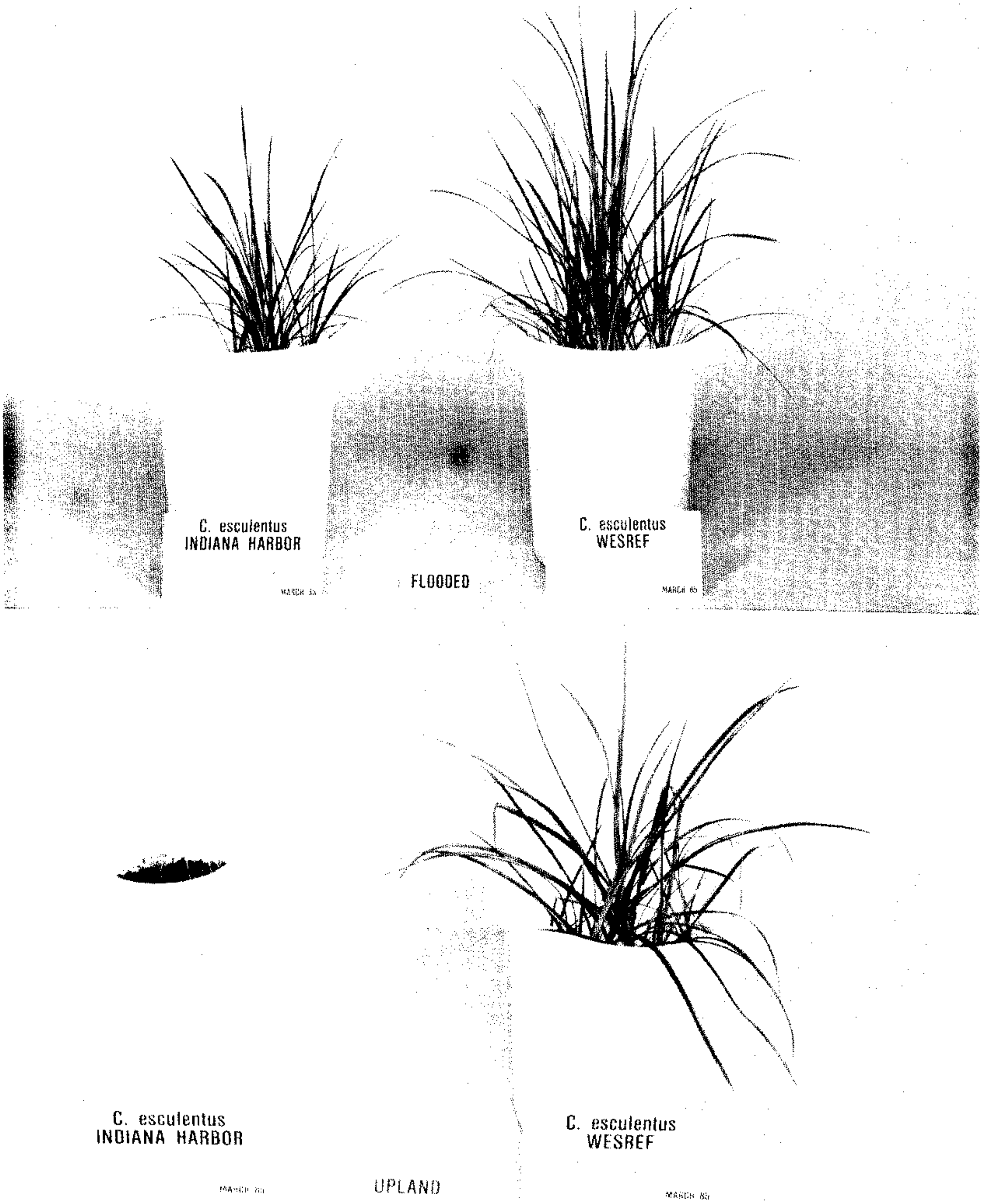

Figure D2. Plant growth of Cyperus esculentus on sediments from Indiana Harbor and the reference soil (WESREF) under flooded and upland conditions

13. The yield of C. esculentus on the Indiana Harbor flooded sediment was 0.245 g tissue (ODW) per kilogram of sediment while the yield on the upland Indiana Harbor sediment was 0.005 g per kilogram of sediment. Normal yield of C. esculentus is about 0.725 g per kilogram of sediment on the flooded condition and about 0.504 g per kilogram of sediment for the upland condition. Normally, plant growth from an upland condition is somewhat reduced when grown on the same soil in a flooded condition. Barko and Smart (1979) have shown that differences in growth and yield of C. esculentus grown on flooded sediments were related to sediment fertility. They demonstrated that all plants grown on flooded sediments were nitrogen limited even though the sediments used in their study contained large amounts of total nitrogen. The sediments that were not nitrogen limited were phosphorus limited. Patrick and Fontenot (1976) showed that vegetative growth of rice was greater under reduced (flooded) conditions than under oxidized (upland) conditions and attributed the better growth to solubilization of phosphorus due to the reducing conditions caused by submergence.

14. Another explanation for the lower yield under upland conditions is the possible decrease in available nitrogen due to the process of denitrification (Patrick and Wyatt 1964, Reddy and Patrick 1977) and ammonia volatilization (DeLaune and Patrick 1970) from the alternate wetting and drying between watering. The combination of reduced nitrogen content and reduced phosphorus availability to the plants grown on the upland sediments could have resulted in substantially lower yields from the upland Indiana Harbor sediment.

15. Even though none of the organic compounds were found in the plant tissue (Table D6), the compounds could have injured the plant roots and severely affected plant growth without entering the plant. This injury would have also affected uptake and translocation of other important compounds necessary for plant nutrition. Also, copper content of C. esculentus was above 12 ug/g in plants grown under the upland condition. Several previous studies (Folsom and Lee 1981; Folsom 1981a, 1981b) have implied that a copper content above 10 ug/g in C. esculentus is detrimental to its growth.

Table D6

Concentration of Organic Contaminants in Cyperus esculentus Grown in Sediment from Indiana Harbor

Compound	Concentration, µg/g/ODW Flooded	 Upland
Aldrin	<0.005	<0.005
PCB-1248	<0.05	<0.05
Naphthalene	<2	<2
Acenaphthylene	<2	<2
Acenaphthene	<2	<2
Fluorene	<2	<2
Phenanthrene	<2	<2
Anthracene	<2	<2
Fluoranthene	<2	<2
Pyrene	<2	<2
Chrysene	<2	<2
Benzo(a)anthracene	<2	<2
Benzo(b)fluoranthene	<2	<2
Benzo(k)fluoranthene	<2	<2
Indeno-1,2,3-c d)pyrene	<2	<2
Dibenzo(a h)anthracene	<2	<2
Benzo(g h i)perylene	<2	<2

* Mean of four replicates.

16. Heavy metal content of plants grown on the upland sediment was generally greater than that grown on the flooded sediment (Table D7) and is consistent with behavior of metal uptake found in other studies (Folsom, Lee, and Bates 1981; Folsom and Lee 1981). Plant cadmium and lead were quite high in the plants grown on the upland sediments (14.5 and 47.0 µg/g, respectively). The cadmium value is above the World Health Organization (WHO) allowable range of 0.5 - 2.0 µg/g Cd (World Health Organization 1972) and should be cause for concern. Lead is greater than that allowed by the European Community (allowable range of 5.0 - 40 µg/g Pb) (European Community, 1974). However, when the total plant uptake (concentration times yield) is considered (Table D8) it is apparent that the stunted plant growth resulted in higher tissue contents of metals under upland conditions. There was less total mobility of metals into plants under upland conditions than under flooded conditions. However, elevated tissue contents of the metals cadmium and lead could present potential adverse food chain impacts.

Table D7

Heavy Metal Content of Cyperus esculentus Grown in Sediment from Indiana Harbor

Metal	Concentration, μg/g	
	Flooded*	Upland**
Zn	34.9*	128
Cd	0.095	14.5
Cu	1.45	12.8
Fe	138	226
Mn	38.4	453
As	<0.025	<0.025
Hg	<0.005	<0.005
Ni	0.549	0.167
Cr	2.43	14.5
Pb	1.51	47.0

* Mean of four replicates.
** Composite of four replicates.

Table D-8

Total Plant Uptake (Concentration Times Yield) of Heavy Metals by C. esculentus Grown in Sediments From Indiana Harbor

Metal	Total Uptake, μg/pot	
	Flooded*	Upland**
Zn	61.5	2.38
Cd	0.198	0.009
Cu	2.64	0.237
Fe	245	4.18
Mn	69.9	8.38
As	--	--
Hg	--	--
Ni	1.03	0.003
Cr	3.71	0.268
Pb	2.75	0.869

* Mean of four replicates.
** Composite of four replicates.

Summary and conclusions

17. Sediments from Indiana Harbor were subjected to the USAEWES plant bioassay procedure. Results of sediment analysis indicated high EC, potentially low available nitrogen and phosphorus, as well as very low concentrations of unknown organics that may limit plant growth. Air drying of the original flooded sediments resulted in reduced levels of OM and two of the PAHs (acenaphthylene and acenaphthene) but not of PCB-1248.

18. Plant growth on the flooded Indiana Harbor sediment was greater than that on the upland sediment. However, heavy metal content of plants grown on the upland sediment was generally greater than that of plants grown on the flooded sediment and is consistent with the behavior of metal uptake found in previous studies. Reduced plant growth under upland conditions could be due to nutrient limitations or inhibition of root function by organic compounds and/or heavy metals, especially Cu. Organic contaminants were not found in plant tissues.

Animal Bioassay

19. Dredged or fill material placed in an upland or in-lake confined disposal facility (CDF) eventually may become a wildlife habitat and resting area for migratory birds. This situation has occurred in many confined disposal facilities around the Great Lakes, such as Times Beach, Buffalo, N.Y., where a prolific wildlife habitat has developed on contaminated dredged material. It is, therefore, important to note that processes such as weathering, leaching, and mobilization of some compounds may result in a material, that, after a period of time, is quite unlike the original sediment. The upland animal bioassay addresses both the immediate response of animals to a newly dredged sediment and the response of animals potentially colonizing the weathered dredged material at some indefinite time in the future.

20. The upland animal bioassay procedures applied are those developed by Edwards (1983) to evaluate the effects of new chemicals for the European Economic Commission (EEC) and the Organization for European Common Development (OECD). The tests have been modified subsequently for use with dredged

material, fill material, and contaminated soils by the WES and TNO (the Netherlands Organization for Applied Scientific Research). The WES-TNO procedure has been applied both as a predictive test and for management guidance for old disposal sites in the United States and Europe (Marquenie and Simmers 1984; Rhett, Simmers, and Lee 1984; Simmers, Lee, and Marquenie 1984).

Materials and methods

21. Earthworms (*Eisenia foetida*) were placed in the original reduced Indiana Harbor sediment as a preliminary screening test prior to the initiation of the earthworm bioassay. An immediate avoidance reaction by the earthworms followed by acute toxicity indicated that bioaccumulation testing for 28 days could not be accomplished until the sediment was rendered less toxic. Various treatments were applied to the sediment to evaluate the effects of aging and drying under upland disposal conditions including: ashing in a muffle furnace for 24 hr at 600°C, drying for 7 and 21 days in sunlight, drying for 21 days in sunlight plus a manure amendment, and aging outdoors in the shade for 6 months. After each aging process, the resulting material was completely air dried, ground with a mortar and pestle, and re-wet to field capacity before adding earthworms. Five worms were added to 50-g triplicate subsamples of each material, and survival was recorded.

22. The 6-month aged sediment was the only material which demonstrated adequate survival for a 28-day bioassay test. This material was aged outdoors in 60 ℓ glass aquaria with regular mixing and RO water added as necessary to prevent complete oxidation and to promote microbial biodegradation. The aquaria were covered to prevent flooding during rainfall and were kept out of direct sunlight. After aging, 2 ℓ of this test material was placed in Plexiglas cylinders (30 × 15 × 3cm) and watered by capillary action from a 2.5 cm-deep basin surrounding the base of the cylinder (Figure D3). Both ends of the cylinder were covered with 340-μ mesh Nitex bolting cloth (Wildco), which was held in place by 2.5 cm lengths of 15 cm schedule 20 PVC pipe. The screen acted to retain the substrate and earthworms.

23. Each bioassay container received 30 g of earthworms (counted and weighed before and after the 28-day test). They were removed from a manure

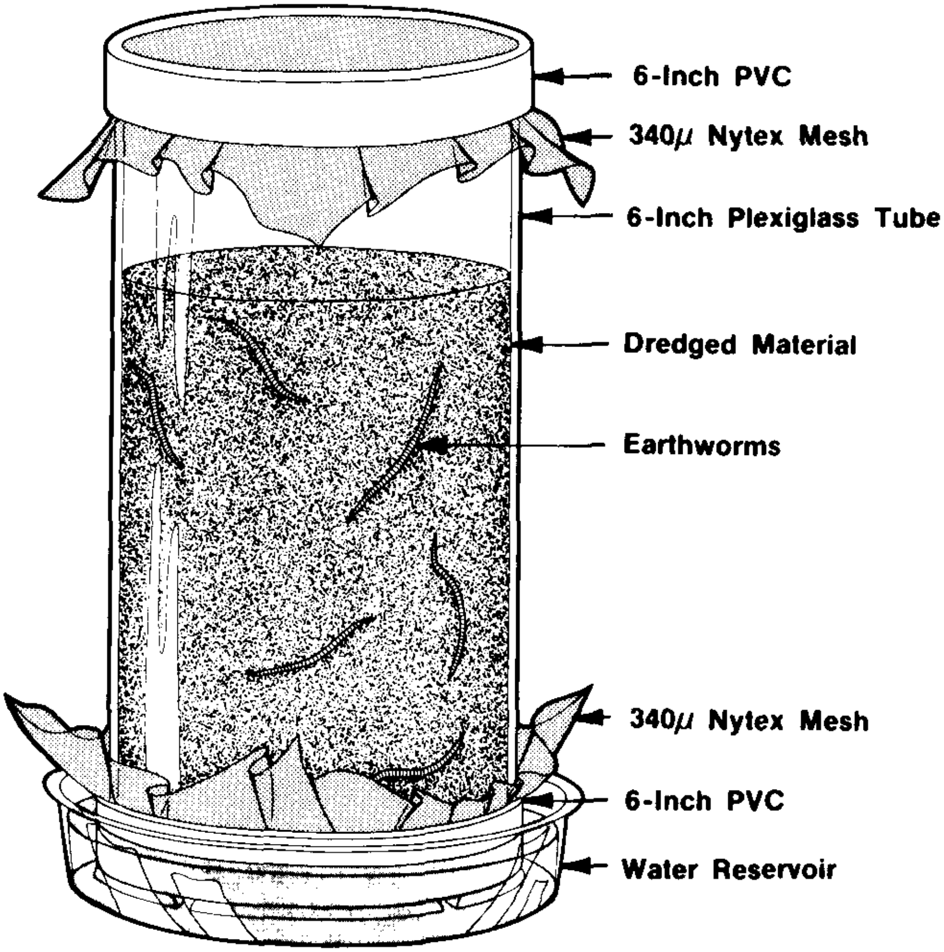

Figure D3. Test cyclinders

growth medium, rinsed with RO water, and placed on paper towels to remove excess water. Then the worms were weighed and placed on the test sediment. The test was conducted in a temperature-controlled chamber at 15°C with continuous lighting. Due to *E. foetida's* negative phototactic response and the transparency of the Plexiglas, the worms were forced to stay within the substrate rather than near the cylinder wall. The capillary watering method provided a moisture stratification allowing the earthworms to choose their best environment.

24. Each earthworm tissue sample for analysis was homogenized using a PT 10/35 Brinkman Homogenizer (Sybron Corp, Westbury, N.Y.), equipped with a PTA 20S titanium blade to reduce potential metal contamination. The resulting homogenate was divided into two subsamples (5 g for heavy metals analysis and 10 g for organic analysis). Tissues and sediment were analyzed for heavy metals using atomic absorption spectroscopy following appropriate USEPA sample digestion procedures (Delfino and Enderson 1978). Test samples were analyzed for cadmium, copper, chromium, lead, nickel, and zinc using a Perkin-Elmer Model 2100 Heated Graphite Atomizer and a Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer. Mercury was determined using a Perkin-Elmer Model 503 Atomic Absorption unit using the cold vapor technique. Arsenic was determined using a Perkin-Elmer Model 305 Atomic Absorption unit with a MHS-10 Hydride Generator. When zinc, cadmium, and chromium levels were high, they were determined using a Beckman IIIB Emission Spectrometer.

25. Techniques for organic analyses followed recommended USEPA procedures (USEPA 1982). Organic compounds in sediments were extracted using a hexane-acetone extraction, and those in tissues were extracted with 4-percent sodium hydroxide. Polychlorinated biphenyls were determined following Soxhlet extraction and silica gel cleanup by means of electron capture gas chromatography. The PAHs fraction was separated by silica gel chromatography and subjected to capillary gas chromatography.

Results and discussion

26. The Indiana Harbor sediment, in its original reduced state, was extremely toxic to the worms. No burrowing occurred, and the worms were dead

or moribund in less than 24 hr. Immediate burrowing of the worms into the manure controls indicated that neither handling nor the physical condition of the worms was the cause of mortality. Various treatments were conducted on the sediments to simulate the aging and weathering of the sediments under upland disposal conditions. No survival occurred in sediments subjected to drying for up to 21 days, drying for 21 days plus a manure amendment, or ashing for 24 hr at 600 °C in a muffle furnace. In contrast, earthworms burrowed actively into the sediment that was aged for 6 months and demonstrated near 100 percent survival for more than 28 days. At this point, a 28-day earthworm bioassay was initiated to evaluate contaminant bioaccumulation from this "aged" Indiana Harbor sediment. The remainder of this discussion applies to the results of the earthworm bioassay on the sediment that was aged for 6 months.

27. The 6-month aging process resulted in substantial changes in the concentrations of organic compounds present in the original Indiana Harbor sediment but had relatively little effect on the metals (Table D9). The concentration of the total PCBs (sum of congeners) in the aged sediment decreased by over 80 percent of the original sediment concentration (Table D10). The most dramatic effect of the aging process was on the PAHs, particularly naphthalene, which dropped to about 2 percent of its original concentration (Table D11). The total of all 16 PAHs analyzed dropped an entire order of magnitude, largely as the result of the loss of naphthalene (see discussion of volatilization in Appendix G).

28. The earthworms burrowed rapidly into the aged sediment and the manure controls. Periodic examination of the test sediment indicated that the worms were actively burrowing throughout the entire volume of sediment in each cylinder and were not in a state of inactivity within the cracks and air pockets. The worms remained active and no dead or moribund worms were observed on the sediment surface throughout the entire 28-day exposure period. Earthworm recovery at the end of the exposure period exceeded 95 percent in both the manure controls and the aged sediments. Tissue biomass was sufficient to allow chemical analysis of the earthworms for toxic metals, PCBs, and PAHs.

29. The concentrations of arsenic, cadmium, copper, lead, and nickel increased significantly in earthworm tissues during the 28-day exposure period,

Table D9

Metal Concentrations* in Indiana Harbor Sediments and Bioassay Earthworms

Metal	Original Sediment	Aged** Sediment	Initial Earthworms †	Bioassay Earthworms ††	CF‡
Arsenic	29.5	25.962 +/- 1.587	1.582 +/- 0.072a	2.808 +/- 0.369b	0.11
Cadmium	20.0	19.094 +/- 2.519	6.082 +/- 0.468a	9.037 +/- 0.823b	0.47
Chromium	650.0	506.729 +/- 36.102	0.000 +/- 0.000a	3.892 +/- 2.822a	0.01
Copper	282.0	237.888 +/- 7.128	11.302 +/- 0.389a	23.112 +/- 3.022b	0.10
Lead	879.0	689.730 +/- 38.902	0.457 +/- 0.122a	6.530 +/- 3.088b	0.01
Mercury	0.530	0.522 +/- 0.904	0.059 +/- 0.103a	0.000 +/- 0.000a	0.00
Nickel	137.0	111.860 +/- 1.401	1.302 +/- 0.295a	3.225 +/- 0.829b	0.03
Zinc	4125.0	3767.454 +/- 114.381	118.426 +/- 5.693a	149.956 +/- 19.096a	0.04

* Mean of three replicates +/- standard deviation expressed as μg/g (=ppm) dry weight. Means in a row followed by the same letter are not significantly different according to Duncan's New Multiple Range procedure at alpha = 0.05.

** 6-month aging.

† Time = 0.

†† Time = 28 days.

‡ Concentration factor (ratio of concentration in worms to that in the aged sediment).

Table D10

PCB Concentrations* in Indiana Harbor Sediments and Bioassay Earthworms

Chlorobiphenyls	Original Sediment	Aged** Sediment	Initial Earthworms†	Bioassay Earthworms††
2,4-Di	<0.002	<0.010 +/- 0.000	<0.008 +/- 0.000a	<0.008 +/- 0.002a
2,4'-Di	4.3	<0.013 +/- 0.006	0.015 +/- 0.008a	0.020 +/- 0.020a
2,4-4'-Tri	17.5	<0.010 +/- 0.000	<0.008 +/- 0.000a	<0.008 +/- 0.002a
2,3',4',5-Tetra	27.0	3.550 +/- 1.210	<0.010 +/- 0.004a	1.365 +/- 0.391b
2,2',4,5'-Tetra	7.8	5.007 +/- 1.782	0.025 +/- 0.011a	1.137 +/- 0.807a‡
2,2',5,5'-Tetra	35.0	<0.010 +/- 0.000	<0.015 +/- 0.013a	<0.008 +/- 0.002a
2,2',4,6-Tetra	17.5	<0.010 +/- 0.000	<0.008 +/- 0.000a	<0.008 +/- 0.002a
2,2',3',4,5-Penta	4.55	1.787 +/- 0.858	0.013 +/- 0.004a	0.614 +/- 0.165b
2,2',4,5,5'-Penta	1.55	<0.010 +/- 0.000	<0.008 +/- 0.000a	<0.008 +/- 0.002a
2,2',3,4,5'-Penta	4.9	1.417 +/- 0.761	<0.008 +/- 0.000a	0.554 +/- 0.164b
2,2',3,4,4',5'-Hexa	2.6	1.149 +/- 0.753	0.008 +/- 0.000a	0.216 +/- 0.064b
2,2',4,4',5,5'-Hexa	1.3	<0.457 +/- 0.774	<0.008 +/- 0.000a	<0.008 +/- 0.002a
2,2',3,3',6,6'-Hexa	<0.002	<0.010 +/- 0.000	<0.008 +/- 0.000a	<0.008 +/- 0.002a
2,2',3,4,5,6'-Hexa	11.5	<0.010 +/- 0.000	<0.010 +/- 0.004a	<0.008 +/- 0.002a
2,2',3,4,4',5,5'-Hepta	1.85	1.660 +/- 1.449	<0.008 +/- 0.000a	0.104 +/- 0.047b
Sum	137.35	15.11		

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* Mean of three replicates +/- standard deviation expressed as µg/g (=ppm) dry weight. Means in a row followed by the same letter are not significantly different according to Duncan's New Multiple Range procedure at alpha = 0.05.

** 6-month aging.

† Time = 0.

†† Time = 28 days.

‡ The analysis of variance indicated that uptake could be considered marginally significant:probability > F = 0.0754.

Table D11

PAH Concentrations* in Indiana Harbor Sediments and Bioassay Earthworms

PAH	Original Sediment	Aged** Sediment	Initial Earthworms†	Bioassay Earthworms††
Naphthalene	2033.333 +/- 57.735a	46.267 +/- 1.258b	d	d
Acenaphthylene	21.667 +/- 0.577	d	d	d
Acenaphthene	105.333 +/- 8.083	d	d	d
Fluorene	78.333 +/- 8.145a	4.287 +/- 0.731b	d	d
Phenanthrene	206.667 +/- 11.547a	14.267 +/- 3.650b	d	d
Anthracene	63.333 +/- 1.528a	74.033 +/- 6.269b	d	35.264 +/- 16.37
Fluoranthene	160.000 +/- 10.000a	36.933 +/- 5.659b	d	d
Pyrene	143.333 +/- 5.774a	74.033 +/- 6.269b	d	35.264 +/- 16.37
Chrysene	95.667 +/- 4.041a	25.500 +/- 5.724b	d	12.218 +/- 5.92
Benzo(a)anthracene	102.000 +/- 13.856a	21.633 +/- 2.363b	d	d
Benzo( )fluoranthene‡	156.667 +/- 15.275a	41.700 +/- 19.213b	d	20.915 +/- 10.49
Benzo(a)pyrene	105.667 +/- 16.921a	33.900 +/- 10.789b	d	18.420 +/- 5.90
Indeno(1,2,3-c,d)pyrene	57.000 +/- 10.440a	18.513 +/- 12.491b	d	9.295 +/- 2.78
Dibenzo(a,h)anthracene	13.667 +/- 6.351a	d	d	d
Benzo(g,h,i)perylene	39.667 +/- 4.163a	4.280 +/- 7.703b	d	4.497 +/- 0.74
Total PAH	3382.333 +/- 142.388a	388.217 +/- 80.765b		131.430 +/- 11.17

Note: d = detection limit.

* Mean of three replicates +/- standard deviation expressed as μg/g (=ppm) dry weight. Means in a row followed by the same letter are not significantly different according to Duncan's New Multiple Range procedure at alpha = 0.05.

** 6-month aging.

† Time = 0.

†† Time = 28 days.

‡ Benzo(b)fluoranthene + Benzo(k)fluoranthene.

whereas, chromium, mercury, and zinc did not (Table D9). Computation of concentration factors (ratios of metal concentrations in bioassay worms to those in the aged sediments), however, showed that most of the metals found in the sediments were not readily available to earthworms.

30. The uptake of PCBs by earthworms was significant during the 28-day exposure period. The earthworms accumulated PCB concentrations that were about 25 percent of those in the aged sediments (Table D10). Of the 15 PCB congeners analyzed in the sediments and worms, significant bioaccumulation occurred in only one tetra-, two penta-, one hexa-, and one heptachlorinated biphenyl congener. Bioaccumulation was marginally significant ($p > F = 0.0754$) in one additional tetrachlorinated congener. Other congeners were near or below detection limits in both worms and sediments.

31. The bioaccumulation of PAHs by earthworms was significant only for five of the 16 compounds analyzed (pyrene, benzo[b]fluoranthene + benzo[k]fluoranthene, benzo[a]pyrene, and indeno[1,2,3-c,d]pyrene). The remaining PAHs were near or below the detection limits in the worms, except chrysene, which also showed marginally significant ($p > F = 0.0701$) bioaccumulation. All PAHs which bioaccumulated significantly were present in the tissues in concentrations about 50 percent of those found in the aged sediments; these PAHs apparently were the least labile of those in the original sediments.

Conclusions

32. Very little is known about bioaccumulation and effects of chemicals on earthworms, except for some pesticides and metals. The initial toxicity of the Indiana Harbor sediment apparently was the result of high concentrations of the volatile (and more water soluble) organic compounds, particularly naphthalene. The presence of the metals probably did not contribute significantly to the observed worm mortality, as the concentrations of metals in both the sediments and earthworms were generally below the levels demonstrated to be toxic or to inhibit growth and reproduction of earthworms (Neuhauser et al. 1984; Malecki, Neuhauser, and Loehr 1982; Hartenstein, Neuhauser, and Narahara 1981; Migula, Baczkowski, and Wielgus-Serafinska 1977). Zinc concentrations

in the sediments, however, were in the range reported to reduce reproduction by earthworms (Neuhauser et al. 1984). The presence of substantial concentrations of copper and zinc in the earthworms should be of little concern, as these metals are essential nutrients and generally are well regulated in animal tissues. Cadmium bioaccumulation may become a potential problem in the food chain, as cadmium is readily mobilized and is known to cause adverse effects at relatively low levels of exposure (Kay, 1985). The effects of PCBs and PAHs on earthworms are essentially unknown. Existing literature indicates that metals, PCBs, and some PAHs are bioaccumulated from sediments by earthworms (Marquenie, Simmers, and Kay, in preparation, Marquenie and Simmers 1984; Simmers, Lee, and Marquenie 1984; Simmers, Wilhelm, and Rhett 1984).

33. Of immediate concern in the upland disposal of Indiana Harbor dredged material would be the potential for acute toxicity to soil invertebrates due to volatile PAHs, especially naphthalene. These compounds would be expected to decrease rapidly with time through a combination of volatilization, microbial activity, and photodegradation. Following the loss of the more labile organic compounds, the sediments possibly would be colonized by earthworms and other soil-dwelling invertebrates. Bioaccumulation of metals and the less labile organic compounds then would be the major concern, as indicated by the earthworm bioassay.

34. The results from the 6-month aging of the Indiana Harbor sediment indicate that, with time, Indiana Harbor sediment placed under confined upland conditions may become habitable and develop into a biologically prolific ecosystem. This has occurred at the Times Beach disposal site at Buffalo, N. Y. (Marquenie, Simmers, and Kay, in preparation) as well as elsewhere in the Great Lakes area. Therefore, upland disposal of Indiana Harbor sediment would require a monitoring and management strategy to address contaminant bioaccumulation as the site became biologically productive.

APPENDIX E: QUANTIFICATION OF SURFACE RUNOFF WATER QUALITY

Introduction

1. Sediments removed from waterways by Corps construction projects sometimes contain high concentrations of contaminants such as heavy metals, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), and pesticides. The potential for causing adverse environmental impacts depends on several factors including the chemical form of the contaminants and the type of disposal environment. Dredged material in its original condition is anaerobic with a pH > 7 where many contaminants are closely bound to the particulates and are poorly soluble and not bioavailable. Movement of contaminants in surface runoff during this period would result mostly from sediment being eroded from the disposal site. The erosion of contaminated sediment during this time may be very high with suspended solids concentrations ranging from 5,000 to 50,000 mg/ℓ. Concentrations of contaminants in unfiltered runoff could also be very high during this period, but dissolved concentrations would be relatively low. When the material is placed in a confined upland disposal site, physiochemical changes occur as the wet anaerobic material dries and oxidizes. The extent to which changes occur may significantly affect the surface runoff water quality, particularly the dissolved portion. As the sediment dries and oxidizes, it becomes more resistant to erosion with suspended solids decreasing to 10 to 1,000 mg/ℓ. Total concentrations of contaminants will be several orders of magnitude less than during the wet stage. If high levels of sulfides are present in the sediment, then oxidation may cause the pH to lower to <4.0 where contaminants such as heavy metals become very soluble in surface runoff.

2. The US Army Engineer Waterways Experiment Station (WES) Rainfall Simulator-Lysimeter System has proven to be very effective in predicting surface runoff water quality from Corps of Engineers project sites such as confined upland dredged material disposal sites. The WES System is a rotating disk type rainfall simulator modified from a design of Morin, Goldberg, and

Seginer (1967).* It incorporates the latest concepts in rainfall simulators to accurately duplicate the drop size and terminal velocities of natural rainfall--a critical factor in erosion and infiltration studies (Westerdahl and Skogerboe 1982). In a study on an overland flow wastewater treatment facility near Utica, Miss., the WES System accurately simulated a natural storm event and hydrograph measured at the field site (Westerdahl and Skogerboe 1982). In another study under the Environmental Impact Research Program (EIRP) the concept of removing a disturbed soil material from a Corps project site and placing it in lysimeters at WES was tested and verified. The WES System accurately predicted soil loss from field plots established on the Tennessee-Tombigbee Waterway Divide Section (Lee and Skogerboe 1984a). Another study on using the WES System for predicting surface runoff water quality from confined upland dredged material disposal sites was conducted under the Field Verification Program (FVP). Material was collected from the proposed dredging site, brought to the WES, and placed in lysimeters to simulate a confined upland disposal site (Lee and Skogerboe 1984b). As the material dried and oxidized rainfall simulations were conducted and the surface runoff water quality monitored. The validity of this test has been field verified under the FVP.

3. Using results from the WES System, planners can make informed decisions concerning proper disposal and surface runoff containment measures prior to dredging. The WES System, however, requires very large and expensive facilities that are not generally available outside of WES. A simplified laboratory test is, therefore, required that will be simple, less expensive, and can be conducted by most Corps laboratories to screen sediments that may cause adverse environmental impacts. When a sediment is found to have the potential for causing environmental problems, the sediment may be brought to the WES for more extensive tests to determine the magnitude of the problem.

4. WES has selected several laboratory procedures from the published literature and applied them to the Indiana Harbor sediment. These procedures included air drying the sediment for various lengths of time, oven drying, a DTPA extract, and a peroxide extract. The purpose of these tests was to

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* See References at the end of the main text (Vol I).

duplicate as closely as possible the natural drying and oxidizing of sediment placed in an upland environment. The air-dried and oven-dried tests determines how quickly a small amount of sediment could naturally be dried and oxidized to the final end point. The DTPA extract has proven to be very useful in predicting the availability of of several heavy metals in plants (Lee, Folsom, and Bates 1983). The peroxide test was originally developed as a test for quickly oxidizing pyrite in acid mine spoils to determine potential soil acidity and lime requirements (Barnhisel 1976).

Materials and Methods

Rainfall Simulator-Lysimeter System

5. Sediment was collected from PCB-contaminated areas in Indiana Harbor, brought to the WES, and placed in three lysimeters measuring 4.57 by 1.22 m. Each lysimeter was loaded with nine 200-ℓ barrels of sediment to a depth of 33.02 cm. Standing water on the sediment was allowed to drain out of the lysimeters. The following day each lysimeter was subjected to a 30-min storm event at a 6.5-cm/hr application rate. Initial sediment moisture was 55 to 67 percent (60-65 percent solids) and pH was 7.9. Runoff rates were measured every minute and 4-ℓ samples were collected for chemical analysis at 5, 15, and 25 min after runoff began to occur. Additional samples were collected for suspended solids (SS) determinations at several points along the hydrograph. The 4-ℓ samples were combined into a composite sample and analyzed for filtered and unfiltered heavy metals, PCBs, PAHs, and pesticides.

6. The lysimeters were then moved outside the greenhouse and covered with semitransparent tops which allowed air movement over the surface of the sediment. Surface moisture and pH were monitored during the drying period. After 6 months of drying and oxidation, storm events were conducted on the three lysimeters. The depth of the sediment decreased to 22.9 cm, the sediment moisture, and the pH to 6.3. Samples were collected and analyzed as in the wet stage test runs.

Simplified laboratory tests

7. These tests were designed to predict contaminant concentrations in runoff water from dredged material disposal areas at various SS concentrations. Such simple screening tests could be performed at most Corps of Engineers field laboratories.

8. The laboratory tests were divided into two categories: those for predicting surface runoff during the wet, anaerobic stage; and those for predicting surface runoff during the dry, oxidized stage. The wet stage would require only the mixing of sediment and water (water extract) at ratios comparable to SS concentrations found in surface runoff during this stage. Past tests indicated that the range of SS could vary from 5,000 to 50,000 mg/ℓ, depending on the type of sediment and means of dredging. For the purpose of these laboratory tests, three sediment-to-water ratios were selected:

a. 1:10 or 100,000 ppm SS (250 g to 2,500 ml reverse osmosis (RO) water).
b. 1:100 or 10,000 ppm SS (25 g to 2,500 ml RO water).
c. 1:1,000 or 1,000 ppm SS (2.5 g to 2,500 ml RO water).

9. Sufficient dry weight equivalents of wet sediment to match the ratios above were placed into 4-ℓ glass jars and filled with RO water. Sediment and water were well mixed and divided into two portions: one for unfiltered contaminant analysis and one for filtered analysis. Samples were analyzed for PCBs, PAHs, Cadmium, Copper, Chromium, Nickel, and Zinc. All tests were replicated three times to match the number of lysimeters.

10. Because of the physicochemical changes that occur when dredged material is placed in an upland environment, the laboratory procedures required to simulate the dry, oxidized sediment were more complex than those for the wet sediment. Sediment in the lysimeter was allowed to dry and oxidize for a period of 6 months before the final runoff tests were conducted; however, that is not practical for a simplified laboratory test that should be quick and inexpensive. A number of procedures were therefore screened in this study and included different lengths of time for natural drying and oxidizing as well as several chemical extracts:

a. Oven drying to 5 percent.
b. Oven drying to 5 percent + peroxide.
c. Air drying to 5 percent.
d. Air drying to 5 percent + 14 days aging.
e. Air drying to 5 percent + 28 days aging.
f. Air drying to 5 percent + peroxide.
g. DTPA extract.

Again, three different sediment-to-water ratios were used that corresponded to the range of SS found in surface runoff from previous studies (100 to 1,000 mg/ℓ):

a. 1:100 or 10,000 ppm SS (25 g to 2,500 ml RO water).
b. 1:1,000 or 1,000 ppm SS (2.5 g to 2,500 ml RO water).
c. 1:10,000 or 100 ppm SS (0.25 g to 2,500 ml RO water).

The purpose of the different lengths of drying time was to determine if sediment could be sufficiently dried and oxidized in a reasonable period of time to predict surface runoff water quality. The DTPA extract has been successfully used by personnel at WES to predict heavy metal uptake of some metals in plants. The peroxide extract was developed by Barnhisel of the University of Kentucky to predict potential acidity and lime requirements on acid mine spoils. The peroxide was used to quickly oxidize pyrite, usually found in acid mine spoils, which forms sulfuric acid. By natural processes, the pyrite might require months or years to completely oxidize, thereby making normal pH and lime requirement tests impractical for mine spoils. The peroxide test quickly oxidizes all the material in the soil or sediment, accomplishing in a short period what might require months by natural processes.

11. For the oven-dried test, wet sediment was placed in an oven at 950°C for 48 hr and then ground up to pass a 20-mesh screen. The sediment was mixed with RO water to attain the appropriate sediment-to-water ratios and divided into unfiltered and filtered portions. Again all tests were replicated three times.

12. Air-dried tests were conducted by placing wet sediment in drying flats in a greenhouse until the sediment reached 5-percent moisture. Some of the sediment was mixed with RO water as in the oven-dried test, and some was allowed to oxidize for an additional 14 and 28 days. Lysimeter tests showed that even after reaching 5-percent moisture, additional time was required to completely oxidize the sediment. After 14 and 28 days, sediment was ground up and mixed with RO water as before.

13. The DTPA extract test was similar to the wet sediment test except that an additional DTPA solution was added to the sediment-water solution. The DTPA solution included several components mixed together and diluted with RO water to 1ℓ and adjusted to pH of 7.3 using HCl or NaOH as needed:

DTPA Solution
1.099 g/ℓ $CaCl_2$ (0.01 M)
14.919 g/ℓ triethanolamine (0.1 M)
1.967 g/ℓ DTPA (0.0005 M)

14. Peroxide was used on both oven-dried and air-dried sediment, and extractions were conducted according to procedures established by Barnhisel (1976). For this procedure a pretest was used to determine the total amount of peroxide required to completely oxidize all the sediment. For the pretest, 10 g of oven-dried sediment was placed in a 4-ℓ glass jar and 10 ml of 30-percent hydrogen peroxide was slowly added. After reaction subsided, another 10 ml was added. This was continued until visible reactions did not occur when additional peroxide was added. This estimated the approximate amount of peroxide required to completely oxidize the sediment. The appropriate amounts of sediment for each sediment-to-water ratio were then mixed with the required volumes of peroxide and the reactions allowed to occur. The solution was then diluted with RO water to 2,500 ml and analyzed for unfiltered and filtered contaminants.

Results

Rainfall Simulator-Lysimeter System

15. Results of the lysimeter test for wet, anaerobic sediment showed high concentrations of contaminants in the unfiltered samples (Table E1). At this stage contaminants were bound up tightly in the SS and, therefore, poorly soluble. The sediment was anaerobic with a high pH in the sediment and in the surface runoff. Concentrations of SS were also high at this stage in the surface runoff and resulted in high concentrations of contaminants in the unfiltered runoff samples.

16. Organic compounds were highest in the unfiltered samples indicating that they were bound up in the SS. The only PCB above detectable limits was PCB-1248 which was also mostly insoluble; however, a detectable concentration was present in the filtered samples. Concentrations of PAHs were also mostly in the unfiltered samples, although naphthalene, acenaphthene, fluorene, and phenanthrene all had detectable concentrations in the filtered samples. Heavy metals were also mostly in the unfiltered samples. Relatively high concentrations of metals were present in the filtered samples, but solubilities were less than 4 percent. Filtered concentrations of arsenic and mercury were below detectable limits. The US Environmental Protection Agency Maximum Criteria for the Protection of Aquatic Life are presented in Table E1 for comparison with surface runoff filtered contaminant concentrations.

17. Significant physicochemical changes occurred in the Indiana Harbor sediment as it dried and oxidized. The percent moisture decreased to about 5 percent, and the sediment pH decreased to 6.3. The sediment in the lysimeters became hard and extensively cracked, causing the SS concentrations to decrease to an average of 56 mg/ℓ. The decline of SS concentrations had a significant effect on the unfiltered contaminant concentrations which decreased by several orders of magnitude. The effects of the physicochemical changes on the filtered concentrations were varied depending on the contaminant.

18. Sediment concentrations of organic compounds decreased significantly due to volatilization (Appendix G) during drying and oxidation so that

Table E1

Surface Runoff Water Quality During Early, Wet, Anaerobic Stage

Parameter	Mean Unfil. Runoff Conc. mg/ℓ	Mean Fil. Runoff Conc. mg/ℓ	USEPA Maximum Criteria mg/ℓ
pH	7.64	7.66	N*
Conductivity S/m	0.0052	0.0052	N
SS	6600	N	N
DDE	< 0.00001	0.00004	N
PCB-1248	0.051	0.0015	0.014
PAH$_s$	18.03	0.148	N
Naphthalene	6.91	0.115	N
Acenaphthylene	0.212	< 0.005	N
Acenaphthene	0.857	0.0131	N
Fluorene	0.780	0.010	N
Phenanthrene	1.67	0.0097	N
Anthracene	0.494	< 0.005	N
Fluoranthene	1.57	< 0.005	N
Pyrene	1.35	< 0.005	N
Chrysene	0.843	< 0.005	N
Benzo(a) anthracene	0.787	< 0.005	N
Benzo(b) fluoranthene	1.12	< 0.005	N
Indeno-1,2,3_C D pyrene	0.195	< 0.005	N
Benzo(g h i) perylene	0.124	< 0.005	N
Heavy metals			
Cadmium	0.154	0.0021**	0.0015-0.0024
Copper	1.79	0.0237**	0.012-0.043
Nickel	0.707	0.0297	1.1-3.1
Zinc	30.9	0.360**	0.180-0.570
Manganese	9.04	0.0170	N
Chromium	4.06	0.056	2.2-9.9
Lead	6.80	0.0670**	0.074-0.400
Iron	627	1.39	N
Mercury	0.0037	< 0.0002	0.0017
Arsenic	0.232	< 0.005	0.440

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* N No values available.

** Concentrations equal or exceed USEPA Maximum Water Quality Criteria.

Table E2

Surface Runoff Water Quality During Dry, Oxidized Stage

Parameter	Mean Unfil. Runoff Conc. mg/ℓ	Mean Fil. Runoff Conc. mg/ℓ	USEPA Maximum Criteria mg/ℓ
pH	6.3	6.3	N*
conductivity (S/m)	4.9	N	N
SS	56	N	N
PCB-1248	< 0.0002	< 0.0002	0.014
PAH			
Naphthalene	0.025 A	0.023 A	N
Acenaphthylene	< 0.005	< 0.005	N
Acenaphthene	< 0.005	< 0.005	N
Fluorene	< 0.005	< 0.005	N
Phenanthrene	0.0069 A	0.0056 A	N
Anthracene	< 0.005	< 0.005	N
Fluoranthene	0.0067	< 0.005	N
Pyrene	0.0061	< 0.005	N
Chrysene	< 0.005	< 0.005	N
Benzo (a) anthracene	< 0.005	< 0.005	N
Benzo (b) fluoranthene	< 0.005	< 0.005	N
Indeno-1,2,3_C D pyrene	< 0.005	< 0.005	N
Benzo (g h i) perylene	< 0.005	< 0.005	N
Heavy metals			
Cadmium	0.0011 A	0.0026 A**	0.0015-0.0024
Copper	0.054 A	0.072 A**	0.012-0.043
Chromium	0.027 A	0.0043 B	0.021
Nickel	0.038 A	0.046 A	1.1-3.1
Zinc	0.34 A	0.53 A**	0.180-0.570
Manganese	0.28 A	0.40 A	N
Lead	0.032 A	0.008 A	0.074-0.400
Iron	5.74 A	0.041 B	N
Mercury	< 0.0002	< 0.0002	0.0017
Arsenic	< 0.005	< 0.005	0.440

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* N No values available

** Concentrations equal or exceed USEPA Maximum Water Quality Criteria. Filtered contaminant concentrations with the same letter as unfiltered concentrations are not significantly different at P=0.05.

unfiltered and filtered concentrations in surface runoff also decreased significantly. Most of the organic compounds were below detectable limits even in the unfiltered samples. Only naphthalene, phenanthrene, fluoranthene, and pyrene were detected in the unfiltered samples. Naphthalene and phenanthrene were also present in the filtered samples.

19. Unfiltered concentrations of heavy metals also decreased significantly from the wet stage; however, many became more soluble. Filtered concentrations of Cadmium, Copper, Nickel, Zinc, Manganese, and Lead were not significantly different from the unfiltered concentrations, indicating that they were mostly soluble. Soluble chromium also increased after drying and oxidation but was still significantly lower than the unfiltered concentrations. The solubility of iron did not change after the sediment dried and oxidized, and mercury and arsenic were below detectable limits.

Simplified laboratory tests

20. Wet, anaerobic sediment. Laboratory test results were very promising and should provide the basis for an effective simplified predictive test that can be conducted by other Corps laboratories. Results for a dilution of 1:10 for the unfiltered wet sediment laboratory test were deleted because of problems with the chemical analysis. The high concentration of SS in the samples, 100,000 ppm, made accurate analysis difficult and the results were extremely varied and consequently have been discarded. Concentrations of SS from the lysimeter tests were between dilutions 1:100 and 1:1,000 (Table E3).

21. Unfiltered organic concentrations were generally accurately predicted by a dilution 1:100; however, lysimeter results for PAHs were slightly higher. Replicate 1 of the lysimeter test was an order of magnitude higher than the other two replicates causing the average concentration to be excessively high. If only second and third replicates are considered, then unfiltered organic concentrations are between a dilution of 1:100 and 1:1,000. Heavy metal concentrations from the lysimeter tests also are between a dilution of 1:100 and 1:1,000.

Table E3

Wet, Anaerobic Sediment Laboratory Test Results, Unfiltered Concentrations (mg/l)

Parameter	Unfiltered Runoff Conc.	Dilution 1:100	Dilution 1:1000
SS	6,600	10,000	1,000
PCB-1248	0.096	1.14	0.066
Naphthalene	6.91	9.0	0.65
Acenaphthylene	0.212	0.11	0.006
Acenaphthene	0.857	0.54	0.049
Fluorene	0.780	0.48	0.040
Phenanthrene	1.67	1.30	0.070
Anthracene	0.494	0.42	0.027
Fluoranthene	1.57	0.84	0.076
Pyrene	1.35	0.83	0.075
Chrysene	0.843	0.39	0.043
Benzo(a) anthracene	0.787	0.38	0.047
Benzo(b) fluoranthene	1.12	< 0.3	0.072
Benzo(k) fluoranthene	1.12	< 0.3	0.072
Indeno-1,2,3_C D pyrene	0.195	< 0.3	< 0.005
Dibenzo (a h) anthracene	< 0.010	< 0.30	< 0.005
Benzo(g h i) perylene	0.124	< 0.30	0.012
Heavy metals			
Cadmium	0.154B	0.2793A	0.0282C
Copper	1.79A	2.456A	0.273B
Chromium	4.06A	5.21A	0.470B
Nickel	0.707A	1.109A	0.120B
Zinc	30.9A	38.8A	3.74B

Different tests with the same letter are not significantly different at P=0.05.

22. Comparison of the different filtered test results was more difficult because of the much lower concentrations in the samples (Table E4). In many cases concentrations were at or near detection limits where precision is more difficult. In general the laboratory tests gave a good indication of the contaminant concentrations that will occur in surface runoff from the lysimeters. A dilution of 1:100 gave the best results but generally slightly underestimated the concentrations of heavy metals measured on the lysimeters. Organic compound concentrations from the lysimeter test were between a dilution of 1:100 and 1:1,000. Concentrations of PCB-1248 from the lysimeter were not significantly different than the dilution of 1:1,000.

23. Dry, oxidized sediment. Except for naphthalene, all organic compound concentrations were at or below detection limits so that comparison of laboratory test results with lysimeter test results would be meaningless. The laboratory tests did indicate that the PAHs would be lost from the sediment due to volatilization, except for trace concentrations of phenanthrene, fluoranthene, and pyrene in the unfiltered samples and naphthalene in both the unfiltered and filtered samples. All the laboratory test results showed PCB-1248 to be below detection limits. Comparisons for the dry, oxidized sediment therefore centered on the heavy metals.

24. Unfiltered concentrations of heavy metals were dependent only on the sediment-to-water ratios and not on the test itself, so to reduce costs many of the unfiltered samples were not analyzed. Table E5 presents results from the oven-dried and the oven-dried + peroxide laboratory tests. No significant differences occurred between the two laboratory tests showing that the presence of a powerful oxidizing agent such as peroxide had little effect on the total concentration of metals in the sediment. These results were to be expected since the total concentrations of heavy metals present in the sediment should not change with time, only the chemical form. The results did show that the lysimeter concentrations were, except for Zinc, slightly less than a dilution of 1:10,000, which compares with the SS concentrations which were also slightly less than a dilution of 1:10,000.

Table E4

Wet, Anaerobic Sediment Laboratory Tests, Filtered Contaminants

Parameter	Dissolved Runoff Conc. mg/ℓ	Dilution 1:1,000 mg/ℓ	Dilution 1:10,000 mg/ℓ	Dilution 1:100,000 mg/ℓ
PCB-1248	0.0016 B	0.011 A	0.0037 B	0.0025 B
PAH				
Naphthalene	0.115 B	2.8 A	0.39 B	0.11 B
Acenaphthylene	< 0.005	0.038	< 0.005	< 0.005
Acenaphthene	0.0131 BC	0.029 A	0.019 B	0.011 C
Fluorene	0.010 B	0.018 A	0.012 B	0.0081 B
Phenanthrene	0.0097 C	0.036 A	0.026 AB	0.020 BC
Anthracene	< 0.005	0.013	0.006	< 0.005
Fluoranthene	< 0.005	0.012	0.0069	0.007
Pyrene	< 0.005	0.012	0.006	0.006
Chrysene	< 0.005	0.006	< 0.005	0.007
Benzo(a) anthracene	< 0.005	0.006	< 0.005	0.007
Benzo(b) fluoranthene	< 0.005	< 0.005	< 0.005	< 0.005
Benzo(k) fluoranthene	< 0.005	< 0.005	< 0.005	< 0.005
Indeno-1,2,3_C D pyrene	< 0.005	< 0.005	< 0.005	< 0.005
Dibenzo(a h) anthracene	< 0.005	< 0.005	< 0.005	< 0.005
Benzo(g h i) perylene	< 0.005	< 0.005	< 0.005	< 0.005
Heavy metals				
Cadmium	0.0021 AB	0.0070 A	0.0009 B	0.0039 AB
Copper	0.0237 B	0.0647 A	0.0063 B	0.006 B
Chromium	0.0567 B	0.211 A	0.019 B	0.009 B
Nickel	0.0297 B	0.043 A	0.012 C	0.004 C
Zinc	0.360 B	0.916 A	0.096 B	0.056 B

Tests with the same letter are not significantly different at P=0.05.

Table E5

Dry, Oxidized Sediment Laboratory Tests, Unfiltered Concentrations*

Heavy Metal	Lysimeter Concentration mg/ℓ	Metal Concentration (mg/ℓ) at Indicated Ratio 1:100	1:1,000	1:10,000
SS	56	10,000	1,000	100
		OVEN DRIED		
Cd	0.0026	0.187	0.0207	0.0039
Cu	0.0011	1.86	0.278	0.0031
Cr	0.027	3.85	0.447	0.0490
Ni	0.038	0.899	0.165	0.042
Zn	0.34	33.1	3.77	1.44
		OVEN DRIED + PEROXIDE		
Cd	0.0011B	0.531A	0.106B	0.0035B
Cu	0.054B	6.40A	0.383B	0.042B
Cr	0.027C	12.7A	0.717B	0.093BC
Ni	0.038C	2.47A	0.332B	0.033C
Zn	0.443B	103A	6.01B	1.34B

* Different tests with the same letter are not significantly different at P = 0.05.

25. Significant differences did occur between the different laboratory tests when filtered metal concentrations are considered (Table E6). Even the highest sediment-to-water ratio for the air-dried + 28 days underestimated the concentrations of Cadmium, Copper, Zinc, and Nickel measured from the lysimeter. Concentrations of these metals appeared to increase slightly as the aging period was increased. However, even the longest drying period of the air-dried + 28 days was insufficient to completely oxidize the sediment. Longer drying periods could be used, probably 6 months or longer, but this would be impractical for a quick, standardized laboratory test. The oven-dried + peroxide, the air-dried + peroxide, and the DTPA tests were all significantly better at predicting the filtered metal concentrations determined from the lysimeter. The oven-dried + peroxide was better than the air-dried + peroxide, but this was probably the result of variations in sediment concentrations and not from differences in the tests. The peroxide tests increased the solubility of Cadmium, Copper, Nickel, and Zinc but did not increase the solubility of Chromium, which was similar to the lysimeter tests. The peroxide tests slightly underestimated the metal concentrations in surface runoff, but the tests did show the increased solubility of the heavy metals and volatilization of the organic compounds. The DTPA test results were highly variable but they did indicate potential for use in predicting surface runoff water quality from dry, oxidized dredged material. Refinements of the testing procedure could improve the variability of this test.

Conclusions and Recommendations

26. Based on the results of this study, the surface runoff from Indiana Harbor sediment placed in an upland environment could result in some adverse environmental impacts. During the early, wet, anaerobic stages, contaminants were mostly bound to the SS in the surface runoff and were poorly soluble. As the sediment dried, the SS concentrations decreased, thereby decreasing the unfiltered contaminant concentrations. Filtered concentrations during this period were low compared with the unfiltered concentrations but were still of concern when compared with the USEPA Maximum Criteria for the Protection of Aquatic Life. Results of the lysimeter tests represented the worst possible case that could occur during the wet, anaerobic stage. Control measures during this period should concentrate on control of the SS in the surface

Table E6

Dry, Oxidized Sediment Laboratory Tests, Filtered Concentrations*

Heavy Metal	Lysimeter Concentration mg/ℓ	Metal Concentration (mg/ℓ) at Indicated Ratio		
		1:100	1:1,000	1:10,000
		Oven Dried		
Cd	0.0026 A	0.0007 A	0.0004 A	0.0005 A
Cu	0.072 A	0.006 B	0.004 B	0.004 B
Cr	0.0043 AB	0.013 A	0.007 AB	0.003 B
Ni	0.046 A	0.031 AB	0.006 B	0.012 B
Zn	0.53 A	0.127B	< 0.030 B	< 0.030 B
		Oven Dried + Peroxide		
Cd	0.0026B	0.0067A	0.0021B	0.0018B
Cu	0.072B	0.212A	0.037C	0.023D
Cr	0.0043C	0.258A	0.120B	0.018C
Ni	0.046B	0.114A	0.017C	0.006C
Zn	0.53C	1.27A	0.714B	0.278D
		Air Dried		
Cd	0.0026 A	0.0009 A	0.0006 A	0.0009 A
Cu	0.072 A	0.005 B	0.003 B	0.003 B
Cr	0.0043 B	0.011 A	0.005 B	0.004 B
Ni	0.046 A	0.011 B	0.005 B	0.007 B
Zn	0.53 A	0.115 C	0.075 C	0.249 B
		Air Dried + 14 Days		
Cd	0.0026 A	0.0008 A	0.0004 A	0.0006 A
Cu	0.072 A	0.011 B	0.004 B	< 0.001 B
Cr	0.0043 C	0.013 A	0.009 B	0.005 C
Ni	0.046 A	0.011 B	0.003 B	0.004 B
Zn	0.53 A	0.125 BC	0.047 C	0.183 B
		Air Dried + 28 Days		
Cd	0.0026A	0.0017A	0.0005A	< 0.0001
Cu	0.072A	0.016B	0.004C	0.002
Cr	0.0043C	0.012A	0.006B	0.0023D
Ni	0.046A	0.010B	0.011B	0.008B
Zn	0.53A	0.323A	0.054A	0.040A
		Air Dried + Peroxide		
Cd	0.0026 A	0.0017 A	0.0027 A	0.0011 A
Cu	0.072 A	0.016 B	0.017 B	0.005 B
Cr	0.0043 C	1.32 A	0.086 B	0.016 C
Ni	0.046 A	0.014 AB	0.042 A	0.003 B
Zn	0.53 A	0.135 C	0.333 B	0.118 C

* Different tests with the same letter are not significantly different at P = 0.05.

Heavy Metal	Lysimeter Concentration mg/ℓ	Metal Concentration (mg/ℓ) at Indicated Ratio 1:100	1:1,000	1:10,000
		DTPA Extract		
Cd	0.0026	0.0287	< 0.010	< 0.010
Cu	0.072 A	0.036 A	0.513 A	0.014 A
Cr	0.0043 B	0.054 A	0.032 AB	0.014 B
Ni	0.046 B	0.283 A	0.046 B	0.193 AB
Zn	0.53 B	5.65 A	1.56 AB	0.244 B

runoff after considering an appropriate mixing zone outside the disposal site. If an appropriate mixing zone does not exist, control measures such as the use of sedimentation basins, control structures, filters, or chemical flocculants should be considered.

27. After the sediment dried and oxidized, the surface runoff water quality constituents of concern changed. Organic compounds were not a problem during this stage since most of the compounds had been lost from the sediment due to volatilization into the atmosphere or adsorption to soil particles. Some naphthalene was present in both the filtered and unfiltered samples but the total PAHs were low. No PCBs were detectable in runoff from the dry, oxidized sediment. Heavy metals were, however, a potential problem. Filtered concentrations of the metals Cadmium, Copper, Nickel, Zinc, Manganese, and Lead were not statistically different from the unfiltered concentrations. These metals were present in mostly soluble forms, which are more difficult to control. Chromium also increased in solubility but not to the extent of the other metals. Filtered concentrations of Cadmium, Copper, Zinc, and Lead were high enough to be of concern as they were greater than or equal to the USEPA Criteria. As the sediment continues to age, hard aggregate chunks will weather and break apart. Concentrations of SS will probably increase by as much as 10 to 20 times as the material becomes more erosive. Concentrations of filtered and unfiltered metals should increase by similar amounts. Therefore, some type of restriction or control measure should be required, or a mixing zone should be considered if the sediment is placed in an upland environment. Control measures might include liming the sediment, vegetating the site, capping, or treating the runoff.

28. Based on the results of the laboratory tests from this study, an extraction procedure does exist that can estimate the physicochemical changes that occur in a dredged material when it dries and oxidizes. The extraction procedures utilized peroxide to quickly oxidize a sediment which would require at least 6 months by natural means or a DTPA extract. Filtered concentrations from wet, anaerobic dredged material were estimated using the simple water-sediment dilution method. Filtered contaminant concentrations from the dry, oxidized sediment required the use of hydrogen peroxide. Further refinement and testing will greatly improve the accuracy and reliability of this

procedure. Additional verification on several different types of dredged material is required to determine the most effective test as well as to establish the reliability of these tests before one can be widely used as a standard procedure for predicting surface runoff water quality from contaminated dredged material. These verification tests should include both freshwater and estuarine dredged material, including dredged material with a wide range of particle-size distributions and organic matter content.

APPENDIX F: EVALUATION OF THE EFFECTIVENESS OF CAPPING IN ISOLATING CONTAMINATED INDIANA HARBOR DREDGED MATERIAL: BIOLOGICAL AND CHEMICAL ASPECTS

Introduction

1. Capping is a physical process in which a contaminated dredged material is covered with a layer of uncontaminated dredged material for the purpose of reducing the ecological impact of the contaminated material and rapidly rendering it harmless. Capping has been utilized by the New England Division and New York District in open-water disposal sites. These field studies have shown that capping is technically feasible and that the caps are stable under normal tidal and wave conditions (O'Conner and O'Conner 1982, Science Applications, Inc. (SAI) 1982). However, the efficiency of capping in isolating contaminants in dredged material from overlying water and from pelagic and benthic biota is unknown (O'Conner and O'Conner 1982). In the New York Bight, a mussel bioaccumulation study at the capping site indicated low body burdens that could have been due to bioconcentration of contaminants from ambient water as much as from the nearby sediments (O'Conner and O'Conner 1982). In Long Island Sound, mussels were also suspended in the water column at the sand- and silt-capped sites of the Stanford-Norwalk capping project. Concentrations of cobalt, copper, mercury, zinc, and vanadium fluctuated in the mussels over time, but these changes were thought to be unrelated to the caps because differences in spatial concentration were not detected (Morton and Kemp 1980). Based on these and other field study results, bioaccumulation of contaminants by test organisms in the water column can result from sources other than dredged material. Therefore, determining the ability of caps to isolate contaminated dredged material from the water column has proven to be a difficult question to answer in the field (Morton and Kemp 1980; O'Conner and O'Conner 1982).

2. Analyses performed on sediments from within two specific reaches in Indiana Harbor indicate that the sediments are contaminated with polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), various metals, and nutrients. In addition, these sediments also contain high levels of several metals, some of which were found to exceed the chronic criterion for the protection of freshwater aquatic life. Capping contaminated dredged material with clean dredged material within Indiana Harbor or Lake Michigan may be an

alternative to other disposal methods, such as confined land disposal. However, capping is still an experimental technique. To demonstrate that capping is an acceptable alternative to other means of disposal for contaminated Indiana Harbor sediments, it must be shown that capping will isolate this dredged material from the water column and the pelagic and benthic biota.

Purpose and Scope

3. The purpose of this study was to identify the minimum thickness of a Lake Michigan sediment that will inhibit sediment-water interactions between contaminated Indiana Harbor dredged sediment and the overlying water column and aquatic biota. Data developed from this work will be used in evaluating the suitability of the confined aquatic disposal concept for Indiana Harbor and, if appropriate, in preparing the preliminary design of the site.

Approach

4. The effectiveness of capping in chemically and biologically isolating contaminated dredged sediments is being actively investigated in the Long-Term Effects of Dredging Operations (LEDO) Program at the US Army Engineer Waterways Experiment Station (WES). The approach used to conduct the present study is the result of this research, and the following procedures were followed.

5. An initial analyses of the contaminated dredged material and the cap material was performed to determine which chemical contaminants were most appropriate to monitor in the studies. The information obtained from this procedure was used to select several key parameters that were monitored in the large-scale reactor studies described below.

6. An experimental technique, being developed for field office use to assess the thickness of cap material needed to chemically isolate contaminated dredged material with capping, was conducted in small (22.6 ℓ) reactor units. In these units, capping effectiveness is determined by following changes in dissolved oxygen and selected inorganic chemical species in the water column overlying each of the thicknesses of cap material tested. The rationale for this approach is as follows. Most contaminated dredged material exerts an oxygen demand on the overlying water column that exceeds the oxygen demands exerted by uncontaminated sediments. To effectively seal a contaminated

dredged material, the cap sediment must be thick enough to prevent the migration of oxygen-demanding materials into the overlying water column. If these materials are able to diffuse through the cap layer, their presence in the water column will cause a dissolved oxygen depletion rate that exceeds that of the cap material alone. In like manner, once the layer of cap material is thick enough to prevent migration of oxygen-demanding materials into the overlying water column, the oxygen depletion rate observed in the water column will be the same as that of the cap material alone. A similar rationale is applicable to ammonium-nitrogen and orthophosphate-phosphorus. These two constituents are released only under anaerobic conditions. Once anaerobic conditions have been achieved, ammonium-nitrogen and orthophosphate-phosphorus will be released. However, if the layer of cap material is thick enough to prevent the diffusion of materials from the underlying contaminated dredged material from reaching the water column, the release rates of these materials will be the same as those from the cap material alone.

7. The ability of the same cap material to isolate the contaminated dredged material from both the overlying water column and aquatic biota was tested using large-scale (250-ℓ) reactor units. The rationale for these tests is based on the fact that organisms tend to accumulate contaminated materials to which they are exposed. Thus, if contaminants are moving into the surface layer of the cap material, the biota living on the surface will be exposed to the contaminants and will accumulate them in their tissues. If the contaminants are moving through the cap material and into the water column, then organisms living in the water column will be exposed to the contaminants and are likely to accumulate these materials in their tissues. Analysis of the tissues of these organisms for key contaminants will then reveal if the contaminants have moved through the cap material and into the overlying water column and aquatic biota.

Methods and Materials

Sediment acquisition

8. Contaminated and capping material samples were obtained from Indiana Harbor in Indiana and Lake Michigan, respectively. Sediments from Indiana Harbor are contaminated, while Lake Michigan sediment is both relatively uncontaminated and a likely material for use in an open-water capping

operation. At each of two locations in Indiana Harbor, a sediment in the navigation channel was obtained using a clamshell dredge and placed into a total of forty 208-ℓ steel barrels. Five 208-ℓ barrels of Lake Michigan sediment were obtained at a site in Lake Michigan using the clamshell dredge. All samples were then transported to the WES within 5 days after collection. Upon arrival at WES, contents of the 40 barrels of Indiana Harbor sediment and the 5 barrels of Lake Michigan sediment were separately composited and mixed, then returned to the barrels for storage.

Small-scale reactor unit experiments

9. The ability of the capping material to chemically seal dredged material from Indiana Harbor containing relatively mobile and oxygen-demanding constituents was determined in 22.6-ℓ, cylindrical, Plexiglas leaching columns. The design and sediment loading arrangement of an individual column is shown in Figure F1. Caps of Lake Michigan sediment ranging from 5 to 30 cm in depth were used. These experiments were conducted in a controlled environment chamber with the temperature regulated at 20° ± 0.5°C.

10. Water supplied from a reverse osmosis unit was used to overlay the test sediments. Once the leaching column was filled, the water was aerated for 3 days by slowly bubbling air through the water column. This procedure ensured that the dissolved oxygen concentration for all units was relatively uniform (±0.5 mg/ℓ) at the start of the experiment. At the end of 3 days, the aeration apparatus was removed and a 4 cm layer of mineral oil was added to seal the surface of the water column from the atmosphere. Water samples were taken initially and at regular intervals for 30 days or until the measured dissolved oxygen concentration was depleted. The overlying water was manually mixed daily without disturbing the sediment using a Plexiglas stirring plunger that was suspended between the sediment and the mineral oil layer. Stirring was performed to prevent the establishment of concentration gradients in the water column and to ensure a well-mixed water column. All experiments were conducted in triplicate.

11. Dissolved oxygen was measured in samples collected by permitting water to flow gently from a long tube attached to the reactor unit sampling port into a standard biochemical oxygen demand (BOD) bottle. Dissolved oxygen was determined with the azide modification of the Winkler Method as described in Standard Methods (American Public Health Association (APHA) 1980).

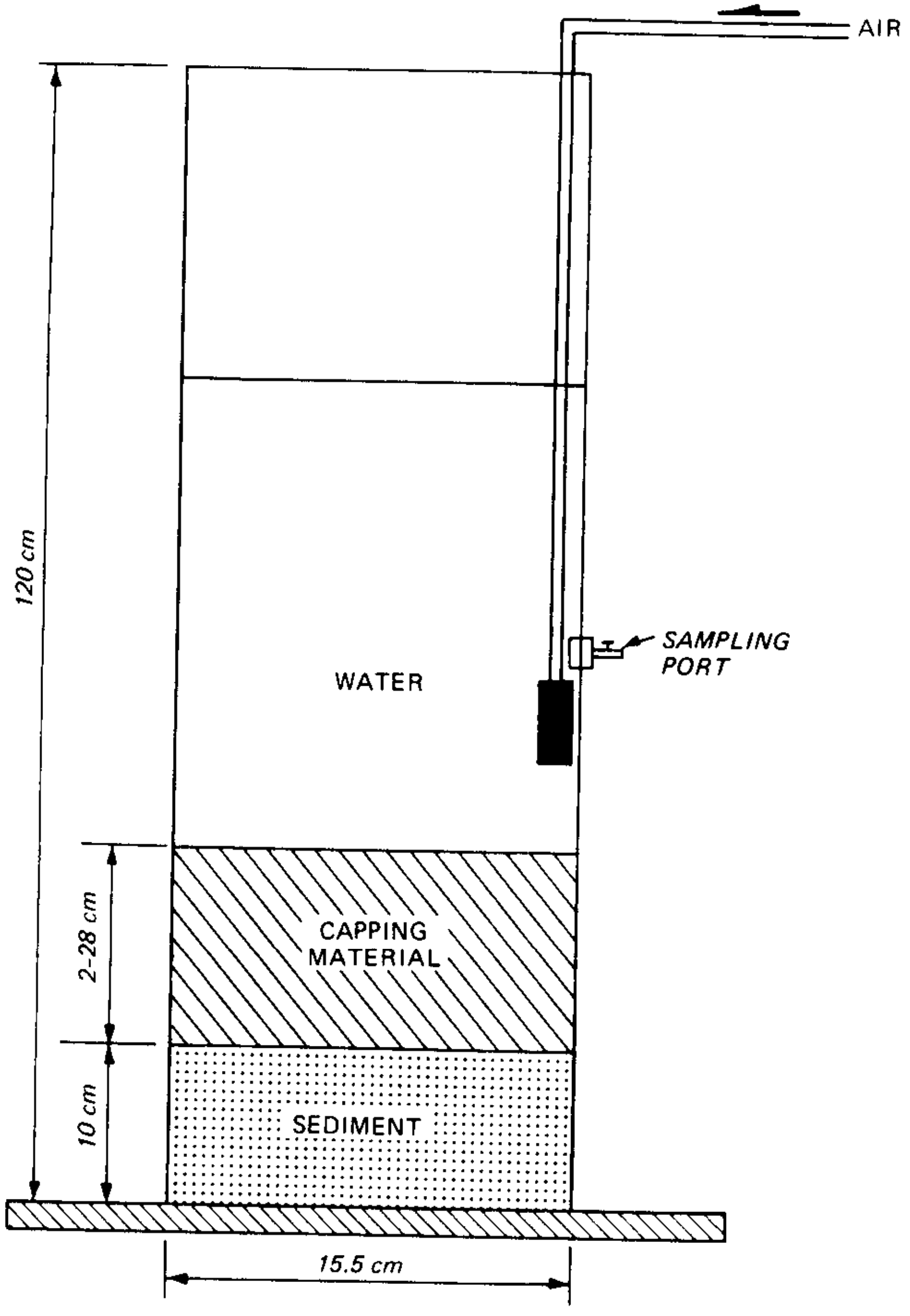

Figure F1. Small-scale reactor unit

12. Samples to be analyzed for ammonium-nitrogen and orthophosphate-phosphorus, relatively mobile compounds that are released under anaerobic conditions, were cleared of particulate matter by passage through a 0.45-μm membrane filter under a nitrogen atmosphere. Samples were preserved by acidification with concentrated HCl to pH 2, followed by immediate freezing and storage at -4°C. Ammonium-nitrogen and orthophosphate-phosphorus were determined using a Technicon Autoanalyzer II, in accordance with procedures recommended by Ballinger (1979).

Large-scale reactor unit experiments

13. Laboratory studies to assess the effectiveness of the cap in isolating Indiana Harbor sediment were conducted in a controlled environment chamber at 20 ± 0.5°C, using modified 250-ℓ flow-through reactor units (Figure F2) described in detail by Gunnison, et al., (1980). These chambers are 121 cm in height and measure 46 cm on a side. Modification included sealing of sampling ports with Plexiglas, removal of the mixing pump from the system, and provision for constant aeration of the water column. With the exception of the control units, to which only Lake Michigan sediment was added, enough Indiana Harbor sediment was added to give a layer 15 cm deep on the bottom of each reactor unit. Indiana Harbor sediment was then capped with a 30-cm layer of the Lake Michigan material. The depth was selected because the results of the small chamber studies demonstrated that 30 cm would completely seal the overlying water column from ammonium-nitrogen releases made by Indiana Harbor sediment. Additional reactor units were set up with 15 cm of Indiana Harbor sediment, but no cap material. A total of three replicates were set up for each of the three treatments (Table F1). Sixty litres of aged tap water were then added as gently as possible to each reactor unit and allowed to equilibrate with aeration for 14 days. A 14-day equilibration time was selected to allow initial compaction to occur and material suspended during water addition to settle. At the end of the equilibration/consolidation period, flow-through of aged tap water was initiated at a rate of 1.46 ℓ/hr. At this flow rate, 50 percent of the overlying water column was replaced every 36 hr (Sprague 1969). The water column in each reactor unit was continuously aerated to ensure a well-mixed aerobic water column.

14. The results of previous capping studies have demonstrated the importance of using at least two organisms to assess capping effectiveness in preventing movements of contaminants into the biota (see Brannon, et al., 1985,

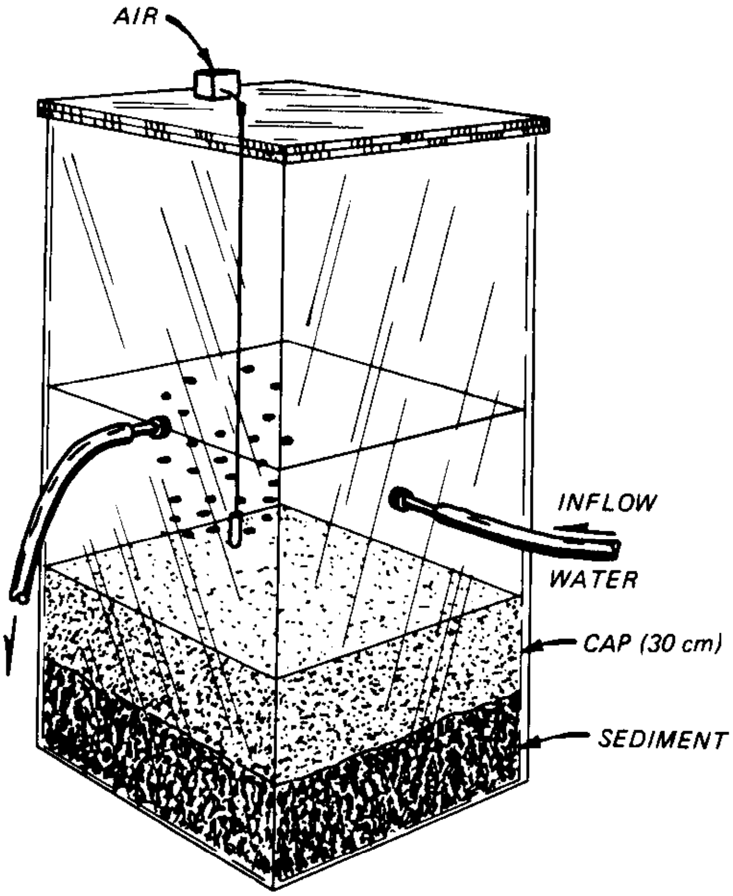

Figure F2. Large-scale reactor unit

Table F1

Experimental Design for Large-scale Reactor Column Experiments

Treatment	Reaction Chamber Replicate Designation
Lake Michigan Sediment only (Control)	IH-2 IH-4 IH-6
Indiana Harbor Sediment only	IH-1 IH-3 IH-5
Indiana Harbor sediment with 30 cm Lake Michigan sediment cap	IH-7 IH-8 IH-9

1986). Normally, one organism is selected that is representative of the benthic surface community. The second organism is often a variety of mussel that can be suspended in the overlying water column. Through discussions with the Chicago District, it was decided that a fish should also be used. The clam (*Anondonta grandis*) and yellow perch fingerlings (*Perca flavescens*) were selected, in consultation with the Chicago District, as bioassay organisms to determine if contaminants were moving through the cap and into the water column, while the red swamp crayfish (*Procambarus clarkii*) was used to assess the effect of capping on contaminant bioaccumulation in benthic organisms and to provide a source of bioturbation. Clams were obtained by scuba divers from the Detroit District from a freshwater lake in the Detroit area. Yellow perch fingerlings were supplied by the U.S. Fish and Wildlife Service Laboratory at LaCrosse, Wis. Crayfish were provided by the Center for Wetland Resources, Louisiana State University, Baton Rouge, La. All animals were acclimated to test conditions in the laboratory for at least 1 month prior to being added to the reactor units.

15. Crayfish were added to the reactor units following 4 days of flow-through operation in the reactor units. A square basket, open on the top, having dimensions of 45 cm on a side, a height of 45 cm, and a mesh size of 2.5 sq mm was then suspended in the water column 5 cm above the sediment surface of each reactor unit. Fifty of the perch fingerlings were added to each basket. A second cylindrical basket containing 30 clams was suspended 5 cm above the bottom of the rectangular basket in each reactor unit.

16. Concurrent with the addition of animals to the reactor units, subsamples of these populations were removed from the holding tanks for initial tissue chemical characterization. Clams were immediately frozen, divided into subsamples for PCB, PAH, and metals analysis, removed from their shells, then placed into hexane-rinsed glass (PCB, PAH) or acid-(HCl) washed plastic (metals) containers and maintained frozen until analyzed. To remove sediment and food from their gut, fish and crayfish were first depurated for 24 hr in water identical to that in the reactor units. They were then divided into subsamples for PCB, PAH, and metals analysis, placed into appropriate glass (PCB, PAH) or plastic (metals) containers, and maintained frozen until analyzed. Fish and crayfish in each reactor unit were fed 5 g of ground TetraMin™ twice each week during the experiment. Clams were fed weekly with a packet of baker's yeast suspended in approximately 250 ml of water from each

reaction chamber; this was then added to the chamber as a slurry. Fifteen clams were removed from each reactor unit at 10- and 40-day intervals and treated in the same manner described for initial clam samples. At the end of 40 days, fish and crayfish were removed from each reactor unit, depurated, and prepared for analysis in the same manner described for initial fish and crayfish samples.

17. Samples of the aged tap water (inflow water) and water in the reactor unit were obtained at the end of 40 days for subsequent chemical analyses. Samples to be used for PCB and PAH analyses were placed in 3.8-ℓ glass jars which had been hexane washed and dried at 105°C for 24 hr. Samples for metal analyses were filtered through 0.45-μm pore size membrane filters. The first 100 ml of filtrate was discarded. The subsequent filtrate was acidified to pH 1 with concentrated HNO_3. Water samples were analyzed for arsenic, cadmium, chromium, lead, and zinc using a Perkin-Elmer Model 2100 heated graphite atomizer and a Perkin-Elmer Model 503 atomic adsorption spectrophotometer. Mercury was determined using a Perkin-Elmer Model 503 atomic adsorption unit coupled to a Perkin-Elmer MHS-10 hydride generator.

18. Water, tissue, and sediment samples were analyzed for ten PCB isomer groups: total monochlorobiphenyls through total decachlorobiphenyls. Isomer group concentrations were determined following Soxhlet extraction, H_2SO_4 cleanup, and quantification in an electron capture gas chromatograph.

19. Sixteen compounds comprising the family of compounds collectively referred to as polyaromatic hydrocarbons (Table F2) were also determined in water, sediment, and tissue samples. Samples were extracted overnight with a Soxhlet using benzene:methanol. The aromatic hydrocarbon fraction was then separated using silica gel chromatography, concentrated, and subjected to capillary gas chromatographic analysis on a Hewlett Packard 5985 gas chromatograph equipped with a flame ionization detector. Individual compounds were quantified using analytical standards and an internal standard. Tissue and sediment samples were analyzed for arsenic, cadmium, chromium, mercury, lead, and zinc using atomic adsorption spectroscopy following sample digestion procedures describe by Ballinger (1979).

20. Total organic carbon (TOC) in sediment samples was determined by dry combustion (Allison 1965). Sediment particle-size distribution was determined using the method of Patrick (1958).

Table F2

Polyaromatic Hydrocarbon Compounds Determined in Water and Tissue Samples

Number of Rings	Name of Compound
Two-ring compounds	Napthalene
Three-ring compounds	Acenaphthalene Acenapthene Phenanthrene Anthracene Fluorene Fluoranthene
Four-ring compounds	Pyrene Chrysene Benzo(a)anthracene
Five-ring compounds	Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Dibenzo(a,h)anthracene
Six-ring Compounds	Indeno(1,2,3-c,d)pyrene Benzo(g,h,i)perylene

Statistical analysis of results

21. Means and standard errors were determined for each parameter within a treatment. To determine the statistical significance of differences between means, data were analyzed using the General Linear Models Procedure of the SAS Institute (SAS Institute, Inc., Cary, N.C.). This version used a Duncan multiple range test to determine differences between means. Statements of significance made in the text refer to the 5-percent level ($p < 0.05$) or less.

Results

Sediment characterization

22. Sediment from Indiana Harbor had higher concentrations of metals and pesticides than did the Lake Michigan cap material (Table F3). For example, the arsenic concentration in Indiana Harbor sediment was nearly triple that in Lake Michigan sediment. Concentrations of other constituents ranged from one to four orders of magnitude greater in the Indiana Harbor sediment compared with those in the Lake Michigan sediment.

23. Indiana Harbor sediment contained much higher levels of PAH compounds than did the cap material (Table F3). The only PAH compound present in detectable quantity in Lake Michigan sediment was naphthalene, and the level of this compound in Indiana Harbor sediment was more than three orders of magnitude greater than in the Lake Michigan material. The remaining PAH compounds found in Indiana Harbor sediment were not detected in Lake Michigan sediment.

24. Sediment from Indiana Harbor was found to contain PCB-1248, which was not detected in Lake Michigan sediment (Table F3). By contrast, Lake Michigan sediment contained a trace amount of PCB-1254, a compound not found in the material from Indiana Harbor. Indiana Harbor sediment also contained substantial quantities of total organic carbon, oil and grease, and a small amount of phenol (Table F3); these were either not present or present in much smaller amounts in Lake Michigan sediment. Indiana Harbor sediment had high percentages of silt, clay, and percent moisture (Table F4).

Small-scale reactor unit experiments

25. Water column oxygen depletion. Small column experiments were conducted to determine the thickness of cap necessary to chemically isolate Indiana Harbor sediment from the water column. The Lake Michigan sediment as supplied contained large amounts of coarse gravel. Discussions with the

Table F3

Comparative Chemical Composition of Indiana Harbor and Lake Michigan Sediments

Parameter	Concentration in Sediment, mg/kg dry weight Indiana Harbor	 Lake Michigan
Metals		
Arsenic	29.5	10.1
Cadmium	20.0	0.1
Chromium	650.0	4.4
Lead	879.0	11.9
Mercury	0.5	BD*
Zinc	4125.0	54.1
Pesticides		
Aldrin	2.55	0.0006
Polyaromatic Hydrocarbons		
Acenapthene	96	BD
Acenapthylene	22	BD
Anthracene	62	BD
Benzo(a)anthracene	86	BD
Benzo(b)fluoranthene	140	BD
Benzo(a)pyrene	87	BD
Benzo(g,h,i)perylene	35	BD
Chrysene	92	BD
Fluoranthene	150	BD
Fluorene	69	BD
Indeno(1,2,3-c,d)pyrene	50	BD
Naphthalene	2000	0.46
Phenanthrene	200	BD
Pyrene	140	BD
Polychlorinated biphenyls		
PCB-1248	7.39	BD
PCB-1254	BD	0.013
Total carbon	2.28% of sediment weight	1.83% of sediment weight
Total inorganic carbon	3.88% of sediment weight	0.47% of sediment weight
Oil and grease	3.9% of sediment weight	1.71% of sediment weight
Phenol	3	BD

* BD = below detection.

Table F4

Selected Physical Characteristics of Indiana Harbor Sediment

Constituent	Concentration
Particle size,* %	
Sand	72.5
Silt	20.0
Clay	7.5
Percent moisture	50-80
Specific gravity of solids	2.50-2.54
Hydraulic conductivity, cm/sec	10-8

*Particle sizes based on US Department of Agriculture classification.

Chicago District indicated that the Lake Michigan material supplied may have had a higher gravel content than is typical of most sediment from this lake. Therefore, to assess the possibility that the gravel content of a cap material would make a difference in the required cap thickness, two small column studies were conducted. The first study used the cap material as supplied, while the second study was conducted with cap material that had been sieved to remove gravel larger than 2.5 mm in diameter.

26. Dissolved oxygen depletion in the water column would not normally be expected to be a problem in the open-water environment because of mixing and reaeration. Previous studies have shown that dissolved oxygen depletion can be used as one of several possible tracers for determining how effectively a cap can isolate an underlying dredged material, such as Indiana Harbor, that exerts a high oxygen demand (Brannon, et al. 1985, 1986).

27. The effect of cap thickness on dissolved oxygen depletion rates in the water overlying the cap material is summarized in Figure F3. Oxygen depletion rates were computed by performing linear regression analyses of net uptake of dissolved oxygen per unit area (milligrams per square metre) of sediment surface versus time. Rates plotted are the means of three replicates and represent values greater than baseline (i.e., oxygen demand of cap alone). As can be seen in Figure F3, 5 cm of the unsieved cap material resulted in no significant decrease in the oxygen depletion rate from that observed with uncapped Indiana Harbor sediment. As the unsieved cap thickness was increased to 30 cm, no significant reduction in the mean oxygen depletion rate was observed. There was no significant difference between the unsieved and sieved Lake Michigan cap with respect to decrease of oxygen depletion rate with depth.

28. Nutrient release rates. Ammonium-nitrogen-release rates to the overlying water, derived in the same manner as oxygen depletion rates, are presented in Figure F4 as a function of the thickness of cap material used. The 5-cm unsieved cap reduced the ammonium-nitrogen release rate by 33 percent from that observed with uncapped Indiana Harbor sediment. The ammonium-nitrogen release rates then decreased linearly until a cap depth of 25 cm was reached. There was no significant difference between sieved and unsieved Lake Michigan cap with respect to ammonium-nitrogen release rates. The 10-cm sieved cap reduced the ammonium-nitrogen release rate 26 percent from that observed with uncapped Indiana Harbor sediment, then decreased linearly to a cap thickness of 30 cm.

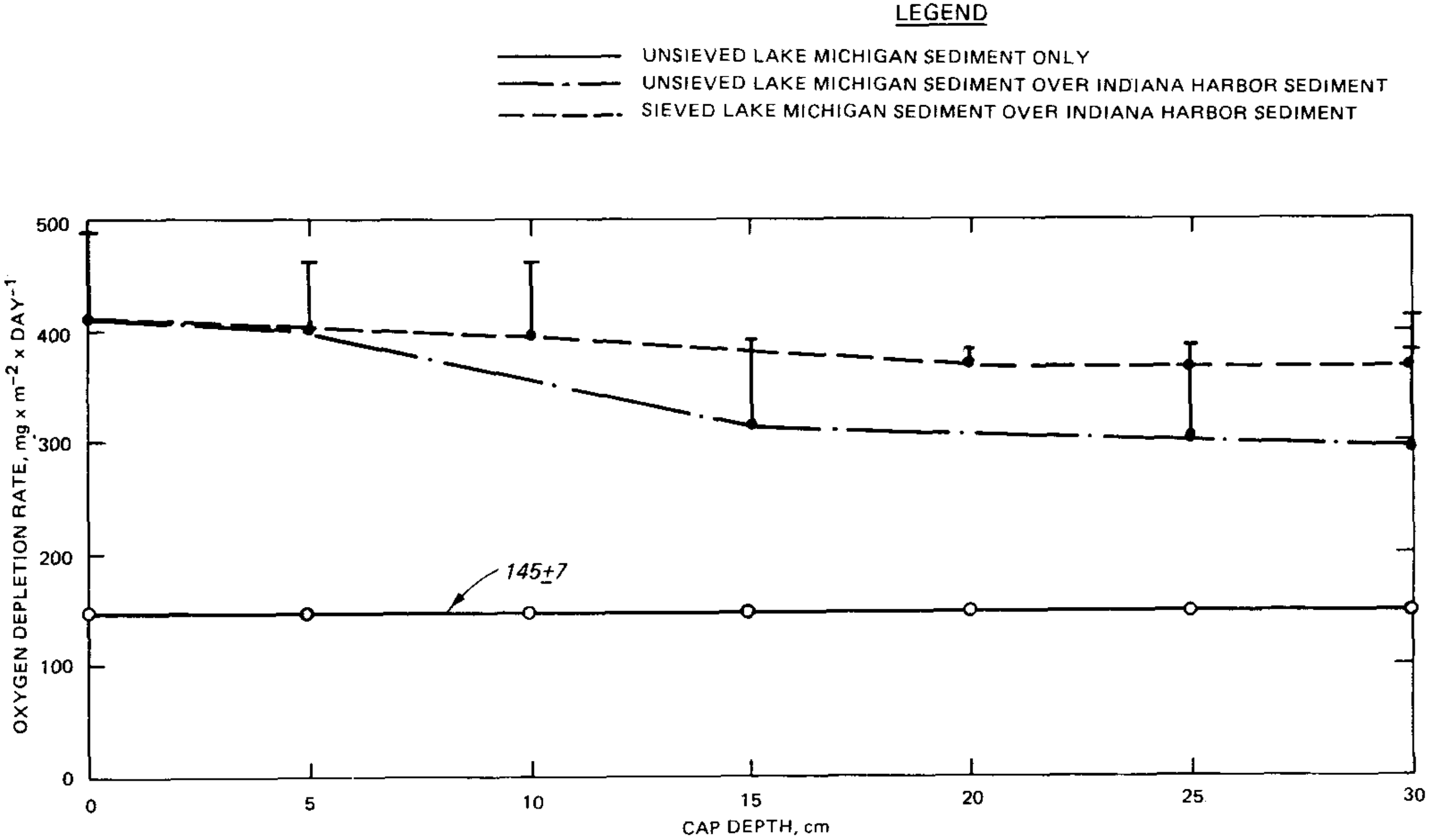

Figure F3. Dissolved oxygen depletion rates

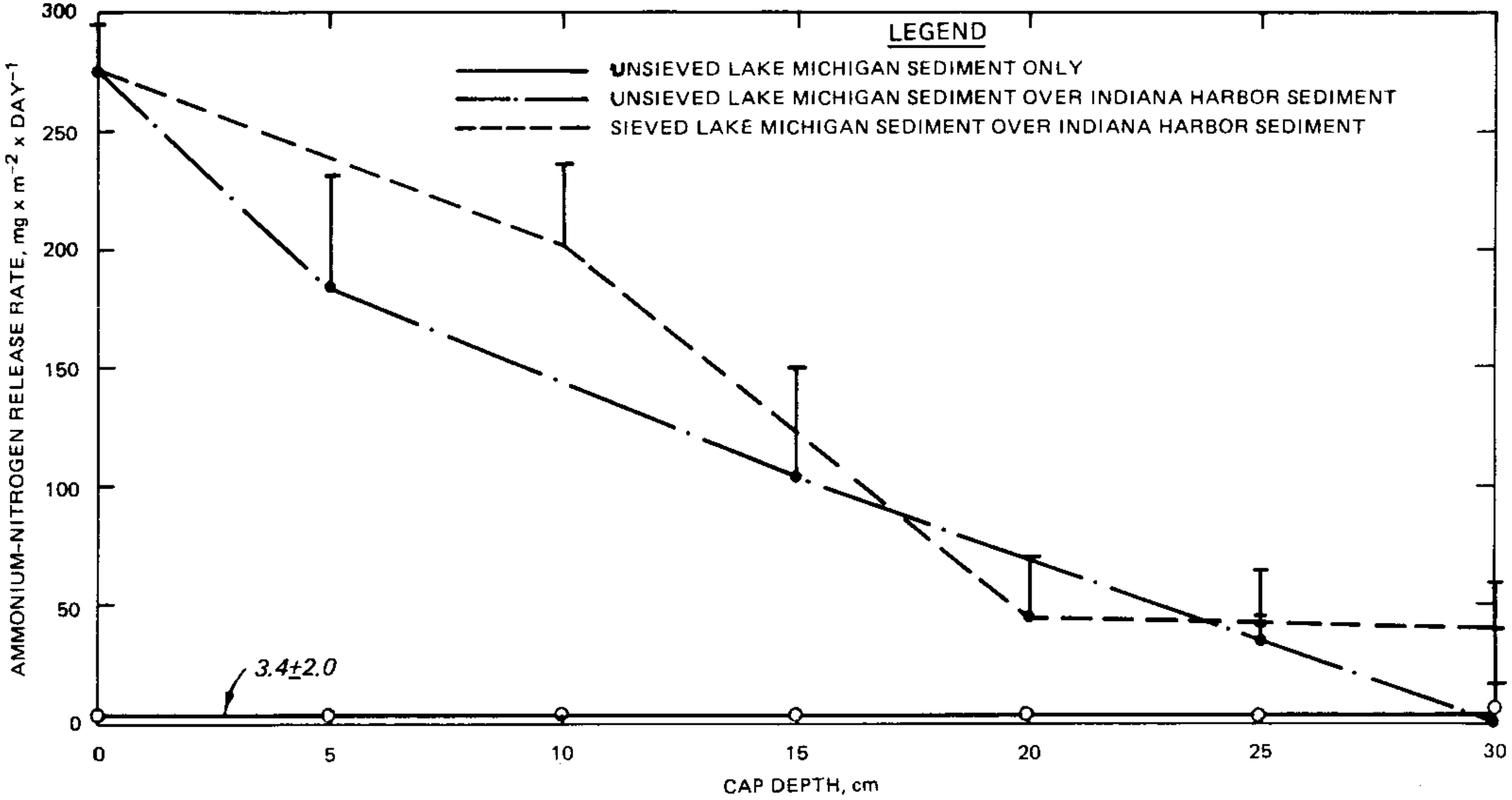

Figure F4. Ammonium-nitrogen release rates

29. There was no significant difference between unsieved and sieved Lake Michigan cap in orthophosphate-phosphorus release rates. Orthophosphate-phosphorus release rates decreased linearly from 5-cm cap depth to a 25-cm cap thickness where there were 46- and 71-percent reductions in release rates, respectively (Figure F5).

30. These results demonstrated that the thickness of the Lake Michigan cap, rather than the texture of the sediment, exerted a considerable influence on sediment-water interactions. In the absence of cap disruption, a cap thickness of at least 30 cm appears to be necessary to completely seal Indiana Harbor sediment from the overlying water column with respect to releases of ammonium-nitrogen. This thickness will also be fairly effective in sealing the water column from releases of orthophosphate-phosphorus, but not from dissolved oxygen demand.

Large-scale reactor unit experiments: contaminant release and uptake

31. Concentration values for selected contaminants were determined in the water column and in fish, clams, and crayfish to assess the ability of a 30-cm cap to isolate Indiana Harbor sediment over a 40-day period. The animals did not suffer excessive mortality in reactor units containing either Lake Michigan sediment only or Indiana Harbor sediment capped with 30 cm of Lake Michigan sediment; 95 percent or more of the animals added initially to the reactor units survived in good condition until sampled and used for tissue analysis. However, in the Indiana Harbor sediment only units, all crayfish and most of the fish were killed within 3 days after initiation of the experiment. In addition, large numbers of clams were killed in the Indiana Harbor sediment only units, leaving less than 20 percent of the initial clam population at the end of the study. In these units, death of the fish and clams was most pronounced during the first 3 days after initiation of the study. After this period, all crayfish were dead, the water column became noticeably less cloudy, and deaths among the fish and clam populations decreased markedly. This observation is purely visual. No direct analysis was made of the suspended solids levels present in uncapped reactor columns during the study.

32. Water column heavy metals. Heavy metal concentrations in the water column above capped sediments did not differ from their respective concentrations in the control (Lake Michigan sediment only) unit water columns (Table 5).

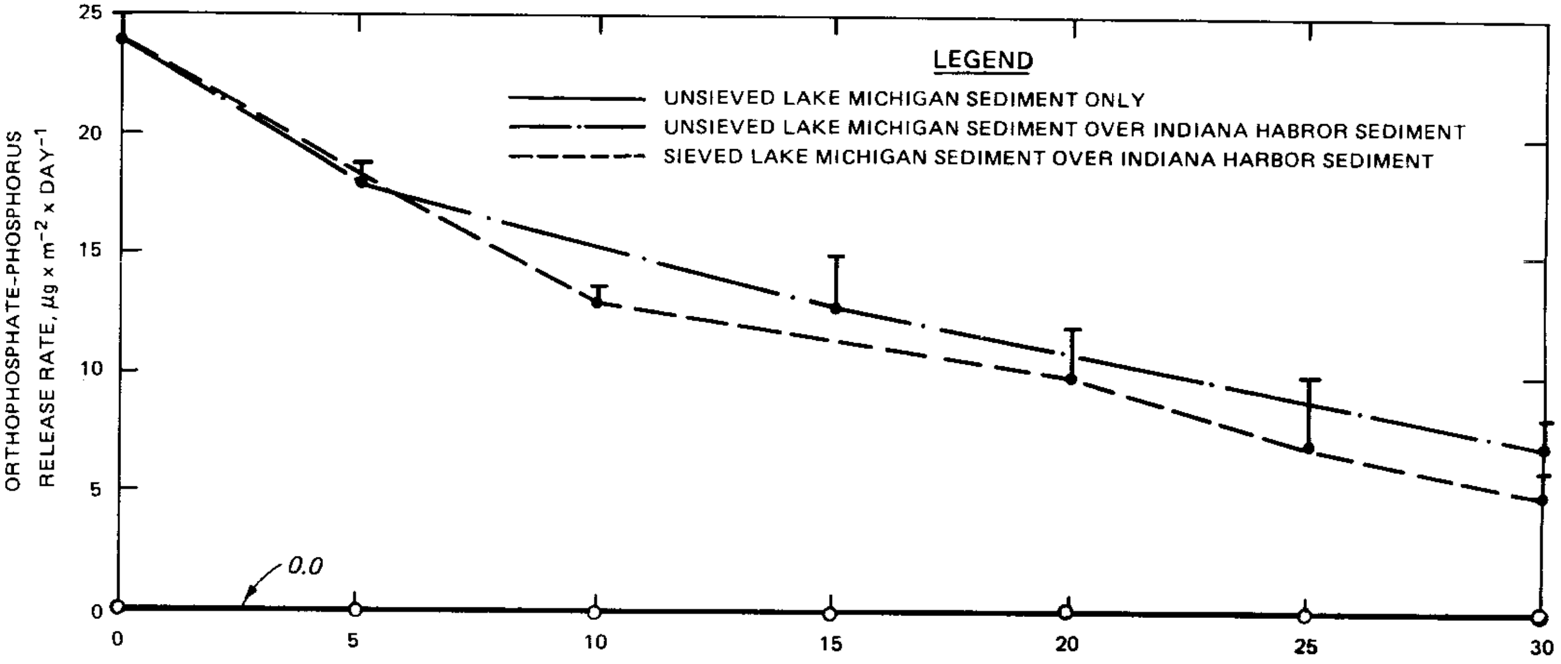

Figure F5. Orthophosphate-phosphorus release rates

Table F5

Heavy Metal Concentrations in the Inflow Water and Reactor Unit Water Columns μg/ℓ Following 40 Days of Incubation in Each of the Treatments.*

Treatment (If Appropriate)	As	Cd	Cr	Pb	Hg	Zn
Inflow Water**	<0.005	0.0001	0.004	0.004	<0.0008	<0.030
Lake Michigan sediment only (control)	<0.005	0.0002 (0.0001)	<0.001	0.003 (0.003)	<0.0008	<0.030
Indiana Harbor sediment only	<0.005	0.0002 (0.0001)	<0.001	0.003 (0.001)	<0.0008	<0.030
Indiana Harbor sediment with cap	<0.005	0.0001 (0)	<0.003	0.003 (0)	<0.0008	<0.030

* Number in parentheses is the standard error of the mean for the value given above it.

** Only one sample taken.

33. Water column PAHs and phenol. Replicate samples for PAHs in the water column were composited to obtain lower detection limits by increasing the volume of water available for extraction for use in the analyses. Even using these techniques, which gave detection limits of 1 ng/ℓ, water column PAH concentrations were very low. Data for water column PAH concentrations in each of the various treatments are summarized in Table F6. Data for the Lake Michigan sediment caps were below detection limits (1 ng/ℓ). There was no apparent enhancement of water column PAH concentrations compared with the inflow or control in any of the treatments, except for the uncapped Indiana Harbor sediment. This treatment demonstrated elevated concentrations of two-, three-, four-, and five-ring compounds as well as total PAHs. Because of the methods used to obtain detection of these compounds in the water (see footnote to Table F6), no significance can be attached to the levels of these compounds in the water over Indiana Harbor sediment as compared with the other treatments.

34. Water column PCBs. Samples analyzed for the presence of PCB isomer groups in the water column revealed the presence of very low, but detectable, levels of these constituents, the total concentration being typically less than 0.40 μg/ℓ (Table F7). The PCB concentration was measured on a single sample of inflow water flowing into the reaction units; this was taken concurrently with other water samples and, because of the lack of replication, has no associated error term. The major contribution to total PCB levels in the inflow water appears to have been in the trichlorobiphenyl and tetrachlorobiphenyl isomer groups. For the three treatments, this is also true for the case of tetrachlorobiphenyls, but not necessarily for the trichlorobiphenyls. There were significantly higher levels of trichlorobiphenyl and tetrachlorobiphenyls in the Indiana Harbor sediment with cap treatments as compared with the control. Nonetheless, these values remained below those in the inflow water, as did the total PCB levels. In all treatments and the inflow water, the most marked changes were confined to PCB compounds containing from two to four chlorine atoms. PCBs containing 8 to 10 chlorine atoms were not detected in the water sample, or in any of the tissue samples, and therefore are not presented in any of the tables.

35. Crayfish heavy metals. Table F8 presents a comparison of crayfish metal concentrations between the various treatments, except for the Indiana Harbor sediment only treatment where all the crayfish died. Heavy metal concentrations in crayfish tissue in the capped Indiana Harbor sediment treatment

Table F6

Water Column PAH and Phenol Concentrations (μg/ℓ) in the Inflow Water and Following 40 Days of Incubation in Each of the Treatments*

	Treatment			
Class of Compound	Inflow Water	Lake Michigan Sediment Only (Control)	Indiana Harbor Sediment Only	Indiana Harbor Sediment With Cap
Two-Ring Compounds	<0.001	<0.001	0.006	<0.001
Three-Ring Compounds	<0.001	<0.001	0.088	<0.001
Four-Ring Compounds	0.005	<0.001	0.058	0.006
Five-Ring Compounds	<0.001	<0.001	0.100	<0.001
Six-Ring Compounds	<0.001	<0.001	<0.001	<0.001
Total PAHs	0.005	<0.001	0.253	0.006
Phenol	<0.010	<0.010	<0.010	<0.010

* Values given were obtained by compositing the replicates of each treatment and then concentrating to increase the detectability of the compounds. Since there was only one value for the replicates, there are no associated error terms.

Table F7

Water Column PCB Concentrations (μg/ℓ) in the Inflow Water and Following 40 Days of Incubation in Each of the Treatments*

	PCB Isomer Group (Number of Chlorine Atoms/Group)**							Total
Treatment	1	2	3	4	5	6	7	PCBs
Inflow Water	<0.5	<0.01	0.11	0.21	<0.01	0.01	0.01	0.34
Lake Michigan Sediment Only (Control)	<0.5	0.03	0.01	0.08	<0.01	<0.01	0.01	0.13
		(0.02)	(0.01)	(0.03)			(0)	(0.03)
Indiana Harbor Sediment Only	<0.5	<0.01	<0.01	0.11	0.003	0.01	0.01	0.14
				(0.01)	(0.003)	(0)	(0)	(0.01)
Indiana Harbor Sediment with Cap	<0.5	0.04	0.04	0.19	<0.01	0.003	0.01	0.29
		(0.01)	(0)	(0.03)		(0)	(0)	(0.03)

* Number in parentheses is the standard error of the mean for the value given above it.

** 1 = Monochlorobiphenyl
2 = Dichlorobiphenyl
3 = Trichlorobiphenyl
4 = Tetrachlorobiphenyl
5 = Pentachlorobiphenyl
6 = Hexachlorobiphenyl
7 = Heptachlorobiphenyl

† Only one sample of inflow water was taken.

Table F8

Heavy Metal Concentrations in Crayfish Tissue (μg/g wet weight) With No Treatment and Following 40 Days of Incubation in Each of the Treatments*

Treatment (If Appropriate)	Metal					
	As	Cd	Cr	Pb	Hg	Zn
None	0.047	0.161	0.356	0.058	<0.0058	14.6
Lake Michigan sediment only (Control)	0.075	0.047	0.416	0.200	<0.0081	18.5
	(0.004)	(0.009)	(0.049)	(0.030)		(0.1)
Indiana Harbor sediment only	NO CRAYFISH SURVIVED THIS TREATMENT					
Indiana Harbor sediment with cap	0.117**	0.013	0.335	0.177	<0.0037	20.5
	(0.007)	(0.004)	(0.013)	(0.012)		(1.8)

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* Number in parentheses is the standard error of the mean for the value given above it.

** Significantly different from the control.

did not generally exceed those of crayfish exposed to the cap material alone (controls) following 40 days of exposure. The only exception was arsenic; in this case, arsenic concentration in the Indiana Harbor with cap treatment significantly exceeded the level of the Lake Michigan sediment only sample.

36. Crayfish PAHs and phenol. Data for PAHs and phenol are presented in Table F9. There was no significant difference between the mean values for any of the compounds examined in crayfish tissues from the controls and the values obtained in crayfish from the capped treatment at 40 days. Unfortunately, the Indiana Harbor sediment only treatment cannot be compared with either the control or the capped treatment because all the crayfish in the Indiana Harbor sediment only treatment died.

37. Crayfish PCBs. Data for PCBs are presented in Table F10. Because the toxicity of the uncapped sediment killed all crayfish within the first week of the study, no PCB accumulation data are available for this treatment. There were minimal accumulations of PCBs in the control and none in the sediment plus cap treatments; PCB levels in these two treatments did not differ significantly from each other (Table F10). Apparently, there were no detectable PCB levels present in the crayfish prior to exposure. The PCB isomers that were detected in the controls were from groups containing three and four chlorine substituents.

38. Clam heavy metals. Data for heavy metals in clam tissue are presented in Table F11. Enough clams in the Indiana Harbor sediment only treatment survived through 10 days to obtain the numbers necessary for chemical analysis. However, by 40 days, only reactor unit IH-5 had sufficient clams remaining for analysis; no replicates were available for comparison. There was no significant difference in the levels of metals accumulated by clams in any of the three treatments at 10 days. The trend at 40 days suggests larger accumulations of metals in the Indiana Harbor sediment only treatment than in the control and capped treatments; however, no significance can be attached to this observation. There was no significant difference between the control and the capped treatments at 40 days.

39. Clam PAHs and phenol. After 10 days of incubation, clam tissue in the Indiana Harbor sediment treatment acquired higher concentrations of three-ring PAH compounds and total PAHs than in the control and capped treatments (Table F12). Both the Indiana Harbor only and the capped treatments had significantly less accumulation of phenol than the control. At 40 days, there

Table F9

PAH and Phenol Concentrations in Crayfish Tissue (μg/g wet weight) With No Treatment and Following 40 Days of Incubation in Each of the Treatments*

	Treatment			
Class of Compound	None	Lake Michigan Sediment Only (Control)	Indiana Harbor Sediment Only	Indiana Harbor Sediment With Cap
Two-ring compounds	0	0.026	NONE SURVIVED	0.039
		(0.008)		(0.018)
Three-ring compounds	0.012	0.046		0.116
		(0.003)		(0.065)
Four-ring compounds	0	0.016		0.028
		(0.006)		(0.021)
Five-ring compounds	0	0.121		0.094
		(0.083)		(0.005)
Six-ring compounds	0	0.004		0
		(0.004)		
Total PAHs	0.012	0.214		0.277
		(0.087)		(0.100)
Phenol	0.565	0.356		0.678
		(0.130)		(0.208)

* Number in parenthesis is the standard error of the mean for the value given above it.

Table F10

PCB Concentrations in Crayfish Tissue (μg/g wet weight) With No Treatment and Following 40 Days of Incubation in Each of the Treatments*

Treatment	PCB Isomer Group (Number of Chlorine Atoms/Group)**							Total PCBs
	1	2	3	4	5	6	7	
None	<.5	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Lake Michigan sediment only (control)	<.5	<.01	.01 (0)	.01 (.01)	<.01	<.01	<.01	.01 (.01)
Indiana Harbor sediment only	NONE OF THE CRAYFISH SURVIVED THIS TREATMENT							
Indiana Harbor sediment with cap	<.5	<.01	<.01	<.01	<.01	<.01	<.01	<.01

* Number in parentheses is the standard error of the mean for the value given above it.

** 1 = Monochlorobiphenyl
2 = Dichlorobiphenyl
3 = Trichlorobiphenyl
4 = Tetrachlorobiphenyl
5 = Pentachlorobiphenyl
6 = Hexachlorobiphenyl
7 = Heptachlorobiphenyl

Table F11

Heavy Metal Concentrations in Clam Tissue (μg/g wet weight) With No Treatment and Following 10 and 40 Days of Incubation in Each of the Treatments*

Treatment (If Appropriate)	Metal					
	As	Cd	Cr	Pb	Hg	Zn
None	0.153	0.186	0.159	0.090	<0.0010	15.7
Lake Michigan sediment only (control)						
10 days	0.133	0.224	0.168	0.120	<0.0010	10.2
	(0.011)	(0.018)	(0.033)	(0.021)		(1.2)
40 days	0.077	0.145	0.144	0.103	<0.0012	7.8
	(0.004)	(0.012)	(0.030)	(0.018)		(0.4)
Indiana Harbor sediment only						
10 days	0.128	0.145	0.156	0.113	<0.0010	8.4
	(0.024)	(0.022)	(0.018)	(0.014)		(1.2)
40 days**	0.066	0.109	0.230	0.380	<0.0011	7.5
Indiana Harbor sediment with cap						
10 days	0.134	0.189	0.191	0.133	<0.0015	10.0
	(0.017)	(0.018)	(0.038)	(0.034)		
(0.2)						
40 days	0.106	0.158	0.203	0.117	<0.0017	10.3
	(0.002)	(0.019)	(0.043)	(0.020)		(1.4)

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* Number in parentheses is the standard error of the mean for the number given above it.

** Only clams from IH-5 survived for 40 days in numbers large enough to permit analysis. Thus, the values given have no associated error term.

Table F12

PAH and Phenol Concentrations in Clam Tissue (μg/g wet weight) With No Treatment and Following 10 and 40 Days of Incubation in Each of the Treatments*

	Treatment 10 days			
Class of Compound	None	Lake Michigan Sediment Only (Control)	Indiana Harbor Sediment Only	Indiana Harbor Sediment With Cap
Two-ring compounds	0	0.024 (0.015)	0.033 (0.019)	0.045 (0.026)
Three-ring compounds	0.042	0.043 (0.004)	0.765** (0.173)	0.037 (0.005)
Four-ring compounds	0.020	0.033 (0.015)	1.050 (0.604)	0.110 (0.018)
Five-ring compounds	0.174	0.298 (0.117)	0.666 (0.238)	0.386 (0.274)
Six-ring compounds	0	0.020 (0.020)	0.139 (0.112)	0
Total PAHs	0.236	0.418 (0.088)	2.660** (0.830)	0.572 (0.234)
Phenol	0	0.062 (0.032)	0**	0**

(Continued)

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* Number in parentheses is the standard error of the mean for the value given above it.

** Significantly different from the control.

Table F12 (Concluded)

Class of Compound	Treatment 40 days None	Lake Michigan Sediment Only (Control)	Indiana Harbor Sediment Only	Indiana Harbor Sediment With Cap
Two-ring compounds	0	0.005 (0.003)	0.011†	0.010 (0.004)
Three-ring compounds	0.042	0.060 (0.020)	0.405	0.020 (0.007)
Four-ring compounds	0.020	0.060 (0.050)	1.500	0.006 (0.002)
Five-ring compounds	0.174	0.060 (0.017)	2.190	0.065 (0.027)
Six-ring compounds	0	0	0.694	0
Total PAHs	0.236	0.515 (0.304)	4.800	0.102 (0.019)
Phenol	0	0	0.057	0

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† Only clams from IH-5 survived in numbers large enough to permit analysis. Thus, the values given in the Indiana Harbor sediment only column have no associated error term.

was no significant difference between the control and the capped treatments for any of the individual classes of PAHs, for total PAHs, or for phenol (Table F12). Due to the high mortality in the Indiana Harbor sediment only treatment, no statistical significance can be attached to the trends demonstrated in this treatment at 40 days; however, there were apparent accumulations of all the classes of PAHs, total PAHs, and, to a lesser extent, phenol.

40. Clam PCBs. Data for PCB levels in clam tissue are presented in Table F13. Sufficient clams survived in two of the three Indiana Harbor sediment only replicates to obtain data for both 10 and 40 days of exposure, although this was in the absence of crayfish-induced bioturbation after the first week of the study. PCB levels in clams from the control and capped sediment treatments did not differ significantly from each other. However, clam tissue samples taken from the Indiana Harbor sediment only treatment at 10 days contained PCB levels that were significantly higher than values in either of the other treatments at 10 or 40 days of exposure (Table F13). Moreover, clam tissue samples from the Indiana Harbor sediment only treatment at 40 days contained PCB levels that were significantly greater than any of the other treatment levels, including levels in samples from the Indiana Harbor sediment only treatment at 10 days. In clams exposed for 10 days to Indiana Harbor sediment, the predominant PCB isomer group present contained four chlorine atoms, with the remaining PCB isomers being approximately equally distributed among compounds containing two, three, five, and six chlorine atoms. By contrast, PCB isomers containing two and three chlorine atoms had not changed in abundance after 40 days of exposure of the clams to Indiana Harbor sediment alone. However, there were significant increases among the isomers containing four, five, and six chlorine atoms in clams exposed to Indiana Harbor sediment alone (Table F13).

41. Fish heavy metals. A large enough mass of fish was not available in the the control treatments to permit separate metals analyses to be made from each replicate and then to allow enough tissue for analyses for PAHs, phenol, and PCBs (the lack of mass was due solely to the low total weight of the fish at the end of the study, not to die-off of fish in this treatment). Because the data for PAHs, phenol, and PCBs were considered more important for the capping evaluation than were the data for metals, the decision was made to use a composite sample for the metals analysis. Nonetheless, the values that were obtained fell within the ranges of variation found for the metals in the capped

Table F13

PCB Concentration in Clam Tissue (μg/g wet weight) With No Treatment and Following 10 and 40 Days of Incubation in Each of the Treatments*

Treatment	PCB Isomer Group (Number of Chlorine Atoms/Group)** 1	2	3	4	5	6	7	Total PCBs
None	<0.5	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
Lake Michigan sediment only (control)								
10 days	<0.5	0	<0.01	<0.01	<0.01	<0.01	<0.01	<0.5
40 days	<0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.5
Indiana Harbor sediment only								
10 Days†	<0.5	0.04	0.04	0.14	0.06	0.06	<0.01	0.34
		(.01)	(0)	(.02)	(0)	(0)		(.04)
40 Days††	<0.5	0.03	0.06	0.26	0.12	0.14	<0.01	0.62
		(0)	(0)	(.02)	(0)	(0)		
Indiana Harbor sediment with cap								
10 days	<0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.5
40 days	<0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.5

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* Number in parentheses is the standard error of the mean for the value given above it.

† Samples from IH-1 were lost during analytical laboratory processing.

†† Only clams from IH-1 and IH-5 survived in numbers large enough to analyze.

** 1 = Monochlorobiphenyl
2 = Dichlorobiphenyl
3 = Trichlorobiphenyl
4 = Tetrachlorobiphenyl
5 = Pentachlorobiphenyl
6 = Hexachlorobiphenyl
7 = Heptachlorobiphenyl

treatment (Table F14). Not enough fish survived in the Indiana Harbor sediment only treatment for analysis of any of the metals; the few fish that remained were saved for analyses for PAHs, phenols, and PCBs.

42. Fish PAHs and phenol. When compared with the time 0 values, fish after 40 days in the Indiana Harbor sediment only treatment appeared to accumulate large amounts of two-, three-, four-, and five-ringed compounds and total PAHs (Table F15). Sufficient fish for chemical analyses survived in only one replicate of the Indiana Harbor sediment only treatment. Of interest is the fact that the capped treatment showed significantly less accumulation of four-ringed compounds than the control while demonstrating a significantly greater accumulation of five-ringed compounds. There was no significant difference in the total PAH levels accumulated, nor in the amount of phenol in these treatments.

43. Fish PCBs. Data on PCB isomer group levels in fish tissue for the various treatments are shown in Table F16. As was true for the PAHs and phenol, no significance can be attached to any accumulation demonstrated by fish in the Indiana Harbor sediment only treatment because only a few fish survived. The largest sources of PCBs for the fish in these two treatments appear to be primarily from isomers with two chlorine substituents and secondarily from isomers with from three to six chlorine substituents, the latter isomers being approximately equally distributed in all fish in the control and capped sediment treatments.

Discussion

44. Results of this study demonstrated that capping can isolate contaminated dredged material from the water column and nonburrowing aquatic organisms. This conclusion is based on observations on the death of the animals in the large-scale reactors containing Indiana Harbor sediment only and on analyses of water and tissue data obtained on samples from all the large-scale reactor units.

45. There was a large amount of variability associated with the bioaccumulation data. This is similar to the bioaccumulation variability observed in the data of Rubenstein, Lores, and Gregory (1983) from aquaria containing *Nereis virens*, *Mercenaria mercenaria*, and *Palaemonetes pugio*. It is highly probable that much of the variability observed represents differences in

Table F14

Heavy Metal Concentrations in Fish Tissue (µg/g wet weight) With No Treatment and Following 40 Days of Incubation in Each of the Treatments*

Treatment (If Appropriate)	Metal					
	As	Cd	Cr	Pb	Hg	Zn
None	<0.019	0.030	0.151	0.004	<0.0115	4.66
Lake Michigan sediment only (control)	COMPOSITE SAMPLE (IH-2, IH-4, IH-6)					
	0.042	0.020	0.391	0.090	<0.0068	29.0
Indiana Harbor sediment only	NOT ENOUGH FISH SURVIVED THIS TREATMENT TO PERMIT ANALYSIS FOR THESE CONSTITUENTS					
Indiana Harbor sediment with cap	0.086	0.017	0.678	0.117	<0.0190	36.1
	(0.034)	(0.003)	(0.186)	(0.061)		(1.6)

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* Number in parenthesis is the standard error of the mean for the value given above it.

Table F15

PAH and PHENOL Concentrations in Fish Tissue (μg/g wet weight) With No Treatment and Following 40 Days of Incubation in Each of the Treatments*

	Treatment			
Class of Compound	None	Lake Michigan Sediment Only (Control)	Indiana Harbor Sediment Only **	Indiana Harbor Sediment With Cap
Two-ring compounds	0	0.031 (0.017)	0.101	0.066 (0.059)
Three-ring compounds	0	0.280 (0.101)	2.310	0.240 (0.121)
Four-ring compounds	0	0.272 (0.015)	0.355	0.158† (0.018)
Five-ring compounds	0	0	0.170	0.054† (0.034)
Six-ring compounds	0	0	0	0
Total PAHs	0	0.583 (0.268)	2.930	0.515 (0.367)
Phenol	0	0	0	0

* Number in parentheses is the standard error of the mean for the value given above it.

** Only fish in IH-1 survived in numbers large enough for analysis. Thus, the values given have no associated error terms.

† Significantly different from the control.

Table F16

PCB Concentration in Fish Tissue (μg/g wet weight) With No Treatment and Following 40 Days of Incubation in Each of the Treatments*

Treatment	PCB Isomer Group (Number of Chlorine Atoms/Group)** 1	2	3	4	5	6	7	Total PCBs
None	<0.5	0.02	0.02	0.04	0.03	<0.01	<0.01	0.11
Lake Michigan sediment only (control)	<0.5	0.17 (0.02)	0.05 (0)	0.05 (0.01)	0.04 (0)	0.03 (0)	<0.01	0.35 (0.03)
Indiana Harbor sediment only†	<0.5	0.02	0.03	0.13	0.04	0.04	<0.01	0.25
Indiana Harbor sediment with cap	<0.5	0.21 (0.04)	0.05 (0.01)	0.05 (0)	0.04 (0.02)	0.04 (0)	<0.01	0.40 (0.06)

* Number in parentheses is the standard error of the mean for the value given above it.

** 1 = Monochlorobiphenyl
2 = Dichlorobiphenyl
3 = Trichlorobiphenyl
4 = Tetrachlorobiphenyl
5 = Pentachlorobiphenyl
6 = Hexachlorobiphenyl
7 = Heptachlorobiphenyl

† Only fish from IH-1 survived in numbers large enough for analysis.

exposure conditions caused by crayfish activity among the chambers. For example, the die-off rates of both fish and clams were observed to decrease in the Indiana Harbor sediment only treatments, once the sediment had killed off all the crayfish and sediment resuspension due to bioturbation had ceased. In the control and the Indiana Harbor with cap treatments, bioturbation activity by crayfish at the cap surfaces had a winnowing effect. The finer silt particles in the sandy-gravelly cap material were suspended in the water column by the crayfish. These particles gave the water column an opaque appearance for the first few days of these studies. However, because the large reaction chambers were equipped with flow-through water supplies, the suspended sediments were gradually swept out of the chambers. Within the first 2 weeks, the cap surfaces gradually became predominantly composed of large sand grains and gravel, and the water columns became transparent as the silt particles were flushed out of the system.

Cap effectiveness

46. Clam tissue analysis and water column chemical data showed that the 30-cm cap of Lake Michigan sediment generally served as an effective barrier to movement of contaminants from dredged material. The only exception to this was the arsenic levels observed in crayfish in the capped Indiana Harbor treatment.

47. It is important to emphasize that the bioturbation in this study may or may not have been as severe as that normally encountered in the field. Crayfish are among the most severe bioturbators of the sediment surface. However, the organisms did not burrow to great depths in the reaction chamber sediments. Among the normal benthic residents of the Great Lakes are *Hexagenia* (mayfly) larvae and chironomid larvae; these can burrow as deep as 10 to 15 cm.* However, these organisms are difficult to capture and maintain in the laboratory, particularly in months other than the late spring. The freshwater benthic macroinvertebrate *Stylodrilus heringianus* also occurs in the Great Lakes and has been observed to burrow to a depth of 4.4 cm in the sediment surface (Krezoski, Robbins, and White 1984). Another benthic organism found in the Great Lakes is the freshwater oligochaete *Tubifex tubifex*; this organism has

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* Personal communication, R. C. Aller, Department of Geophysical Sciences, University of Chicago).

been observed to disturb the sediment surface, causing a uniform distribution of labelled particles over the upper 6 cm, decreasing exponentially below to undetectable levels by 9 cm (Robbins, et al. 1979).

48. Freshwater capping studies have not been carried out to the same extent as in marine and estuarine environments, where many examples of the effects of bioturbation have been reported. For example, Rhoads, McCall, and Yingst (1978) reported that polychaetes observed recolonizing a dredged material disposal site in Long Island Sound were *Streblospio benedictii*, *Capitella capitata*, and *Nephtys incisa*. Of these polychaete species, *Nephtys*, at 50 mm, was the longest measured. For *Nephtys*, an increase in worm size was shown to produce a corresponding increase in burrow length and depth (Davis and Miller 1979, Davis 1980). The data of Davis (1980) showed that the largest 1- to 2-year-old *Nephtys* (0.6 g wet weight) burrowed to a depth of approximately 8 cm. The *Nereis virens* used in a study by Brannon, et al., (1986) were among the largest of the polychaete species, often measuring up to 450 mm in length (Arnold 1968). The particular *Nereis* used by Brannon, et al. were generally 300 mm or longer, weighed from 3 to 4 g (wet weight), and burrowed to much greater depths (at least 50 cm) than the smaller polychaete species. In these studies, bioturbation was observed to be much greater than would be expected of the polychaete assemblage in an ocean disposal site. Brannon, et al. (1985, 1986) found that the *Nereis* were able to totally disrupt (breach) a 5-cm cap, resulting in a failure of the cap to prevent movement of contaminants out of the dredged material and into the water column and biota. From this work, it is evident that the bioturbation depth at a field site must be determined prior to capping operations so that the contaminated dredged material truly can be isolated from all burrowing organisms.

49. Brannon, et al. (1985, 1986) found that in the absence of bioturbation, a 5-cm cap appeared to be generally effective in preventing the movement of metals, PAHs, and PCBs into the overlying water and biota. This was in agreement with the results of Rubenstein, Gillian, and Gregory (1984), who showed that simply isolating organisms (fish) from contact with contaminated sediment with a 1-mm mesh screen significantly reduced PCB body burdens compared with organisms allowed to contact the sediment. In the work reported here, once the crayfish in the reactor units containing Indiana Harbor sediment only had died, Indiana Harbor sediments were no longer suspended into the water column, the flow-through waters moved the previously suspended sediments out

of the water column, and the mortality rates of the fish and clams in the water columns decreased. Physical isolation of contaminated sediment through capping, therefore, appears to be a viable means of effectively reducing death and contaminant bioaccumulation by water column organisms.

Thickness and relative effectiveness of cap material

50. Results of the small column studies demonstrated that cap thicknesses as shallow as 5 cm can exert an influence on sediment-water interactions. A 5-cm cap resulted in a 33-percent reduction in release of ammonium-nitrogen from Indiana Harbor sediment into the water column. A cap thickness of 30 cm was sufficient to completely prevent the transfer of ammonium-nitrogen from Indiana Harbor sediment into the overlying water. Similarly, a 30-cm cap decreased the release of orthophosphate-phosphorus by 78 percent.

51. In studies of different thicknesses and types of capping material, Brannon, et al. (1985, 1986) found that cap materials with higher proportions of clay and silt were more effective in preventing the movement of contaminants into the overlying water and biota than sand. This enhanced effectiveness relative to sand was thought to have been due to the greater adsorptive capacity for contaminants by clays and silt compared with sand.

52. The studies of Brannon, et al. (1985, 1986) also demonstrated the importance of engineering considerations in capping operations. Capping with sand sealed Black Rock sediment with a 54-percent solids content from the overlying water. Lowering the solids content of the Black Rock sediment to 30 percent, however, allowed dredged material to mix freely with the sand and prevent formation of an effective cap. These authors stressed the importance of closely examining the engineering properties of a dredged material and proposed cap material prior to capping to determine their compatibility. These observations are of particular relevance to the study presented here because our attempts to achieve a 30-cm cap in the large column studies were opposed by the tendency of the Lake Michigan cap material to sink into the underlying Indiana Harbor sediment. Based on the data obtained in this study, the percent solids of clamshell-dredged Indiana Harbor sediment is between 30 and 50 percent. It may be that the low solids level of Indiana Harbor sediment resulted in a process similar to that observed by Brannon, et al. (1985, 1986). The effects that strong compaction have on dissolved oxygen depletion rates and other biological and chemical phenomena are unknown.

53. The observed compaction process indicates that a field demonstration project will have to be carefully monitored to ensure that the recommended cap thickness is attained. It is also important to point out that there may have to be a trade-off between the effectiveness of the cap and its persistence in the aquatic environment. Morton and Miller (1980) reported that a sand cap was found to be physically more stable than a silt cap--trends apparently opposite to those observed by Brannon, et al. (1985, 1986) for cap effectiveness.

Summary and Conclusions

54. Analysis of dissolved oxygen, ammonium-nitrogen, and orthophosphate-phosphorus in the small column studies revealed that increasing cap thicknesses caused a decreasing transfer of ammonium-nitrogen and orthophosphate-phosphorus into the overlying water. A 30-cm cap had no significant effect in decreasing the dissolved oxygen depletion rate of Indiana Harbor sediment; however, the efficiency of a 30-cm cap of Lake Michigan sediment in preventing releases of ammonium-nitrogen and orthophosphate-phosphorus from Indiana Harbor sediment was 100-percent for ammonium-nitrogen and 78 percent for orthophosphate-phosphorus. Sieving Lake Michigan sediment to remove coarse pieces of gravel did not significantly alter these results. A 30-cm cap of Lake Michigan sediment overlying Indiana Harbor sediment was highly effective in preventing the transfer of heavy metals, PAHs, phenol, and PCBs from the contaminated sediment into the overlying water and aquatic biota. Indiana Harbor sediment itself was found to be extremely toxic to aquatic life, particularly in the presence of bioturbation. Some of the benthic fauna indigenous to the Great Lakes region have been reported to burrow as deep as 10 to 15 cm. Therefore, it is recommended that a 20-cm-thick increment be added to the Lake Michigan sediment cap tested here to ensure that these organisms do not penetrate into that portion of the cap needed to maintain an effective chemical seal. Thus, the minimum cap depth of Lake Michigan sediment recommended to prevent release of contaminants from Indiana Harbor sediment is 50 cm.

APPENDIX G: LEACHATE TESTING RESULTS

Introduction

1. Bottom sediments contaminated with organic matter, heavy metals, polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs) are present in most urban waterways. Dredging and disposal of these sediments are often delayed because of concern over potential adverse environmental impacts. When the potential for adverse environmental impacts exists, disposal of contaminated material must be planned to restrict contaminant mobility. To design facilities and systems necessary to satisfy site-specific requirements for environmental protection, a prime requirement is information on potential contaminant mobility. Lacking specific quantitative information, project engineers are forced to adopt contaminant containment strategies that are possibly more conservative than necessary, resulting in costs that may be unnecessary.

2. Confined disposal is one option for Indiana Harbor dredged material. When contaminated dredged material is placed in a confined disposal facility (CDF), the potential exists for leachate generation that may adversely impact ground waters. At present, there is no routinely applied laboratory testing protocol capable of predicting, or even approximating, leachate quality from confined dredged material disposal sites. Testing procedures to predict leachate quality are, therefore, needed to fully evaluate the confined disposal alternative for Indiana Harbor dredged material. If leachate quality and quantity can be predicted, the potential impacts of CDF disposal of contaminated dredged material can be evaluated, allowing the most cost-effective site design to be utilized.

Objectives and Approach

3. The objectives of this study were twofold. The primary objective was to assess the leaching potential of Indiana Harbor sediment. Since standard procedures applicable to dredged material for assessing leaching potential were not available, a supporting objective was to develop, evaluate, and apply appropriate testing procedures for estimating leachate contaminant levels in Indiana Harbor sediment.

4. The technical approach used in this study was based on recommendations of a technical working group assembled to review methods for predicting leachate quality (Environmental Laboratory 1984).* It is an intergrated procedure that involves coupling results from batch and continuous flow column tests with a mass transport equation. Comparison of predicted and observed column effluent quality is the basis for evaluating the processes that govern contaminant leaching from Indiana Harbor sediment.

Materials and Methods

5. Upon arrival at the US Army Engineer Waterways Experiment Station (WES), sediment used in leaching tests was refrigerated at 4 °C in sealed containers until used. Sediment used for aerobic testing was placed in 38-ℓ glass aquaria to a depth of approximately 8 cm. The aquaria were then placed in a covered enclosure (open to the air) at ambient temperatures. At least once each week the sediment was thoroughly stirred to expose fresh sediment to the air. When necessary, distilled-deionized water was added to the sediment to prevent it from completely drying out. At the end of 6 months the sediment was removed from the aquaria, placed in a 115-ℓ mortar mixer, and thoroughly mixed for 2 hr. The sediment was then refrigerated at 4 °C until used for aerobic leachate testing.

6. Two types of leachate tests were conducted, batch and column tests. Batch tests were conducted to investigate the intrinsic contaminant release properties of the sediment under anaerobic and aerobic conditions. Column tests were conducted to verify the assumptions involved in batch testing and evaluate the feasibility of extrapolating batch results to continuous flow systems. The test procedures and a protocol for integrating the results from the batch and column tests are described below.

Batch testing

7. Kinetic tests. In this report kinetic testing refers to a series of shake tests conducted to determine the shake time necessary to achieve steady-state soluble contaminant concentrations in the batch tests. The general experimental sequence used to conduct kinetic testing is presented in Table G1; more details on the proceudres can be found in the following discussion.

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* See References at the end of the main text (Vol I).

Table G1

Experimental Sequence for Determining Appropriate Shaking Times in Indiana Harbor Kinetic Testing

STEP 1	Place sediment in appropriate centrifuge tube (stainless steel or polycarbonate), and sufficient deoxygenated-distilled water to maintain water-to-sediment ratio of 4:1.
STEP 2	Place centrifuge tubes horizontally on shaker and shake at 160 cycles per minute.
STEP 3	Remove tubes (enough for triplicate samples for organics and for metals) from shaker at appropriate intervals: 1, 2, and 7 days for organic contaminants and 6, 24, 48, 72, and 96 hr for metals.
STEP 4	Centrifuge for 30 min at 6,500 × g for organics and 9,000 × g for metals. Prior to filtering, pass centrifuged leachate through acid-washed glass wool for metals and acetone-washed glass wool for organics. Repetition of Step 4 using clean centrifuge tubes is necessary for leachate for organic analyses.
STEP 5	Filter centrifuged, deoiled leachate through 0.45-μm pore size membrane filters for metals and through a Whatman GF/D glass fiber prefilter and a Gelman AE glass fiber filter of 1 μm nominal pore size.
STEP 6	Acidify leachate for organic analysis with HCL and leachate for metals with Ultrex nitric acid. Store leachate for organic analysis in acetone-rinsed glass bottles and leachate for metals analysis in plastic bottles.

Note: The test sequence was carried out twice for metals. The tubes were shaken vertically the first time and horizontally the second time. Centrifuge tubes were removed at intervals of 24, 48, and 72 hr during the horizontal shaking procedure.

8. For kinetic testing of metals, triplicate 250-ml polycarbonate centrifuge tubes each fitted with leakproof, airtight tops, were loaded with sufficient sediment and deoxygenated, distilled-deionized water to obtain a 4:1 water-to-sediment dry weight ratio. All operations were conducted in a glove box under a nitrogen atmosphere. Sufficient centrifuge tubes were loaded to allow sampling, in triplicate, at 6 hr, 24 hr, 48 hr, 72 hr, and 96 hr. Samples were placed upright on a mechanical shaker and shaken at 160 cycles per minute for the allotted time. Three tubes were then removed from the shaker and centrifuged at 9,000 × g for 20 min. The supernate was passed under nitrogen through acid-washed (1:1 HCl) glass wool to remove oil. The supernate was then filtered under a nitrogen atmosphere through 0.45-μm pore size membrane filters. The filtrate was acidified to pH 1 with concentrated Ultrex nitric acid and stored in plastic bottles until analyzed. The test procedure was repeated as previously described, except that shaking was conducted with the leaching vessel on its side; sampling times were 24 hr, 48 hr, and 72 hr.

9. Kinetic testing for organic contaminants was conducted in specially fabricated 450-ml stainless steel centrifuge tubes. Twenty-four acetone-rinsed centrifuge tubes were loaded with sufficient sediment and deoxygenated, distilled-deionized water to obtain a 4:1 water-to-sediment dry weight ratio. The total mass of sediment and water added was regulated to allow the tube to be safely centrifuged at 6,200 rpm (6,500 g). All operations were conducted in a nitrogen atmosphere. The tubes were then laid on their sides and shaken at 160 cycles per minute for periods of 1 day, 2 days, and 7 days. At the appointed time, the samples were centrifuged for 30 min. The supernate was then passed through acetone-rinsed glass wool, and recentrifuged in clean centrifuge tubes to remove the oil residue. The recentrifuged supernate was then filtered through a Whatman GF/D glass fiber prefilter and a Gelman AE glass fiber filter with a nominal pore size of 1.0 μm. Neither filter contained binders or detectable quantities of the organic contaminants analyzed during this study. Filtration was conducted in a nitrogen atmosphere followed by acidification with 1 ml of concentrated HCl to prevent iron precipitation and scavenging of organic contaminants from solution. Samples were then stored in the dark in acetone-rinsed 2-ℓ glass bottles until analyzed.

10. Liquid-solids ratio testing. Following determination of the shake time necessary to obtain steady-state concentrations in the leachate, testing to determine the proper liquid-solids ratio was conducted. The general test

sequence is presented in Table G2. Selection of an appropriate liquid-solids ratio is governed by available analytical capabilities as well as the necessity to conform as closely as possible to field conditions. These restraints are discussed in detail later in this report.

11. For metals, anaerobic Indiana Harbor sediment was placed in acid-washed, 250-ml polycarbonate centrifuge tubes in liquid-solids ratios of 2:1; 4:1, and 8:1 using double, distilled-deionized water. The tubes were sealed, mechanically shaken horizontally for 24 hr, and centrifuged. The supernate was filtered through 0.45-μm membrane filters, acidified, and stored in plastic bottles prior to analysis as previously described. The anaerobic integrity of the samples was maintained throughout the preparation, shaking, and filtration of the sample.

12. Similar procedures were followed for organic contaminants except that 24-hr shaking was conducted in 450-ml stainless steel centrifuge tubes. Filtration and other sample preparation procedures are as described for kinetic testing.

13. Sequential batch testing and challenge testing. Sequential batch leaching tests were applied first to anaerobic sediment following selection of a 4:1 liquid-solids ratio and a shaking time of 24 hr. General test procedures for metal and organic contaminants are detailed in Table G3.

14. Batch tests were designed to determine metal releases from anaerobic Indiana Harbor sediments and provide sufficient leachate to challenge fresh sediment. To obtain this leachate, three 500-ml polycarbonate centrifuge bottles with leakproof caps were loaded under a nitrogen atmosphere with anaerobic Indiana Harbor sediment and deoxygenated, distilled-deionized water at a 4:1 liquid-solids ratio and mechanically shaken for 24 hr. The bottles were then centrifuged at 9,000 × g for 30 min. Following oil removal by passage through glass wool, half of the supernate from each 500-ml centrifuge bottle was filtered through a 0.45-μm membrane filter. A portion of the unfiltered supernate was then analyzed immediately for pH using a combination electrode and a millivolt meter, and conductivity using a Yellow Springs Instrument Company conductivity meter and cell. Enough of the remaining unfiltered supernate was weighed into a 250-ml polycarbonate centrifuge tube containing fresh Indiana Harbor sediment to obtain a 4:1 liquid-solids ratio. This procedure, whereby part of the initial leachate was set aside for analysis and the remainder used to challenge fresh anaerobic Indiana Harbor sediment, was

Table G2

Test Sequence for Determining the Appropriate Water to Sediment Ratio for Use During Batch Testing Procedures

STEP 1	Place sediment in appropriate centrifuge tubes: 250 ml polycarbonate for metals and 450-ml stainless steel for organic contaminants. Add water to each tube to bring final water-to-sediment ratio to 2:1, 4:1, 8:1.
STEP 2	Shake mixtures horizontally at 160 cycles per minute for 24 hr.
STEP 3	Centrifuge for 30 min at 6,500 × g for organics and 9,000 × g for metals. Prior to filtering, centrifuged leachate is passed through acid-washed glass wool for metals and acetone-washed glass wool for organics. Samples for organic analysis required repetition of step 3 using clean stainless steel centrifuge tubes to remove oil.
STEP 4	Filter Leachate through 0.45-μm membrane filters for metals or through a Whatman GD/F glass fiber prefilter followed by passage through a Gelman AE glass fiber filter of 1.0 μm nominal pore size.
STEP 5	Acidify leachate for organic analysis with HCL and leachate for metals analysis with Ultrex nitric acid. Store leachate for organic analysis in acetone-rinsed glass bottles and leachate for metals analysis in plastic bottles.

Note: The anaerobic integrity of the sample was maintained during sample addition to centrifuge tubes, shaking, centrifugation, and filtration.

continued for 5 days. Fresh deoxygenated, distilled-deionized water was added to each 500-ml centrifuge tube to replace the leachate removed for analysis and challenge of fresh sediment. All operations were conducted in a nitrogen atmosphere. This procedure was repeated for aerobic sediments, except that aerobic sediment leachate was used to challenge anaerobic sediment.

15. Because of the number of stainless steel centrifuge tubes needed to obtain enough leachate for analysis of one sample (4) and the limited number of stainless steel centrifuge tubes (24), organic testing was conducted differently from metals testing in that the challenge testing of fresh sediment was not conducted concurrently. Twelve centrifuge tubes were loaded with equal amounts of either anaerobic or aerobic sediment and equal amounts of distilled-deionized water to obtain a 4:1 liquid-solids ratio. The tubes were then sealed and shaken horizontally for 24 hr at 160 cycles per minute, then centrifuged and filtered as previously described for the kinetic tests. The only modification consisted of adding the small amount of glass wool used in the prefiltering step to trap oil back to the centrifuge tube prior to addition of fresh distilled-deionized water. This was done to prevent loss of oil from the sediment. As discussed later, the oil contains a sizable portion of the organic contaminants associated with Indiana Harbor sediment. These tests were conducted using both anaerobic and aerobic sediment. Tests with anaerobic sediment were conducted in a nitrogen atmosphere. A subsample of filtered leachate was set aside from both the anaerobic and aerobic tests for analysis of total organic carbon. In each case, the leachate was replaced with distilled deionized water, remixed, shaken for 24 hr, then processed as previously described. This cycle was repeated five times.

16. Anaerobic/anaerobic leachate challenge testing for organic contaminants was conducted separately as shown in Table G3, but could not be replicated because of equipment limitations. The procedure required all 24 of the stainless steel centrifuge tubes to obtain one challenge leachate sample.

17. Interstitial water extraction. Interstitial water samples for metal and organic contaminant analysis were obtained by centrifugation of the Indiana Harbor sediment. To obtain samples for metals from anaerobic Indiana Harbor sediment, triplicate 250-ml polycarbonate centrifuge tubes, fitted with leakproof, airtight tops, were loaded with sediment in a glove box in a nitrogen atmosphere. The centrifuge tubes were then centrifuged at 9,000 × g for 30 min, and the supernate filtered in a nitrogen atmosphere through 0.45-μm

Table G3

Test Sequence for Sequential Batch Leaching and Challenge Testing of Anaerobic Indiana Harbor Sediment for Metals and Organic Contaminant Analysis

STEP 1	Load sediment into appropriate centrifuge tubes: 500 ml polycarbonate for metals and 450 ml stainless steel for organic contaminants. Add sufficient water to each tube to bring final water-to-sediment ratio to 4:1. Sufficient stainless steel tubes must be loaded to obtain enough leachate for analysis and for use in leaching fresh sediment.
STEP 2	Go through steps 2 and 3 in Table G2.
STEP 3	For half of the leachate, carry through steps 4 and 5 in Table G2, setting aside a small amount of leachate prior to acidification for analysis of pH and conductivity. Introduce the remaining centrifuged leachate into 250-ml polycarbonate centrifuge tubes for metals and 450-ml stainless centrifuge tubes for organic contaminants. Carry these centrifuge tubes through steps 2 through 5 in Table G2.
STEP 4	Return to step 2 after replacing leachate removed in the initial set of centrifuge tubes with deoxygenated-distilled water. Repeat the entire procedure five times.

Note: Testing sequence is the same for aerobic sediments except that aerobic sediment leachate is used to challenge anaerobic sediment and anaerobic integrity is not maintained.

pore size membrane filters following passage through acid-washed glass wool to remove oil. The filtrate was then acidified to pH 1 with concentrated Ultrex grade nitric acid and stored in plastic bottles until analysis. Procedures for obtaining interstitial water for metals analysis from aerobic Indiana Harbor sediment were similar to those described for anaerobic sediment except that all steps in the operation were conducted without a nitrogen atmosphere.

18. Interstitial water for analysis of organic contaminants was obtained by centrifugation of anaerobic Indiana Harbor sediment in 450-ml stainless steel centrifuge tubes. For separation of interstitial water from anaerobic Indiana Harbor sediment, six tubes were loaded with sediment, then centrifuged for 30 min at 6,500 × g. The supernate was then passed through acetone-rinsed glass wool, and recentrifuged in clean centrifuge tubes to remove residual emulsified oil. Complete removal of the oil from the anaerobic interstitial water required nine centrifugations. When finally clear of oil, the interstitial water was filtered through a Whatman GF/D glass fiber prefilter and a Gelman AE glass fiber filter with a nominal pore size of 1.0 μm. All steps in the operation were conducted in a nitrogen atmosphere. Following filtration, the interstitial water was acidified with 1 ml of concentrated hydrochloric acid then stored in the dark in acetone-rinsed 2-ℓ glass bottles until analyzed. Aerobic interstitial water was obtained in a similar manner except that aerobic conditions were maintained during the procedure.

Column testing

19. Loading and operation. Column leaching tests were conducted in divided-flow permeameters designed to minimize wall effects and provide for pressurized operation (Figure G1). The bottom ring divides flow, separating the leachate flowing through the center of the column from that flowing down the walls, thereby minimizing wall effects on effluent quality. The applied pressure (25 psi) forced water through the sediment at rates sufficient to allow sample collection in a reasonable period.

20. Permeameter tests were run to simulate leaching of anaerobic and aerobic sediment, prepared as previously described. Because of the large leachate volume needed to conduct organic analyses (1 ℓ), separate permeameter tests were run for metals and organic analysis. Each test was run in triplicate. A total of 12 permeameters were operated, three each for anaerobic metals, anaerobic organics, aerobic metals, and aerobic organics.

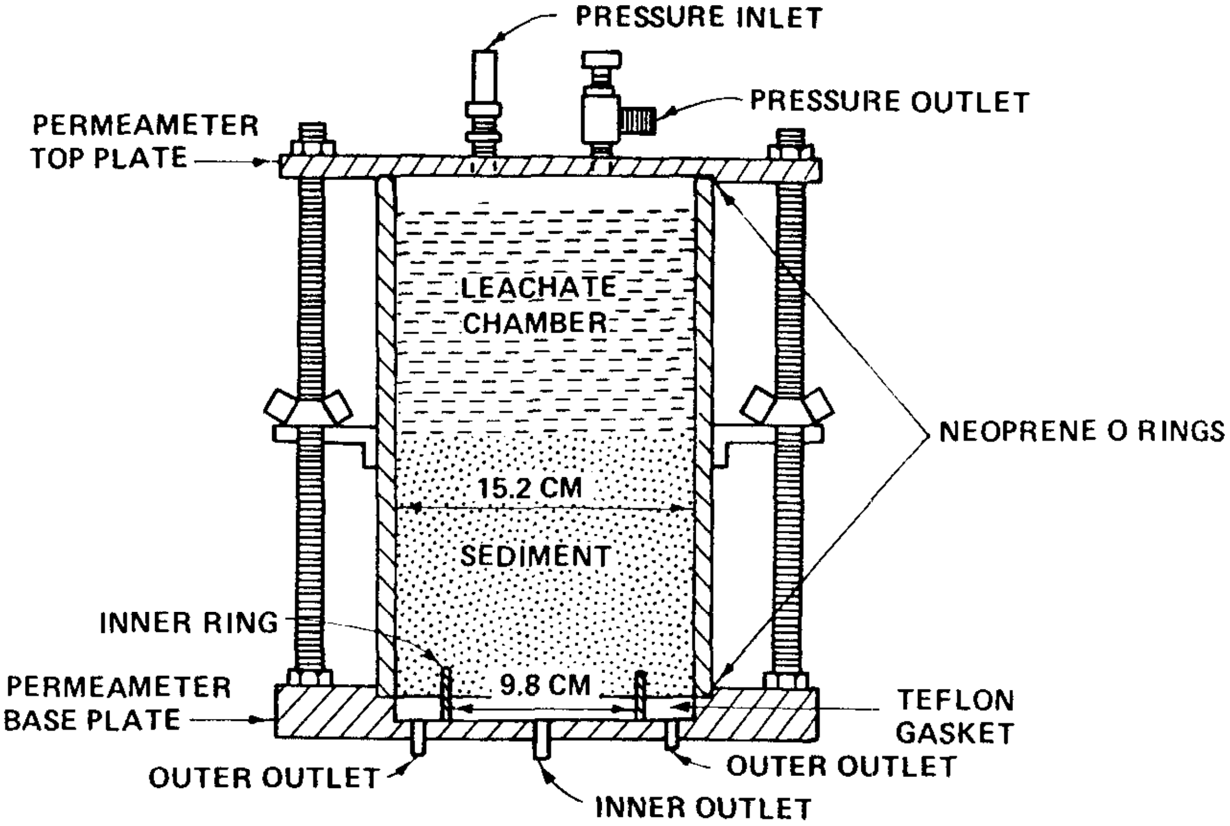


Figure G1. Divided-flow permeameter used for continuous-flow column test

21. Indiana Harbor sediment was loaded into the permeameters in several lifts each having an average thickness of 5 cm, the number of lifts added depended on the target column height. As each lift of water-saturated sediment was added, the permeameter was vigorously agitated on a vibrating table to remove trapped air. The weight and height of each lift was measured and recorded following vibration. Sediment height averaged 18 cm in permeameters used to obtain leachate for metal analyses and 36 cm in permeameters used to obtain leachate for organic contaminant analyses. A longer column of sediment was placed in the permeameters used for organic testing because the volume of sample required for organic analysis is greater than that required for metals analysis. The sediment porosity in the permeameters was determined by measuring the weight and volume of sediment added to the permeameter, then measuring the weight and volume of a separate sediment sample before and after oven drying at 105 °C; weight loss upon drying was then equated to the volume of water in the permeable voids. The pore volume in each permeameter was then calculated for the inner sediment column extending from the bottom of the permeameter to the top of the sediment column.

22. Following sediment addition, distilled-deionized water was added to the permeameters; the apparatus was sealed and pressurized with either nitrogen or air, depending on whether the test was conducted on anaerobic or aerobic sediment, respectively. It was necessary to periodically add water to the permeameters during testing. Leachate from all three permeameter outlets was drained through Teflon tubing to 1,000-ml graduated cylinders. The cylinder receiving flow from the center outlet of each permeameter was isolated from the atmosphere by a water trap. The collection cylinder head-space was purged with nitrogen immediately prior to applying pressure and after each sample was collected.

23. Flow from the permeameters were regulated by adjusting the operating pressure. The permeability of the sediment decreased for the first week of operation. As permeability decreased, operating pressure was increased until a maximum value of 172 kPa (25 psig) was reached in all permeameters. A daily record of flow from all three outlets of each permeameter was maintained.

24. Following completion of permeameter testing, the sediment in each permeameter was carefully removed as an intact core. Samples for moisture determination were obtained from slices made along the vertical axis of the core. Moisture content was determined by oven drying at 105 °C. The ratio of

initial moisture content to final moisture content was used to calculate the final porosity of the sediment.

25. Sampling. Permeameter effluent sampling for metals was conducted as frequently as possible as the first pore volume moved through the column, then at less frequent intervals. Effluent from permeameters set up for metals testing was also analyzed for dissolved organic carbon, conductivity, and pH. Effluent from permeameters set up for organic analysis was sampled at approximately 0.5 pore volume intervals. These samples were analyzed for specific organic contaminants and dissolved organic carbon.

26. Leachate samples for metals and organic contaminants from anaerobic sediment were filtered in a nitrogen atmosphere using procedures previously described for batch testing, except that centrifugation and filtration through glass wool were omitted. Since the leachate from the permeameters did not contain emulsified oil, procedures for oil removal were not needed. A portion of unfiltered leachate for metals determination was analyzed immediately for pH using a combination electrode and a millivolt meter, and for conductivity using a Yellow Springs Instrument Company conductivity meter and cell.

27. Dispersion coefficient determination. The dispersion coefficient, D_p, was determined by operating a separate permeameter using anaerobic sediment and distilled-deionized water containing bromide as a tracer (constant concentration = 1,000 mg/ℓ). Effluent samples were collected periodically, filtered (0.45-μm filter), and analyzed for bromide using a specific ion meter with a bromide probe. From these data the dispersion coefficient was computed using the F-curve method described by Levenspiel (1972). This method assumes that dispersion is small, i.e., $D_p/VL < 0.01$. The term D_p/VL is a dimensionless ratio, termed the dispersion number, that characterizes the amount of dispersion in flow-through systems. The value V is the average pore water velocity in the column, and L is the column length.

Chemical analysis

28. Leachate and sediment samples were analyzed for concentrations of selected congeners (PCBs) of Aroclor 1248, PAHs, and heavy metals (arsenic, cadmium, chromium, lead, zinc, and mercury). Specific organic contaminants are identified in Table G4. Concentrations of Aroclor 1248 congeners and PAH compounds in sediment samples were determined following Soxhlet extraction, Florosil cleanup, and quantification in either a Hewlett Packard 5985A gas chromatograph/mass spectrophotometer equipped with a flame ionization detector

Table G4

Organic Compound Identification Key

No.	Compound	No.	Compound
1.	Napthalene	16.	2,4'-dichlorobiphenyl
2.	Acenaphthalene	17.	2,4,4'-trichlorobiphenyl
3.	Acenapthene	18.	2,3',4',5-tetrachlorobiphenyl
4.	Fluorene	19.	2,2',4,5'-tetrachlorobiphenyl
5.	Phenanthrene	20.	2,2',5,5'-tetrachlorobiphenyl
6.	Anthracene	21.	2,2',4,6-tetrachlorobiphenyl
7.	Fluoranthene	22.	2,2',3',4,5-pentachlorobiphenyl
8.	Pyrene	23.	2,2',4,5,5'-pentachlorobiphenyl
9.	Chrysene	24.	2,2',3,4,5'-pentachlorobiphenyl
10.	Benzo (a) anthracene	25.	2,2',3,4,4',5'-hexachlorobiphenyl
11.	Benzo (b) fluoranthene	26.	2,2',4,4',5,5'-hexachlorobiphenyl
12.	Benzo (a) pyrene	27.	2,2',3,3',6,6'-hexachlorobiphenyl
13.	Indeno (1 2 3-c d) pyrene	28.	2,2',3,4,5,6'-hexachlorobiphenyl
14.	Benzo (g h i) perylene	29.	2,2',3,4,4',5,5'-heptachlorobiphenyl
15.	2,4-dichlorobiphenyl	30.	Total arochlor 1248 congeners

(PAHs) or a Hewlett Packard 5880A gas chromatograph equipped with an electron capture detector (PCBs). Concentrations of PAH and Aroclor 1248 congeners in leachate samples following methylene chloride extraction were determined on the same equipment as for sediment samples. Sediment samples were analyzed for arsenic, cadmium, chromium, lead, and mercury following appropriate sample digestion procedures (Ballinger 1979). Arsenic in leachate and sediment samples was determined by hydride generation (Ballinger 1979) using a Perkin-Elmer 305 atomic adsorption spectrometer coupled with a Perkin-Elmer Model MHC-10 hydride generator. Leachate samples and digested sediment samples were analyzed for cadmium, chromium, and lead using a Perkin-Elmer Model 5000 atomic adsorption spectrometer coupled with a Perkin-Elmer Model 500 hot graphite atomizer. Zinc was analyzed using directly coupled plasma emission spectroscopy on a Beckman Spectraspan IIIB plasma emission spectrometer. Total organic carbon in leachate and sediment samples was determined using an Oceanographic International 543B organic carbon analyzer and standard procedures (Ballinger 1979).

Theoretical Basis for Leachate Quality Prediction

Design basis for batch and column leaching tests

29. The purpose of this section is to describe the equations used to predict leachate quality and show how they relate to the experimental methods described earlier. For this discussion, it is assumed that water transports contaminants from the dredged material to the boundaries of a CDF. Leaching is defined to be interphase transfer of contaminants from the dredged material solids to the aqueous phase as water moves past the dredged material solids. Upon contact with percolating water, contaminants associated with sediment particles can go into solution, increasing contaminant levels in the leachate.

30. For contaminant leaching by water percolating through porous media, the governing one-dimensional partial differential equation for steady-state flow conditions is given below (Lapidus and Admundson 1952; Rao et al. 1979; Grove and Stollenwerk 1984):

$$\partial C/\partial t + \rho/\theta\ (\partial q/\partial t) = D_p(\partial^2 C/\partial z^2) - V(\partial C/\partial z) \qquad \text{(G1)}$$

where

C = aqueous phase contaminant concentration, mg/ℓ

t = time, sec

ρ = bulk density, kg/ℓ

θ = porosity, dimensionless

q = solid phase contaminant concentration, mg/kg

D_p = bulk dispersion coefficient, cm^2/sec

z = direction, cm

V = average pore water velocity, cm/sec

Equation G1 is sometimes referred to as the permeant-porous media equation. The derivation of this equation is based on a balance of mass fluxes into and out of any arbitrary volume within a column of sediment (Figure G2). The first term on the right-hand side represents dispersive transport of contaminant, the second term represents convective transport (bulk flow). The first term on the left-hand side, sometimes referred to as the accumulation term, represents the change in aqueous phase contaminant concentration with time; the second term on the left-hand side, sometimes referred to as the source or reactive term, represents interphase transfer of contaminant from the sediment solids to the aqueous phase. Laboratory procedures are available for obtaining coefficients in the bulk flow and dispersion terms of the equation, but standard procedures have not been developed for quantifying the contaminant source term for dredged material. The primary objective of the laboratory tests performed in this study was to provide an accurate description of the source term for Indiana Harbor sediment.

31. The first step in applying Equation G1 is the development of a conceptual model for the source term, i.e., a mathematical formulation of the term. The second step is quantification of the coefficients in the mathematical formulation selected. Several conceptual models for the source term have been proposed (Hornsby and Davidson 1973; Rao et al. 1979; Valocchi 1985). A source term formulation that assumes that interphase transfer processes are "fast" with respect to bulk fluid flow is often used because the assumption presents advantages in computational efficiency and eliminates the need for rate coefficients (Jaffe and Ferrara 1983; Valocchi 1985). For this assumption, desorption processes are in a state of local equilibrium. The local equilibrium assumption usually applies when pore water velocity is 10^{-5} cm/sec

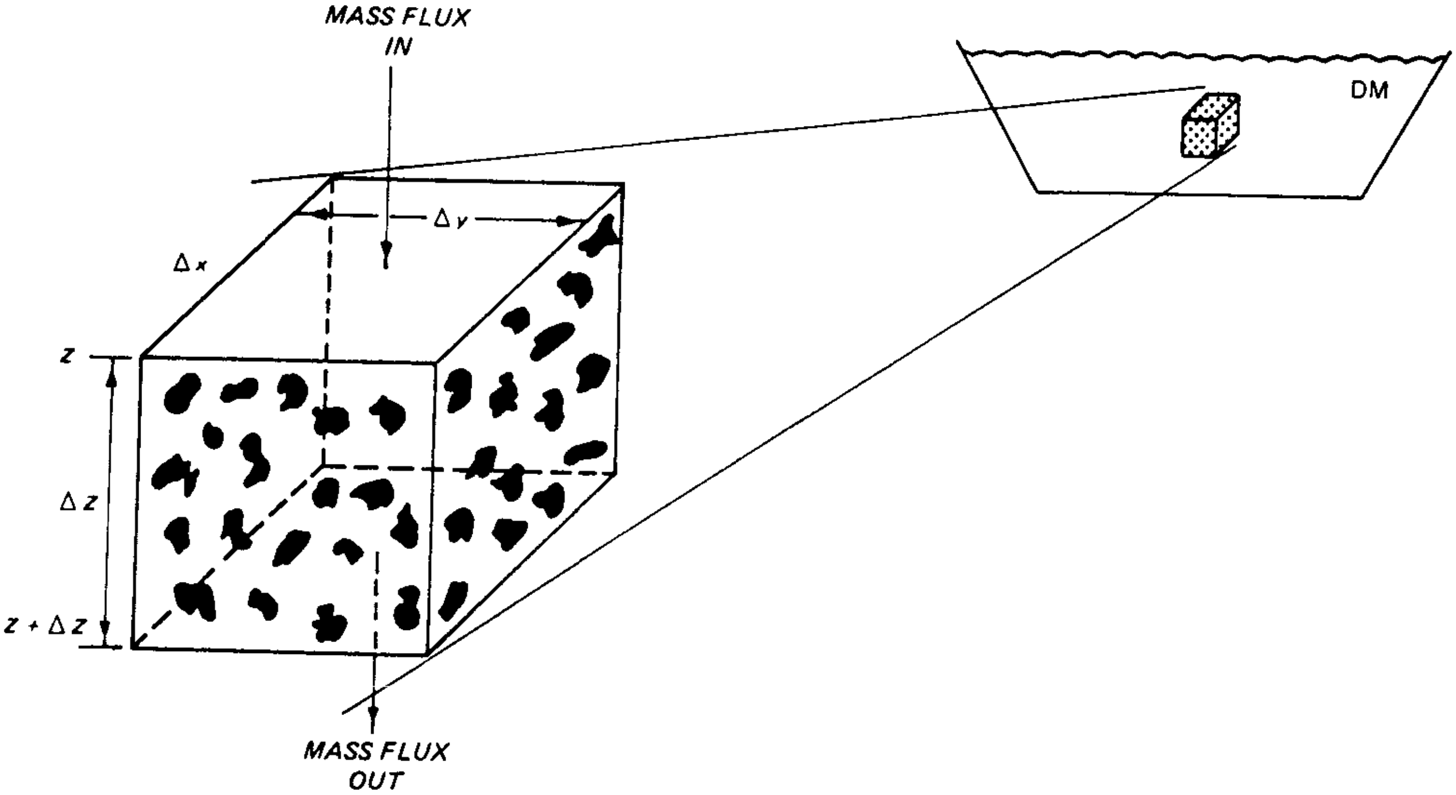


Figure G2. Representative element for dredged material in a confined disposal facility or less (Valocchi 1985). Add the assumption that desorption is a linear process, and the source term for interphase transfer can be formulated as equilibrium-controlled, linear desorption. The permeant-porous media equation with equilibrium-controlled, linear desorption is given below (Grove and Stollenwerk 1984):

$$(\partial C/\partial t) + (\rho K_d/\theta)\ (\partial C/\partial t) = D_p(\partial^2 C/\partial z^2) - V(\partial C/\partial z) \tag{G2}$$

where K_d is the distribution coefficient, ℓ/kg. The leach tests described in this report were conducted to test the hypothesis that contaminant leaching from Indiana Harbor sediment is described by Equation G2, i.e., the source term can be described as equilibrium-controlled, linear desorption. Mathematically, equilibrium-controlled, linear desorption can be written in several forms. These are briefly reviewed below.

32. A first-order kinetic equation for a reversible reaction at the sediment solids-water interface is as follows:

$$dq/dt = -K_F q + K_R C \quad \text{(batch)} \tag{G3a}$$

$$\partial q/\partial t = -K_F q + K_R C \quad \text{(continuous flow)} \tag{G3b}$$

where K_F and K_R are the forward and reverse reaction rates, respectively. If the percolation of water through the sediment is slow in relation to the rates at which contaminants cross the sediment-water interface, the sediment solids-water interface approaches steady-state as the reaction proceeds to equilibrium. For steady-state conditions, Equations G3a and G3b can be written as follows:

$$q = K_d C \tag{G4}$$

where K_d is equal to K_R/K_F. The solid phase concentration q in Equations G3 and G4 applies to the reversible component of the bulk sediment concentration. If q is defined as the bulk sediment contaminant concentration, then the nonreversible component must be added to Equation G4 as follows:

$$q = K_d C + q_r \tag{G5}$$

where q_r is the nonreversible component that is resistant to leaching. Equation G5 is a general relationship for a batch system at steady state. In a continuous flow system, q and C at any point do not remain constant over time but change as percolating water leaches contaminants. Applying Equation G5 to a continuous flow system yields

$$\partial q/\partial t = K_d\ (\partial C/\partial t) \tag{G6}$$

Equation G6 describes a local, linear equilibrium at the sediment solids-water interface in a continuous flow system. Substitution of Equation G6 into Equation G1 yields Equation G2.

33. Equation G5 is the basis of design for the sequential batch leaching tests, described earlier. By sequentially leaching a portion of sediment with successive aliquots of clean water, a table of C and corresponding q values can be generated and plotted. Such a plot is called a desorption isotherm, and its slope is K_d. If the desorption isotherm goes through the origin, then q_r is equal to zero. The physical significance of q_r is interpreted as a contaminant fraction that is resistant to leaching.

34. As shown in Figure G3, the difference between the initial sediment contaminant concentration q_o and the component resistant to leaching q_r is the total leachable contaminant concentration q_L. Thus, it is important to know if the isotherm goes through the origin. If it does not, then evaluation of the leaching potential on the basis of bulk sediment concentration can be seriously misleading.

35. The isotherm intercept q_r has a direct bearing on how K_d should be determined. For q_r equal to zero, one other point on the isotherm is all that is required to compute K_d. Distribution coefficients are frequently determined using the batch equilibrium method, i.e., without sequential leaching. Such procedures produce single-point distribution coefficients that implicity assume that the isotherm goes through the origin. When q_r is greater than zero, at least two points on the isotherm are required to compute its slope, since q_r is not known prior to conducting the leach test. Thus, a slope-derived K_d does not require assumptions regarding q_r. Sequential batch leaching tests provide multipoint isotherms from which slope-derived K_d and q_r values can be obtained by fitting the isotherm data to Equation G5.

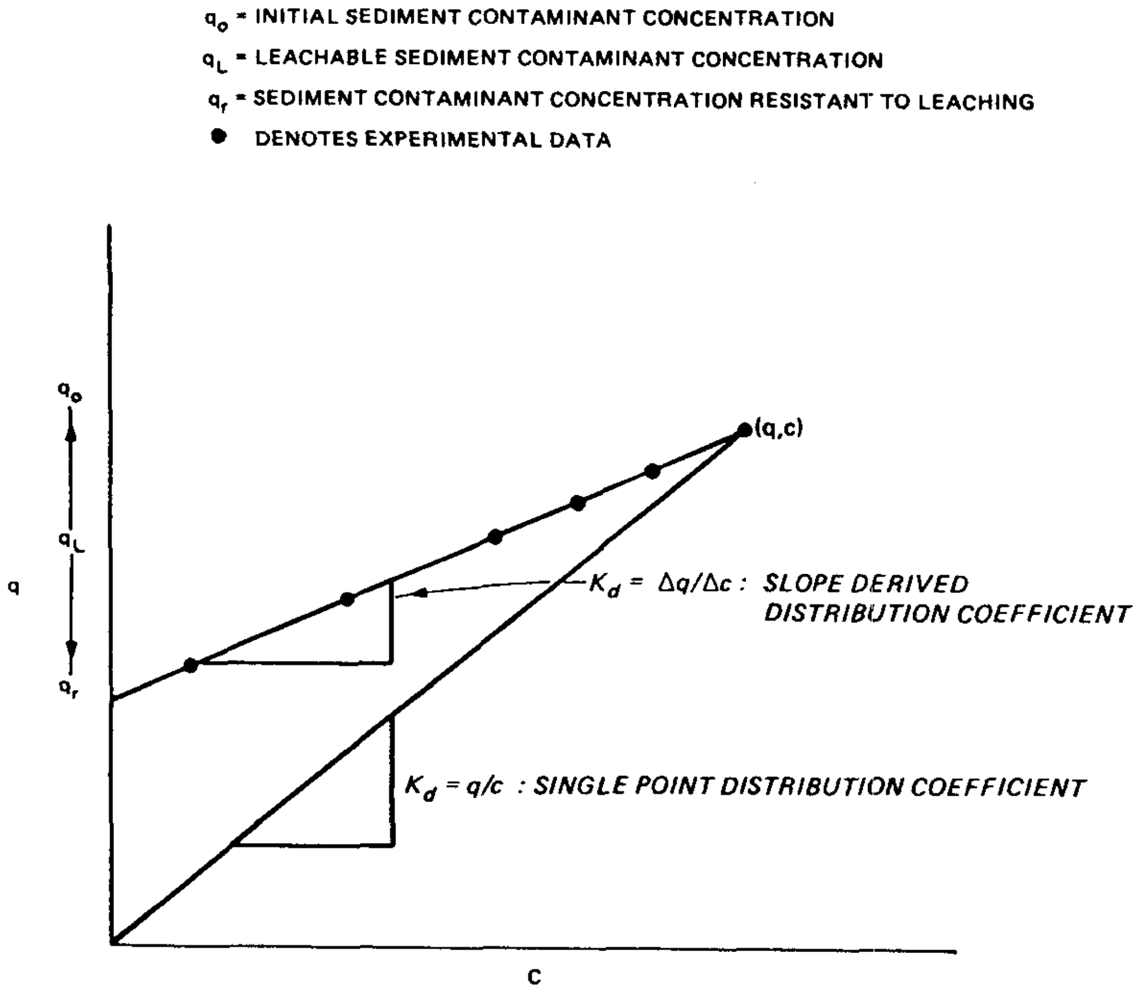


Figure G3. Ideal desorption isotherms for slope-derived and single-point distribution coefficients

The difference between single-point and slope distribution coefficients is illustrated in Figure G3.

36. The above discussion presents the basic theory behind the development and use of the sequential, batch leach tests for Indiana Harbor sediment. It is clear that sequential batch leaching tests, designed to evaluate K_d and q_r , do not provide a complete picture of how the contaminant concentration varies with time and position in a continuous flow system. According to the permeant-porous media equation, as water percolates through a column of dredged material the contaminant concentration in the leachate over time is determined not only by the source term but also by the effects of dispersion and advection. Further, the velocity of the water at the aqueous-solid phase interface in a shake test is higher than that in a continuous-flow system and can affect interphase transfer.

37. In a column test, film effects can be an important factor that inhibits interphase transfer (Grove and Stollenwerk 1985). In a continuous-flow column, a boundary layer can develop around the sediment particles. Depending on the thickness of the boundary layer and the molecular diffusivity of the contaminant, the boundary layer can limit the rate of transfer of contaminant from the sediment solids to the pore water. Another type of film effect can also be important if the sediment contains oil and grease. The oil and grease coats the particle surfaces and reduces the effective area for interphase transfer. In batch tests, film effects are effectively eliminated by vigorous agitation. To observe the combined effects of interphase transfer with advective and dispersive transport (hydraulic flux), and to verify the assumption that coefficients determined in batch tests can be used to describe the source term in continuous flow systems, data from continuous flow laboratory columns are needed.

Integrated approach

38. As previously stated, the integrated approach consists of using results from batch leach tests, column leach tests, and Equation G2 to test the hypothesis that contaminant leaching from Indiana Harbor sediment can be described as equilibrium-controlled, linear desorption. Application of the integrated approach is illustrated in Figure G4. Details of the integrated approach are presented below.

39. Before Equation G2 can be used to predict permeameter leachate quality as a function of volume throughput (time), specific parameters are

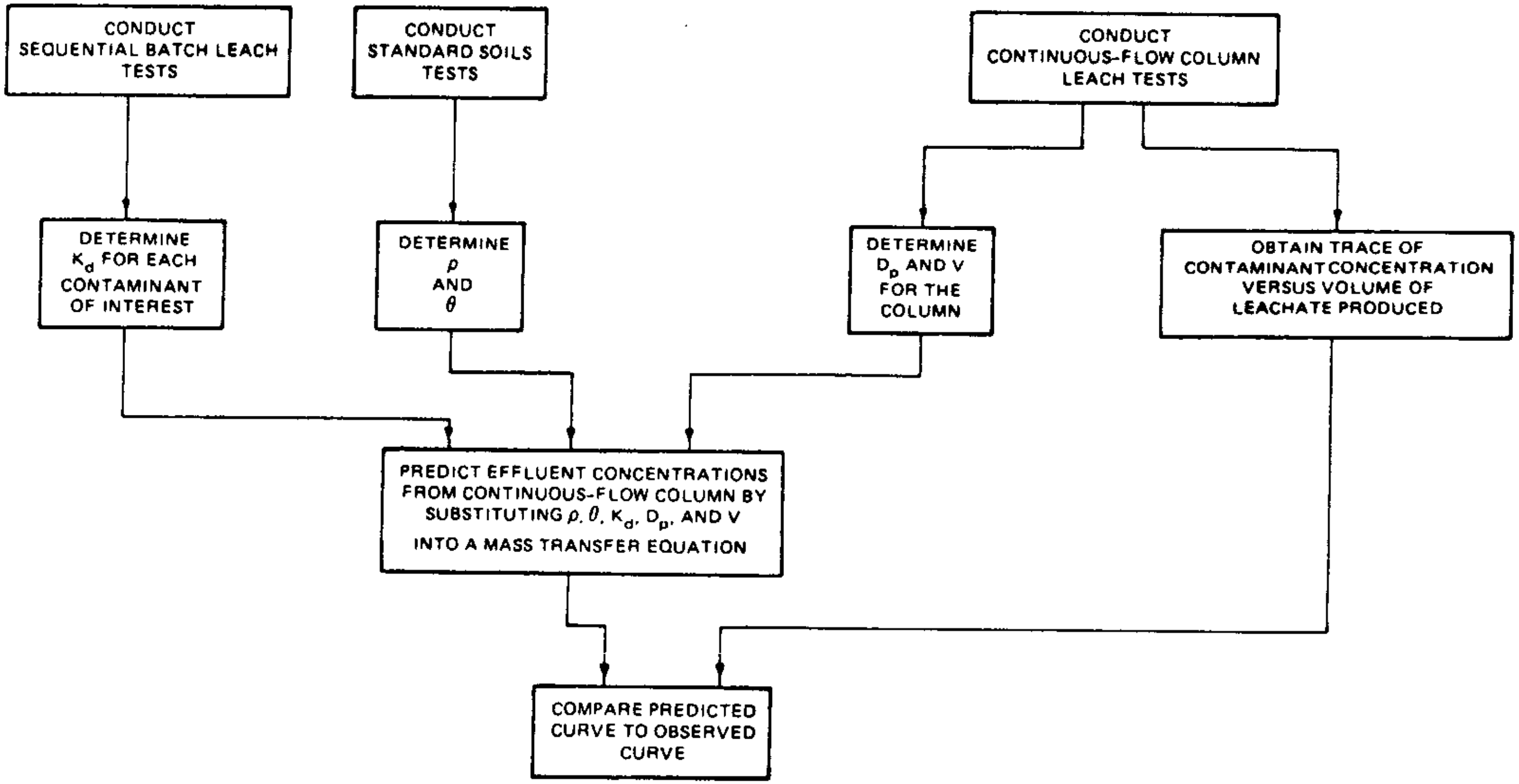


Figure G4. Schematic of integrated approach for examining the source term required. These include porosity and bulk density (obtainable from standard soils tests) and average pore water velocity (obtainable from column operating records). In addition, dispersion in the permeameters must be measured. Distribution coefficients and the initial pore water contaminant concentrations are evaluated independently of the column. Distribution coefficients are determined in sequential batch leach tests, and the initial pore water contaminant concentration is determined by analysis of the interstitial water or estimated using distribution coefficients.

40. Once the needed information has been obtained, column and batch leaching data can be combined using the permeant-porous media equation to provide an integrated picture of leachate quality as a function of time or the volume of water passing through the dredged material. An analytical solution to this equation for equilibrium-controlled, linear desorption is presented below (Ogata and Banks 1961).

$$C(z,t) = C_I + (C_o - C_I)\ 0.5\ \mathrm{erfc}\ \frac{Rz - Vt}{2(DRt)^{0.5}} + 0.5\ \exp\frac{Vz}{D}\ \mathrm{erfc}\ \frac{Rz + Vt}{2(DRt)^{.5}} \qquad \text{(G7)}$$

where

z = distance from top of the sediment column, cm

C_I = initial contaminant concentration in the interstitial water, mg/ℓ

C_o = contaminant concentration in the water entering the sediment, mg/ℓ, equal to zero for the test procedures used in this study

$R = 1 + \frac{\rho K_d}{\theta}$ = retardation coefficient, dimensionless

D = longitudinal dispersivity = D_p/V, cm

The initial and boundary conditions used to obtain Equation G7 are as follows:

$$C(z,0) = C_I$$
$$C(0,t) = C_o$$
$$\partial C/\partial z\ (\infty,t) = 0$$

41. If test procedures are free from error, the solution obtained from Equation G7 should agree with observed effluent concentrations from the permeameters. Thus, the integrated approach can be used to verify the mathematical form of an assumed source term. If the predicted and observed effluent

curves agree, it may be concluded that transfer of contaminant from the dredged material solids is adequately described as equilibrium-controlled, linear desorption. If not, other source term formulations can be tried. Once a reasonable description of contaminant transfer has been found, a planning level assessment of potential leachate problems can be made by solving the advection-dispersion equation for the initial and boundary conditions that apply in the field. However, caution must be exercised in generalizing conclusions obtained at one set of conditions to others since the source term is, in part, dependent on the hydrodynamic properties of the continuous-flow system (Valocchi 1985).

The role of the distribution coefficient

42. A significant amount of the discussion thus far has been directed toward equilibrium distribution coefficients. Because of the central role played by K_d, its practical significance in a field situation deserves discussion. The distribution coefficient affects pore water contaminant concentration in two ways. First, the initial contaminant concentration in the pore water depends on K_d, and second, K_d controls the shape of predicted curves. The initial pore water contaminant concentration before dredging or leaching is often referred to as the interstitial water contaminant concentration. The relationship between the sediment solids and the interstitial water contaminant concentration is given by

$$C_I = q_L/K_d \tag{G8}$$

where q_L is the leachable solid phase contaminant concentration (mg/kg). This equation assumes that the contaminant is distributed or partitioned between sediment solids and aqueous phases such that the chemical potentials in the two phases are equal, i.e., the sediment-pore water system is at equilibrium. Equation G8 shows that the higher K_d, the lower the initial water phase contaminant concentration.

43. A value for the initial water phase contaminant concentration must be available in order to evaluate Equation G7. Simply stated, C_I is the starting point for predictive curves developed using Equation G7. C_I can be measured by extracting the interstitial water from the sediment and analyzing it, or C_I can be estimated using Equation G8 if K_d is known and is not equal to zero.

44. The value of K_d also affects the shape of the curve predicted by Equation G7. The higher K_d, the longer the initial concentration will tend to persist. The effect that K_d has on persistence is illustrated in Figure G5. In this figure, leachate concentration, assuming the same leachable sediment concentration q_L, is graphed as a function of pore volume for two values of K_d. As shown, the initial concentration is lower for the higher K_d. However, this concentration tends to persist while the leachate concentration for the lower value of K_d washes out. When K_d is equal to zero, the leachate concentration theoretically drops to zero once the initial pore water has been displaced.

45. The significance of persistence with regard to flux analysis is readily apparent. For high distribution coefficients, the leachate concentration is essentially constant. For low distribution coefficients, the flux analysis should include the dependency of concentration on the number of pore volumes of water that have passed through the sediment. If K_d is zero, then the flux analysis can be based on the movement of interstitial water and the contaminant concentration in the interstitial water.

Results and Discussion

Sediment chemical concentrations

46. In this appendix, organic contaminants are referred to by number because of the complexity of compound names and the number of organic contaminants analyzed (29). A key to organic compound identification is contained in Table G4. Specific congeners of Aroclor 1248 were analyzed and reported instead of PCB aroclors in order to achieve the enhanced limits of detection possible with congeners (0.01 μg/ℓ for congeners compared with 0.10 μg/ℓ for aroclors). Congeners were selected for quantitation based on their preponderance in Aroclor 1248, the major PCB source of contamination in Indiana Harbor sediment. Metal concentrations in Indiana Harbor sediment and interstitial water are presented in Table G5. The sediment contained low concentrations of mercury, but high concentrations of zinc, lead, copper, and chromium. The total organic carbon concentration was 7.39 percent sediment dry weight. Oil and grease analysis was 3.88 percent sediment dry weight. In previous work, sediment samples from Indiana Harbor Canal contained from 2.8 to 4.4 percent by weight oil and grease (US Environmental Protection Agency (USEPA) 1977).

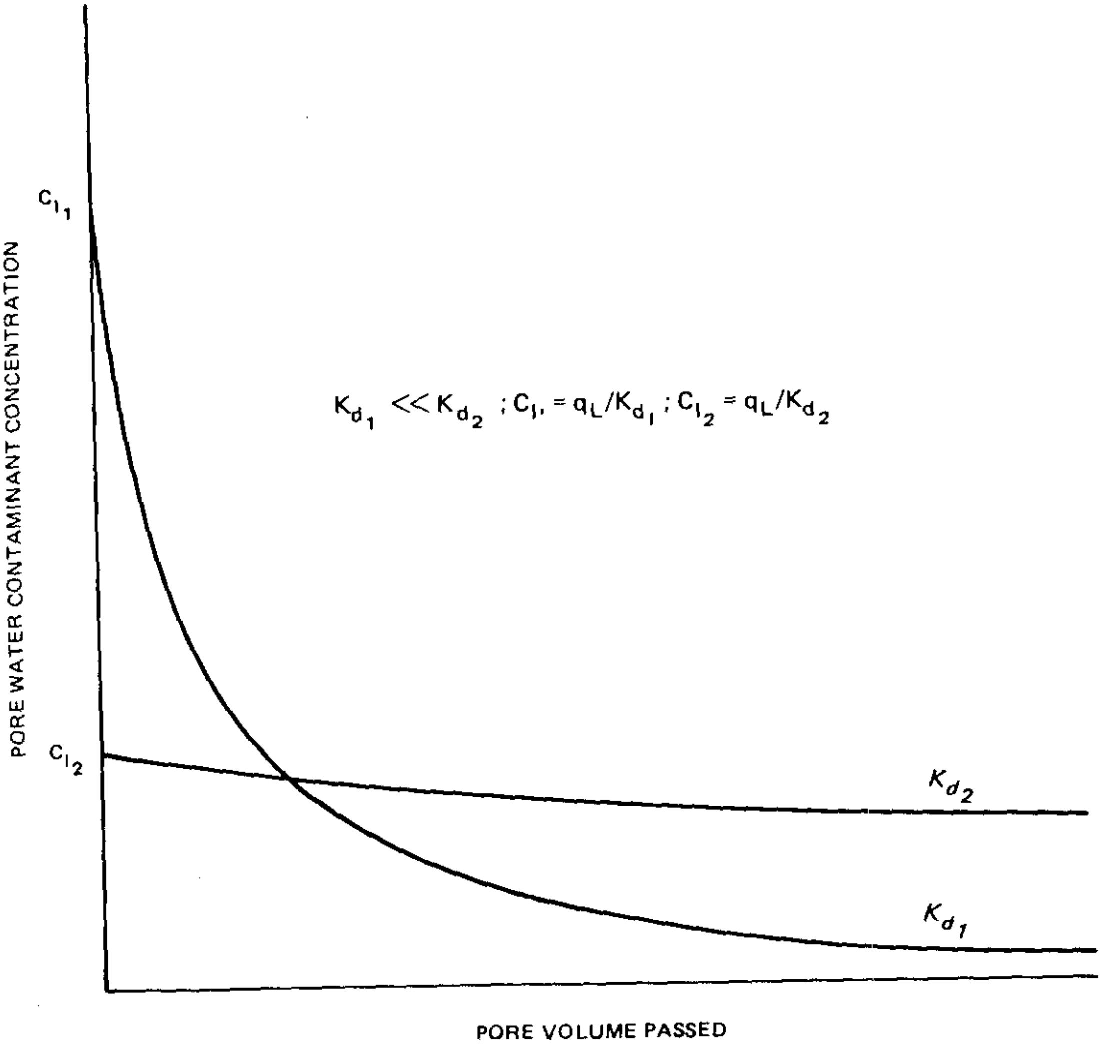


Figure G5. Dependency of contaminant persistence on k_d

Table G5

Metal Concentration in Indiana Harbor Sediment and Interstitial water (standard error)

Metal	Sediment, μg/g	Interstitial Water, μg/ℓ
Arsenic	29.5	0.0137 (0.0057)
Cadmium	20.0	0.0047 (0.0008)
Copper	282.0	
Lead	879.0	0.089 (0.028)
Zinc	4,125.0	0.327 (0.124)
Chromium	650.0	0.06 (0.022)
Mercury	0.5	

47. The oil presented special problems for the batch leaching tests. When the anaerobic sediment was centrifuged, oil was separated from the sediments. As shown in Table G6, oil separated from anaerobic Indiana Harbor sediment was highly contaminated with organic compounds. The oil contaminant concentrations were correlated with total sediment concentration ($r = 0.983$, $P < 0.01$), indicating that the oil was a primary repository of organic contaminants. Oil, however, was not observed in leachate from the permeameters. Misleadingly high batch leachate organic contaminant concentrations would result if the oil dislodged from the sediment during shaking were not removed prior to analyzing the leachate. It was therefore necessary to remove the oil from the batch leachate prior to analysis. To completely remove the oil, extensive centrifugation and filtration were required that involved one-of-a-kind stainless steel centrifuge bottles specially manufactured for this study.

48. Organic contaminant concentrations in Indiana Harbor sediment measured before and after 6 months of wet exposure to air are presented in Table G6. Changes in sediment organic concentration following exposure to the air for 6 months were dramatic. Sediment concentrations for PAH compounds changed substantially during the 6-month oxidation period, decreasing from 3,229 μg/g dry weight PAH to 515 μg/g dry weight PAH, a decrease of 86 percent. In addition, an 83-percent decrease in sediment total Aroclor 1248 congener concentration was noted in aerobic sediment compared with anaerobic sediment.

49. A thorough analysis of the processes involved in the losses noted above was beyond the scope of this study. However, a brief discussion of the implications may be useful. Volatilization and biological degradation are two processes that were probably involved. Since the aerobic sediment was not exposed to direct sunlight, photooxidation was probably minimal. Of the two processes that could have been responsible for the reduction in PAH and PCB concentrations, volatilization is probably the process primarily responsible. Under the passive aeration that was provided, aerobic biological processes occurred, but at a limited rate. Further, PAHs and PCBs are toxic compounds that are biodegraded slowly. Volatilization of organic compounds from moist sediment depends on Henry's Law constant and can be significant if the Henry's Law constant is high, as is the case with PAHs and PCBs. The fact that PCBs make excellent transformer oil because of their low vapor pressures should not be misconstrued to imply that volatilization of PCBs is negligible in

Table G6

Oil and Sediment Organic Contaminant Concentration

Compound*	Anaerobic Sediment Contaminant Concentration in Oil from Anaerobic Sediment, mg/ℓ	Anaerobic Sediment Contaminant Concentration, μg/g	Aerobic Sediment Contaminant Concentration, μg/g
1	1,165	2,000	81.9
2	33	22	<7
3	155	96	10.8
4	115	69	11.6
5	278	200	35.5
6	77	62	12.8
7	197	150	63.45
8	177	140	85.2
9	73	92	42.8
10	90	86	30.9
11	101	140	64.7
12	125	87	48.55
13	47	50	15.75
14	30	35	11.8
15	<0.002	<0.002	<0.002
16	4.3	10.8	0.13
17	17.5	19.5	2.14
18	27.0	31.9	5.24
19	7.8	3.5	1.14
20	35.0	19.5	6.99
21	17.5	19.3	2.14
22	4.55	5.2	0.94
23	1.55	1.7	<0.00001
24	4.9	5.7	0.87
25	2.6	3.7	0.59
26	1.3	2.2	0.36
27	<0.002	<0.002	<0.002
28	11.5	12.4	2.30
29	1.85	1.98	0.31

* See Table G4.

environmental media, where as often as not Henry's Law constant determines volatility (Mackay et al. 1983).

50. The losses shown in Table G6 are not indicative of the volatilization that would occur in a CDF. The Indiana Harbor sediment used for aerobic leachate analysis was kept moist, and turned weekly for 6 months. This may represent a gross exaggeration of conditions at the surface layer in an upland CDF. The losses were dramatic and do indicate that volatilization may be a significant route of contaminant loss under certain circumstances. The potential for volatilization is greatest when the dredged material is moist, not saturated with water. Repeated wetting and drying of exposed sediments would promote volatilization. Volatilization would be far less in the inundated condition with several feet of water above the dredged material. Dried material has the least potential for volatilization because in this condition volatilization is dependent on vapor pressure, not Henry's Law constant. Indiana Harbor sediments which were air dried without rewetting for plant uptake experiments (Appendix D) showed less volatile loss of PAHs than occurred from moist sediments and no loss of PCBs.

Kinetic batch testing

51. Kinetic testing was performed to determine shake time necessary to reach steady-state leachate contaminant concentrations. As part of this evaluation, the method of shaking the sediment-water mixtures was also investigated. Kinetic and shaking procedure results for metals are presented in Tables G7-G9. As shown in table G7, shaking the centrifuge tubes in a vertical position resulted in metal concentrations, except for Pb, that peaked at 24 hr, after which no significant changes were observed. No release of mercury was observed. Mercury was therefore dropped from further monitoring. For tubes shaken horizontally (Table G8), leachate metal concentrations following 24 hr of shaking were as high or higher than leachate concentrations obtained using longer shake times. It was, therefore, determined that a 24-hr shake time was sufficient to attain steady-state leachate concentrations for metals. In cases where the metal concentration decreased when shaken longer than 24 hr, a 24-hr shake time represents a worst case leachate concentration. Similar results were obtained for most of the organic compounds, Table G9. It was, therefore, concluded that a 24-hr shake time was appropriate for batch testing of both metal and organic contaminants.

Table G7

Metal Concentration* in Anaerobic Indiana Harbor Sediment Leachate as a Function of Shaking Time [μg/ℓ (standard error)]

Time hr	As	Zn	Cd	Pb	Hg
6	8 (1)	480 (170)	5 (2)	80 (30)	<2
24	11 (2)	1,030 (90)	10 (6)	50 (30)	<2
48	12 (10)	890 (510)	10 (2)	100 (60)	<2
72	13 (10)	520 (150)	4 (1)	100 (40)	<2
96	12 (2)	850 (450)	7 (5)	140 (60)	<2

Table G8

Metal Concentrations in Anaerobic Indiana Harbor Sediment Leachate as a Function of Horizontal Shaking time [μg/ℓ (standard error)]

Time hr	As	Zn	Cd	Pb	Cr
24	38 (1)	1240 (210)	9 (1)	263 (50)	210 (30)
48	44 (3)	721 (210)	5 (1)	161 (50)	99 (40)
72	44 (1)	550 (110)	4 (0.2)	109 (12)	66 (1)

Table G9

Summary of Indiana Harbor Organic Contaminant Kinetic Testing Data [μg/ℓ (standard error)]

	Time of Shaking, days		
Compound	1	2	7
1	ND	ND	ND
2	ND	ND	ND
3	1.9 (0.85)	ND	ND
4	3.4 (2.1)	ND	ND
5	ND	ND	ND
6	2.6 (1.7)	ND	ND
7	3.3 (2.0)	11 (1.7)	8 (3.5)
8	8 (3.5)	7 (2.3)	8 (1.4)
9	3 (0.07)	4 (0.6)	3 (0.7)
10	3 (2.1)	4 (0.6)	3 (0.7)
11	6 (5.7)	7 (1.7)	3 (2.8)
12	14 (5.7)	18 (2.9)	13 (2.8)
13	ND	ND	ND
14	ND	ND	ND
15	ND	ND	ND
16	0.09 (0)	0.07 (0.04)	0.1 (0.06)
17	0.28 (0.007	0.25 (0.03)	0.38 (0.16)
18	0.44 (0.02)	0.35 (0.05)	0.21 (0.11)
19	0.10 (0.0)	0.10 (0.003)	0.25 (0.09)
20	0.28 (0.007)	0.24 (0.003)	0.50 (0.01)
21	0.28 (0.007)	0.25 (0.03)	0.38 (0.16)
22	0.09 (0.005)	0.06 (0.003)	0.09 (0.04)
23	0.05 (0.005)	0.02 (0.0)	0.04 (0.02)
24	0.08 (0.007)	0.06 (0.003)	0.10 (0.04)
25	0.08 (0.005)	0.04 (0.01)	0.07 (0.04)
26	0.02 (0.01)	ND	ND
27	ND	ND	ND
28	0.22 (0.02)	0.19 (0.01)	0.28 (0.14)
29	0.05 (0.007)	0.02 (0.0)	0.05 (0.01)
30	2.04 (0.10)	1.63 (0.17)	2.42 (0.49)

52. Centrifuge tubes shaken horizontally showed increased reproducibility (smaller coefficients of variation) between replicates for leachate metal concentration when compared with leachate obtained by shaking the sediment- water mixture in a vertical position (Table G10). The increase in reproducibility was apparently a function of the enhanced mixing obtained in the horizontal position. Subsequent batch leach tests were therefore conducted with the centrifuge tubes in a horizontal position.

Selection of liquid-solids ratio for batch testing

53. Batch leaching tests were also conducted to determine the minimum liquid-solids ratio that could be used in the sequential batch leach tests. For a wide range of contaminants, distribution coefficients have been shown to be dependent on the liquid-solids ratio at which they are determined (O'Connor and Connolly 1980; Di Toro and Horzempa 1982a; Voice, Rice, and Weber 1983; Di Toro 1985). Coefficients developed at one liquid-solids ratio may not be appropriate at another if the liquid-solids ratios differ by orders of magnitude. The liquid-solids ratio is approximately 1:1 for unconsolidated dredged material in a CDF after sedimentation. To be a practical laboratory procedure, the liquid-solids ratio used in sequential batch leach tests must be of sufficient magnitude to produce enough leachate for organic contaminant analyses (approximately 1ℓ) and be as close to the field condition as practical. In order to determine the maximum acceptable liquid-solids ratio, a comparison of single-point distribution coefficients obtained at differing ratios was conducted.

54. Indiana Harbor sediment presented unique problems that complicated the comparison of single-point distribution coefficients for the interstitial water-sediment system with those for water-sediment mixtures at the 2:1 and higher liquid-solids ratios. Indiana Harbor sediment is highly contaminated with oil and grease--so much so that a separate oil phase was obtained during centrifugation. Repeated high-speed centrifugation was required to break up the oil dispersion in the aqueous phase, particularly during the interstitial water extraction.

55. The effect of the liquid-solids ratio on single-point distribution coefficients for metals in anaerobic Indiana Harbor sediment is presented in Table G11. Single-point distribution coefficients measured for the sediment-interstitial water system were generally higher than those obtained using higher liquid-solids mixtures, a result of higher metal concentrations in the

Table G10

Coefficient of Variation Measured in Kinetic Testing of Indiana Harbor Sediment for Heavy Metals Using Shaking Techniques With Upright (U) and Horizontal (H) Tubes

	Coefficient of Variation, percent							
Time	As		Zn		Cd		Pb	
hr	U	H	U	H	H	H	U	H
24	2.7	2.6	15.5	24.2	100.0	9.2	60.0	27.0
48	16.7	8.0	100.0	40.6	30.0	26.0	60.0	40.6
72	15.4	3.2	50.0	27.1	50.0	7.7	40.0	27.1

Note: Coefficients of variation are given only where direct comparisons can be made (24-, 48-, and 72-hours sampling times).

Table G11

Single-Point Heavy Metal Distribution Coefficients [ml/g (standard error)] for Anaerobic Indiana Harbor Sediment at Various Water to Sediment Ratios

Ratio	As	Cd	Cr	Pb	Zn
Interstitial water (1:1)	2,852 (837)	4,472 (769)	13,600 (3900)	13,866 (6393)	16,118 (4756)
2:1	648 (87)	2,377 (127)	2,700 (300)	2,721 (985)	3,179 (560)
4:1	767 (41)	3,603 (239)	9,500 (4000)	4,133 (971)	5,752 (139)
8:1	901 (60)	2,913 (393)	4,700 (1000)	5,110 (1084)	4,681 (827)

leachate than in the interstitial water. A similar situation was found for single-point distribution coefficients for the aerobic sediment (Table G12). These differences were probably a result of the high oil and grease content of the sediment, as discussed below.

56. The effects of oil in the sediment on the distribution of metals between sediment and interstitial water have not been documented. But, since the interstitial water tests did not involve shaking, it is highly probable that the oil inhibited desorption, causing the interstitial water contaminant concentrations to be low relative to leachate concentrations at the other liquid-solids ratios. This resulted in higher single-point distribution coefficients for the interstitial water-sediment system.

57. The variability of the single-point distribution coefficients for most metals, for both anaerobic (Table G11) and aerobic (Table G12) sediment, was high. This was a function of the high sediment contaminant concentration and the low levels of heavy metals measured in the leachate. For example, if a parameter has an equilibrium sediment concentration of 1,000 μg/g dry weight sediment, and the leachate concentration is 0.003 μg/ml, the distribution coefficient would be 333,333. If the leachate concentration were 0.002 μg/ml, however, the distribution coefficient would rise to 500,000. There is, therefore, an apparent high degree of variability in the single-point distribution coefficients when in reality there is no environmental or analytical difference between the two leachate concentrations. The problem is exacerbated when leachate concentrations are near the analytical detection limits, increasing the variability of measured leachate concentrations.

58. As shown in Table G13, leachate concentrations for organic contaminants using a 4:1 liquid-solids ratio were generally higher or similar to concentrations measured in the interstitial water (1:1 ratio). The interstitial water concentrations in Table G13, however, are the result of analysis of a single sample. Preparation of this sample required nine separate centrifugations in stainless steel centrifuge tubes at 6,500 g for 30 min to completely break the oil dispersion. It is, therefore, possible that organic contaminant losses through volatilization and adsorption occurred during the repeated handling. Due to the difficulty in obtaining this sample and the opportunities present for contaminant losses, interstitial water concentrations for organic contaminants are suspect.

Table G12

Single-Point Heavy Metal Distribution Coefficients [ml/g (standard error)] for Aerobic Indiana Harbor Sediment at Various Water-to-Sediment Ratios

Ratio	As	Cd	Cr	Pb	Zn
Interstitial water (1:1)	2369 (211)	<2,000,000*	73600 (10980)	128600 (82300)	17700 (334)
2:1	707 (60)	28857 (12140)	25257 (3600)	101700 (4070)	20200 (6240)
4:1	986 (38)	45470 (21200)	47900 (4700)	139500 (6990)	26500 (3040)
8:1	1540 (114)	21693 (4137)	94000 (0)	154000 (22000)	41700 (1800)

< indicates minimum value of single-point distribution coefficient based on analytical detection limit.

Table G13

Steady-State Leachate Concentrations [ng/ml(standard error)] for Anaerobic Indiana Harbor Sediment at Various Sediment to Water Ratios

Compound	Ratio				
	1:1*	2:1	4:1	8:1	12:1.
1	<5	<5	1230 (260)	<5	<5
2	<5	<5	5.5 (8)	10 (0.8)	11 (0.00)
3	12	7.5 (1.4)	16 (2)	30 (1)	26 (0.8)
4	1.1	4 (3)	10 (1)	19 (1)	14 (1.4)
5	3.9	8.7 (4)	20 (2)	25 (0.8)	15 (0.4)
6	<5	5.0 (0.5)	3.7 (0.6)	5 (0.0)	3 (0.2)
7	19	16 (4)	9.3 (1.8)	12 (0.4)	6 (0.2)
8	16	13 (2.5)	9.2 (2)	8 (0.6)	5 (0.1)
9	10	8 (0.5)	3.1 (2)	6 (0.1)	<3
10	8	7 (0.7)	3 (1)	5 (0.3)	<3
11	9	7 (0.6)	<5	6 (0.4)	<5
12	<5	<5	<5	<5	<5
13	<5	<5	<5	<5	<5
14	<5	<5	<5	<5	<5
15	<0.01	<0.01	<0.01	<0.01	<0.01
16	0.05	0.06 (0.01)	0.11 (0.06)	0.05 (0.01)	0.06 (0.02)
17	<0.01	0.43 (0.08)	0.16 (0.04)	<0.01	<0.01
18	0.17	0.44 (0.04)	0.16 (0.08)	0.16 (0.05)	0.11 (0.01)
19	0.06	0.06 (0.01)	0.08 (0.02)	0.02 (0.00)	0.04 (0.004)
20	0.28	0.36 (0.04)	0.50 (0.10)	0.15 (0.07)	0.18 (0.004)
21	<0.01	0.40 (0.08)	0.18 (0.03)	<	<0.01
22	0.04	0.07 (0.004)	0.08 (0.01)	0.06 (0.01)	0.05(0.02)
23	<0.01	<0.01	<0.01	<0.01	<0.01
24	0.04	0.07 (0.01)	0.05 (0.01)	0.04 (0.01)	0.03 (0.00)
25	0.03	0.04 (0.00)	0.04 (0.02)	0.06 (0.04)	0.03 (0.01)
26	0.01	0.02 (0.00)	0.03 (0.006)	0.02 (0.00)	0.02 (0.008)
27	<0.01	<0.01	<0.01	<0.01	0.01
28	0.09	0.17 (0.02)	0.10 (0.02)	0.09 (0.01)	0.07 (0.01)
29	0.01	0.02 (0.00)	0.02 (0.00)	0.04 (0.01)	0.03 (0.01)

* Interstitial water extraction

59. Leachate concentrations in the 4:1 liquid-solids ratio tests were generally similar to those obtained in the 2:1 liquid-solids ratio testing for all contaminants. For example, single-point distribution coefficients for anaerobic and aerobic metals at the 4:1 liquid-solids ratio were within the standard error of those measured using a 2:1 liquid-solids ratio. It was, therefore, found appropriate to use a 4:1 water-to-sediment ratio for the sequential batch and challenge leach testing. This was the highest water to sediment ratio tested that was deemed operationally suitable from the standpoint of minimizing oil problems and the number of centrifugations necessary to obtain a sample that did not contain oil. This was an important consideration because oil was not observed in the leachate from the permeameters, and, therefore, would not be expected in the leachate in a field situation.

Sequential batch and challenge leach testing

60. General leachate quality. Leachate conductivity gradually decreased during both the anaerobic and aerobic testing (Table G14). Leachate from aerobic sediments was generally lower in conductivity than that from anaerobic sediments initially, but the situation was reversed by the end of the leaching period. Challenging fresh anaerobic sediment with leachate from either anaerobic or aerobic sediment increased the conductivity in the leachate.

61. Leachate pH from anaerobic sediment ranged from 7.4 to 7.6 with only a slight drop as leaching continued (Table G15). Challenging anaerobic sediment with leachate from anaerobic sediment did not result in any marked changes in leachate pH. Leachate from aerobic sediments was approximately one pH unit lower than leachate from anaerobic sediment. Challenging fresh anaerobic sediment with leachate from aerobic sediment lowered the pH of leachate from the anaerobic sediment compared with either leachate from anaerobic sediment or leachate from anaerobic sediment challenged by anaerobic sediment leachate. This difference in pH between anaerobic and aerobic leachate was not of a magnitude sufficient to cause pronounced differences in metal solubility.

62. Metal releases sequential batch leach tests. The steady-state sediment q and leachate C metal concentrations obtained from the sequential batch leach tests for anaerobic and aerobic conditions are presented in Tables G16 and G17, respectively. In general, the anaerobic sequential batch tests produced well-defined desorption isotherms and the aerobic sequential batch tests produced ill-defined clusters. The predictable and linear

Table G14

Conductivity (μmhos/cm) in Indiana Harbor Serial Batch Leachate

Test	Time, days				
	1	2	3	4	5
Anaerobic	1540 (30)	675 (30)	450 (35)	330 (17)	290 (6)
Anaerobic Challenged	2037 (30)	1100 (0)	770 (35)	600 (0)	570 (17)
Aerobic	1038 (64)	585 (20)	495 (3)	398 (3)	495 (3)
Aerobic Challenged	1678 (35)	840 (30)	585 (6)	550 (3)	550 (13)

Table G15

Serial Batch Leachate pH [mean (standard error)] for Indiana Harbor

Test	Time, days 1	 2	 3	 4	 5
Anaerobic	7.6 (0.03)	7.6 (0.03)	7.5 (0.03)	7.5 (0)	7.4 (0.03)
Anaerobic Challenged	7.6 (0.05)	7.6 (0)	7.5 (0.03)	7.4 (0.03)	7.2 (0)
Aerobic	6.6 (0.03)	6.6 (0)	6.7 (0.03)	6.6 (0.03)	6.8 (0.03)
Aerobic Challenged	7.0 (0)	6.8 (0.03)	6.6 (0.03)	6.7 (0)	6.7 (0)

Table G16

Steady-State Sediment and Leachate Concentrations [mean (standard error)] for Indiana Harbor Sediments Following Anaerobic Sequential Leaching

Time days	Concentration				
	As	Cr	Pb	Cd	Zn
			Sediment, µg/g		
1	29.36	281.18	877.45	19.96	4119.8
	(0.01)	(0.14)	(0.34)	(0.0006)	(1.0)
2	29.28	280.91	876.78	19.94	4117.3
	(0.02)	(0.12)	(0.32)	(0.007)	(0.9)
3	29.23	280.85	876.64	19.93	4116.3
	(0.02)	(0.12)	(0.35)	(0.02)	(1.2)
4	29.17	280.83	876.59	19.92	4115.8
	(0.02)	(0.12)	(0.35)	(0.02)	(1.3)
			Leachate, µg/ml		
1	0.034	0.195	0.370	0.009	1.27
	(0.002)	(0.031)	(0.08)	(0.001)	(0.22)
2	0.020	0.062	0.156	0.004	0.60
	(0.001)	(0.012)	(0.04)	(0.0006)	(0.14)
3	0.016	0.014	0.033	0.004	0.22
	(0.002)	(0.002)	(0.01)	(0.003)	(0.06)
4	0.012	0.005	0.011	0.001	0.12
	(0.001)	(0.001)	(0.001)	(0.003)	(0.02)

Table G17

Steady-State Sediment and Leachate Concentrations [mean (standard error)] for Indiana Harbor Sediment Following Aerobic Sequential Leaching

Time	Concentration				
days	As	Cr	Pb	Cd	Zn
			Sediment, μg/g		
1	29.5	281.98	878.97	19.98	4124.5
	(0.00)	(0.00)	(0.005)	(0.006)	(0.06)
2	29.48	281.96	878.93	19.97	4124.32
	(0.00)	(0.003)	0.006)	(0.008)	(0.06)
3	29.45	281.91	878.89	19.97	4124.05
	(0.003)	(0.01)	(0.007)	(0.008)	(0.05)
4	29.42	281.87	878.81	19.97	4123.71
	(0.004)	(0.02)	(0.02)	(0.007)	(0.02)
5	29.39	281.85	878.78	19.97	4123.47
	(0.003)	(0.02)	(0.02)	(0.007)	(0.02)
			Leachate, μg/ml		
1	<0.005	0.004	0.009	0.006	0.126
	(0.00)	(0.0003)	(0.001)	(0.002)	(0.016)
2	0.005	0.007	0.01	0.0013	0.044
	(0.0002)	(0.0007)	(0.0009)	(0.0009)	(0.001)
3	0.009	0.013	0.01	0.0006	0.066
	(0.0009)	(0.002)	(0.002)	(0.002)	(0.005)
4	0.006	0.01	0.019	0.0007	0.085
	(0.0007)	(0.002)	(0.004)	(0.0001)	(0.014)
5	0.009	0.006	0.055	0.0006	0.061
	(0.004)	(0.002)	(0.0009)	(0.00008)	(0.008)

desorption of metals under anaerobic conditions is compared in Figures G6-G8 to the ill-defined clusters observed for metal desorption from the aerobic sediment. The points plotted in Figures G6-G8 represent pooled data from all the replicates. As indicated in these figures, more zinc, cadmium, chromium, lead, and zinc were released by the anaerobic sediment than from the aerobic sediment. This is consistent with the lack of a pronounced pH drop in the aerobic sediment. Brannon and Patrick (1985) have previously reported that Indiana Harbor sediment is high in iron concentration. Under aerobic conditions, these and other sediments were observed to fix both native and added antimony in more immobile sediment iron fractions (Brannon and Patrick 1985). Similar fixation processes for heavy metals were apparently active during the 6 months that Indiana Harbor sediment was exposed to air. Thus, exposure to air decreased the mobility of metals under aerobic leaching conditions.

63. In order to examine the assumption that the release of metals is governed by linear desorption, the values of q and C obtained from sequential batch leach tests were regressed onto Equation G5. The results are presented in Table G18 for anaerobic testing and Table G19 for aerobic testing. The replicate data for each contaminant were not pooled, and each experimental replicate for each contaminant was examined individually. This allowed the three replicates for each contaminant to be compared. Values for K_d and q_r determined by least squares analysis are presented in Tables G18 and G19 along with supporting statistics.

64. With one exception (cadmium), the regression coefficients for the anaerobic sediment are high, indicating good fit. The probability that the values for the distribution coefficients in Table G18 result by chance is small. Thus, the regression statistics support the assumption that the release of metals from anaerobic Indiana Harbor sediment is governed by linear desorption (Equation G5). In addition, it should be noted that 99 percent or more of the bulk sediment metal concentrations was resistant to leaching.

65. It is apparent from Figures G5-G7 that batch aerobic desorption data for zinc and cadmium were highly clustered. Thus, the release of metals from the aerobic sediment did not follow a well-defined desorption isotherm similar to the anaerobic results. The regression statistics in Table G19 showed that Equation G5 is not a satisfactory model for the aerobic metal data due to poor fit. The fit was poor as indicated by the r^2 values because the data were clustered. For clustered desorption isotherms, meaningful values for K_d and

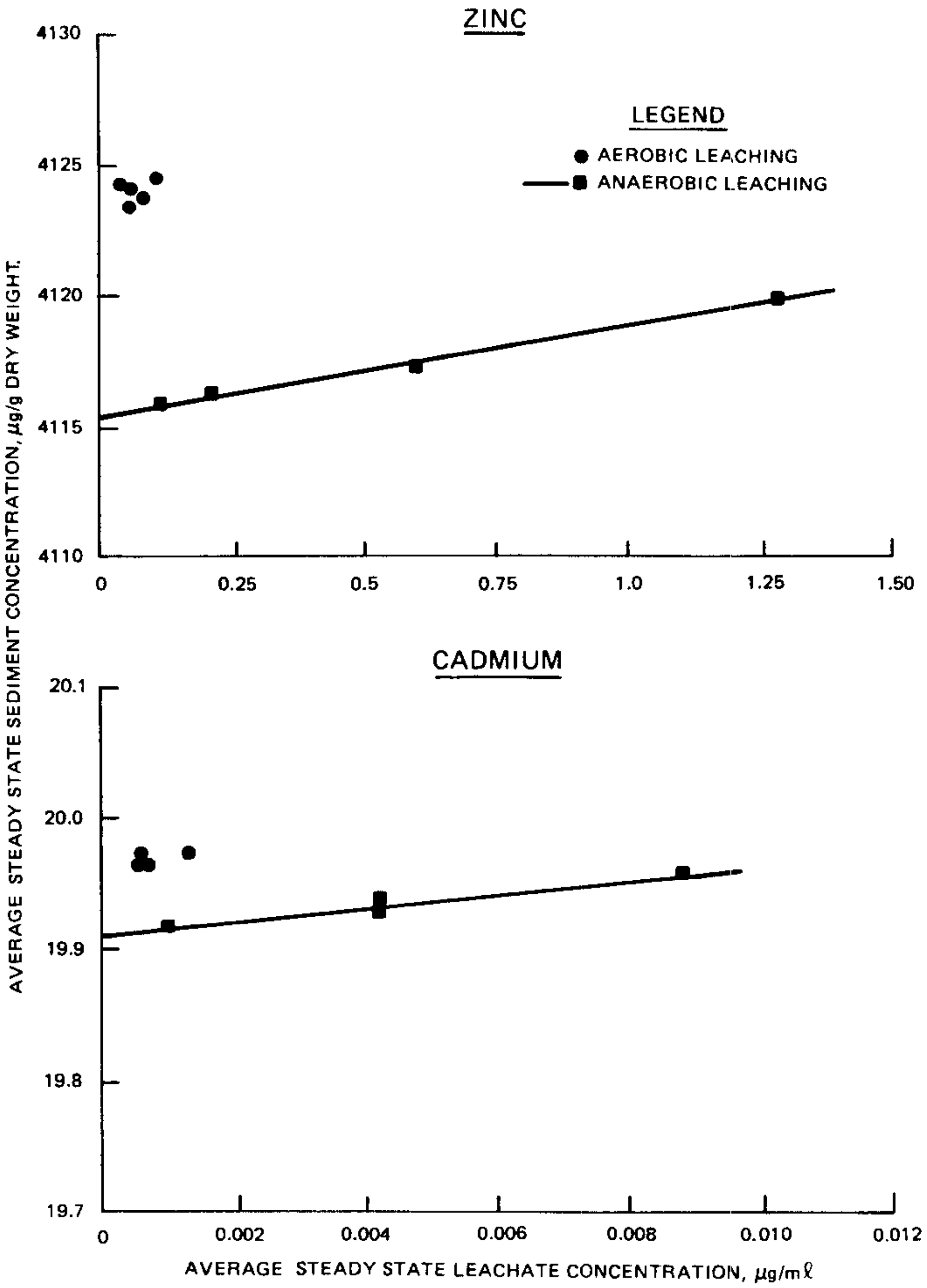


Figure G6. Desorption isotherms for zinc and cadmium in Indiana Harbor sediment

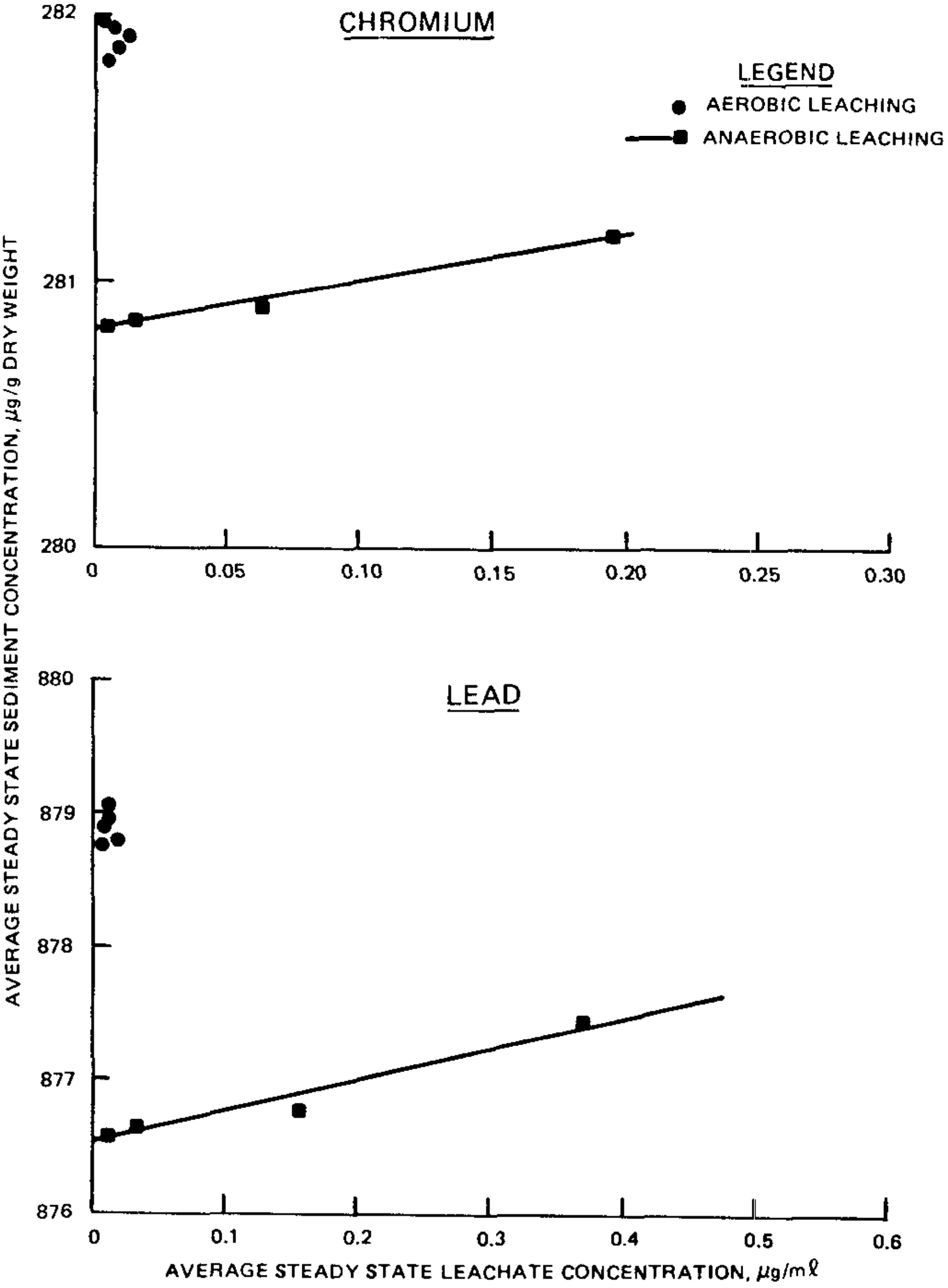
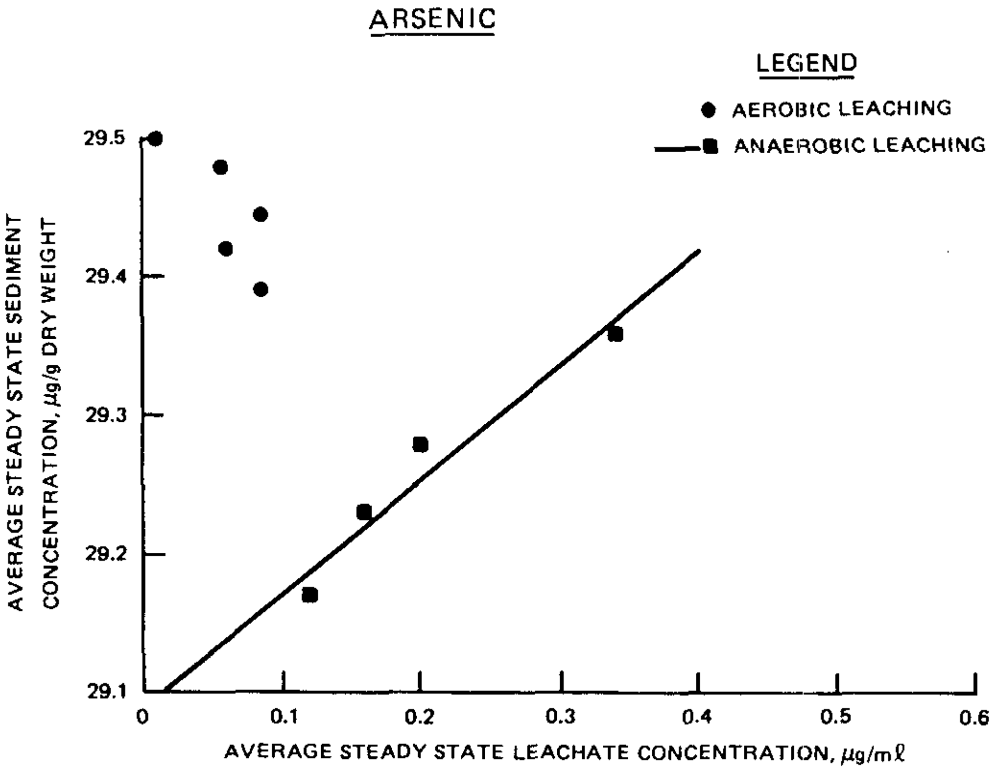


Figure G7. Desorption isotherm for lead and chromium in Indiana Harbor sediment



'Figure G8. Desorption isotherms for arsenic in Indiana Harbor sediment

Table G18

Linear Regression of q versus C for Sequential Batch Leaching of Metals From Anaerobic Indiana Harbor Sediment*

Metal	Replicate	n	r^2	K_d ℓ/kg	SE ℓ/kg	Ave. K_d ℓ/kg	q_r mg/kg	q_r/q_o %
Arsenic	1	4	0.898	7.47	1.77	7.46	29.1	98.8
	2	4	0.83	8.21	2.61		29.1	99.0
	3	4	0.95	6.70	1.01		29.1	98.8
Cadmium	1	4	0.63	3.30	1.76	2.86	19.94	99.7
	2	4	0.82	2.17	0.73		19.94	99.7
	3	4	0.214	3.10	4.20		19.89	99.4
Chromium	1	4	0.84	2.73	0.84	1.85	648.91	99.9
	2	4	0.99	1.53	0.093		648.94	99.8
	3	4	0.99	1.29	0.059		648.59	99.8
Lead	1	4	0.79	2.99	1.09	2.39	876.21	99.6
	2	4	0.84	2.90	.88		877.22	99.8
	3	4	0.97	1.29	.15		876.17	99.6
Zinc	1	4	0.66	3.88	1.96	3.01	4115.57	99.7
	2	4	0.996	2.59	0.102		4117.78	99.8
	3	4	0.899	2.56	0.60		4113.56	99.7

* n = number of points in each replicate (steps in sequential leaching).
r^2 = Correlation coefficient.
K_d = slope of the regression line.
SE = Standard error of the mean.
q_r = intercept of regression line.
q_o = bulk sediment concentration at the beginning of leaching.

Table G19

Linear Regression of q Versus C for Sequential Batch Leaching of Metals from Aerobic Indiana Harbor Sediment

Metal	Replicate	n	r^2	K_d ℓ/kg	SE ℓ/kg	Ave. K_d ℓ/kg	q_r mg/kg	Ave.* q_r mg/kg	q_r/q_o %
Arsenic	1	4	.795	-19.7	7.06				
	2	4	.064	-3.33	8.98	-13.43	29.45		
	3	4	.114	-8.51	16.74		29.49	29.39	99.6
	4	4	.766	-22.2	8.67		29.59	(.003)*	
Cadmium	1	5	.70	2.62	.968		19.85		
	2	5	.033	2.22	6.9	1.41		19.85	
	3	5	.10	.83	1.41		19.97	19.97	99.8
	4	5	.0	.0	.0		19.96	(.007)*	
Chromium	1	5	.119	-5.67	8.86		281.96		
	2	5	.018	-1.92	8.07	-2.93	281.91	281.85	99.9
	3	5	.33	-7.3	6.00	(-4.52)	281.96	(.02)*	
	4	5	.042	3.17	8.71		281.91		
Lead	1	5	.192	-5.65	6.69		878.93		
	2	5	.168	-4.44	5.71	-0.035	878.92	878.78	<99.9
	3	5	.005	-1.27	9.65		878.88	(0.02)*	
	4	5	.528	11.5	5.66		878.81		
Zinc	1	4	.05	3.52	8.78		4123.77		
	2	4	.04	3.50	9.69	3.56	4123.72	4123.47	<99.9
	3	4	.20	3.67	4.12		4123.65	(0.02)*	

* Average sediment concentration at the end of sequential leaching.

q_r cannot be obtained by regression analysis alone. Sediment chemistry relating to the physicochemical locations of contaminants within fine-grained sediment and the selective partitioning of contaminants within different geochemical phases must be recognized in order to fully evaluate the desorption isotherms.

66. The primary reason that well-defined isotherms were not obtained for aerobic metals is that the amount of contaminant released was very low. This implies that most of the metals in the aerobic sediment are resistant to leaching, i.e., q_r is large relative to the bulk concentration. If q_r is large, then the leachable concentration, q_L , is small. For very small q_L , differences in leachate concentration between steps in the sequential leaching procedure, regardless of the value for K_d , will be small relative to the combined precision of the leaching tests and the chemical analytical procedures. The data will be scattered about the true desorption isotherm, depending on the variability associated with the leaching and chemical analysis procedures. Thus, the clustering or scatter associated with the desorption isotherms for aerobic metals is probably due to small q_L (large q_r) relative to the testing variability.

67. There is a well-established geochemical basis for a leaching resistant concentration q_r for metals in dredged material. Metals are partitioned among several geochemical forms (phases) ranging from a fraction that is ionically attached or sorbed to the dredged material solids (exchangeable phase) to an extremely stable residual that is part of mineral crystalline lattices (Brannon et al. 1976). Geochemical partitioning in order of decreasing mobility is ion exchangeable phase, easily reducible and moderately reducible phases, organic and sulfide phases, and a residual phase. The leaching resistant concentration, q_r , probably represents the geochemical phases beyond the easily reducible phase. This includes metals bound within iron and manganese oxide and hydroxide partitions, metals bound in organic matter as complexes and compounds precipitated as sulfide salts, and metals occurring as part of mineral crystalline lattices. The leachable concentration, q_L , therefore, consists primarily of metals in the interstitial water and the exchangeable and easily reducible phases, as was shown for metals release from sediment into overlying water (Brannon, Plumb, and Smith 1978). This includes metals ionically attached to the dredged material solids and metals occluded within iron and manganese oxide and hydroxide partitions. Thus, the overall

mobility of a metal contaminant in dredged material depends on the geochemical partitioning of the metal (Brannon, Plumb, and Smith 1978).

68. Since the regression analysis for aerobic metals was not satisfactory, estimates for q_r were based on the total mass of metal removed in the aerobic, sequential leach tests. These values are presented in Table G19. As indicated, greater than 99 percent of the bulk metal concentrations were not removed by sequential leaching. The data obtained in the sequential batch leach tests for anaerobic and aerobic sediment show that the metals in Indiana Harbor sediment are highly resistant to leaching.

69. Organic contaminant releases in sequential batch tests. Steady-state dissolved organic carbon (DOC) concentrations in the filtered leachate from sequential batch leach tests for anaerobic and aerobic conditions are presented in Table G20. For reference, concentrations of TOC in the sediment interstitial water prior to leaching were 985 and 750 mg/ℓ in anaerobic and aerobic sediments, respectively. As shown in Table G20, the leachate DOC decreased with each step in the sequential leach procedure until the fourth step. At this point, DOC became constant at 25 mg/ℓ in the anaerobic tests and 45 mg/ℓ in the aerobic tests. The data produced a well-defined isotherm for anaerobic sediment as shown in Figure G9. The isotherm is curvilinear. A plot for aerobic data is not available because TOC in the aerobic sediment was not measured. The sequential leach data, however, indicate that a curvilinear isotherm similar to the one shown in Figure G9 would also be obtained for aerobic organic carbon desorption. Curvilinear isotherms can be modeled by the Langmuir adsorption-desorption equation (Equation H6). Application of this equation to curvilinear desorption isotherms is discussed in Appendix H. Langmuir coefficients for the anaerobic organic carbon isotherm were determined using least squares analysis of the linearized form of the Langmuir equation (Equation H7). Langmuir coefficients for the anaerobic TOC isotherm were $Q = 73492$ mg/kg and $b = 3.864$ ℓ/mg ($r = 0.9999$). Q and b are defined as the monolayer sorption capacity and the Langmuir distribution constant, respectively. These data show that the distribution of TOC between solid and aqueous phases follows a nonlinear isotherm, well known from adsorption theory.

70. An analysis of the various components that make up the DOC in the filtered leachate is not available. However, it is probable that much of the material is naturally occurring humic acids, substances that are known to sorb

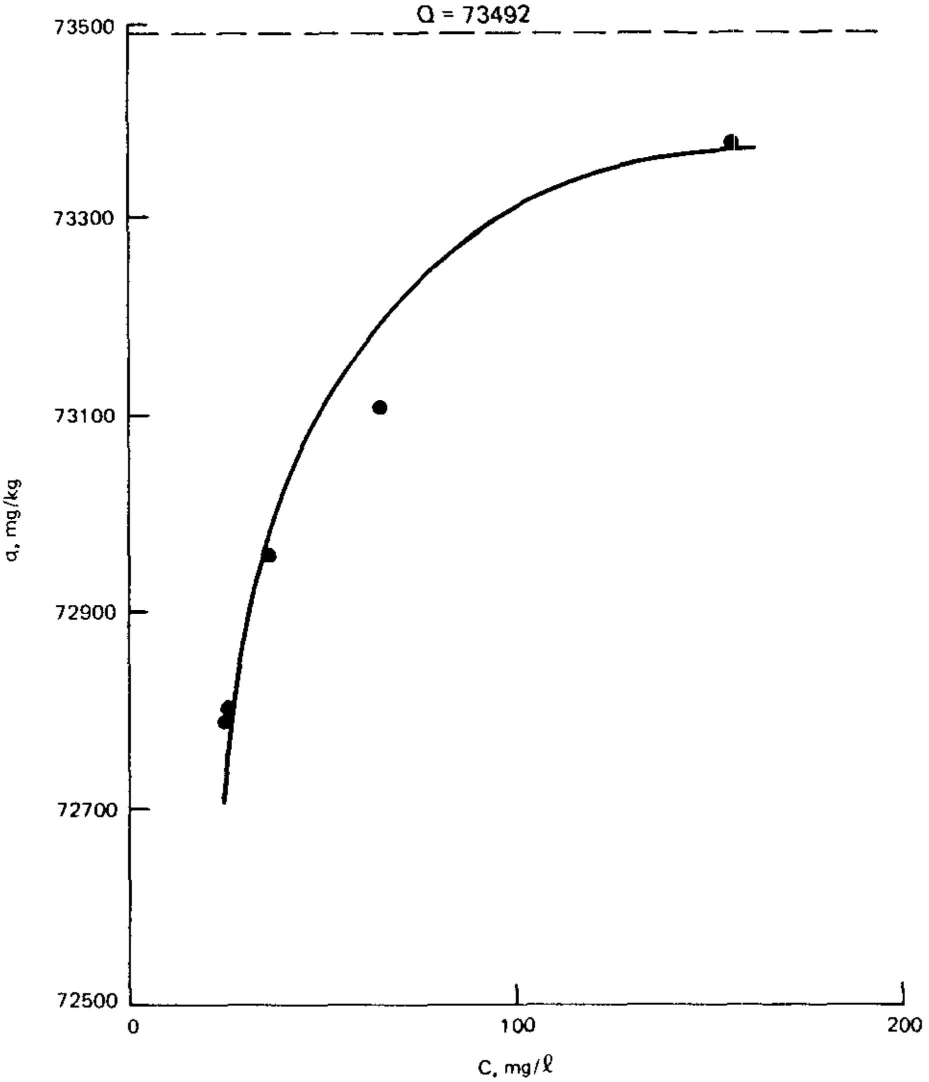


Figure G9. Desorption isotherm for dissolved organic carbon in anaerobic Indiana Harbor sediment

Table G20

Steady-State DOC Concentration [mg/ℓ (standard error)] in Leachate for Sequential Batch Leach Tests for Anaerobic and Aerobic Sediment

Treatment	Sequential Leach Number				
	1	2	3	4	5
Anaerobic	156 (19)	65 (3)	39 (2)	25 (3)	24 (4)
Aerobic	204 (7)	76 (5)	50 (2)	40 (2)	45 (3)

to sediments and soils. These substances could act to stabilize in solution weakly soluble and highly sorbed contaminants such as PCB congeners (Voice, Rice, and Weber 1983; Gschwend and Wu 1985). Thus, DOC was considered a potentially important index of overall organic contaminant mobility. If gross aqueous phase organic carbon has an effect on the partitioning of hydrophobic organic compounds, then the sequential leaching of these compounds should mimic the desorption characteristics for DOC. It is probable, however, that certain components of the aqueous phase organic carbon, not gross DOC, affect the partitioning of organic compounds (Voice, Rice, and Weber 1983; Gschwend and Wu 1985). If this is the case, the DOC measurement will lack the resolution necessary to measure the effect.

71. The steady-state sediment q and leachate C concentrations for PAHs and Aroclor 1248 congeners obtained from the sequential batch leach tests for anaerobic and aerobic leaching are presented in Tables G21-G24. When plotted, these data produced clustered isotherms that did not show a well-defined relationship between q and C. This is illustrated in Figures G10 and G11, respectively, for anaerobic naphthalene and an anaerobic PCB congener (see number 19 in Table G4). These desorption isotherms, typical of the PAH and PCB isotherms obtained for anaerobic leaching, bear little resemblance to the well-defined desorption isotherm for anaerobic DOC shown in Figure G9.

72. Slope-derived distribution coefficients for the organic contaminants were obtained from the sequential batch leach data by regressing the q and C values onto Equation G5. The regression statistics for anaerobic coefficients are presented in Table G25. The regression statistics showed that regression of Equation G5 onto the data produced very poor fit and that the distribution coefficients obtained by regression were not meaningful. No attempt was made to regress the linearized Langmuir equation onto the data because all the PAH and PCB desorption isotherms were clustered. As previously noted for the aerobic metals, when isotherm data are clustered, a well-defined relationship between q and C cannot be determined. It is clear that the clusters shown in Figures G10 and G11 cannot be described using straight lines or simple curves.

73. Release of organic contaminants from aerobic Indiana Harbor sediment showed the same clustering effect as did organic contaminant release from the anaerobic sediment. The statistics for the regression of Equation G5 onto the aerobic PAH and PCB sequential leach data are presented in Table G26. These

Table G21

Steady-State Sediment Organic Contaminant Concentration [ug/g dry weight (standard error)] for Indiana Harbor Sediment Following Anaerobic Sequential Leaching

Compound	Sequential Leach Number				
	1	2	3	4	5
1	1993.83 (1.322)	1986.25 (2.29)	1975.10 (1.98)	1962.23 (3.17)	1951.33 (4.19)
2	21.97 (0.004)	21.95 (0.007)	21.91 (0.006)	21.88 (0.009)	21.84 (0.01)
3	95.92 (0.01)	95.83 (0.02)	95.72 (0.01)	95.62 (0.02)	95.51 (0.02)
4	68.95 (0.005)	68.89 (0.007)	68.82 (0.01)	68.76 (0.01)	68.70 (0.01)
5	199.90 (0.01)	199.81 (0.01)	199.72 (0.02)	199.64 (0.01)	199.56 (0.006)
6	61.98 (0.003)	61.97 (0.002)	61.95 (0.003)	61.94 (0.002)	61.94 (0.008)
7	149.95 (0.009)	149.91 (0.009)	149.87 (0.007)	149.85 (0.01)	149.83 (0.009)
8	139.95 (0.007)	139.91 (0.007)	139.88 (0.009)	139.86 (0.008)	139.85 (0.01)
9	91.98 (0.009)	91.96 (0.01)	91.95 (0.01)	91.94 (0.01)	91.94 (0.01)
10	85.99 (0.006)	85.97 (0.007)	85.96 (0.008)	85.95 (0.007)	85.95 (0.007)
11		No Detectable Release*			
12		No Detectable Release*			
13		No Detectable Release*			
14		No Detectable Release*			
15		No Detectable Release**			
16	10.800(0.0001)	10.799(0.0002)	10.798 (0.0006)	10.798(0.0006)	10.797(0.0007)
17	19.499(0.0002)	19.499(0.0002)	19.499 (0.0003)	19.499(0.0003)	19.499(0.0003)
18	31.899(0.0004)	31.899(0.0001)	31.898 (0.0006)	31.898(0.0007)	31.898(0.0007)
19	3.499(0.0001)	3.499(0.0001)	3.499 (0.0001)	3.499(0.0001)	3.499(0.0001)
20	19.498(0.0006)	19.487(0.0005)	19.496 (0.0004)	19.495(0.0005)	19.495(0.0006)
21	19.299(0.0002)	19.299(0.0002)	19.299 (0.0002)	19.299(0.0002)	19.299(0.0002)
22	5.200(0.0001)	5.199(0.0001)	5.199 (0.0002)	5.199(0.0002)	5.199(0.0002)
23		No Detectable Releases **			
24	5.700(0.0001)	5.700(0.0001)	5.699 (0.0001)	5.699(0.0002)	5.699(0.0002)
25	3.700(0.0001)	3.700(0.0001)	3.700 (0.0001)	3.700(0.0001)	3.700(0.0001)
26	2.200(0.00003)	2.200(0.00003)	2.200 (0.0001)	2.200(0.0001)	2.200(0.0001)
27		No Detectable Releases **			
28	12.400(0.0002)	12.400(0.0001)	12.399 (0.0003)	12.399(0.0003)	12.398(0.0003)
29		No Detectable Releases **			

* Detection limit = 0.005 mg/ℓ.

** Detection limit = 0.00001 mg/ℓ.

Table G22

Steady-State Leachate Organic Contaminant Concentrations [ug/ml (standard error)] for Indiana Harbor Sediment Following Sequential Leaching

Compound	Sequential Leach Number									
	1		2		3		4		5	
1	1.23	(0.026)	1.52	(0.30)	2.23	(0.18)	2.57	(0.27)	2.18	(0.25)
2	0.006	(0.0008)	0.005	(0.001)	0.007	(0.0006)	0.0007	(0.0007)	0.007	(0.0003)
3	0.016	(0.002)	0.017	(0.003)	0.022	(0.002)	0.021	(0.002)	0.021	(0.006)
4	0.010	(0.001)	0.011	(0.001)	0.013	(0.001)	0.012	(0.001)	0.012	(0.000)
5	0.020	(0.002)	0.018	(0.001)	0.018	(0.001)	0.015	(0.001)	0.016	(0.001)
6	0.004	(0.001)	0.003	(0.0002)	0.003	(0.000)	0.002	(0.000)	0.002	(0.000)
7	0.009	(0.002)	0.009	(0.001)	0.007	(0.001)	0.004	(0.000)	0.003	(0.000)
8	0.009	(0.002)	0.009	(0.001)	0.006	(0.000)	0.004	(0.000)	0.002	(0.000)
9	0.003	(0.002)	0.005	(0.004)	0.002	(0.001)	0.001	(0.0001)		<0.001
10	0.002	(0.001)	0.004	(0.0003)	0.002	(0.0002)	0.001	(0.001)	<0.001	
11	<		<		<0.005		<0.005		<0.005	
12	<0.005		<0.005		<0.005		<0.005		<0.005	
13	<0.005		<0.005		<0.005		<0.005		<0.005	
14	0.005		<0.005		<0.005		<0.005			
15	<0.00001		<0.00001		<0.00001		<0.00001			
16	0.00011	(0.00006)	0.00007	(0.00002)	0.00007	(0.00001)	0.00009	(0.00001)	0.00012	(0.00012)
17	0.00016	(0.00004)	0.00009	(0.00004)	<0.00001		<0.00001		<0.00001	
18	0.00016	(0.00008)	0.00011	(0.00004)	0.00008	(0.0002)	0.00008	(0.00002)	0.00005	(0.00001
19	0.00008	0.00002)	0.00003	(0.00002)	0.00003	(0.0003	0.0003	(0.000003)	(0.00003	(0.00001)
20	0.0005	(0.00011)	0.00019	(0.00004)	0.00016	(0.00003)	0.00014	(0.00001)	<0.00001	
21	0.00018	(0.00003)	0.00009	(0.00004)	<0.00001		<0.00001		<0.00001	
22	0.0008	(0.00001)	0.00005	(0.00004)	0.00004	(0.00001)	0.00003	(0.000003)	0.00003	(0.00001)
23	<0.00001		<0.00001		<0.00001		<0.00001		<0.00001	
24	0.00005	(0.00001)	0.00004	(0.00002)	0.00004	(0.00001)	0.00003	(0.000003)	0.00002	(0.00003)
25	0.00003	(0.00002)	0.00003	(0.00002)	0.00002	(0.00001)	0.00002	(0.000003)	0.00002	(0.00001)
26	0.00003	(0.00001)	0.00001	(0.000003)	0.00002	(0.00001)	0.00001	(0.000003)	0.00001	(0.00000)
27	<0.00001		<0.00001		<0.00001		<0.00001		<0.00001	
28	0.00011	(0.00002)	0.00008	(0.00005)	0.00006	(0.00002)	0.00004	(0.00007)	0.00003	(0.00006)
29	<0.00001		<0.00001		<0.00001		<0.00001		<0.00001	

Table G23

Steady-State Sediment Organic Contaminant Concentrations [ug/g (standard error)]

for Indiana Harbor Sediments Following Aerobic Leaching

Compound	Sequential Leach Number				
	1	2	3	4	5
1	81.73 (0.026)	81.72 (0.022)	No Further Changes in Sediment Concentration		
2	No Change in Sediment Concentration				
3	10.74 (0.0007)	10.72 (0.001)	10.71 (0.0019)	No Further Changes in Sediment Concentration	
4	11.54 (0.00026)	No Further Changes in Sediment Concentration			
5	36.49 (0.0008)	No Further Changes in Sediment Concentration			
6	No Change in Sediment Concentration				
7	63.44 (0.001)	63.43 (0.0006)	63.41 (0.0008)	63.40 (0.002)	63.39 (0.0005)
8	85.18 (0.001)	85.17 (0.001)	85.15 (0.001)	85.13 (0.001)	85.12 (0.0006)
9	No Change in Sediment Concentration				
10	No Change in Sediment Concentration				
11	No Change in Sediment Concentration				
12	No Change in Sediment Concentration				
13	No Change in Sediment Concentration				
14	No Change in Sediment Concentration				
15	No Change in Sediment Concentration				
16	0.131 (0.00003)	0.131 (0.00003)	0.130 (0.00003)	0.130 (0.00003)	0.130 (0.00007)
17	No Change in Sediment Concentration				
18	5.240 (0.00003)	5.240 (0.00006)	5.239 (0.00003)	5.238 (0.00007)	5.238 (0.00007)
19	1.1398 (0.00003)	1.1397 (0.00006)	1.1395 (0.00009)	1.1393 (0.0001)	1.1393 (0.00007)
20	6.9894 (0.00009)	6.9887 (0.00009)	6.9881 (0.0003)	6.9872 (0.0002)	6.9870 (0.0003)
21	No Change in Sediment Concentration				
22	0.9438 (0.00003)	0.9437 (0.00006)	0.9435 (0.00006)	0.9432 (0.00006)	0.9431 (0.00006)
23	No Change in Sediment Concentration				
24	0.5849 (0.00007)	0.5848 (0.00006)	0.5846 (0.0001)	0.5845 (0.00009)	0.5744 (0.00009)
26	0.3549 (0.00006)	0.3548 (0.00006)	0.3547 (0.00007)	0.3546 (0.00007)	0.3545 (0.00007)
27	No Change in Sediment Concentration				
28	2.2997 (0.00003)	2.2996 (0.0001)	2.2992 (0.0001)	2.2988 (0.0001)	2.2986 (0.0002)
29	0.3088 (0.00009)	0.3088 (0.00009)	0.3086 (0.00001)	0.3086 (0.00009)	0.3086 (0.00009)

Table G24

Steady-State Leachate Organic Contaminant Concentrations [ug/ml (Standard Error)] for Indiana Harbor Sediment Following Aerobic Leaching

Compound	Sequential Leach Number 1	2	3	4	5
1	0.052 (0.006)	0.004 (0.001)	<0.004	<0.004	<0.004
2	<0.005	<0.005	<0.005	<0.005	<0.005
3	0.003 (0.0002)	0.004 (0.0003)	0.003 (0.0002)	<0.002	<0.002
4	0.0015 (0.00006)	<0.001	<0.001	<0.001	<0.001
5	0.0036 (0.0003)	<0.002	<0.002	<0.002	<0.002
6	<0.005	<0.005	<0.005	<0.005	<0.005
7	0.0032 (0.0003)	0.003 (0.0003)	0.0028 (0.0001)	0.0025 (0.0003)	0.0024 (0.0003)
8	0.0041 (0.0003)	0.0041 (0.0004)	0.0038 (0.0003)	0.0044 (0.0005)	0.0038 (0.0004)
9	<0.005	<0.005	<0.005	<0.005	<0.005
10	<0.005	<0.005	<0.005	<0.005	<0.005
11	<0.005	<0.005	<0.005	<0.005	<0.005
12	<0.005	<0.005	<0.005	<0.005	<0.005
13	<0.005	<0.005	<0.005	<0.005	<0.005
14	<0.005	<0.005	<0.005	<0.005	<0.005
15	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
16	0.00008 (0.00001)	0.00003 (0.00001)	0.00003 (0.00001)	0.00005 (0.00001)	0.00003 (0.00001)
17	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
18	0.00009 (0.00001)	0.00011 (0.00001)	0.00014 (0.00002)	0.00015 (0.00001)	0.00007 (0.00002)
19	0.00004 (0.00001)	0.00003 (0.000003)	0.00005 (0.00001)	0.00004 (0.00001)	0.00003 (0.00000)
20	0.00016 (0.00002)	0.00017 (0.000000)	0.00014 (0.00007)	0.00022 (0.00001)	0.00005 (0.00004)
21	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
22	0.00004 (0.00001)	0.00003 (0.00000)	0.00005 (0.00001)	0.00007 (0.00001)	0.00003 (0.00000)
23	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
24	0.00004 (0.00001)	0.00003 (0.00000)	0.00004 (0.00000)	0.00004 (0.00001)	0.00003 (0.00000)
25	0.00004 (0.00001)	0.00002 (0.00000)	0.00004 (0.00001)	0.00003 (0.00001)	0.00003 (0.00000)
26	0.00002 (0.00001)	0.00003 (0.00002)	0.00002 (0.00001)	0.00002 (0.00001)	0.00002 (0.00001)
27	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
28	0.00006 (0.00001)	0.00005 (0.00002)	0.00009 (0.00001)	0.00009 (0.00001)	0.00006 (0.00001)
29	0.00005 (0.00002)	0.00001 (0.00000)	0.00004 (0.00001)	0.00002 (0.00001)	0.00002 (0.00001)

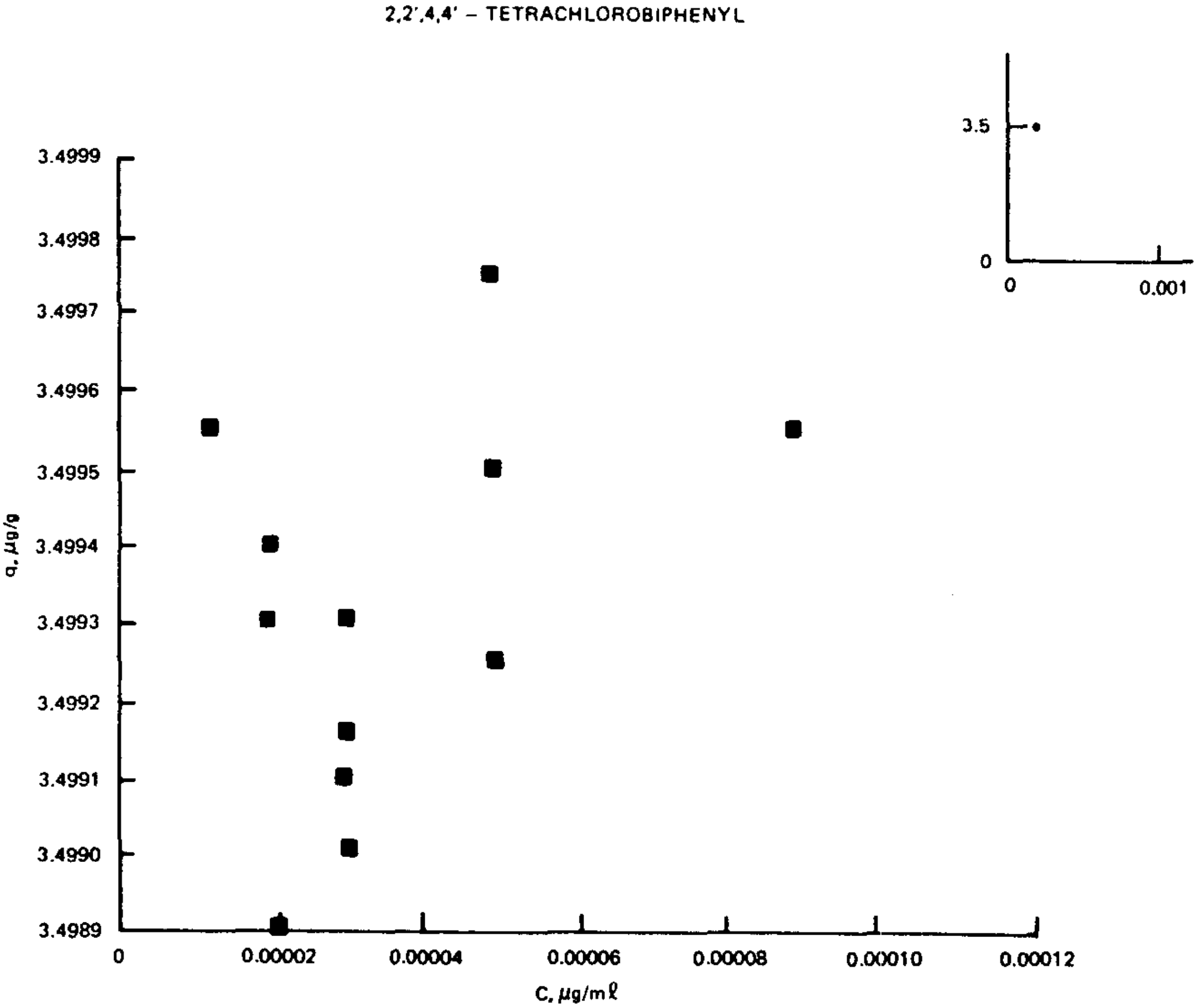


Figure G10. Desorption isotherm for 2, 2', 4,4' -tetrachlorobiphenyl

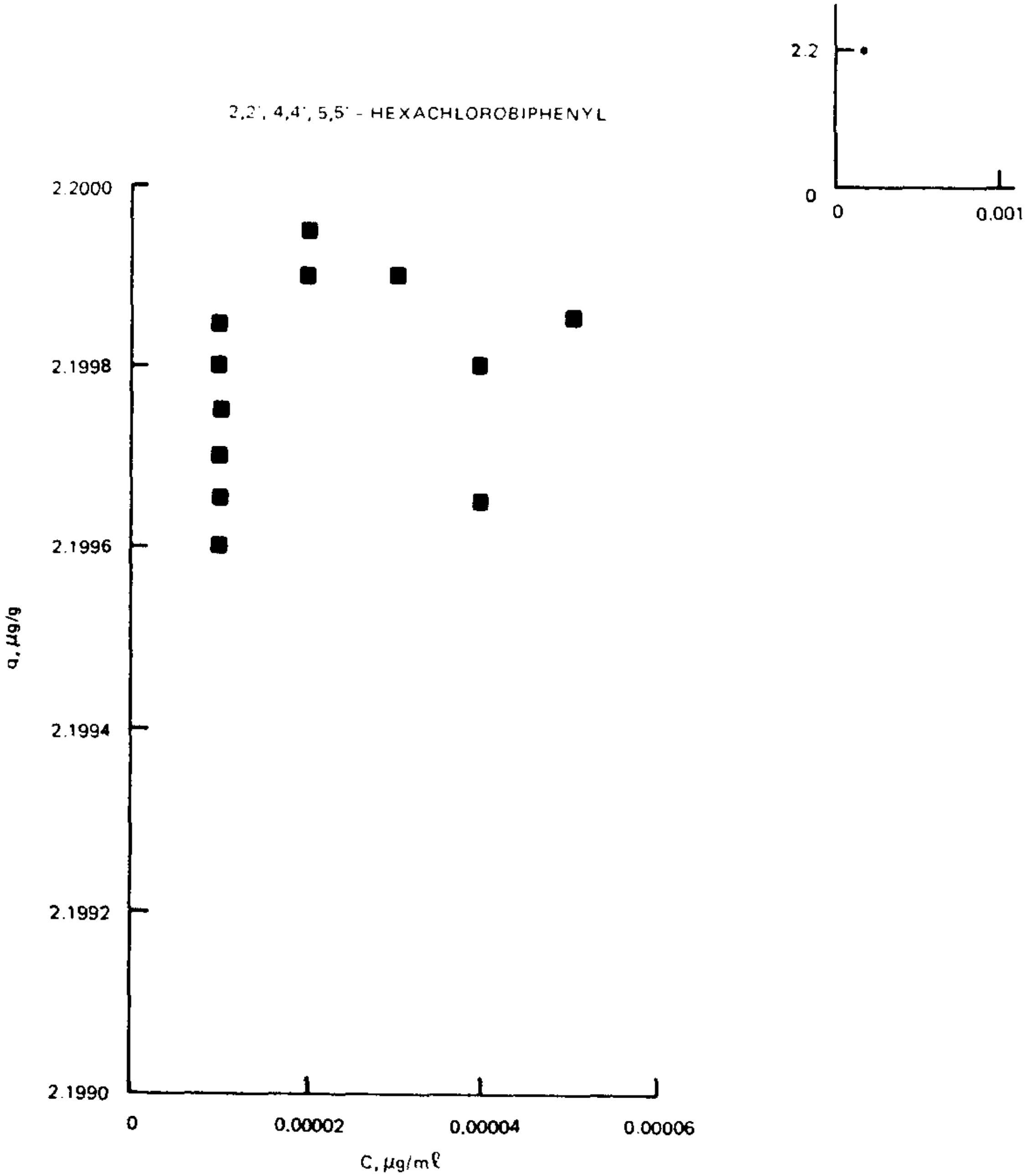


Figure G11. Desorption isotherm for 2,2',4,4',5,5' -hexachlorobiphenyl

Table G25

Linear Regression of q Versus C for Sequential Batch Leaching of Organic Contaminants from Anaerobic Indiana Harbor Sediment

Compound	Replicate	n	r^2
1	1	5	0.34
	2	5	0.78
	3	5	0.64
2	1	5	0.144
	2	5	0.56
	3	5	0.26
3	1	5	0.188
	2	5	0.75
	3	5	0.45
4	1	5	0.03
	2	5	0.66
	3	5	0.182
5	1	5	0.64
	2	5	0.51
	3	5	0.72
6	1	5	0.76
	2	5	0.64
	3	5	0.86
7	1	5	0.93
	2	5	0.80
	3	5	0.54
8	1	5	0.54
	2	5	0.96
	3	5	0.97
9	1	5	0.14
	2	5	0.07
	3	5	0.014
10	1	5	0.63
	2	5	0.77
	3	5	0.32

(Sheet 1 of 3)

Table G25 (Continued)

Compound	Replicate	n	r^2
11	1	5	BDL*
	2	5	
	3	5	
12	1	5	BDL
	2	5	
	3	5	
13	1	5	BDL
	2	5	
	3	5	
14	1	5	BDL
	2	5	
	3	5	
15	1	5	
	2	5	BDL
	3	5	
16	1	5	0.01
	2	5	0.19
	3	5	0.74
17	1	5	0.29
	2	5	0.95
	3	5	0.86
18	1	5	0.56
	2	5	0.89
	3	5	0.41
19	1	5	0.45
	2	5	0.61
	3	5	0.107
20	1	5	0.310
	2	5	0.67
	3	5	0.63
21	1	5	0.03
	2	5	0.88
	3	5	0.98

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* All leachate samples were below the detection limit (see Table G38 for detection limits)

(Sheet 2 of 3)

Table G25 (Concluded)

Compound	Replicate	n	r^2
22	1	5	0.116
	2	5	0.67
	3	5	0.04
23	1	5	BDL
	2	5	
	3	5	
24	1	5	0.17
	2	5	0.82
	3	5	0.13
25	1	5	0.23
	2	5	0.63
	3	5	0
26	1	5	0
	2	5	0.5
	3	5	0.47
27	1	5	BDL
	2	5	
	3	5	
28	1	5	0.09
	2	5	0.68
	3	5	0.13
29	1	5	BDL
	2	5	
	3	5	

(Sheet 3 of 3)

Table G26

Linear Regression of q Versus C for Sequential Batch Leaching of Organic Contaminants From Aerobic Indiana Harbor Sediment

Compound	Replicate	n	r^2
1	1	5	0.31
	2	5	0.5
	3	5	0.5
2	1	5	BDL*
	2	5	
	3	5	
3	1	5	0.61
	2	5	0.57
	3	5	0.67
4	1	5	0.5
	2	5	0.5
	3	5	0.75
5	1	5	0.40
	2	5	0.58
	3	5	0.60
6	1	5	BDL
	2	5	
	3	5	
7	1	5	0.35
	2	5	0.67
	3	5	0.25
8	1	5	0.35
	2	5	0.127
	3	5	0.04
9	1	5	BDL
	2	5	
	3	5	
10	1	5	BDL
	2	5	
	3	5	

---

* All leachate samples were below the detection limit (see Table G38 for detection limits.

(Sheet 1 of 3)

Table G26 (Continued)

Compound	Replicate	n	r^2
11	1	5	BDL
	2	5	
	3	5	
12	1	5	BDL
	2	5	
	3	5	
13	1	5	BDL
	2	5	
	3	5	
14	1	5	BDL
	2	5	
	3	5	
15	1	5	BDL
	2	5	
	3	5	
16	1	5	0.122
	2	5	0
	3	5	0.43
17	1	5	BDL
	2	5	
	3	5	
18	1	5	0
	2	5	0.18
	3	5	0
19	1	5	0.703
	2	5	0.102
	3	5	0.03
20	1	5	0.29
	2	5	0.024
	3	5	0.028
21	1	5	BDL
	2	5	
	3	5	

(Sheet 2 of 3)

Table G26 (Concluded)

Compound	Replicate	n	r^2
22	1	5	0.04
	2	5	0.21
	3	5	0
23	1	5	BDL
	2	5	0.66
	3	5	0.5
24	1	5	0.48
	2	5	0.33
	3	5	0.24
25	1	5	0.23
	2	5	0.69
	3	5	0.09
26	1	5	0.1
	2	5	0.02
	3	5	0.007
27	1	5	0.05
	2	5	0
	3	5	BDL
28	1	5	0.27
	2	5	0.29
	3	5	0.12
29	1	5	0.23
	2	5	0.23
	3	5	0.08

(Sheet 3 of 3)

data also showed that the aerobic distribution coefficients obtained by regression were not meaningful.

74. Contaminant released during the aerobic testing was less than the releases observed from anaerobic sediment. Batch leachate concentrations were lower from aerobic sediment for all compounds studied (Table G24). This was, in part, a result of the large losses of organic contaminants from sediment during the 6-month transition from anaerobic to aerobic conditions discussed previously and in part possibly a result of fixation.

75. The clustering that characterizes the PAH and PCB desorption isotherms indicates that these contaminants were tightly bound to the sediment solids or, alternately, that the distribution coefficient varied during the sequential leaching procedure, or both. The clustering effect for tightly bound sediment contaminants is due to a very large K_d. Literature values for sediment-water partitioning of PCBs, for example, range from 10^3 to 10^6 ℓ/kg (Pavlou 1980, Neely 1983). If distribution coefficients are high, the aqueous phase concentrations are low in each step of the sequential leaching due to partitioning. Clustered data result because the differences in leachate concentrations are within the noise level of the combined variability of the batch leaching and chemical analytical procedures.

76. It is also possible that K_d varied during the sequential leaching procedure. Distribution coefficients for PCBs have been estimated using sediment TOC and the octanol-water partitioning coefficient (Karickhoff, Brown, and Scott 1979). The distribution coefficient is proportional to sediment TOC and the octanol-water partitioning coefficient as follows:

$$K_d = 0.63\, f_{oc} K_{oc} \qquad \text{(G9)}$$

where

f_{oc} = fraction of the solids, by weight, composed of organic carbon
K_{ow} = octanol-water partition coefficient

Equation G9 indicates that K_d is directly proportional to sediment TOC. During sequential leaching, sediment TOC varied no more than 10 percent from step 1 to step 4. Therefore, if K_d was variable during the sequential leaching, the variability was probably not related to sediment TOC. As discussed earlier, components of the aqueous phase TOC are a more likely source of variability.

77. In order to calculate meaningful distribution coefficients for the PAHs and PCBs from the sequential, batch leach data, two assumptions were necessary. First, the bulk sediment concentration was assumed to be leachable, i.e., q_r is equal to zero. Second, the batch data cluster about some point (C,q) that represents the overall or net distribution coefficient for the sequential leaching. Using these assumptions, an approximate K_d was calculated by computing the average K_d from all the single-point estimates provided by the data from the sequential batch leach tests. The distribution coefficients determined by this method are presented in Table G27. These values are in the upper range of the values reported in the literature.

78. It is realized that there may be a non-reversible component, up to 90 percent, for PAHs and PCBs (Di Toro and Horzempa 1982, Di Toro 1985). If there is a significant nonreversible component, then the explanation for the clustering is similar to the explanation previously developed for the aerobic metals data. A high K_d and a high q_r (low q_L) have the same practical significance, i.e., aqueous phase concentrations near the detection limits. For the former, partitioning holds the leachable contaminant in the solid phase, and, for the latter, the leachable concentration is small to begin with. Clustering results in each case because the concentrations that are measured in the leachate are low enough to be influenced by the combined variability inherent in sequential batch leaching and testing near the detection limits.

79. The basis for a nonreversible component for organic contaminants, however, is not as well established as the geochemical partitioning basis for metals. The physical basis for a leaching resistant component for organic contaminants is as follows. The leaching resistant component is adsorbed to surfaces in intraparticle pores. The water in intraparticle pores is immobile. In order to be leached, the contaminant in the intraparticle pore must diffuse to the particle surface. Since diffusion is a slow process, the intraparticle component is not leached in short-term tests and appears to be nonreversibly sorbed to the sediment. If 90 percent of the bulk sediment concentration is assumed to be nonreversibly sorbed, the K_d values in Table G27 become one order of magnitude lower. There is no change, however, in an estimated C_I (Equation G8) because q_L is also one order of magnitude lower.

Table G27

Single-Point Distribution Coefficients for PAHS and Aroclor 1242 Congeners, Cluster Centroid Method*

Compound	Distribution Coefficient, ℓ/kg	
	Anaerobic	Aerobic
1	1 160	27 400
2	3 440	2 790
3	5 120	3 900
4	5 980	5 260
5	11 700	13 600
6	25 700	> 2 560
7	26 800	23 400
8	29 700	21 500
9	32 200	> 8 560
10	37 300	> 6 180
11	> 28 000	>12 940
12	> 17 400	>
	> 10 000	> 3 150
14	> 7 000	> 2 360
15	UD	UD
16	163 000	4 160
17	2 430 000	42 800
18	423 000	55 400
19	145 000	31 000
20	614 000	241 000
21	2 400 000	> 2 610
22	194 000	24 800
23	> 1 660 000	UD
24	266 000	27 300
25	375 000	23 700
26	203 000	22 300
27	UD	UD
28	410 000	47 600
29	> 33 000	26 100
Total PAH	1 600	30 800
Total congeners	256 000	38 700

* Refer to text for description of method

> = Leachate below detection limit.

UD = Undefined, not detected in sediment.

Total Aroclor 1242 Congeners.

As discussed later, there is no difference in the shape of predicted concentration curves for K_d in the range of E+02 to E+06. Since there is no practical significance to determining a leaching resistant component for the clustered desorption isotherm data obtained in this study for organic contaminants, the conservative assumption that all of the organic contaminant is reversibly adsorbed was used to calculate K_d .

80. For the above assumption, the data from the sequential batch leach procedure can be interpreted as replicate, single-point estimates of the distribution coefficient. Thus, the batch equilibrium method (no sequential leaching) appears appropriate for determining distribution coefficients for PAHs and PCBs in contaminated sediments.

81. Metal releases in challenge tests. When leachate from anaerobic and aerobic Indiana Harbor sediment was used to challenge anaerobic Indiana Harbor sediment, there was little further release of metals from the sediment. Steady-state sediment and leachate metal concentrations for anaerobic Indiana Harbor sediment challenged with leachate from anaerobic and aerobic sediment are presented in Tables G28 and G29, respectively. After the initial contact with fresh leachate there was little change in the desorption characteristics of the anaerobic sediment for metals. This was expected in the anaerobic/anaerobic challenge because the leachate was already in a steady state relationship with the anaerobic Indiana Harbor sediment. However, when anaerobic sediment was challenged with leachate from aerobic sediment, it was expected that the aerobic leachate would assume the character of the anaerobic leachate. Since aerobic leachate concentrations were generally lower than anaerobic leachate concentrations, the aerobic/anaerobic challenge was expected to show an increase in leachate concentrations. However, the challenge did not result in substantially increased leachate concentrations for all metals. Arsenic and chromium concentrations increased to near that observed in anaerobic leachate. Cadmium, chromium, lead, and zinc did not, suggesting that the effect that aerobic leachate has on the desorption characteristics of anaerobic sediment is apparently metal specific. In no case did the aerobic leachate increase the amount of metal leached from the anaerobic sediment. For cadmium, chromium, lead, and zinc the leachability appeared to be reduced.

82. Organic contaminant releases in challenge tests. Anaerobic Indiana Harbor sediment was also subjected to challenge testing, although only one replicate could be run because of equipment limitations. Single-point,

Table G28

Steady-State Sediment and Leachate Metal Concentration [mean (standard error)] in Anaerobic Indiana Harbor Sediment Challenged with Leachate from Anaerobic Indiana Harbor Sediment

Time, days	As	Cr	Pb	Cd	Zn
			Sediment Concentration, μg/g		
1	29.46	281.64	878.64	19.99	4123.29
	(0.11)	(0.009)	(0.04)	(0.003)	(0.16)
2	29.44	281.24	878.39	19.99	4121.63
	(0.03)	(0.22)	(0.27)	(0.016)	(1.42)
3	29.43	281.33	878.96	19.99	4122.76
	(0.03)	(0.09)	(0.43)	(0.032)	(1.69)
4	29.43	281.33	878.87	19.98	4121.09
	(0.03)	(0.09)	(0.45)	(0.033)	(1.24)
5	29.44	281.33	879.19	19.99	4122.86
	(0.03)	(0.09)	(0.29)	(0.023)	(0.61)
			Leachate Concentration, μg/mℓ		
1	0.033	0.21	0.22	0.009	0.98
	(0.002)	(0.004)	(0.02)	(0.004)	(0.02)
2	0.027	0.027	0.22	0.012	1.49
	(0.004)	(0.03)	(0.009)	(0.006)	0.15
3	0.021	0.14	0.09	0.012	0.89
4	0.016	0.11	0.05)	0.0007	0.87
	(0.001)	(0.03)	(0.04)	(0.003)	(0.18)
5	0.013	0.02	0.04	0.005	0.16
	(0.0003)	(0.002)	(0.005)	(0.0002)	0.02)

Table G29

Steady State Sediment and Leachate Concentration [mean (standard error)] for Anaerobic Indiana Harbor Sediment Challenged with Leachate from Aerobic Indiana Harbor

Time, days	Cs	Cr	Pb	Cd	Zn
			Sediment Concentration, μg/g		
1	29.43 (0.008)	281.96 (0.01)	878.99 (0.009)	20.00 (0.003)	4125.08 (0.009)
2	29.34 (0.03)	281.95 (0.01)	878.98 (0.02)	20.00 (0.005)	4124.98 (0.05)
3	29.31 (0.01)	281.95 (0.02)	878.95 (0.03)	20.00 (0.005)	4124.91 (0.09)
4	29.27 (0.02)	281.95 (0.02)	878.98 (0.04)	20.01 (0.005)	4124.96 (0.10)
5	29.24 (0.02)	281.95 (0.03)	878.97 (0.05)	20.01 (0.006)	4124.98 (0.09)
			Leachate Concentration, μg/mℓ		
1	0.025 (0.0007)	0.017 (0.003)	0.013 (0.003)	0.002 (0.0005)	0.148 (0.008)
2	0.033 (0.002)	0.017 (0.002)	0.014 (0.002)	0.001 (0.0002)	0.077 (0.016)
3	0.019 (0.0005)	0.014 (0.001)	0.018 (0.003)	0.0008 (0.00009)	0.081 (0.014)
4	0.020 (0.0000)	0.011 (0.002)	0.011 (0.003)	0.0007 (0.0001)	0.076 (0.014)
5	0.017 (0.003)	0.006 (0.0007)	0.008 (0.0004)	0.0005 (0.0001)	0.049 (0.007)

organic contaminant distribution coefficients for this challenge testing are presented in Table G30. Anaerobic distribution coefficients for the anaerobic sediment determined during the first phase of the challenge testing did not differ substantially (within error limits) from coefficients reported previously, even though the challenge testing was conducted 3 months later. When leachate from the first phase of the challenge testing was used to challenge fresh anaerobic Indiana Harbor sediment, partition coefficients for organic contaminants did not change appreciably. This is evident from the results presented in Table G30, even though no statistical statements can be made due to the lack of replication. Steady state leachate and sediment organic contaminant concentrations obtained prior to challenge testing are presented in Tables G31 and G32, respectively. These test results did not generally differ substantially from those reported previously for anaerobic leachate testing. When this leachate was used to challenge fresh anaerobic Indiana Harbor sediment, leachate concentrations of organic contaminants did not change substantially (Table G33). This was paralleled by very little change in organic contaminant concentrations in fresh anaerobic sediment exposed to leachate from anaerobic sediment (Table G34). These results indicate that distribution coefficients for organic contaminants in Indiana Harbor sediment should be fairly constant as leachate is exposed to fresh unleached sediment.

Permeameter testing

83. Continuous flow column leaching tests were conducted in divided flow permeameters as previously described using both anaerobic and aerobic Indiana Harbor sediment. The data generally indicate that as the number of pore volumes of water passed through the sediment increased, the contaminant concentrations in the leachate decreased. Specific results are presented below and discussed in the following section.

84. Anaerobic permeameters: metals, conductivity, and DOC. Measured values of anaerobic permeameter leachate metal and DOC concentrations and conductivity with corresponding pore volumes are listed in Table G35. Pooled data from this table for metals, dissolved organic carbon, and conductivity are plotted on Figures G12-G15. Predicted permeameter leachate concentrations are plotted on the figures for metals using the solution of Ogata and Banks (1961), Equation G7, for system specific parameters as follows: $V = 1.4$ E-05 cm/sec, $D_p = 2.6$ E-05 cm^2/sec, $\rho = 0.742$ kg/ℓ, and $\theta = 0.61$. The

Table G30

Single-Point Distribution Coefficients (ml/g) for Organic Contaminants from Challenge Testing of Anaerobic Indiana Harbor Sediment

	Sequential Leach Number				
Compound	1	2	3	4	5
1	1626	1318	879	777	917
2	4000	4400	3200	3250	3320
3	6000	5650	4360	4570	4570
4	6590	6350	5190	5600	5750
5	3400	3770	3830	4510	4395
6	16760	20000	20670	33880	39490
7	16130	16670	22060	34090	43230
8	15220	16470	23730	37840	82350
9	29680	17040	61330	65710	92000
10	35830	19240	53750	86000	> 86000
11	>28000	>28000	> 28000	> 28000	> 28000
12	>17400	>17400	> 17400	> 17400	> 17400
13	>10000	>10000	> 10000	> 10000	> 10000
14	> 7000	> 7000	> 7000	> 7000	> 7000
15	None Detected in Sediment				
16	95580	161200	154300	124100	90000
17	121900	209700	1950000	> 1950000	> 1950000
18	203200	282300	425300	425300	679000
19	42170	129600	106100	129630	116670
20	39000	104300	121900	142300	> 1950000
21	109000	214400	1930000	> 1930000	> 1930000
22	67800	98100	130000	173000	173000
23	>166000	>166000	>166000	>166000	>166000
24	114000	154000	154000	211000	248000
25	123000	123000	161000	161000	218000
26	73000	314000	132000	220000	169000
27	None Detected in Sediment				
28	110000	155000	207000	288000	413000
29	>198000	>198000	>198000	>198000	>198000

Table G31

Steady-State Leachate Concentrations (ug/ℓ) for Indiana Harbor Sediment Following Anaerobic Leaching Prior to Challenge Testing

Compound	Sequential Leach Number 1	2	3	4
1	650	950	1800	1800
2	<5	5.1	5.8	5.1
3	14	17	19	16
4	10	13	12	9.1
5	18	21	16	13
6	3.3	8.5	1.8	2.9
7	9.5	11	6.2	3.8
8	8.8	9.8	5.9	3.1
9	2.8	3.4	1.5	<1
10	3.1	3.2	1.5	5
11	7	5.9	3.2	5
12	<5	<5	<5	<5
13	<5	<5	<5	<5
14	<5	<5	<5	<5
15	<0.01	<0.01	<0.01	<0.01
16	0.07	0.06	0.03	<0.01
17	0.37	0.33	0.12	0.26
18	0.75	0.68	0.20	2.5
19	0.13	0.12	0.05	0.19
20	0.71	0.73	0.34	<0.01
21	0.37	0.33	0.12	0.26
22	0.13	0.10	0.03	<0.01
23	<0.01	<0.01	<0.01	<0.01
24	0.12	0.10	0.03	0.38
25	0.01	<0.01	0.02	<0.01
26	0.04	<0.01	0.01	<0.01
27	<0.01	<0.01	<0.01	<0.01
28	0.28	0.24	0.08	<0.01
29	0.04	0.04	0.01	<0.01

Table G32

Steady-State Sediment Concentration (ug/g Dry Weight) for Indiana Harbor Sediment Following Anaerobic Leaching Prior to Challenge Testing

Compound	Sequential Leach Number 1	2	3	4
1	1997.4	1993.6	1986.4	1979.2
2	21.98	21.96	21.94	21.92
3	95.94	95.88	95.80	95.74
4	68.96	68.91	68.86	68.82
5	199.93	199.84	199.78	199.78
6	61.99	61.95	61.95	61.94
7	149.96	149.92	149.89	149.88
8	139.96	139.93	139.90	139.90
9	91.99	91.98	91.97	91.95
10	85.99	85.97	85.97	85.95
11	139.97	139.95	139.94	139.92
12	86.98	86.96	86.94	86.92
13	50	50	50	50
14	35	35	35	35
15	NONE DETECTED IN SEDIMENT			
16	10.79	10.79	10.79	10.79
17	19.499	19.497	19.497	19.496
18	31.897	31.894	31.894	31.884
19	3.499	3.499	3.499	3.498
20	19.497	19.494	19.493	19.493
21	19.299	19.297	19.297	19.296
22	5.199	5.199	5.199	5.199
23	NONE RELEASED FROM SEDIMENT			
24	5.699	5.699	5.699	5.698
25	3.700	3.6999	3.6998	3.6998
26	2.199	2.199	2.199	2.199
27	NONE RELEASED FROM SEDIMENT			
28	12.3899	12.3889	12.3886	12.3886
29	1.9798	1.9797	1.9796	1.9796

Table G33

Steady-State Leachate Concentrations (ug/l) for Anaerobic Indiana Harbor Sediment Following Challenge Testing with Anaerobic Indiana Harbor Leachate

Compound	Sequential Leach Number 1	2	3	4
1	<5	1600	1700	1900
2	4.8	19	17	22
3	<5	6.2	5.5	7.1
4	<5	13	11	14
5	<5	21	17	21
6	<5	4.3	2.9	3.9
7	9.1	12	7	8
8	8.8	11	6.4	7.5
9	5	4.3	2.4	3
10	3.5	3.4	1.9	2.2
11	5.5	6.1	3.7	3.8
12	<5	<5	<5	<5
13	<5	<5	<5	<5
14	<5	<5	<5	<5
15	<0.01	<0.01	<0.01	<0.01
16	<0.01	0.07	0.08	0.06
17	0.52	0.33	0.22	0.20
18	<0.01	0.64	0.42	0.36
19	0.29	0.11	0.08	0.07
20	<0.01	0.60	0.44	0.46
21	0.52	0.33	0.22	0.20
22	0.34	0.10	0.09	0.08
23	0.34	<0.01	<0.01	<0.01
24	0.35	0.10	0.07	0.06
25	0.32	0.08	0.07	<0.01
26	0.28	0.04	0.04	0.02
27	<0.01	<0.01	<0.01	<0.01
28	0.47	0.23	0.17	0.14
29	0.28	0.04	0.03	0.03

Table G34

Steady-State Sediment Concentrations (μg/g Dry Weight) for Anaerobic Indiana Harbor Sediment Following Challenge Testing with Anaerobic Indiana Harbor Leachate

Compound	Sequential Leach Number			
	1	2	3	4
1	2002.6	2000.0	2000.4	1999.8
2	96.03	96.03	96.04	96.02
3	22.00	22.00	22.00	21.99
4	69.02	69.02	69.02	69.01
5	200.05	200.05	200.05	200.02
6	61.99	61.99	61.99	61.98
7	150.00	149.99	149.99	149.98
8	140.00	139.99	139.99	139.98
9	91.99	91.99	91.99	91.99
10	86.00	85.99	85.99	86.00
11	140.01	140.01	140.00	140.01
12	87.00	87.00	87.00	87.00
13	50.00	50.00	50.00	50.00
14	35.00	35.00	35.00	35.00
15	10.80	10.80	10.80	10.80
16	19.50	19.50	19.50	19.50
17	31.90	31.90	31.90	31.91
18	3.499	3.499	3.499	3.500
19	19.50	19.50	19.50	19.50
20	19.29	19.29	19.29	19.29
21	5.199	5.199	5.199	5.199
22	1.659	1.659	1.659	1.659
23	5.199	5.199	5.199	5.198
24	1.659	1.659	1.659	1.659
25	5.699	5.699	5.699	5.700
26	3.699	3.698	3.698	3.698
27	21.99	21.99	21.99	21.99
28	12.39	12.39	12.39	12.39
29	1.979	1.979	1.979	1.979

Table G35

Indiana Harbor Anaerobic Metals Permeameter Tests: Metal Concentration Dissolved Organic Carbon, and Conductivity vs. Pore Volume

Cummu-lative Pore Volume	Metal Concentration, mg/ℓ					DOC	Conductivity
	As	Cd	Cr	Pb	Zn	mg/ℓ	µmhos
				Permeameter No. 1			
0.14	0.015	0.0020	0.011	0.005	0.047	90.3	*
0.41	0.013	0.0005	0.011	0.003	<.030	50.5	3200.0
0.68	0.010	0.0010	0.008	0.003	<.030	61.3	3200.0
1.04	0.006	0.0026	0.008	0.003	<.030	37.2	2900.0
1.47	0.006	0.005	0.009	0.004	<.030	93.0	2100.0
2.41	0.009	0.0004	0.008	0.003	<.030	67.8	1200.0
				Permeameter No. 2			
0.22	0.013	0.0017	0.011	0.004	0.191	48.5	*
0.40	0.008	0.0014	0.009	0.003	0.030	57.1	3200
0.64	0.006	0.0004	0.009	0.005	0.030	76.1	3400
0.94	0.007	0.0008	0.009	0.002	<.030	39.8	2500
1.30	0.006	0.0010	0.010	0.004	<.030	91.2	2000
1.92	<.005	0.0003	0.008	0.003	<.030	51.6	1200
2.76	<.005	0.0003	0.007	0.002	<.030	27.8	620
3.35	<.005	0.0004	0.008	0.003	<.030	29.1	640
3.92	<.005	0.0010	0.008	0.004	<.030	22.5	580
5.34	<.005	0.0004	0.006	0.002	<.030	14.0	760
6.16	<.005	0.0042	0.006	0.002	<.030	9.2	750
				Permeameter No. 3			
0.15	0.011	0.0070	0.010	0.006	0.081	63.9	*
0.50	0.009	0.0009	0.009	0.002	<.030	45.1	2800
0.87	0.010	<.0001	0.006	0.002	<.030	79.7	1800
1.28	0.006	0.0003	0.007	0.003	<.030	80.0	2300
1.78	<.005	0.0003	0.008	0.002	<.030	89.2	1900
2.38	<.005	0.0005	0.011	0.003	<.030	56.2	1150
3.18	<.005	0.0003	0.008	0.003	<.030	45.6	860
4.42	<.005	0.0004	0.008	0.003	<.030	29.5	760
5.22	<.005	0.0004	0.007	0.006	0.032	22.9	620
6.91	<.005	0.0005	0.005	0.001	<.030	13.3	710
7.94	<.005	0.0042	0.004	<.001	<.030	11.8	705

* No data.

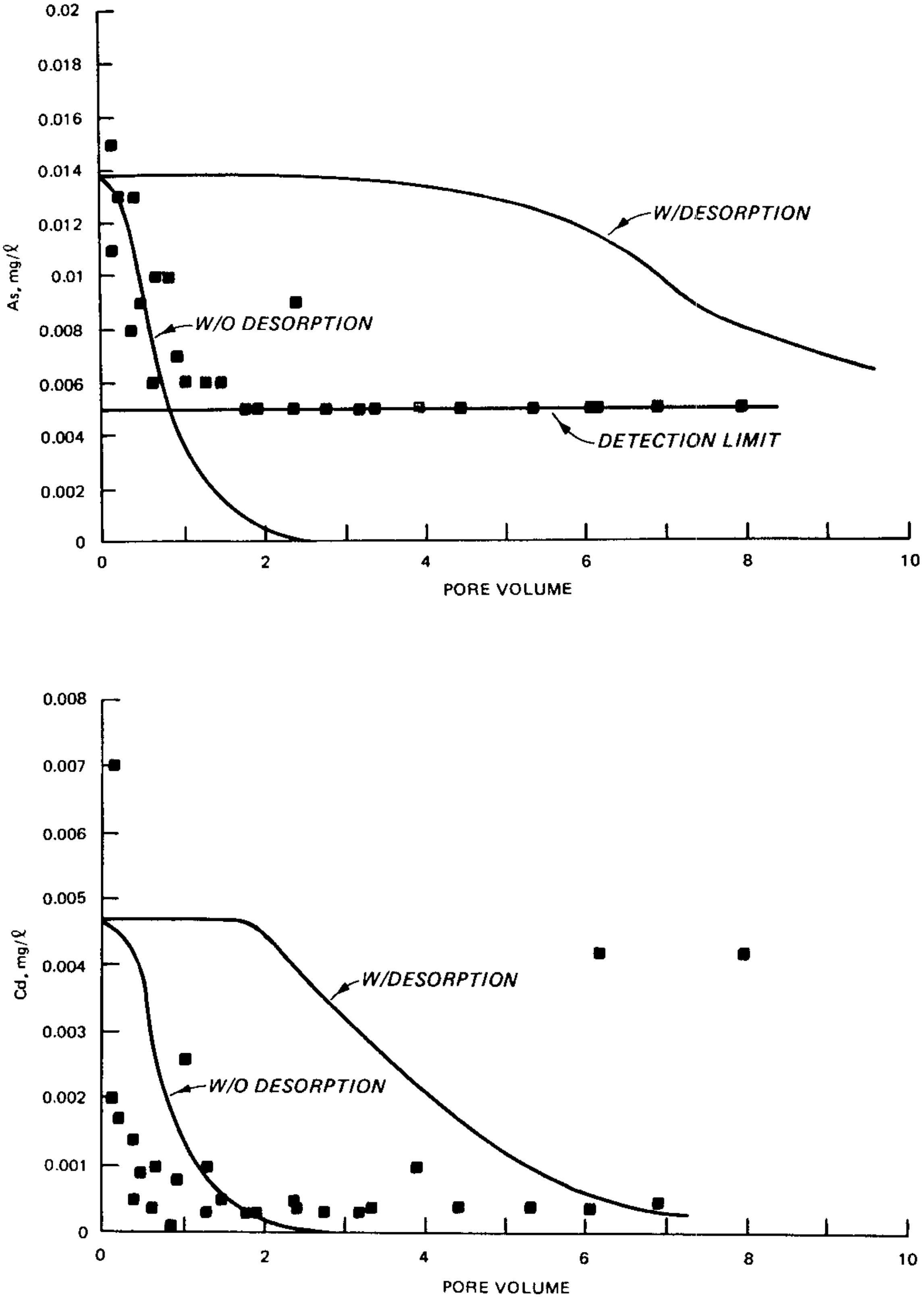
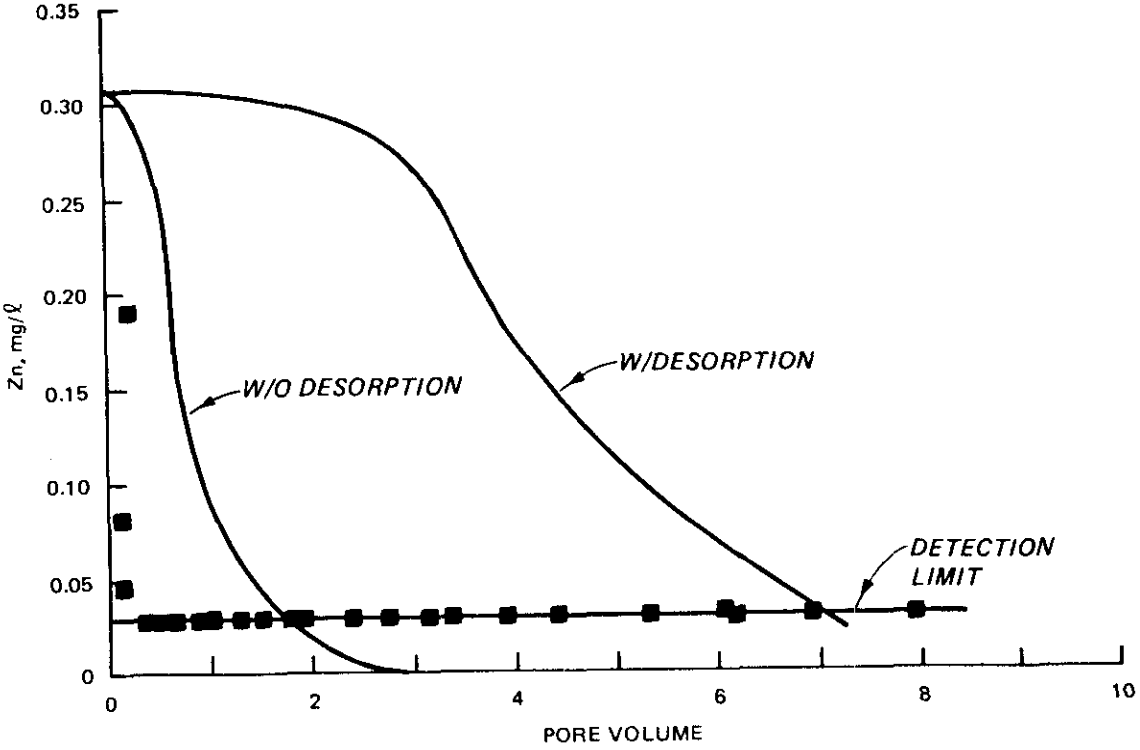


Figure G12. Comparison of arsenic and cadmium concentrations in anaerobic permeameter leachate with predicted values



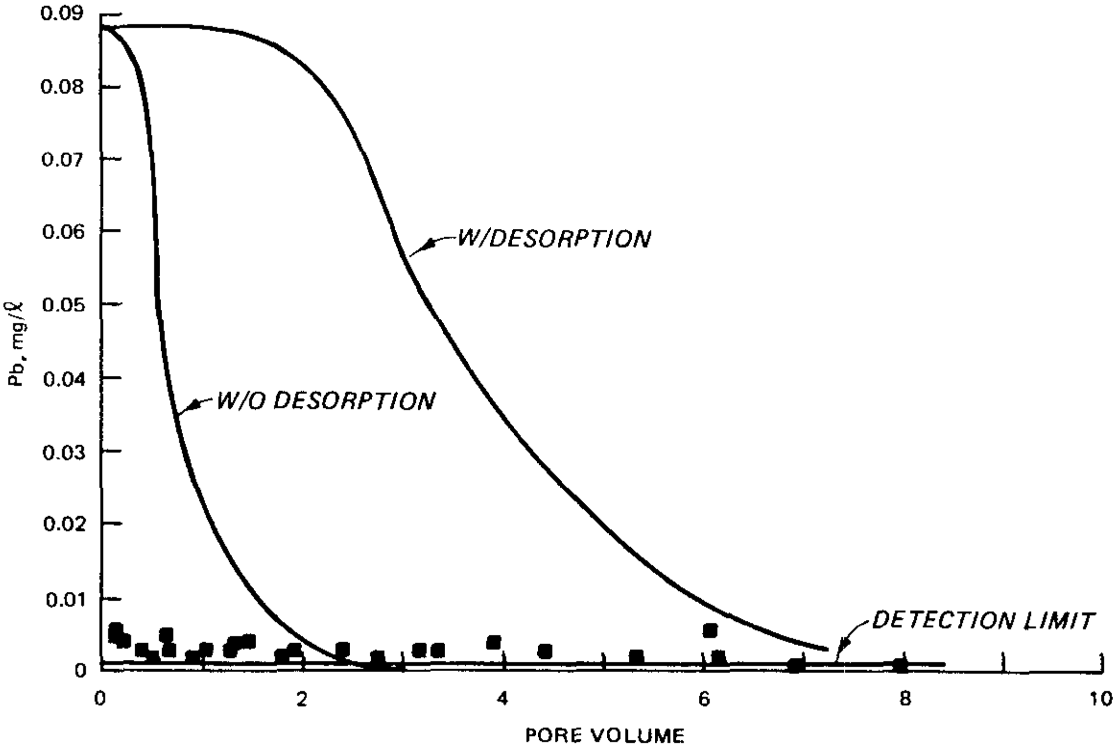


Figure G13. Comparison of zinc and lead concentrations in anaerobic permeameter leachate with predicted values

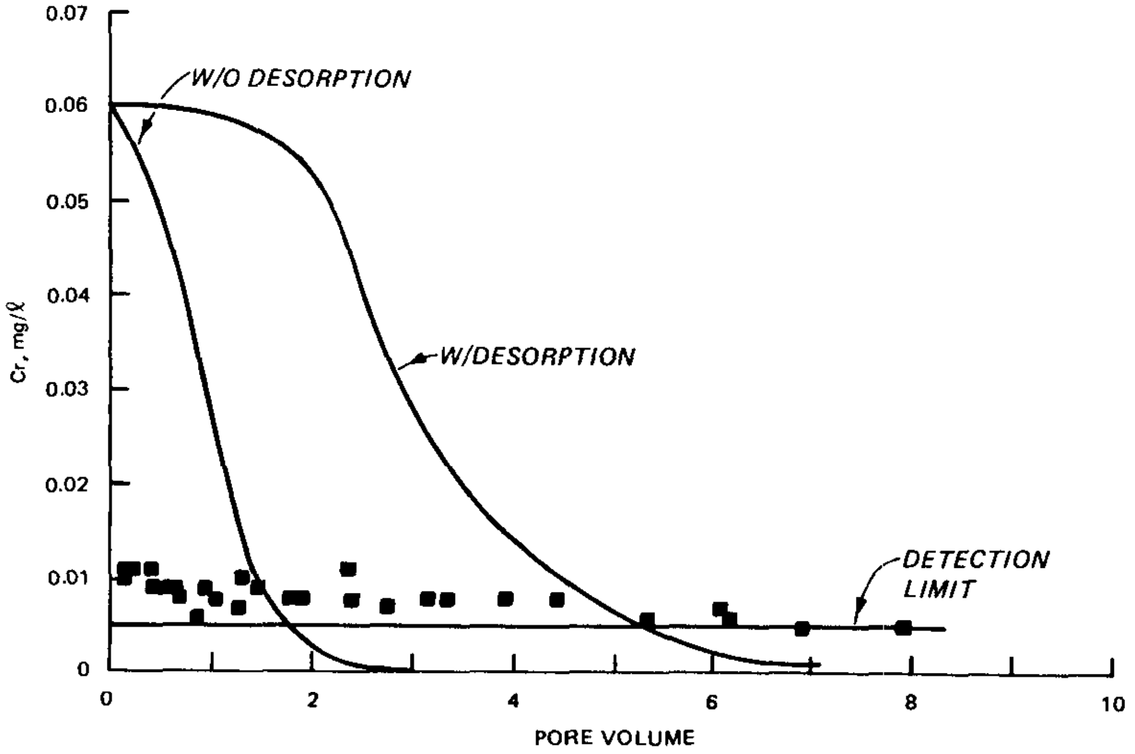


Figure G14. Comparison of chromium concentrations in anaerobic permeameter leachate with predicted values

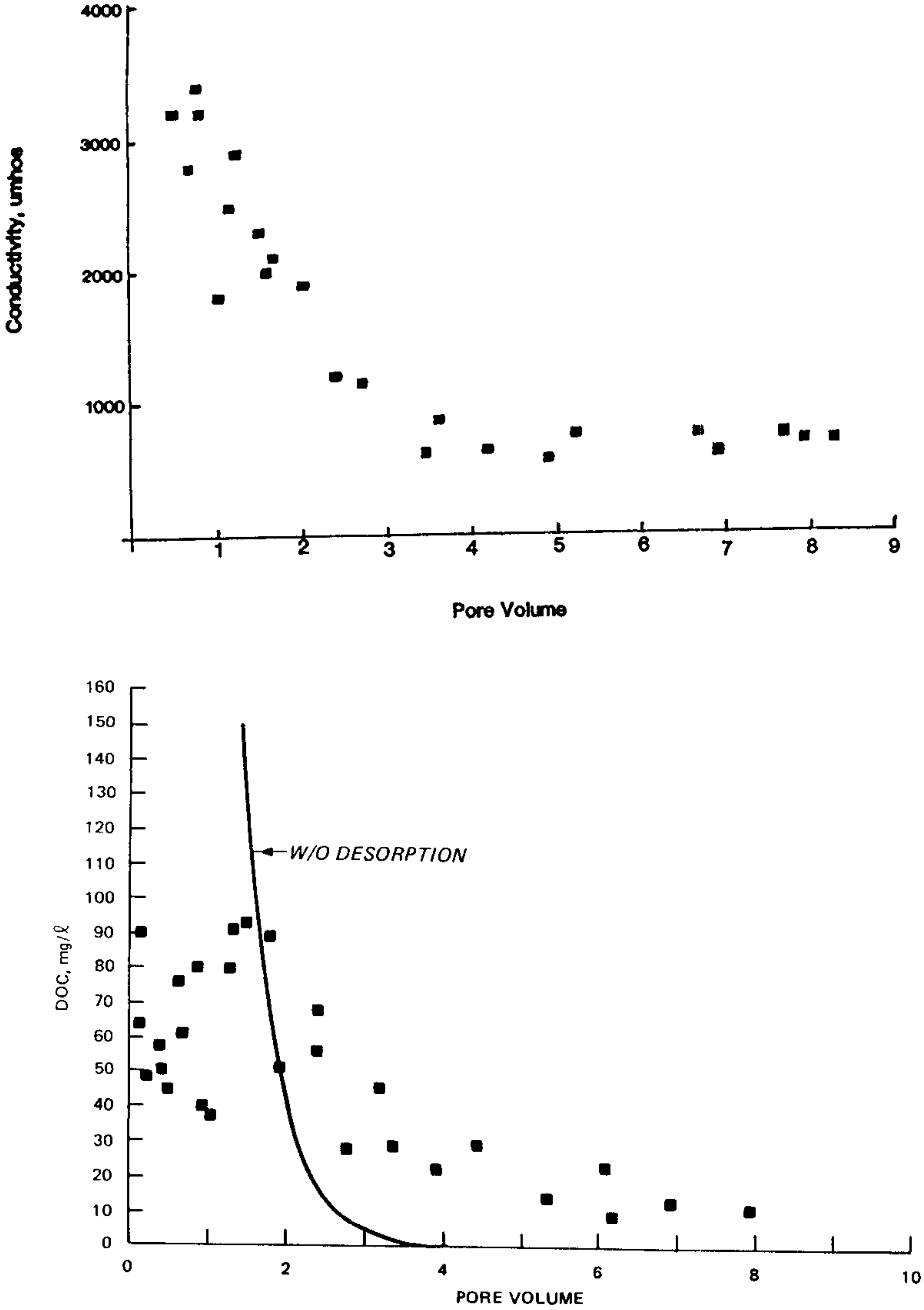


Figure G15. Conductivity and dissolved organic carbon in anaerobic permeameter leachate during metal leach test values for K_d are listed in Table G18, and the C_I values are listed in Table G5.

85. Predicted concentrations have been plotted for two conditions. The first assumes that contaminant leaching in the permeameters is governed by equilibrium-controlled, linear desorption and that the equilibrium distribution coefficient is adequately described by the K_d obtained using sequential batch leach tests. The second condition assumes that desorption does not occur; that is, K_d is equal to zero. In both cases, the interstitial water concentrations measured during batch testing were used as the initial pore water concentrations. A comparison of the predicted curves to the observed data is provided below.

- a. After the interstitial water was displaced, no desorption of lead or zinc was observed.
- b. Arsenic and cadmium showed some desorption although not as much as predicted.
- c. Chromium concentrations were above detection limits but did not follow either predictive curve.
- d. Observed DOC concentrations were somewhat erratic; however, the shape of the plot suggests that desorption was involved during the release of organic carbon.
- e. The conductivity data showed a typical washout curve with some desorption occurring.

86. Anaerobic permeameters: organic compounds and DOC. The concentrations of most of the 29 organic compounds listed in Table G4 were below detection limits in the anaerobic permeameter leachate. Table G36 is a summary of the organic compounds that were not detected. In particular, no PAHs were detected in the anaerobic permeameter leachates. One of the Aroclor 1248 congeners, organic compound number 19 was above the detection limit (0.00001 mg/ℓ) in only one sample. The other Aroclor 1248 congeners appeared more than once but not in all samples. The concentrations of each congener that was detected and the total Aroclor 1248 congener concentrations for each anaerobic permeameter are presented as a function of pore volume in Table G37.

87. Predicted and observed curves were prepared for total Aroclor 1248 congener concentration. The predicted curve was prepared using Equation G7 and system specific parameters as follows: $V = 6.4\ \text{E-06 cm/sec}$, $D_p = 2.4\ \text{E-05 cm}^2\text{/sec}$, $\rho = 0.741\ \text{kg/ℓ}$, and $\theta = 0.61$. The K_d value that was used is listed in Table G27, and the C_I value is listed in Table G38. As with the anaerobic metals, two predictive curves were developed. One assumed that

Table G36

Summary of Organic Contaminants that were Below the Detection Limit in Anaerobic Permeameter Leachates

Compound	Detection Limit mg/ℓ
1	0.005
2	0.005
3	0.005
4	0.005
5	0.005
6	0.005
7	0.005
8	0.005
9	0.005
10	0.005
11	0.005
12	0.005
13	0.005
14	0.005
15	0.00001
20	0.00001
27	0.00001

Table G37

Aroclor 1248 Congeners and DOC Concentrations (mg/ℓ)

in Leachates from Anaerobic Permeameters

Pore Volume	Compound 16	17	18	19	21	22	23	24	25	26	28	29	DOC	Total Detected Aroclor 1248 Congeners
Permeameter No. 4														
0.40	0.00002	0.00002	0.00004	<0.00001	0.00002	0.00002	<0.00001	0.00003	<0.00001	0.00003	0.00006	0.00006	173	0.00030
1.19	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	0.00001	104	-
1.98	<0.00001	0.00001	0.00001	<0.00001	0.00001	0.00001	0.00001	0.00001	0.00002	<0.00001	0.00002	0.00001	72	0.00011
2.76	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00002	0.00002	<0.00001	<0.00001	0.00005	<0.00001	45	0.00009
Permeameter No. 5														
0.35	0.00002	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00003	<0.00001	0.00001	<0.00001	<0.00001	160	0.00006
1.05	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	0.00001	90	-
1.76	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	0.00001	0.00001	<0.00001	<0.00001	<0.00001	<0.00001	70	0.00003
2.46	0.00002	0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	43	0.00003
Permeameter No. 6														
0.35	0.00002	0.00002	0.00003	<0.00001	0.00002	<0.00001	<0.00001	<0.00001	<0.00001	0.00002	0.00002	<0.00001	160	0.00013
1.04	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	0.00001	118	-
1.73	<0.00001	<0.00001	<0.00001	0.00006	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	72	0.00007
2.45	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00009	<0.00001	<0.00001	<0.00001	45	0.00009

Note: Compound numbers 15, 20, and 27 were <0.00001 mg/1 in all samples.

Table G38

Comparison of C_I to C_{max} for Anaerobic Permeameter

Compound	C_I, mg/ℓ	C_{max}, mg/ℓ**
1	1.172	<0.005
2	0.006	<0.005
3	0.019	<0.005
4	0.012	<0.005
5	0.017	<0.005
6	0.002	<0.005
7	0.006	<0.005
8	0.005	<0.005
9	0.003	<0.005
10	0.002	<0.005
11	0.005	<0.005
12	0.005	<0.005
13	0.005	<0.005
14	0.005	<0.005
15	UD	<0.00001
16	0.00007	0.00002
17	0.00001	0.00002
18	0.00008	0.00004
19	0.00002	0.00006
20	0.00003	<0.00001
21	0.00001	0.00002
22	0.00003	0.00002
23	<0.00001	0.00001
24	0.00002	0.00003
25	0.00001	0.00009
26	0.00002	0.00003
27	UD	<0.00001
28	0.00003	0.00006
29	0.00006	0.00006
Total PAH	1.82029	<0.005
Total PCB	0.00054	0.00030

* C_I = Calculated using Equation G8.

** C_{max} = maximum value observed in anaerobic permeameter leachate.

UD not detected in sediment.

contaminant leaching is governed by equilibrium-controlled, linear desorption, and the other assumed that no desorption was occurring, i.e., K_d was equal to zero. Figure G16 is a plot of total Aroclor 1248 congener concentration versus pore volume for the three permeameters. This figure also shows the two predicted curves referred to above. Figure G17 is a plot of effluent DOC versus pore volume. This figure presents pooled data from all three permeameters. Examination of these plots and the data presented in Table G37, provides the following observations:

- a. PAHs were not detected in the anaerobic permeameter leachates.
- b. Leachate concentrations of Aroclor 1248 congeners from anaerobic permeameters were generally near or below the detection limit (0.000010 mg/ℓ).
- c. Total Aroclor 1248 congener concentration ranged from below detection limits to 0.00030 μg/ℓ.
- d. Total Aroclor 1248 congener concentration was more reproducible among the three permeameters than were specific congener concentrations.
- e. DOC showed a well-defined washout curve.
- f. The total Aroclor 1248 congener concentration did not persist as predicted.

88. Aerobic permeameters: metals, conductivity, and DOC. Measured values of aerobic permeameter leachate metal and DOC concentrations and conductivity with corresponding pore volumes are listed in Table G39. Plots of metals and DOC concentrations and conductivity versus pore volume for aerobic sediment are presented in Figures G18-G21. A comparison of the aerobic plots to the anaerobic plots presented in Figures G12-G15 is provided below:

- a. In general, observed metal values showed more scatter than anaerobic permeameter metals data.
- b. Metal concentrations obtained from aerobic permeameters were, in general, equal to or greater than the corresponding concentrations from the anaerobic permeameters.
- c. Conductivity showed a well-defined washout curve that plotted above the conductivity curve for the anaerobic permeameters.
- d. DOC showed a well-defined washout curve that plotted above the curve for anaerobic sediment.

89. Anaerobic permeameters: organic compounds and DOC. As with the anaerobic permeameters, the concentrations of most of the 29 organic compounds listed in Table G4 were below the detection limits in the aerobic permeameter leachates. The compounds not detected are listed in Table G40. The concentration of each congener that was detected and the total Aroclor 1248 congener

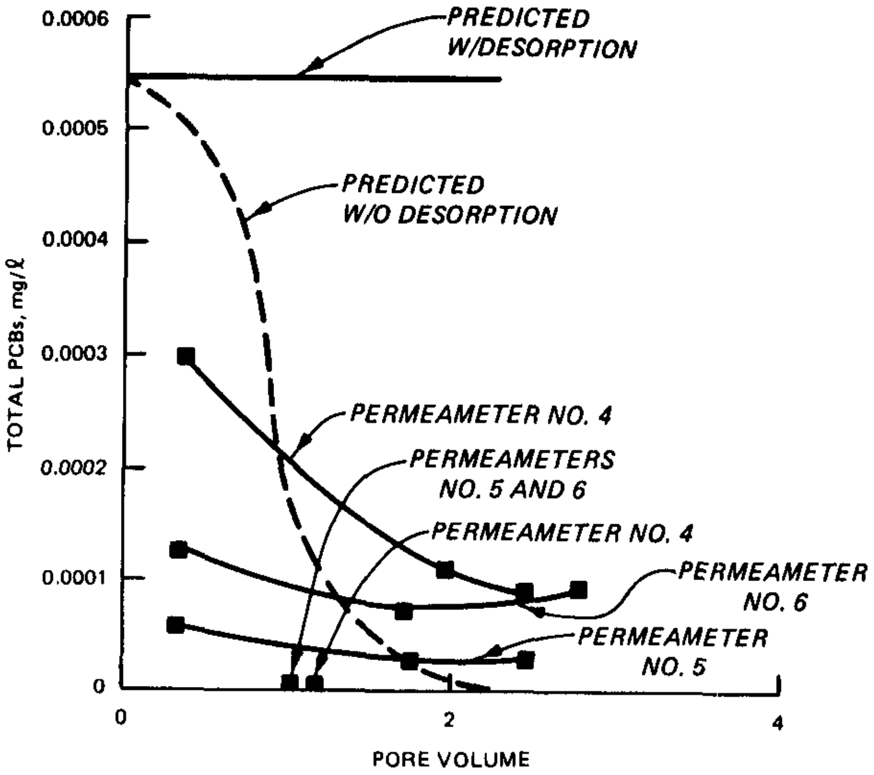


Figure G16. Total PCB concentrations in anaerobic permeameter leachate

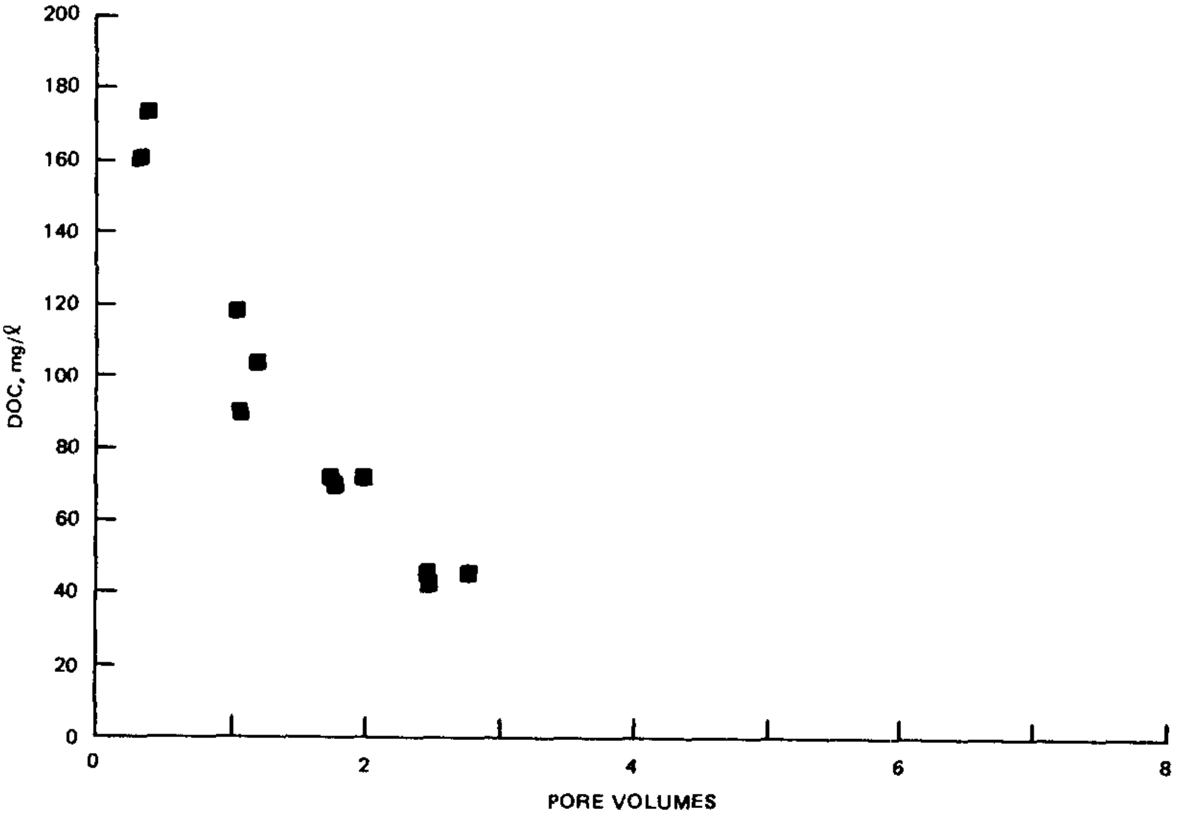


Figure G17. Dissolved organic carbon concentration in anaerobic permeameter leachate during organic leach test

Table 39

Metal and DOC Concentrations and Conductivity in Leachate from Aerobic Permeameters

Pore	Metal Concentration, mg/ℓ					DOC	Conductivity
Volume	As	Cd	Cr	Pb	Zn	mg/ℓ	μmhos
Permeameter 1A							
0.27	0.008	0.0414	0.009	0.002	0.305	603	4500
0.72	0.003	0.0462	0.008	0.001	0.289	621	4300
1.06	0.009	0.0412	0.009	0.004	0.454	604	4500
1.50	0.012	0.0094	0.008	0.003	0.088	394	1190
1.62	0.013	0.0104	0.008	0.003	0.082	333	3900
2.64	0.016	0.0005	0.007	0.009	<0.03	246	3350
3.04	0.015	0.0005	0.006	0.004	<0.03	197	3300
4.40	0.013	0.0005	0.004	<0.001	<0.03	119	2800
5.18	0.011	0.0022	0.003	0.005	0.059	90	2600
7.22	0.010	0.0004	0.003	0.002	<0.03	*	2300
8.98	*	*	*	*	*	64	1975
10.54	0.009	0.0008	0.003	0.002	0.03	45	1725
Permeameter 2A							
0.14	0.011	0.0125	0.009	0.003	0.113	637	4100
0.44	0.010	0.0995	0.010	0.002	0.116	542	4400
0.74	0.010	0.0134	0.009	0.003	0.107	604	4600
1.10	0.013	0.0103	0.011	0.002	0.070	433	4300
1.46	0.014	0.0116	0.008	0.004	0.063	307	4000
2.36	0.005	0.0130	0.002	0.003	0.027	20	740
3.29	<0.005	0.0005	<0.001	0.001	<0.03	20	600
Permeameter 3A							
0.14	0.012	0.0130	0.009	0.001	0.089	549	4100
0.47	0.012	0.0276	0.007	0.003	0.114	560	4400
0.80	0.012	0.0025	0.008	0.001	0.104	541	4400
1.18	0.012	0.0100	0.009	0.006	0.084	434	4000
1.54	0.012	0.0127	0.008	0.002	0.002	292	3750
2.36	0.013	0.0009	0.007	0.001	0.036	227	3100
3.16	0.009	0.0003	0.004	0.002	<0.030	121	2350
3.92	0.015	0.0006	0.004	0.008	<0.030	88	2300
4.65	0.011	0.0031	0.006	0.005	0.044	87	2100
6.38	0.011	0.0019	0.003	0.001	0.041	76	2300
8.00	0.010	0.0009	0.003	0.001	<0.030	54	1850
9.57	0.009	0.0002	0.003	0.001	<0.030	49	1675

* No sample collected.

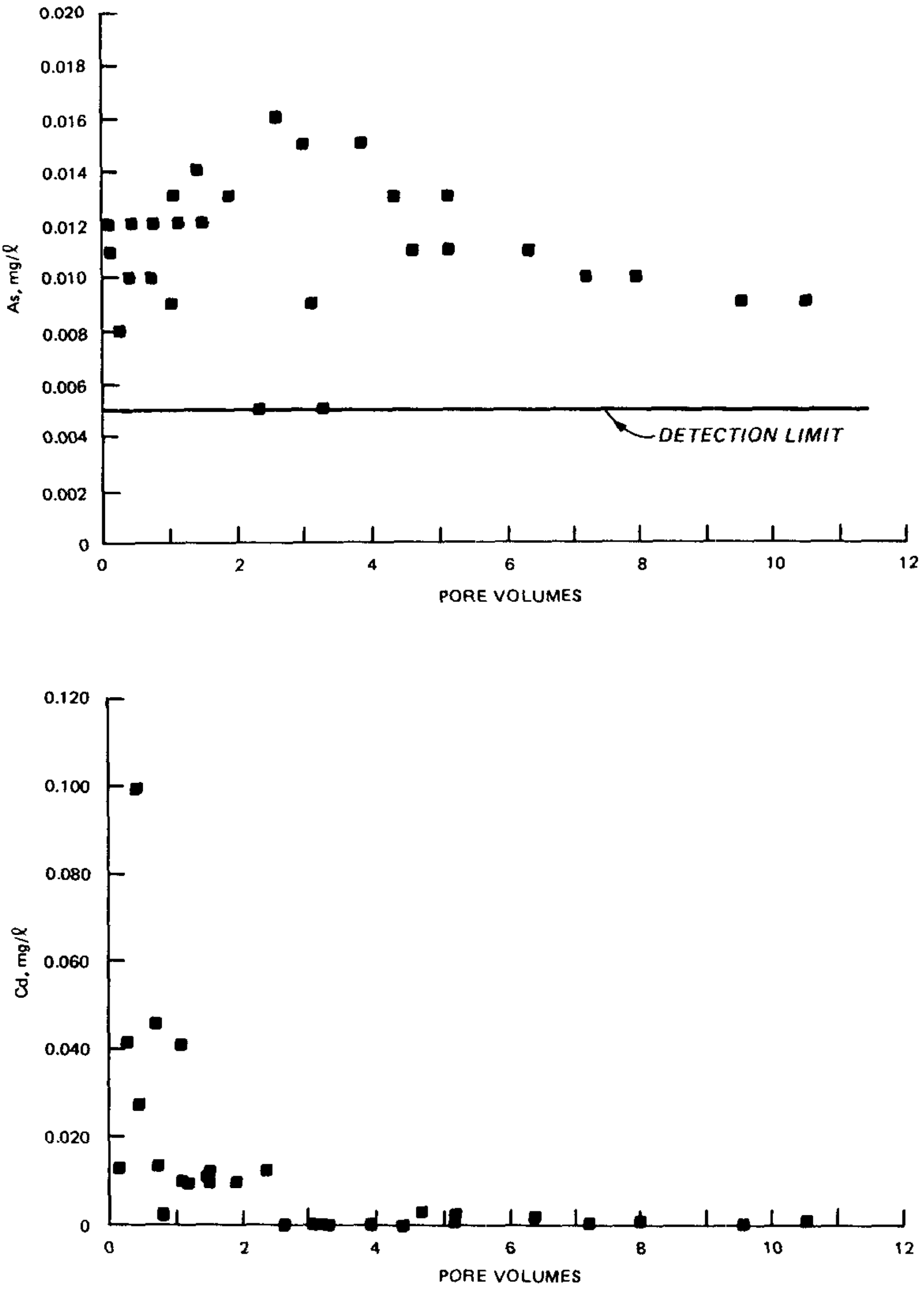
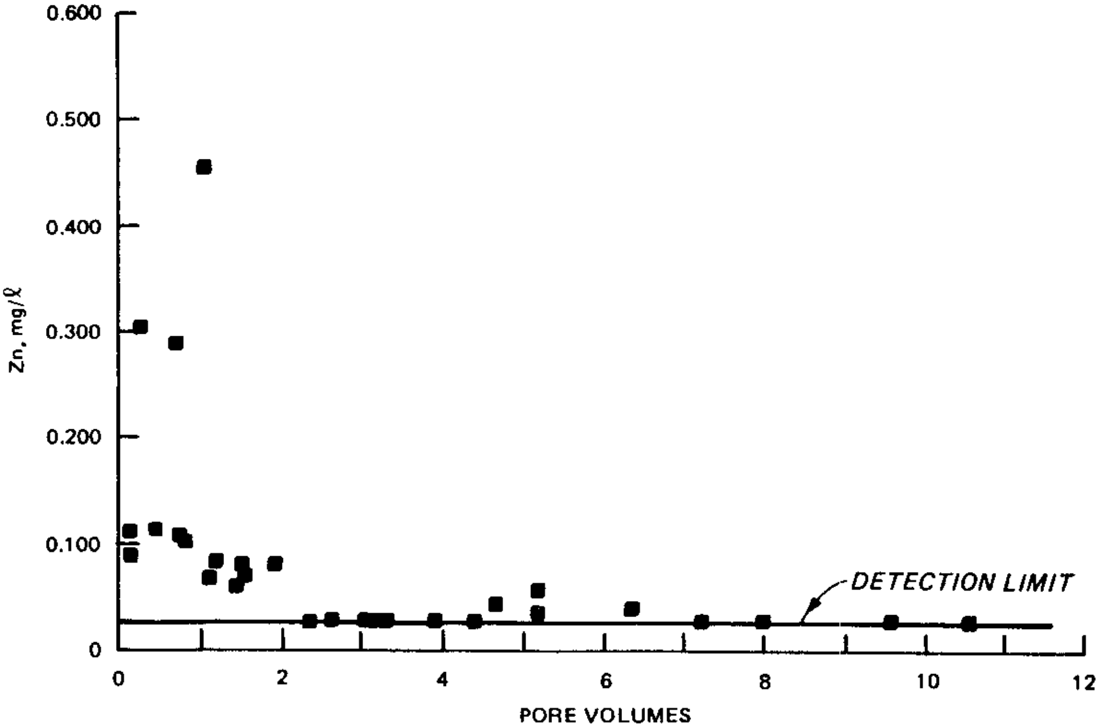


Figure G18. Arsenic and cadmium in aerobic permeameter leachate



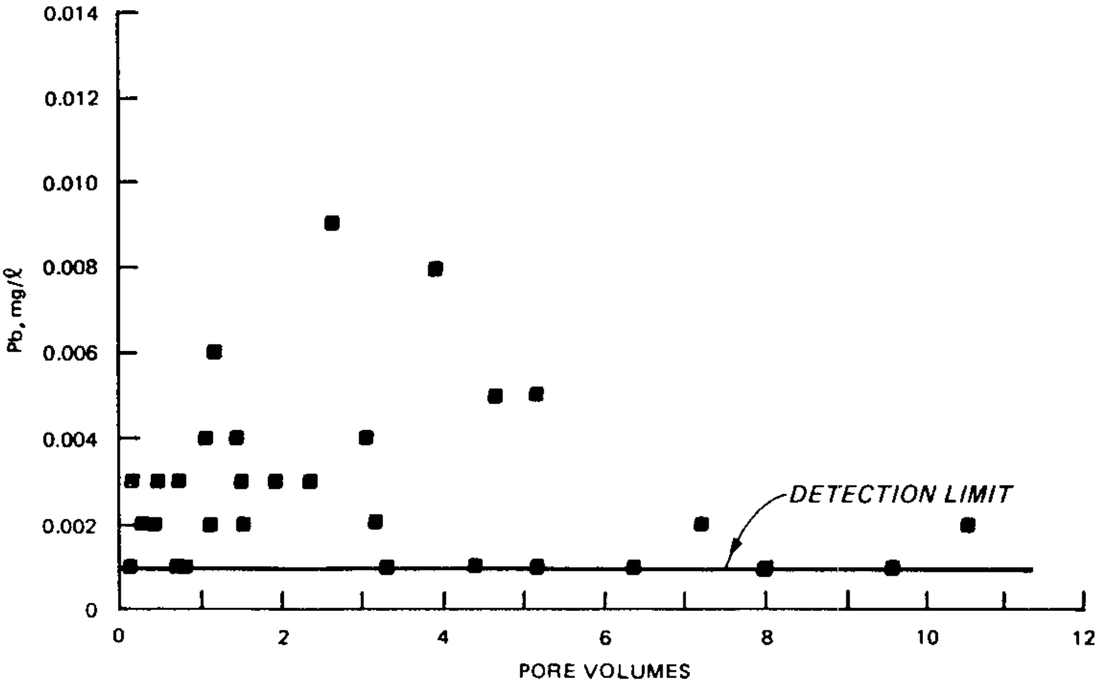


Figure G19. Zinc and lead in aerobic permeameter leachate

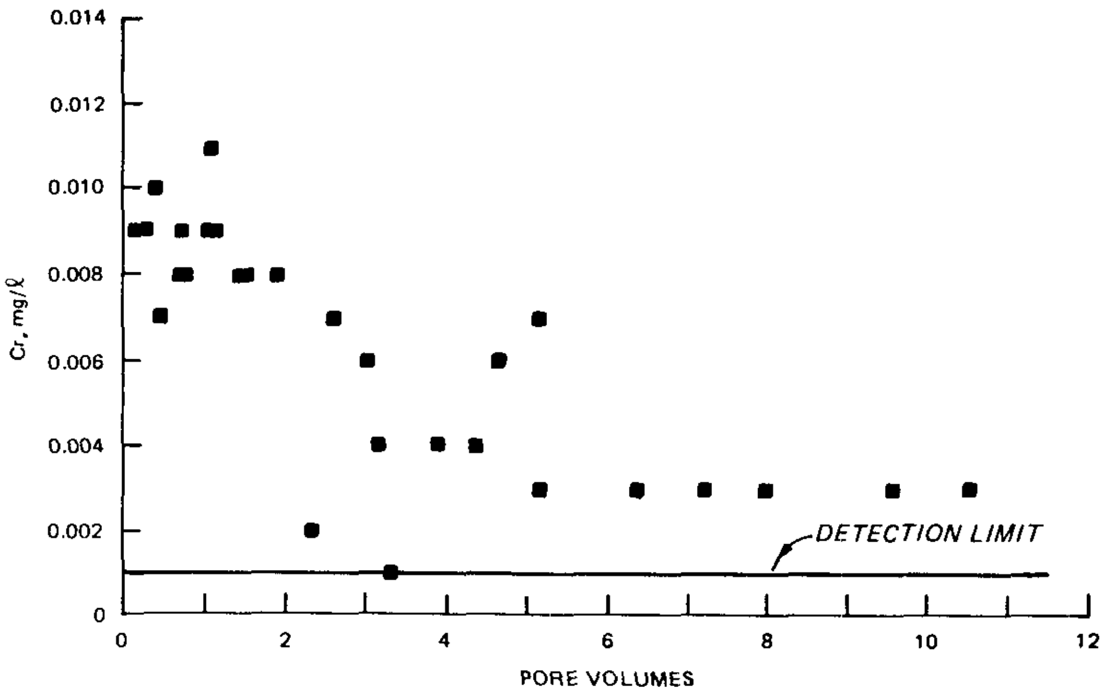


Figure G20. Chromium in aerobic permeameter leachate

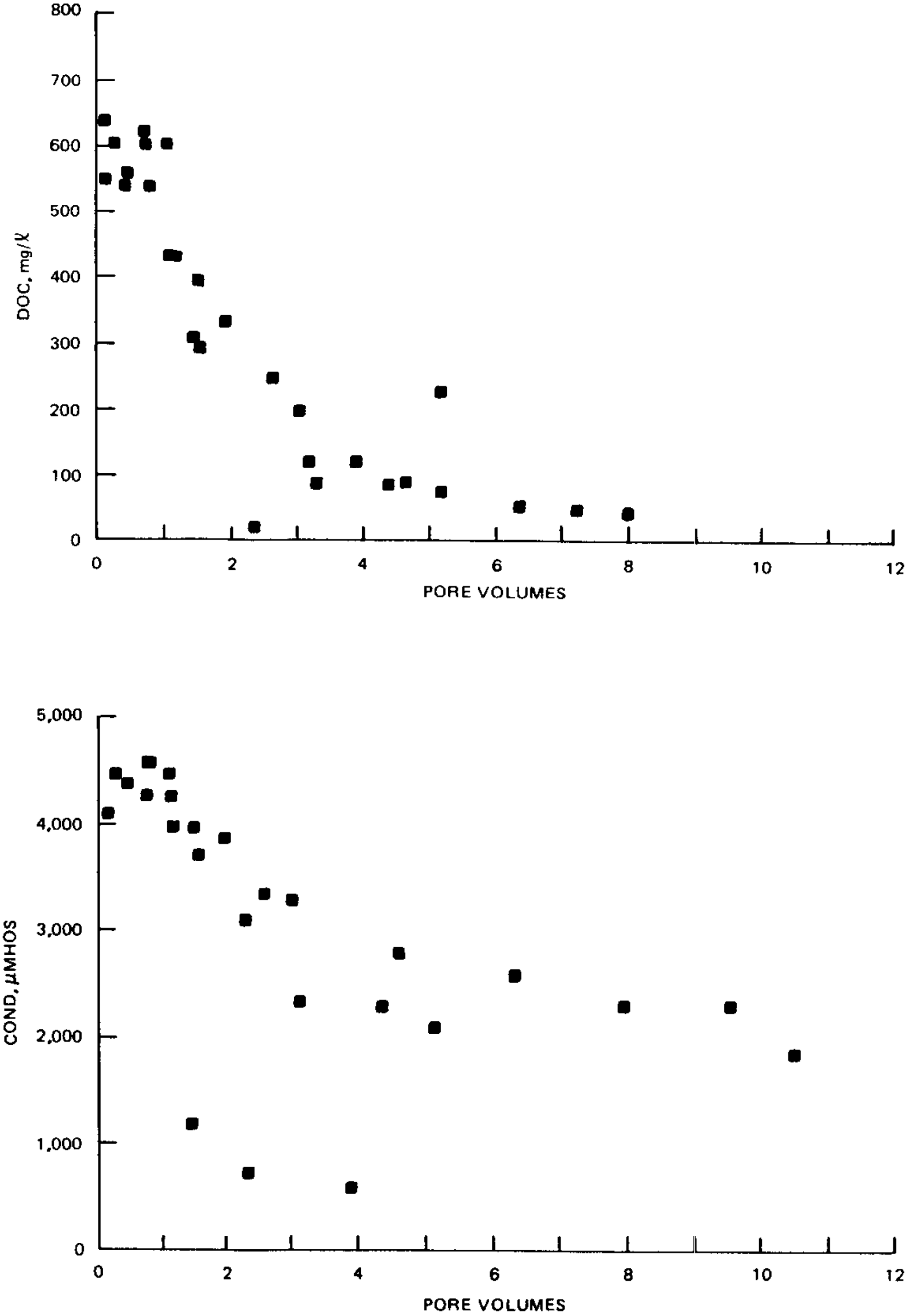


Figure G21. Dissolved organic carbon and conductivity in aerobic permeameter leachate during metal leach test

Table G40

Summary of Organic Contaminants that were Below the Detection Limit in Aerobic Permeameter Leachates

Compound	Detection Limit mg/ℓ
2	0.005
3	0.005
4	0.005
5	0.005
6	0.005
7	0.005
8	0.005
9	0.005
10	0.005
11	0.005
12	0.005
13	0.005
14	0.005
15	0.00001
27	0.00001

concentration and the corresponding pore volumes for each aerobic permeameter are listed in Table G41. Plots similar to those for anaerobic sediment are shown in Figure G22 for total Aroclor 1248 congener concentration and Figure G23 for DOC. Examination of these plots and Table G41 provides the following observations:

- a. Naphthalene was detected in only two samples. No other PAHs were detected.
- b. Total Aroclor 1248 congener concentration ranged from below detection limits to 0.07136 mg/ℓ.
- c. Leachate from one of the aerobic permeameters was consistently higher in Aroclor 1248 congeners than the other two permeameters.
- d. DOC showed a well defined washout effect not observed for total Aroclor 1242 congeners.

90. Consolidation during permeameter testing. At the start of the permeameter leaching tests, a well-mixed slurry of sediment was placed in the permeameters at uniform density and moisture content. Initially, the sediment was oversaturated and in a fluid state. Once the permeameters were placed in operation, a downward velocity was imparted to the slurry by momentum transfer from the moving water to the fluidized particles. Particles reaching the bottom were retained by the Teflon fabric in the bottom. Consolidation occurred from the bottom up (denser layers at the bottom) as additional particles accumulated at the bottom. At the conclusion of the permeameter leaching tests, the moisture content was spatially variable. Along the vertical axis, the sediment had consolidated by 20 percent. Thus, the void volume and porosity decreased during the testing, and since resistance to flow increases as porosity decreases, the permeability of the sediment decreased as the permeameter tests proceeded. Column operating records indicated that the permeability of anaerobic permeameters was 8.66×10^{-8} cm/sec at the beginning of the tests and 6.9×10^{-8} cm/sec at the end of the tests. For the aerobic permeameters, the initial permeability was 1.5×10^{-7} cm/sec, and the final permeability was 1.2×10^{-7} cm/sec. This decrease in permeability over the approximately 6 months that the tests lasted was flow induced and related to the pressurized operation of the permeameters. In the field, self-weight consolidation is much slower than the flow-induced consolidation observed in the permeameters. Thus, field sediment properties do not change as rapidly.

Discussion of permeameter results and integrated approach

91. Agreement between observed and predicted contaminant concentrations varied depending on the contaminant of interest. Predictions were

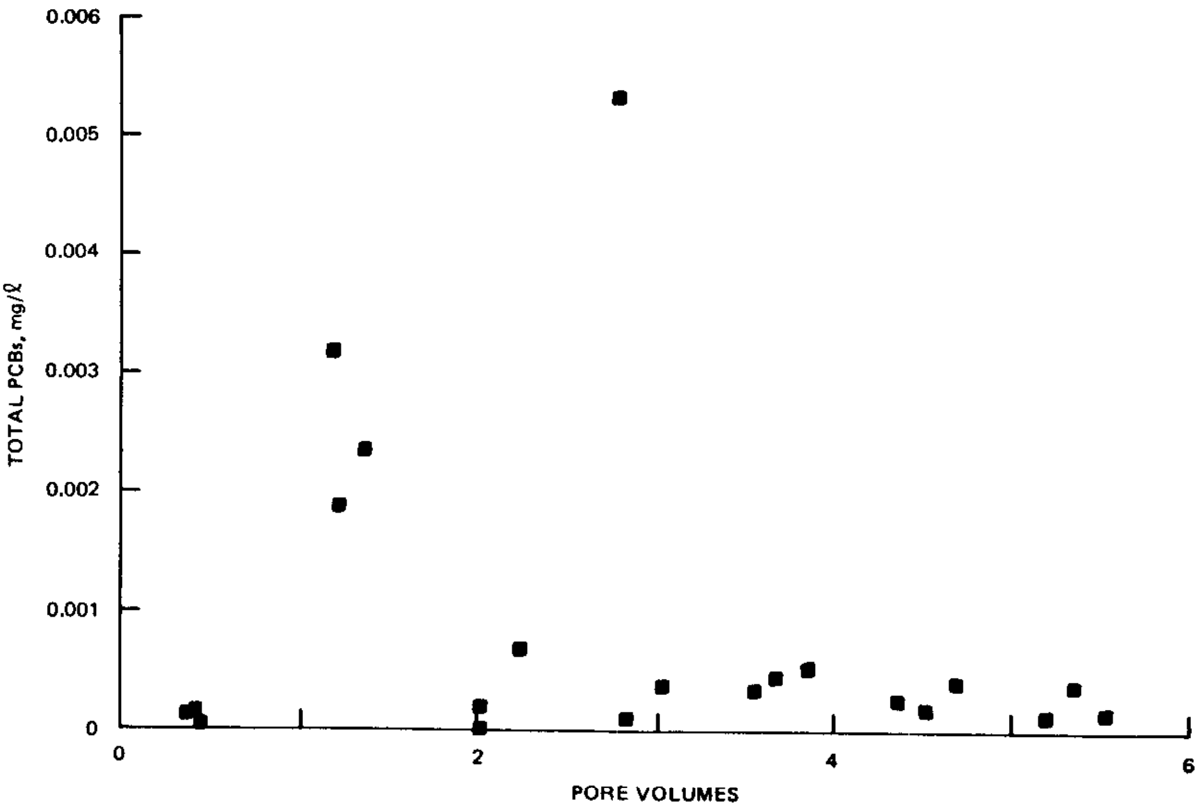


Figure G22. Total PCB concentrations in aerobic permeameter leachate

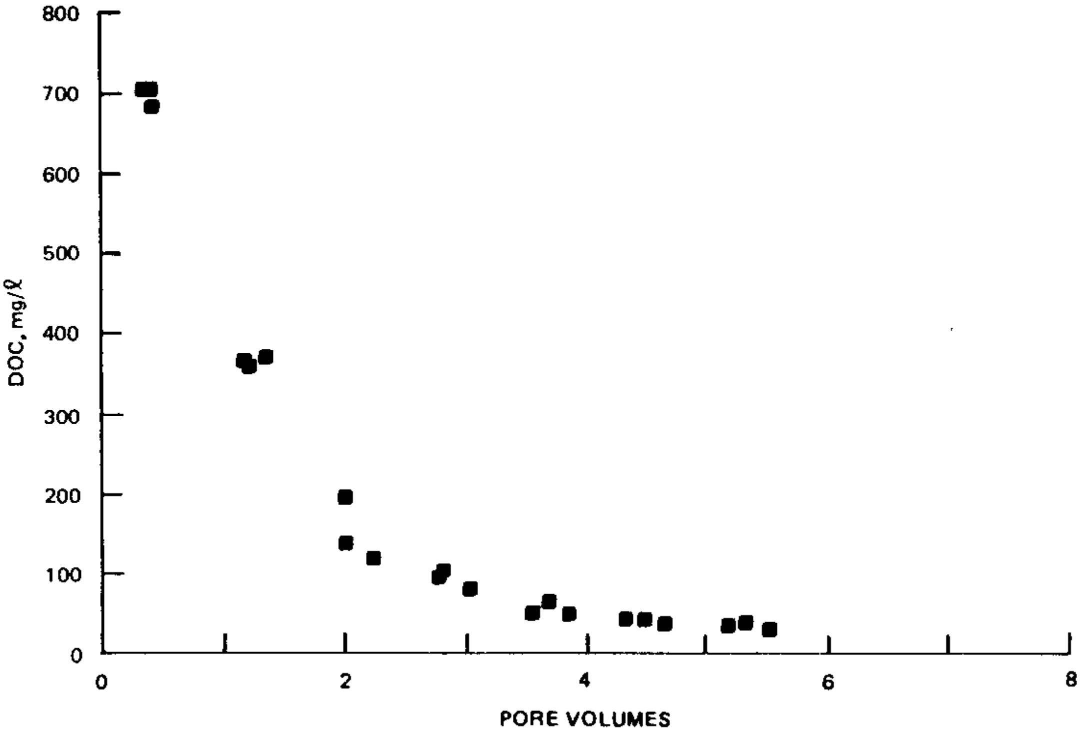


Figure G23. Dissolved organic carbon concentrations in aerobic permeameter leachate during organic leach test

Table G41

Aroclor 1248 Congener and DOC Concentrations (mg/ℓ) in Leachates from Aerobic Permeameters

Pore Volume	Organic Compound Number 1	16	17	18	19	20	21	22	23	24	25	26	28	29	DOC	Total Detected Aroclor 1248 Congeners
Permeameter No. 7																
0.44	<0.006	0.00004	<0.00001	<0.00001	<0.00001	0.00004	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	684	0.00008
1.36	0.0066	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00038	0.00100	<0.00001	<0.00001	0.00100	<0.00001	372	0.00238
2.24	<0.006	<0.00001	<0.00001	<0.00001	0.00069	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	120	0.00069
3.03	<0.006	0.00007	<0.00001	<0.00001	0.00023	0.00002	<0.00001	0.00003	0.00001	<0.00001	0.00001	0.00001	<0.00001	<0.00001	80	0.00038
3.86	<0.006	0.00006	<0.00001	<0.00001	<0.00001	0.00006	<0.00001	<0.00001	0.00005	<0.00001	0.00017	0.00008	0.00005	0.00005	50	0.00052
4.68	<0.006	0.00012	0.00002	<0.00001	<0.00001	0.00005	0.00002	<0.00001	<0.00001	<0.00001	0.00009	<0.00001	0.00009	0.00004	36	0.00042
5.53	<0.006	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00018	<0.00001	<0.00001	28	0.00018
Permeameter No. 8																
0.37	<0.006	0.00003	0.00001	<0.00001	<0.00001	0.00008	0.00001	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	705	0.00013
1.19	<0.006	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00180	0.00001	0.00140	<0.00001	<0.00001	365	0.00320
2.01	<0.006	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	197	-
2.78	0.066	<0.00001	0.00082	<0.00001	<0.00001	<0.00001	0.00082	0.00133	0.00115	<0.00001	0.00001	<0.00001	<0.00001	0.00124	98	0.00536
3.57	<0.006	0.00006	<0.00001	<0.00001	<0.00001	0.00006	<0.00001	<0.00001	0.00005	<0.00001	0.00001	0.00008	0.00005	0.00005	52	0.00035
4.36	<0.006	0.00008	<0.00001	<0.00001	<0.00001	0.00004	<0.00001	<0.00001	<0.00001	<0.00001	0.00003	0.00005	0.00007	<0.00001	42	0.00027
5.19	<0.006	0.00011	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	35	0.00013
Permeameter No. 9																
0.41	<0.006	0.00005	0.00002	<0.00001	<0.00001	0.00006	0.00002	<0.00001	<0.00001	<0.00001	0.00001	<0.00001	<0.00001	<0.00001	705	0.00015
1.22	<0.006	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	0.00190	<0.00001	<0.00001	360	0.00190
2.01	<0.006	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00020	0.00001	<0.00001	<0.00001	<0.00001	137	0.00020
2.83	<0.006	0.00003	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	0.00001	0.00001	0.00001	0.00001	0.00001	<0.00001	0.00002	101	0.00009
3.68	<0.006	0.00006	<0.00001	0.00003	<0.00001	0.00009	<0.00001	<0.00001	0.00005	<0.00001	0.00011	<0.00001	0.00007	0.00006	64	0.00047
4.51	<0.006	0.00006	<0.00001	<0.00001	<0.00001	0.00004	<0.00001	<0.00001	<0.00001	<0.00001	0.00005	<0.00001	0.00005	<0.00001	41	0.00020
5.34	<0.006	0.00010	0.00004	<0.00001	0.00001	<0.00001	0.00004	0.00001	<0.00001	<0.00001	0.00001	0.00020	<0.00001	<0.00001	36	0.00039

conservative, i.e., higher than observed. The differences between predicted and observed are discussed below.

92. Anaerobic permeameters. The anaerobic metals showed lower releases during the permeameter tests than predicted. For chromium, lead, and zinc, departure of predicted from observed began with the initial value. The average value for the interstitial water extractions for these metals did not provide a good estimate for C_I , the starting point for the predicted curves. The average interstitial water concentrations for chromium, lead, and zinc were well above the concentrations in the first permeameter leachate samples. Consequently, the predicted curves started out higher than the observed permeameter data. If the standard error for the interstitial water extractions is considered, the starting point for the predicted curve can be placed closer to the observed data, but still not with the observed range. Chromium and lead were at or near the detection limit throughout the permeameter tests. Zinc was initially measurable in the permeameter leachate, but after the first sample, zinc concentrations were below the detection limit.

93. The starting point of the predicted curves for arsenic and cadmium was in the range of metal concentrations observed in the first sample collected from the anaerobic permeameters. However, the concentrations of arsenic and cadmium in the permeameter leachates decreased more rapidly than the batch K_d predicted. This indicates that the batch K_d for arsenic and cadmium overestimated the apparent K_d for the permeameters. This difference in batch K_d and apparent permeameter K_d is probably related to the high oil and grease concentrations originally present in the sediment. In the sequential batch tests the oil and grease were dislodged from the sediment by the vigorous shaking inherent in the procedure. In the permeameters the oil and grease remained coated on the sediment solids. This coating inhibited metal sorption processes between the sediment solids and the pore water.

94. The differences between interstitial water metal concentrations and the initial concentrations in permeameter leachates are not as easily explained. The differences here are probably also due to problems with the oil and grease content of the sediment. During the centrifugation process, much of the oil and grease associated with the sediment separated and became a third phase. This process may have removed the inhibition to releases caused by the oil and grease sufficiently to result in higher interstitial water metal concentrations.

95. The predicted concentrations for total Aroclor 1248 congeners were also conservative (larger) compared with the observed concentrations. As shown in Figure G16, the predicted leachate concentration did not change from C_I. The observed concentrations tended to persist, although some decrease was noted. When K_d is large, the source term completely overwhelms the other terms in the permeant-porous media equation. Figure G24 shows the results of a sensitivity analysis. Once K_d exceeds a numerical value of 100 ℓ/kg, the leachate concentration is constant for a long time. Evaluation of Equation G7 to predict contaminant concentration is not necessary when K_d is on the order of 10^2 or greater. The predicted leachate concentration may simply be considered constant at C_I. This simplification has application to the field situation also because the field V and D_p will generally be lower than those applicable to the permeameters.

96. As previously discussed, the interstitial water extraction conducted in the batch testing for the organic compounds did not produce reliable values. Equation G8 was used to estimate C_I for the curve shown in Figure G16 using the K_d value in Table G27 and the bulk sediment concentrations listed in Table G6. The estimated value was reasonably close to the initial permeameter leachate concentrations. Estimates of C_I for all the organic compounds are presented in Table G38. These values are also estimates based on the K_d values in Table G27 and the bulk sediment concentrations listed in Table G6.

97. Table G38 also presents the maximum concentration measured in the permeameter leachates for each organic compound. The differences between C_I and C_{max} are an indication of how conservative predictions based on batch leach data are relative to observed data from a continuous-flow system. Theoretically, C_I should always be greater than C_{max}. A situation where C_{max} is greater than C_I implies that the continuous-flow system in the permeameters has departed significantly from model assumptions, or it may indicate chemical analytical problems. Comparison of the C_I and C_{max} data for the anaerobic permeameters showed that the predictive curve is very conservative for PAHs. For specific Aroclor 1242 congeners, C_I and C_{max} were about the same.

98. Application of the integrated approach to anaerobic leaching showed that the assumption of equilibrium-controlled, linear desorption was overly conservative for metals and PAHs. The assumption appears valid for PCB congeners, although there was some departure from theoretical persistence. If

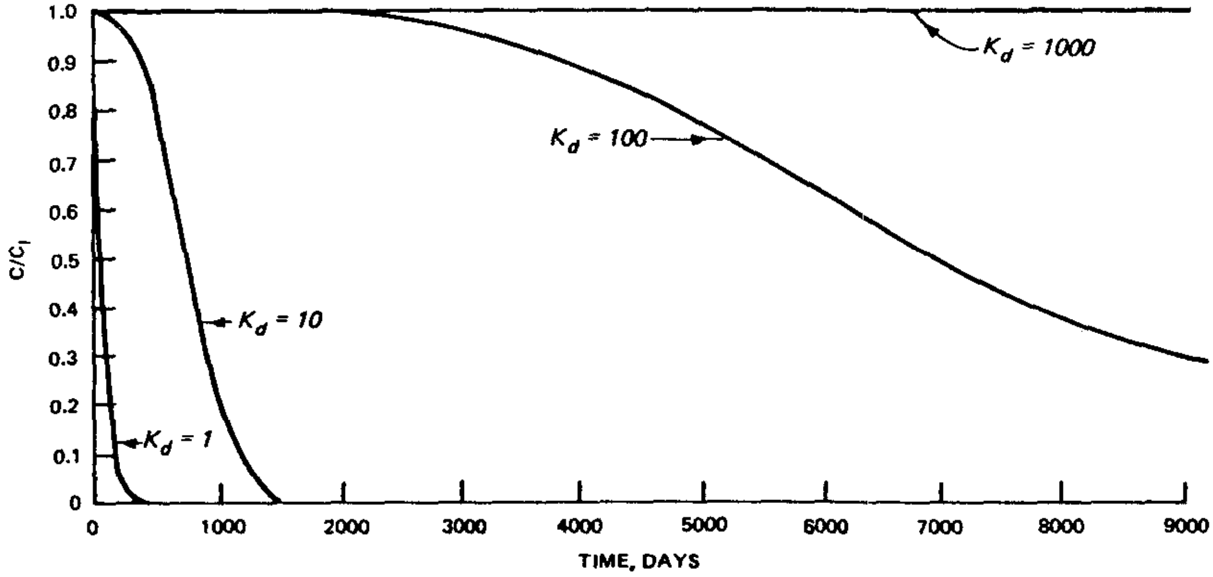


Figure G24. Fraction initial concentration remaining in permeameter leachate for various distribution coefficients predictions are needed that are closer to the observed permeameter leachate concentrations, a nonequilibrium source term formulation based on diffusive transport through a boundary layer or on desorption kinetics may be required for metals and PAHs.

99. Aerobic permeameters. Predicted curves for contaminant concentrations in leachates from the aerobic permeameters were not developed because the leaching conditions with regard to oxygen content in the leachate from the aerobic permeameters were substantially different from that in the aerobic, sequential batch leach tests. The aerobic permeameter testing involved placing partially oxidized sediment in a flooded column. Due to residual sediment oxygen demand, the "aerobic" permeameters probably became anaerobic soon after being placed in operation. Neither oxygen concentration nor oxidation-reduction potential were measured in the permeameter leachate. However, color and turbidity changes indicative of ferrous iron precipitation were evident in the permeameter leachate. Initially, the leachate was reddish-orange (ferric oxyhydroxides) and turbid, then turned black and turbid and remained so throughout the remainder of the test. Therefore, since aerobic batch and permeameter leach tests did not undergo equivalent leaching conditions, batch-determined distribution coefficients were not considered applicable to leaching in the "aerobic" permeameters.

100. Another point requiring explanation is the relative scatter in the aerobic column data compared with the anaerobic column data. This scatter is probably related to changes in desorption properties of the sediment resulting from changes in the sediment oxidation-reduction potential. In the anaerobic testing, the sediment was originally obtained and maintained in an anaerobic condition. Thus, the sediment was well poised in terms of oxidation-reduction potential throughout the permeameter testing. The time dependent changes in the oxidation-reduction potential of the sediment in the "aerobic" permeameters apparently altered the desorption characteristics of the sediment as the permeameter tests were being run.

101. The observed concentrations for total Aroclor 1248 congeners showed an unexpected rapid increase between 1 and 2 pore volumes and a subsequent decrease in concentration. Similar peaks were evident for specific Aroclor 1248 congeners. Theoretically, such peaks should not be observed. Several possible explanations are:

a. Initially, contaminants were adsorbed onto the surfaces of collection vessels and tubing leading from the permeameters to the collection vessels.

b. The permeameter hydraulics were such that clean water reached the bottom quickly and diluted the initial samples.

c. The peaks are experimental artifacts caused by contamination during sample preparation and analysis.

d. The peaks represent the true variability of aerobic permeameter leach testing of organic contaminants.

e. The peaks are related to changes in sediment geochemistry and desorption properties.

102. It is difficult to reconcile the first two explanations with all of the data. If contaminants are initially adsorbed and the delayed peaks represent the time required for the permeameter leachate and the collection apparatus to reach equilibrium, the concentrations should not have subsequently decreased. The plot of DOC for the aerobic permeameters (Figure G23) showed a classic washout curve and no indication that the permeameters were not functioning properly hydraulically or that slugs of oil were being released from the permeameters. On the basis of this analysis, it is likely that explanations d and e, alone or in combination, account for the peaks. Since the peaks represent a significant increase in contaminant concentration further study is needed to determine the cause or causes.

103. The aerobic permeameter tests, as discussed above, did not simulate contaminant leaching in a crust of oxidized sediment in a mature CDF. It is difficult, probably impossible, to determine exactly what type of field situation the aerobic permeameter tests represent. It should be noted that the leaching environment that began in a moist, aerobic condition followed by a flooded, anaerobic condition had higher metals, Aroclor 1248 congeners, and DOC concentrations than the strictly anaerobic environment. These data show that the desorptive properties of dredged material may change for the worse in an upland CDF in particular, if the oxidation-reduction potential varies widely. This does not necessarily mean that contaminant flux will be worse since interphase contaminant transfer must be coupled with hydraulic flux in order to estimate contaminant flux. Further study is needed to fully understand the implications of these findings.

104. Limitations of the predictive equation. The equation used to develop the predictive curves, Equation G7, is restricted to constant coefficients. This means that the variables D_p , V , ρ , θ , C_I and K_d are

constants. Several of these parameters depend on sediment porosity. The dispersion coefficient D_p and the pore water velocity V are flow-related variables that are affected by changes in porosity. During permeameter testing some sediment consolidation was observed that caused the porosity and therefore D_p, V, ρ, θ, and the sediment pore volume used to calculate the pore volume throughput for the observed points to change as testing progressed. A more sophisticated mathematical description of the permeameter test involving solution of a partial differential equation with variable coefficients could be used to develop predictive curves that account for consolidation. Although a more sophisticated predictive equation would be expected to improve the accuracy of the predicted curves, such an equation was not used in this study for two reasons.

105. First, the prediction of contaminant concentrations in the permeameter leachate is relatively insensitive to ρ, θ, and V, moderately sensitive to D_p, and extremely sensitive to C_I and K_d. Since C_I and K_d are not related to consolidation, the use of a predictive model that accounts for the effects of consolidation would not change the starting point for the predictions, C_I, or significantly change the shape of the predicted curve, K_d.

106. Second, development of the functional relationships for consolidation and the pore volume through the permeameters and the relationship between consolidation and the flow-related variables would require a separate set of equations and numerical analysis of these equations by a computer model. The effort required to develop reliable input needed for a complicated model was not within the scope of this study.

107. The final limitation of the predictive equation relates to biodegradation. Equation G7 does not include a term for biodegradation. For contaminants with high distribution coefficients, Equation G7 predicts that the initial leachate concentration will persist indefinitely. In this case, the the biodegradation term could become important. The rates at which organic compounds are biodegraded depend on the structure of the compounds and the metabolic capacities of the microbial community resident in the dredged material. As biokinetic rates for specific organic contaminants applicable to dredged material become available, the inclusion of a biodegradation term in the predictive equation will become more practical.

Conclusions

108. An integrated approach to leachate testing involving batch and column leach tests, and a mass transport equation was developed that appears to be a useful tool for investigating the processes that govern contaminant leaching from sediment solids. Results of the test procedures described in this appendix showed that metal and organic contaminants associated with Indiana Harbor sediment are tightly bound to the sediment. The leachate data provided in this appendix, in part, provide the basis for performing contaminant flux analysis for proposed CDF's. Conclusions are provided below.

General

109. General conclusions include:

- a. Evaluation of the governing principles of leachate formation and transport showed that interphase transfer of contaminants from the sediment solids to the aqueous phase must be coupled with hydraulic flux in order to adequately evaluate contaminant leaching. Without hydraulic flux, leachate is not transported, and without interphase transfer, contaminated leachate is not formed.
- b. Open-air aging of Indiana Harbor sediment under moist conditions for 6 months resulted in losses of PAHs and PCBs on the order of 80 percent. If volatilization is assumed to be the mechanism primarily responsible for reduction of PAH and PCB in the aged sediment, volatilization could be a major pathway for PAH and PCB release in a CDF.
- c. The amount of contaminant released from batch and column leach tests was near or below the detection limits in many cases. Testing near the detection limits added variability to the data that was unavoidable.

Batch testing

110. Batch testing conclusions include:

- a. The presence of contaminated oil imposed severe operational and analytical difficulties on all phases of batch testing. Complete separation of oil from leachate samples was required in order to obtain valid distribution coefficients.
- b. Less than 1 percent of the bulk metal concentrations in Indiana Harbor sediment were leachable in the sequential batch leach tests.
- c. Organic contaminants in Indiana Harbor sediment are tightly adsorbed to the sediment. Batch equilibrium distribution coefficients ranged from 10^3 to 10^4 for PAHs and from 10^3 to 10^6 ℓ/kg for PCBs.
- d. The batch procedures for determining distribution coefficients for organic compounds can be simplified by using the batch equilibrium method instead of the sequential leach procedure.

e. An understanding of the diversity of chemical interactions and sediment geochemistry is required in order to interpret data from batch leach tests. Data reduction and analysis by statistical procedures alone can be seriously misleading.

Permeameter testing

111. Permeameter testing conclusions include:

a. Metal and PAH concentrations in anaerobic permeameter leachates were not controlled by linear equilibrium desorption. A film effect related to the oil in the sediment probably inhibited interphase transport of metals and PAHs.

b. Aroclor 1248 congeners were generally near or below the detection limit (0.00001 mg/ℓ) in leachate from the anaerobic permeameters.

c. Metal and organic contaminant concentrations were significantly higher in leachate from the aerobic permeameters than from the anaerobic permeameters. The potential for contaminant release is higher in CDFs that allow the dredged material to become oxidized than in CDFs that maintain anaerobic leaching conditions.

d. The aerobic permeameter leach tests did not entirely satisfy testing objectives. The utility of information obtained from aerobic permeameter leach tests was limited to comparison with anaerobic permeameter data and could not be used to verify coefficients determined in aerobic batch leach tests.

Integrated approach

112. Integrated approach conclusions include:

a. The assumption of equilibrium-controlled linear desorption for the source term in the permeant-porous media equation conservatively predicted leachate contaminant concentrations. More accurate predictions will require a nonequilibrium formulation for the source term.

b. Leachate concentrations may be assumed constant at interstitial water levels for contaminants with significant partitioning onto the solid phase (high K_d). In such instances, accurate contaminant flux analysis depends primarily on proper formulation of the hydraulic transport equations.

c. Fundamental differences in the design and conduct of batch and continuous-flow leach tests imply that some phenomena are observable with only one procedure or the other. Oil films or other phenomena that affect interphase transfer of contaminants from the sediment solids to the aqueous phase are observable only by comparing the results of batch and column studies.

d. The sequential batch leach tests were a poor indication of the relative mobility of contaminants in aerobic permeameter leach tests. Further study is needed to fully understand the utility and limitations of aerobic test procedures.

e. The results reported here constitute the first time batch and permeameter leach tests and mass transport equations have been used to assess the leaching potential of contaminated sediment.

Additional study, development, and verification of the integrated approach are needed before it can be adopted for routine application.

APPENDIX H. PROCEDURES FOR EVALUATING SOLIDIFICATION/ STABILIZATION TECHNOLOGY

Introduction

1. Solidification/stabilization is a state-of-the-art technology for the treatment and disposal of contaminated materials. The technology has been applied in Japan to bottom sediments containing toxic substances (Kita and Kubo 1983; Nakamura 1983; Otsuki and Shima 1982)* and in the United States to industrial wastes (Pojasek 1979; Malone, Jones, and Larson 1980) Tittlebaum et al. (1985) reviewed the current technology and its potential application to wastes high in organic contaminants. Experiences in Japan with bottom sediments and in the United States with industrial sludges indicate that solidification/stabilization is a promising contaminant immobilization technology for materials that show a potential for leaching.

2. The technical feasibility of reducing contaminant mobility in Indiana Harbor sediment by solidification/stabilization was investigated in a series of laboratory-scale applications of selected solidification/stabilization processes. The processes evaluated were portland cement, portland cement with fly ash, portland cement with fly ash and/or sodium silicate, portland cement with Firmix (a proprietary additive), Firmix, portland cement with WEST-P (a proprietary polymer), Firmix with WEST-P, and lime with fly ash. Most of these processes are commercially available. Patents have been issued for some.

Materials and Methods

3. Some of the data presented in this report were furnished by sources outside the Government. The PQ Corporation, Valley Forge, Pa., supplied the data in Table 14 of the main body of this report. Table 14 presents unconfined compressive strength data for the process that used portland cement with fly ash and/or sodium silicate. The PQ Corporation also supplied samples of this process for leach testing. Five variations of the process were sent to the US Army Engineer Waterways Experiment Station (WES) for leach testing. The materials and methods used at the WES are described below.

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* See References at the end of the main text (Vol I).

4. Sediment acquisition, mixing, and transportation procedures have been previously described in Part II. The sediment was stored at 4 °C until used. The contents of the sediment container (55-gal drum) were mixed prior to use. No processing (e.g. dewatering) was applied prior to applying the various solidification/stabilization processes. Type I portland cement was used in the processes involving portland cement; class C fly ash was used in the processes involving fly ash; and hydrated lime was used in the lime with fly ash process. The proprietary additive Firmix is a solidification agent that is commercially available. Firmix was obtained from Trident Engineering, Baltimore, Md. The proprietary polymer WEST-P was obtained from Philip W. West, retired Professor of Chemistry, Louisiana State University. The polymer is still in the research and testing stage of development and was not commercially available at the time this report was prepared.

Laboratory processing

5. The process additives were mixed with sediment in a Hobart C-100 mixer (2.5-gal capacity) for 5 min per additive. After mixing the freshly prepared solidified sediment was cast in 2-in. cube molds for unconfined compressive strength testing, standard Corps of Engineers (CE) compaction molds for trafficability and chemical leach testing, and 2.8-in. diam cylindrical molds for permeability testing. The samples were cured at 98-percent relative humidity and 23 °C until tested. A standard cure time of 28 days was used in all of the testing unless otherwise noted.

Experimental design

6. Each process was applied in three formulations except the portland cement process. Four portland cement formulations were tested. The formulations for each process differed in respect to the dosage of setting agent used, not the types of agents used. By testing different processes in varying formulations, data were obtained for making comparisons among processes and process formulations.

7. The experimental matrix for the physical/chemical testing is presented in Table H1. The matrix was developed to give a general indication of the effectiveness of solidification/stabilization for Indiana Harbor sediment. Thus, the testing does not focus on detailed analysis of products from all of the processes included in the evaluation. Unconfined compressive strength was the key test for physical stabilization, and the serial, graded batch leach procedure was the key test for chemical stabilization. Leach tests were

Table H1

Experimental Matrix for Testing of Solidified/Stabilized Indiana Harbor Sediment*

Process	Test UCS	T	P	SCT	Leach
Portland Cement	X	X	X	X	X
Lime-Fly Ash	X	X		X	X
Portland Cement-Fly Ash	X			X	X
Portland Cement-Fly Ash-Sodium Silicate					X
Portland Cement-Firmix	X			X	X
Portland Cement-WP	X			X	X
Firmix-WP					X
Firmix	X			X	X

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* UCS = unconfined compressive strength.
T = trafficability.
P = permeability.
SCT = strength-cure time curve.
Leach = chemical leach testing.
WP = proprietary polymer WEST-P.

conducted on each process formulation and unconfined compressive strength testing was conducted on all of the process formulations, except the 0.4 portland cement:1 sediment formulation.

Physical properties tests

8. Unconfined compressive strength. Unconfined compressive strength (UCS) was determined according to the American Society for Testing and Materials (ASTM) Compressive Strength of Hydraulic Cement Mortars (C-109) procedure. A minimum of three replicates and in some cases six replicates were run for each determination.

9. Permeability. Triaxial, upflow permeability (hydraulic conductivity) was determined on 2.8-in. diam cylinders 3 in. in length by the standard CE procedure described in EM 1110-2-1906 (McIver and Hale 1970). Duplicates were not run.

10. Trafficability. Trafficability was determined on 4-in.-diam cores cast in standard CE compaction molds using a cone penetrometer. Trafficability is reported in terms of cone index (CI) in pounds per square inch. The CI is the resistance to penetration of a 30-deg right-circular cone. The standard cone penetrometer has a base area of 0.5 sq in., and the high-range penetrometer has a base area of 0.2 sq in. It was convenient to use the standard cone penetrometer on samples with a CI less than 100 psi and to use the high range penetrometer for samples greater than 300 psi. For samples in between the above ranges, both penetrometers give satisfactory results. Five replicates were made for each CI determination.

Serial, graded batch leach tests

11. Background. The serial, graded batch leach procedure is a simplification of the sequential batch leach tests described in Appendix G. In the serial, graded procedure, a sample is leached one time at several liquid-solids ratios (Houle and Long 1980). A table of solid phase and aqueous phase concentrations is developed from analyses of the leachates produced. These data are plotted to produce a desorption isotherm. This procedure is simpler than the sequential leach procedure because the mass of solids being leached has to be measured and handled only once. In the sequential procedure the mass of solids, the solid phase contaminant concentration, and the moisture content and contaminant concentration in the moisture remaining with the solids must be accounted for at each step in the sequence.

12. From the desorption isotherm, contaminant-specific coefficients can be obtained that describe the interphase transfer of contaminant from the solid phase to the aqueous phase. The interpretation of data from serial, graded batch leach tests is similar to the interpretation previously described in Appendix G for data from sequential batch leach tests. Of particular importance is Equation G5.

$$q = K_d C + q_r \tag{G5}$$

Equation G5 assumes that a fraction of the solid phase contaminant concentration is resistant to leaching and the solid to liquid phase transfer of the leachable fraction is governed by a reversible process. In this model, the relationship between the solid phase concentration q and the aqueous phase concentration C is linear. Two parameters describe the relationship, a distribution coefficient K_d that relates leachable solid phase concentration to aqueous phase concentration and the solid phase concentration resistant to leaching q_r. Similar models have been used in various studies on contaminant mobility in sediments (Jaffe and Ferrara 1983; Di Toro and Horzempa 1982b). Equation G5 has not previously been demonstrated as a practical leaching model for solidified/stabilized sediment.

13. Serial, graded batch leach tests can provide the information needed for a permeant-porous media mass transport equation, given certain simplifying assumptions. (Permeant-porous media equations are discussed in Appendix G.) Water is assumed to be the transport medium for the contaminants. Only contaminants on surfaces in contact with moving pore water are available for leaching. Contaminants that are not solubility limited are released by ion exchange and desorption of adsorbed contaminants. It is further assumed that the water moves so slowly through the solidified/stabilized material that ion exchange and desorption can be modeled as equilibrium controlled.

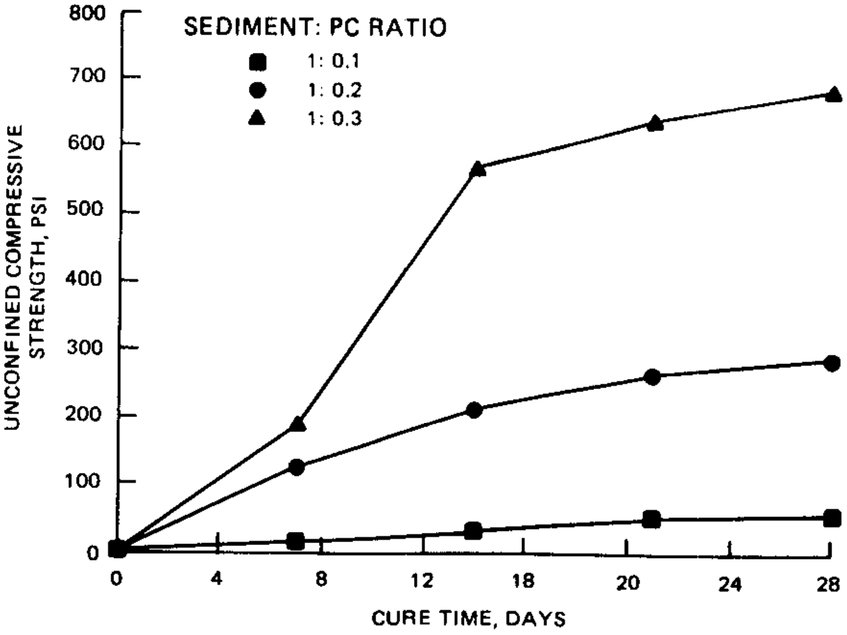
14. The equilibrium assumption is a common assumption in the practical application of permeant-porous media equations (Grove and Stollenwerk 1985; Vallochi 1985). The basis for this assumption involves both hydraulics and chemical kinetics. The transfer of contaminant from the solid phase to the aqueous phase is assumed to be fast in relation to the rate at which water percolates through the solidified/stabilized material. As water percolates

through the material, a piecewise equilibrium in space and time is established such that the contaminants are distributed between solid and aqueous phases according to the chemical thermodynamics of the solid and aqueous phases. This distribution is described by a desorption isotherm, i.e., a plot of solid phase concentration versus aqueous phase concentration, as in Figure G-2. The term "desorption" is used here to represent the net result of all reversible processes.

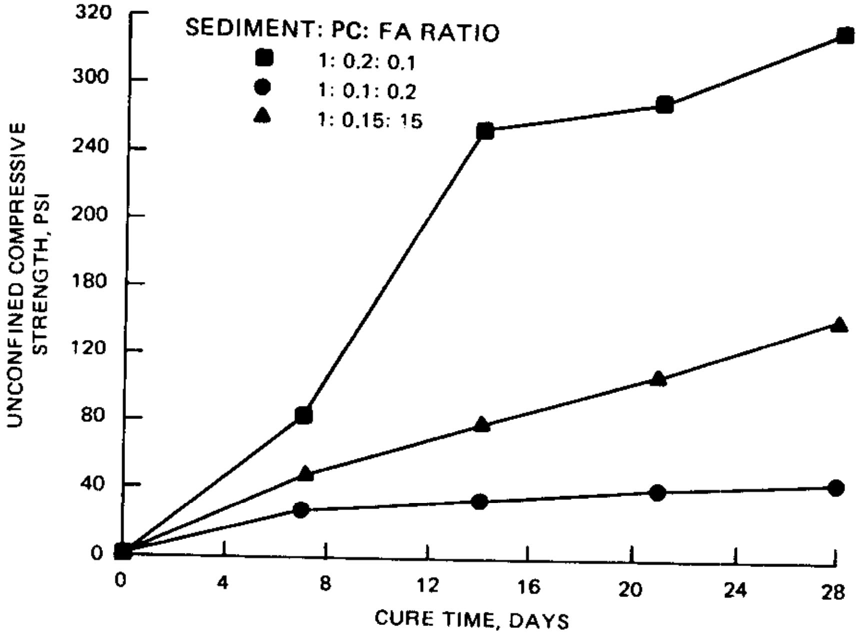
15. The serial, graded batch leach procedure also assumes that the liquid-solids ratio does not affect the chemistry of the leaching process, i.e., the distribution coefficient is not dependent on liquid-solids ratio. The literature indicates that this assumption is probably not correct for untreated sediment, although the reason for this is not entirely clear (Voice, Rice, and Weber 1983; Di Toro et al. 1986). For solidified/stabilized sediment, changes in the chemistry of the aqueous phase with varying liquid-solids ratio probably have a more profound effect on interphase contaminant transfer than changes in the concentration of solids. Specifically, if pH varies significantly, the solubility of metals will vary. The excess alkalinity of the solidification reagents, however, tends to stabilize pH.

16. Chemical leach tests. Serial, graded batch leach tests were run on samples taken from the center of the 4-in.-diam specimens cast in compaction molds. The 4-in. specimens were broken apart in order to obtain the samples for chemical leach testing. The samples were ground on a Brinkman centrifugal grinding mill to pass a 0.5-mm screen before leach testing. The leach procedure consisted of contacting solidified sediment samples with distilled-deionized water on a mechanical shaker for 24 hr in liquid-solids ratios of: 100 ml:50 g, 100 ml:10 g, 100 ml:5 g, and 100 ml:1 g. In some of the tests, a 100 ml:20 g liquid-solids ratio was included. The extractions were run in triplicate in 250-ml polyethylene bottles laid in the horizontal position. After shaking, the mixtures were filtered through 0.45-μ membrane filters and analyzed for arsenic, cadmium, chromium, lead, zinc, and organic carbon. Organic carbon was not included in the analysis of leachates from portland cement with fly ash and/or sodium silicate. Blanks were prepared by carrying deionized-distilled water through the same shaking and filtration procedures. Chemical analysis procedures are described in Appendix G.

17. The chemical leach data were reduced to tables of solid and aqueous phase concentrations using the calculations described below. The solid phase

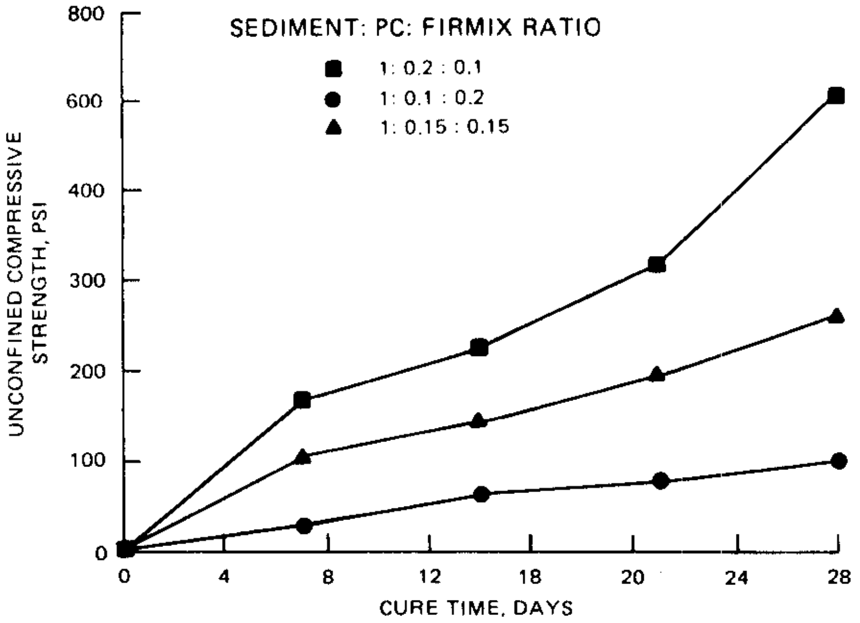


a. Portland Cement

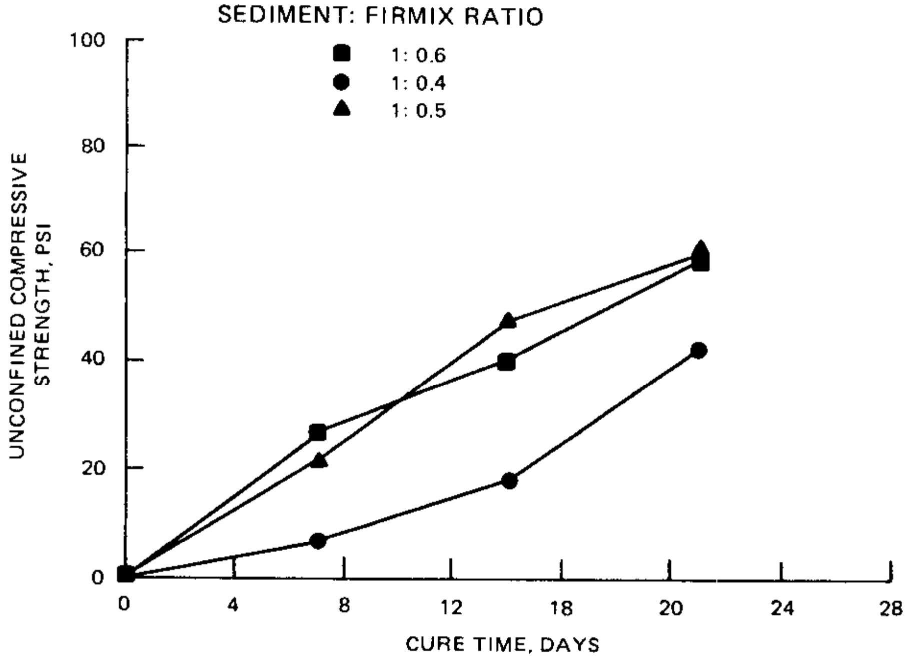


b. Portland Cement with Fly Ash

Figure H1. Unconfined Compressive Strength-Cure Time Curves for Indiana Harbor Sediment Solidified/Stabilized Using Portland Cement and Portland Cement with Fly Ash Processes



a. Portland Cement with Firmix



b. Firmix

Figure H2. Unconfined Compressive Strength-Cure Time Curves for Indiana Harbor Sediment Solidified/Stabilized Using Portland Cement with Firmix and Firmix Processes contaminant concentration after leaching is given by

$$\left\{\begin{array}{l}\text{Solidified Sediment}\\ \text{Contaminant}\\ \text{Concentration}\\ \text{After}\\ \text{Leaching}\end{array}\right\} = \left\{\begin{array}{l}\text{Solidified Sediment}\\ \text{Contaminant}\\ \text{Concentration}\\ \text{Before}\\ \text{Leaching}\end{array}\right\} - \left\{\frac{\begin{array}{l}\text{Mass of Contaminant}\\ \text{Leached}\end{array}}{\begin{array}{l}\text{Mass Solidified}\\ \text{Sediment Leached}\end{array}}\right\}$$

or

$$q = q_o - C(V/M) \qquad \text{(H1)}$$

where

q = total contaminant concentration in the solid phase after leaching, mg/kg

q_o = initial contaminant concentration in the solid phase, mg/kg

C = contaminant concentration in the leachate, mg/ℓ

V = volume of aqueous phase (leachate), ℓ

M = mass of solidified sediment leached, kg

Equation H1 relates to a single contaminant. Since the liquid-solids ratio L/S is given by

$$L/S = V/M$$

Equation H1 can be written as

$$q = q_o - C(L/S) \qquad \text{(H2)}$$

Equation H-1 was used to calculate the solid phase concentration q corresponding to the aqueous phase concentration determined by chemical analysis for the liquid-solids ratio used. Since all the tests used 100 ml of distilled-deionized water, the liquid-solids ratio is 100 ml divided by the mass of solidified/stabilized sediment leached in grams.

18. The initial solid phase concentration q_o for each contaminant is given by the following equation:

$$q_o = \frac{S_x}{(1 + w)\ (1 + R)} \qquad \text{(H-3)}$$

where

S_x = contaminant concentration in the sediment before solidification, mg/kg (dry weight basis)

w = moisture content of the wet sediment, kg water/kg sediment solids

R = dosage of solidification/stabilization reagents, kg reagents/kg wet sediment processed

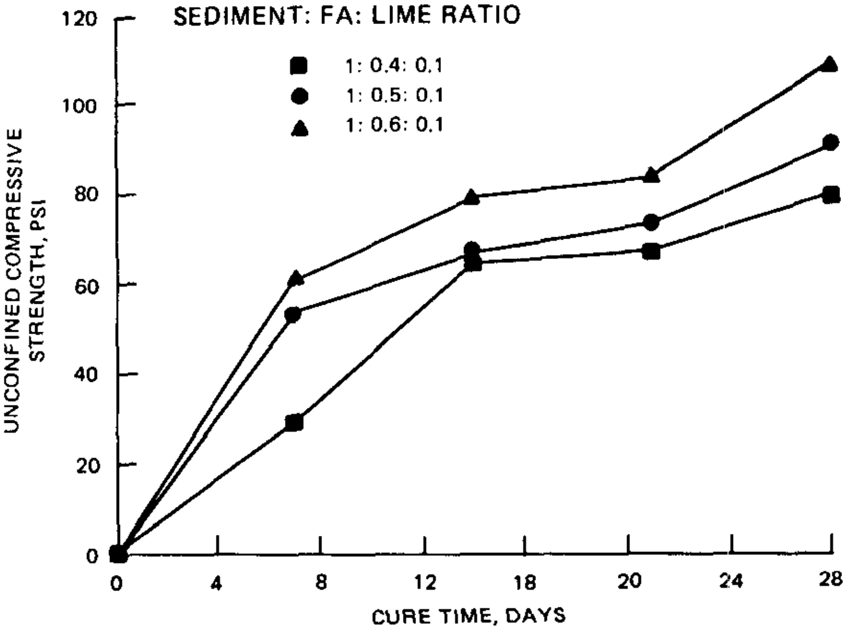
The moisture content of the sediment was 88 percent, and values for S_x are given in Table 1 in the main body of this report.

19. From the tables of solid phase contaminant concentration q and aqueous phase contaminant concentration C desorption isotherms were developed by plotting q versus C. Determination of the distribution coefficient K_d and the solid phase contaminant concentration resistant to leaching q_r varied slightly, depending on the liquid-solids ratios at which contaminants were detected in the leachates. When the aqueous phase concentration was above the detection limit at three or more liquid-solids ratios and the data were not clustered K_d and q_r were determined by least squares analysis of the line of best fit. For clustered data q_r was determined by averaging the solid phase concentrations. Clustering is discussed in the results section of this appendix. When the aqueous phase concentrations were below the detection limit at the 10:1 and/or 2:1 liquid-solids ratios, a distribution coefficient was not calculated. The solid phase contaminant concentration at the next highest liquid-solids ratio with aqueous phase concentration below the detection limit was used as an estimate of the contaminant concentration resistant to leaching. In this case q_r was reported as a greater than value.

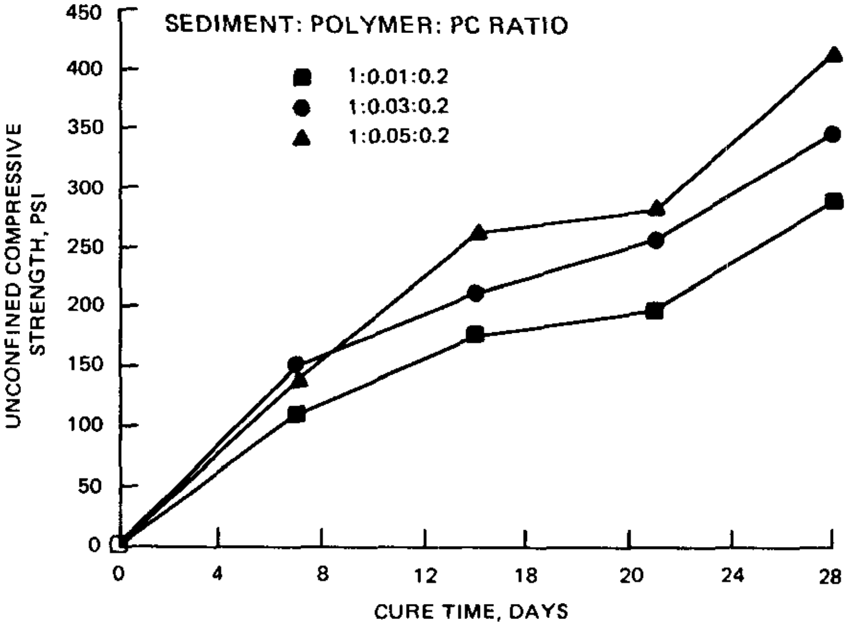
Results

Physical properties

20. Unconfined compressive strength. UCS for portland cement, portland cement with fly ash, portland cement with Firmix, portland cement with WEST-P, Firmix, and lime with fly ash processes was measured at cure times of 7, 14, 21, and 28 days. These data are presented in Figures H1-H3. The points in



a. Fly Ash with Lime



b. Portland Cement with Polymer

Figure H3. Unconfined Compressive Strength-Cure Time Curves for Indiana Harbor Sediment Solidified/Stabilized Using Fly Ash with Lime and Portland Cement with WEST-Polymer Processes the figures are averages of either three or six replicates. The 7- and 21-day data are averages of three replicates and the 14- and 28-day data are averages of six replicates.

21. The UCS data showed, as expected, that the higher the additive dosage, the higher the strength of the solidified product. For example, the 28-day UCS for the 0.1 portland cement:1 sediment weight ratio was 56.7 psi, for the 0.2:1 weight ratio of portland cement to sediment the 28-day UCS was 290 psi, and the 28-day UCS for the formulation using a 0.3:1 weight ratio of portland cement to sediment was 682 psi. In the processes involving portland cement and another additive, the strength of the product increased as the proportion of portland cement increased. This is shown in Figures H1b and H2a for the portland cement with fly ash and the portland cement with Firmix processes, respectively. The data also showed increased strength with higher dosage of fly ash in the fly ash with lime process, Figure H3a. The process using Firmix as the setting agent showed increased strength for dosages above a 0.4:1 weight ratio of Firmix to sediment relative to the strength of the 0.4:1 product. However, the strength versus cure time curves for the 0.5:1 and the 0.6:1 weight ratios of Firmix to sediment were very similar and probably not significantly different.

22. Strength versus cure time curves were developed for the portland cement with WEST-P in order to complement the chemical leach studies conducted on Indiana Harbor sediment solidified with this process. The purpose of the polymer is to reduce the leachability of organic contaminants. As indicated in Figure H3b, the optimum polymer dosage was the 0.03:0.2:1 polymer:portland cement:sediment formulation.

23. The UCS data in Figures H1b and H2a show the relative effect of portland cement substitution using either fly ash or Firmix. The UCS for 0.2 portland cement:1 sediment and 0.3 portland cement:1 sediment formulations were compared with the UCS for the 0.1 fly ash:0.2 portland cement:1 sediment and the 0.1 Firmix:0.2 portland cement:1 sediment formulations. The data for this comparison are summarized in Table H2. It should noted that these formulations have a total additive-to-sediment weight ratio of 0.3:1. Substitution with fly ash produced a product with strength no better than that of the 0.2:1 portland cement process. These results indicate that there would be no economic advantage to using the fly ash used in this study as a portland cement substitute. To achieve a given USC, processes with and without fly ash

Table H2

Comparison of UCS for Various Portland Cement/Additive Formulations

Formulation	UCS, psi, for Indicated Cure Time, days 7	14	21	28
0.2:1 (PC:S)	126	215	268	290
0.3:1(PC:S)	190	567	640	682
0.1:0.2:1 (FM:PC:S)	168.3	226.2	319.1	507.9
0.1:0.2:1 (FA:PC:S)	82.4	254.8	270.3	312.8

* S = sediment.
PC = portland cement.
FM = Firmix.
FA = fly ash with lime.

require about the same amount of portland cement. Substitution with Firmix provided a product strength in between that for the 0.2:1 and 0.3:1 portland cement:sediment formulations. Thus, portland cement substitution with Firmix could reduce the cost of achieving a given strength criterion, depending on the relative cost of Firmix to portland cement.

24. The gain in strength with cure time that is evident in Figures H1-H3 showed that the sediment solidified in spite of the potential for interference from the various contaminants in the sediment. If the setting reactions responsible for solidification were not occurring, the products would not gain strength as they cured. This is a significant finding in light of what is known about the potential for interference (Jones et al. 1985). Oil and grease, in particular, can interfere with the development of a hardened mass (Clark, Colombo, and Neilson 1982). On-going research at WES on contaminants that interfere with solidification processes applied to industrial sludges has shown that the level of oil and grease in Indiana Harbor sediment can interfere with setting reactions. Initially, it was thought that solidification might not be technically feasible for Indiana Harbor sediment due to the oil and grease and other contaminants in the sediment. However, the steady gain in strength with cure time that was recorded for most of the process formulations showed that the contaminants in the sediment do not interfere with the setting reactions to the extent that the sediment cannot be solidified.

25. There is, however, evidence of retardation in set time. An often-used rule of thumb is that portland-cement-based processes achieve 95 percent of final strength in 28 days. With the exception of the portland cement curves, the strength versus cure time curves for the various processes showed that strength is continuing to develop beyond 28 days. For example, the setting of the Firmix process was slow compared with the rate normally encountered with clean sediments. Firmix usually reaches maximum strength in about 30 days with clean sediments.*

26. The range in product strengths, 48.5 to 682 psi, is indicative of the versatility and flexibility of solidification as a treatment process for immobilizing the contaminated solids in Indiana Harbor Sediment. For comparison, the UCS of concrete, clays of various consistency, and solidified industrial sludge are shown in Table H3. Solidified/stabilized Indiana Harbor

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* Personal communication, Mitchell Kaplan, Trident Engineering, Baltimore, Md.

Table H3

UCS of Various Materials

Material	Type	UCS, psi
Clay	Very soft	<3.5
	Soft	3.5-7
	Medium	7-14
	Stiff	14-28
	Hard	28-56
	Very hard	56
Concrete	Low strength	2,000
	Medium strength	5,000
Soil-like solidifed waste (Bartos and Palermo 1977)	FGD sludge	23-43
	Electroplating sludge	32
	Nickel/cadmium battery sludge	8
	Brine sludge	22
	Calcium fluoride sludge	25

sediments had strengths above the range normally associated with hard clay and solidified industrial sludge and below the range normally associated with soft concrete.

27. Permeability. The permeabilities of portland cement:sediment formulations of 0.1:1, 0.2:1, and 0.3:1 (weight ratios) were 1.4×10^{-5}, 3.9×10^{-6}, and 6.7×10^{-6} cm/sec, respectively. Permeability partly determines the rate at which contaminants can be released by chemical leaching. The permeabilities for the portland cement products are in the range of published values for solidified wastes (Bartos and Palmero 1977). The solidified dredged materials were more permeable than consolidated sediments (see leachate analysis, Appendix G), though there is disagreement in the literature as to whether these methods of permability analysis are applicable to solidified wastes.

28. Trafficability. The cone index (CI) for the portland cement and the fly ash with lime processes was measured at various cure times. These data are presented in Table H4. The use of CI as an indicator of trafficability is described in Army TM 5-330. A review of the CI requirements for landfill construction equipment showed that a CI greater than 75 psi will permit repeated passes of tracked vehicles and most all-wheel-drive vehicles. If traffic is limited to tracked bulldozers and loaders, a minimum CI of 50 psi is satisfactory. The CI data showed that all of the portland cement formulations except for the weakest (0.1:1 weight ratio of portland cement:sediment) were trafficable after 1 day. If traffic is limited to tracked vehicles, the lime with fly ash formulations were trafficable after 1 day. In considering trafficability, a conservative approach is recommended because field application of CI to solidified material has not been demonstrated.

29. In addition to being an index of trafficability, CI is a rapid and simple measurement that could be developed for field acceptance testing (Myers 1986). CI correlates to the amount of critical solidification agent in a process formulation, is indicative of the strength of the solidified product, and follows a predictable increase that is a function of cure time.

Chemical leach data

30. General. A summary of the analysis of 16 blanks is presented in Table H5. Table H5 lists the range, mean, standard deviation, limit of the 95-percent confidence interval for the mean, and detection limits for arsenic, cadmium, chromium, lead, zinc, and organic carbon. The blanks were generally near or below the chemical analytical detection limits. Arsenic and organic

Table H4

CI Versus Cure Time for Solidified/Stabilized Indiana Harbor Sediment*

	CI, psi,					
Process**	Day 1	Day 3	Day 7	Day 14	Day 21	Day 28
Portland Cement						
0.1 PC:1 Sed	-	32	59	133	258	294
0.2 PC:1 Sed	-	152	550	>750	>750	>750
0.3 PC:1 Sed	-	550	>750	>750	>750	>750
0.4 PC:1 Sed	-	>750	>750	>750	>750	>750
Lime with Fly Ash						
0.1 L:0.4 FA:1 Sed	80	131	190	404	436	492
0.1 L:0.5 FA:1 Sed	83	203	228	542	-	706
0.1 L:0.6 FA:1 Sed	151	220	385	708	-	>750

* Average of five determinations.

** Weight ratios of additive(s) to wet sediment.

PC = portland cement.
Sed = sediment.
L = lime.
FA = fly ash.

Table H5

Summary Statistics for Chemical Analysis of Blanks (N=16)

Statistic	As	Cd	Cr	Pb	Zn	OC*
Detection Limit	0.005	0.0001	0.001	0.001	0.030	1.0
Number of blanks with concentration below the detection limit	16	3	5	5	11	16
Range	<0.005	<0.0001 to 0.0010	<0.001 to 0.005	<0.001 to 0.006	<0.030 to 0.046	<1.0
Mean, mg/ℓ**	<0.005	0.00048	0.0019	0.0022	<0.021	<1.0
Standard deviation mg/ℓ	-	0.00027	0.0014	0.0017	0.0011	-
95% confidence interval	≤0.005	≤0.007	≤0.003	≤0.003	≤0.030	≤1.0

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* OC = organic carbon

** Values less than the detection limit were assigned a value of one half the detection limit.

Values below the detection limit excluded, n = 13.

carbon were below the detection limit in each blank. Zinc was detected in five of sixteen blanks. Cadmium, chromium, and lead, were above the detection limits in the majority of the blanks. Leachate samples with contaminant concentrations within the 95-percent confidence interval were reported as less than the 95-percent confidence limit. Except for cadmium, the 95-percent confidence interval determination used one half of the detection limit for values that were below the detection limit. Because most of the leachate samples were within the range of values reported for the cadmium blanks, determination of the 95-percent confidence interval for the cadmium blank excluded the below detection limit values.

31. For the liquid-solids ratios used in this study, the range in pH for a given process formulation was typically less than 0.5. Leachate pH as a function of liquid-solid ratio for selected processes is presented in Table H6. These data indicate that the liquid-solids ratio probably does not significantly affect interphase transfer through a pH effect.

32. Desorption isotherm data. The results from the serial, graded batch leach tests conducted on solidified/stabilized Indiana Harbor sediment are presented in Tables H7-H33. The tables are organized by process and process formulation. Each table contains data for one process formulation. The first column in each table lists the liquid-solids ratio. The remaining entries in each table list aqueous phase contaminant concentration C and the corresponding solid phase concentration q for five metals, and organic carbon (if analyzed). Differences in solid phase concentration for identical aqueous phase concentrations at the same liquid-solids ratio reflect slight differences in the amount of solids weighed for leach testing. The aqueous phase concentration C refers to the contaminant concentration in the filtered (0.45-μm) leachate.

33. Less than values for the aqueous phase concentration C were reported when the aqueous phase concentration was less than the detection limit (including blank if significant). The solid phase concentration was reported as a greater than value when C was below the detection limit. Most of the cadmium leachate concentrations were within the range of concentrations found in the blanks. Arsenic and zinc were sometimes below the detection limit and sometimes not, depending on the solidification/stabilization process and the additive dosage. Chromium and lead were above the detection limit in most of

Table H6

Variation in pH with Liquid-Solids Ratio For Solidified/Stabilized Indiana Harbor Sediment

Process	Liquid-Solids Ratio	pH
0.6 Firmix:1 sediment	100	9.71
	20	9.68
	10	9.62
	5	9.73
	2	10.02
0.05 WEST-P:0.5 Firmix:1 sediment	100	10.31
	20	10.26
	10	10.58
	5	10.47
	2	10.57
0.15 portland cement:0.15 fly ash: 1 sediment	100	10.34
	20	10.69
	10	10.85
	5	10.75
	2	10.80

Table H7

Desorption Isotherm Data for Portland Cement Formulation

0.1 PC:1 Sediment*

L/S ml/g	Arsenic C mg/ℓ	 q mg/kg	Cadmium C mg/ℓ	 q mg/kg	Chromium C mg/ℓ	 q mg/kg	Lead C mg/ℓ	 q mg/kg	Zinc C mg/ℓ	 q mg/kg	OC C mg/ℓ	 q mg/kg
100	0.006	13.71	<0.0007	>9.601	0.015	312.72	<0.003	>424.70	<0.030	>1991.7	13	10320.4
100	0.007	13.60	<0.0007	>9.600	0.013	312.90	<0.003	>424.70	<0.030	>1991.7	13	10308.9
100	<0.005	>13.80	<0.0007	>9.601	0.015	312.71	<0.003	>424.70	<0.030	>1991.7	12	10414.5
20	0.009	14.12	<0.0007	>9.656	0.030	313.44	<0.003	>424.94	<0.030	>1994.1	55	10506.1
20	0.008	14.14	<0.0007	>9.656	0.043	313.18	0.004	424.92	<0.030	>1994.1	56	10486.3
20	0.009	14.12	<0.0007	>9.656	0.034	313.36	<0.003	>424.94	<0.030	>1994.1	53	10546.9
10	0.010	14.20	<0.0007	>9.663	0.057	313.45	0.011	424.89	<0.030	>1994.4	92	10685.2
10	0.012	14.18	<0.0007	>9.663	0.053	313.49	0.010	424.90	0.032	1994.4	95	10655.4
10	0.012	14.18	<0.0007	>9.663	0.046	313.56	0.010	424.90	0.037	1994.3	98	10625.1
2	0.015	14.27	<0.0007	>9.669	0.025	313.95	0.014	424.97	0.097	1994.5	322	10961.4
2	0.016	14.27	<0.0007	>9.668	0.019	313.97	0.017	424.97	0.129	1994.4	331	10943.7
2	0.017	14.27	<0.0007	>9.669	0.013	313.98	0.018	424.96	0.113	1994.5	404	10797.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H8

Desorption Isotherm Data for Portland Cement Formulation

0.2 PC:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>12.61	<0.0007	>8.791	<0.003	>287.90	0.007	389.31	<0.030	>1825.0	13	9350.1
100	<0.005	>12.61	0.0014	8.722	0.011	287.11	0.006	389.41	<0.030	>1825.0	13	9350.1
100	<0.005	>12.60	0.0014	8.721	0.012	287.01	0.007	389.30	<0.030	>1825.0	11	9543.6
20	<0.005	>13.00	0.0049	8.762	0.008	287.88	0.027	389.46	0.043	1827.1	42	9797.3
20	<0.005	>13.00	0.0015	8.830	0.010	287.84	0.021	389.58	0.037	1827.3	42	9797.2
20	<0.005	>13.00	0.0017	8.826	0.008	287.88	0.024	389.52	<0.030	>1827.4	40	9837.4
10	<0.005	>13.05	0.0011	8.849	0.010	287.92	0.037	389.63	0.033	1827.7	71	9926.3
10	<0.005	>13.05	0.0015	8.845	0.008	287.94	0.044	389.56	0.030	1827.7	68	9956.3
10	<0.005	>13.05	<0.0007	>8.853	0.010	287.92	0.035	389.65	0.035	1827.6	71	99[illegible].1
2	0.014	13.07	<0.0007	>8.859	0.006	287.99	0.083	389.83	0.047	1827.9	206	10224.1
2	0.013	13.07	<0.0007	>8.859	0.009	287.99	0.094	389.81	0.059	1827.9	211	10214.1
2	0.014	13.07	<0.0007	>8.859	0.007	287.99	0.085	389.83	0.054	1827.9	207	10222.[illegible]

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H9

Desorption Isotherm Data for Portland Cement Formulation

0.3 PC:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.58	<0.0007	>8.113	0.012	265.09	0.009	359.0	0.030	1684.2	9	8934
100	<0.005	>11.57	<0.0007	>8.112	0.008	265.47	0.007	359.2	<0.030	>1684.2	9	8919
100	<0.005	>11.57	<0.0010	>8.082	0.012	265.08	0.007	359.2	0.030	1684.2	7	9120
20	<0.005	>11.97	<0.0007	>8.168	0.007	265.97	0.065	358.6	0.056	1686.1	41	9000
20	<0.005	>11.97	<0.0007	>8.168	0.010	265.91	0.056	358.8	0.055	1686.1	35	9119
20	<0.005	>11.97	<0.0007	>8.168	0.006	265.99	0.065	358.6	0.050	1686.2	36	9099
10	<0.005	>12.02	<0.0007	>8.175	0.011	265.98	0.073	359.2	0.049	1686.7	67	9149
10	<0.005	>12.02	<0.0007	>8.175	0.008	266.01	0.079	359.1	0.059	1686.6	67	9150
10	<0.005	>12.02	<0.0007	>8.175	0.009	266.00	0.079	359.1	0.056	1686.6	67	9150
2	0.011	12.05	0.0010	8.180	0.011	266.06	0.096	359.7	0.069	1686.0	210	9399
2	0.013	12.05	<0.0007	>8.181	0.013	266.05	0.081	359.7	0.074	1687.0	215	9389
2	0.013	12.05	<0.0007	>8.181	0.011	266.06	0.147	359.6	0.085	1687.0	210	9399

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H10

Desorption Isotherm Data for Portland Cement Formulation

0.4 PC:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>10.71	<0.0007	>7.527	0.015	245.75	0.014	332.75	0.042	1562.3	5	8617.4
100	<0.005	>10.71	<0.0007	>7.528	0.013	245.95	0.016	332.56	0.037	1562.8	5	8620.3
100	<0.005	>10.71	<0.0007	>7.527	0.016	245.65	0.014	332.76	0.046	1561.9	5	8619.3
20	<0.005	>11.11	<0.0007	>7.583	0.014	246.80	0.063	332.89	0.072	1565.1	32	8476.7
20	<0.005	>11.11	<0.0007	>7.583	0.014	246.80	0.078	332.59	0.067	1565.2	32	8476.4
20	<0.005	>11.11	<0.0007	>7.583	0.008	246.92	0.078	332.59	0.066	1565.2	39	8337.4
10	<0.005	>11.16	<0.0007	>7.590	0.008	246.98	0.087	333.28	0.076	1565.8	52	8596.5
10	<0.005	>11.16	<0.0007	>7.590	0.010	246.96	0.084	333.31	0.067	1565.8	55	8566.8
10	<0.005	>11.16	<0.0007	>7.590	0.009	246.97	0.115	333.00	0.075	1565.8	55	8566.6
2	0.007	11.20	<0.0007	>7.596	0.010	247.03	0.105	333.94	0.067	1566.4	187	8742.4
2	0.007	11.20	<0.0007	>7.596	0.017	247.01	0.115	333.92	0.073	1566.4	188	8740.7
2	0.008	11.19	<0.0007	>7.596	0.017	247.01	0.102	333.95	0.070	1566.4	192	8732.4

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H11

Desorption Isotherm Data for Fly Ash and Portland Cement

0.2 Fly Ash:0.1 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.57	<0.0007	8.112	0.018	264.37	0.007	359.79	<0.030	>1684.2	13	8518.6
100	<0.005	>11.57	<0.0007	8.112	0.019	264.28	0.009	359.59	<0.030	>1684.2	11	8720.8
100	<0.005	>11.57	<0.0007	8.112	0.023	263.88	0.010	359.49	0.042	1683.0	15	8321.6
20	0.007	11.93	<0.0007	8.168	0.053	265.03	0.015	359.71	<0.030	>1686.6	52	8779.0
20	0.006	11.95	<0.0007	8.168	0.036	265.37	0.010	359.81	<0.030	>1686.6	50	8819.2
20	0.007	11.93	<0.0007	8.168	0.040	265.29	0.013	359.75	<0.030	>1686.6	51	8798.8
10	0.010	11.97	<0.0007	8.175	0.042	265.66	0.012	359.83	<0.030	>1686.9	85	8968.7
10	0.009	11.98	<0.0007	8.175	0.041	265.67	0.012	359.83	<0.030	>1686.9	82	8998.6
10	0.011	11.96	<0.0007	8.175	0.046	265.62	0.010	359.85	0.032	1686.9	84	8978.7
5	0.012	12.01	<0.0007	8.179	0.038	265.89	0.013	359.86	0.038	1687.0	145	9093.6
5	0.013	12.01	<0.0007	8.179	0.025	265.95	0.015	359.85	0.039	1687.0	144	9098.7
5	0.012	12.01	<0.0007	8.179	0.026	265.95	0.015	359.85	0.039	1687.0	142	9108.7
2	0.020	12.03	<0.0007	8.181	0.026	266.02	0.018	359.87	0.051	1687.1	302	9214.6
2	0.019	12.04	<0.0007	8.181	0.005	266.07	0.021	359.86	0.053	1687.1	306	9206.6
2	0.022	12.03	<0.0007	8.181	0.004	266.07	0.018	359.87	0.052	1687.1	306	9206.6

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H12

Desorption Isotherm Data for Fly Ash and Portland Cement

0.1 Fly Ash:0.2 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.58	<0.0007	>8.113	0.019	264.38	0.004	359.49	<0.030	>1684.2	14	8425.6
100	<0.005	>11.57	<0.0007	>8.112	0.012	265.08	0.008	359.09	<0.030	>1684.2	12	8622.2
100	<0.005	>11.58	<0.0007	>8.113	0.015	264.78	0.004	359.49	<0.030	>1684.2	13	8525.1
20	<0.005	>11.97	<0.0007	>8.168	0.020	265.71	0.015	359.59	<0.030	>1686.6	46	8899.5
20	<0.005	>11.97	<0.0007	>8.168	0.027	265.57	0.014	359.61	<0.030	>1686.6	48	8859.4
20	<0.005	>11.97	<0.0007	>8.168	0.028	265.55	0.013	359.63	<0.030	>1686.6	49	8839.8
10	0.006	12.01	<0.0007	>8.175	0.023	265.86	0.015	359.74	<0.030	>1686.9	80	9019.0
10	0.006	12.01	<0.0007	>8.175	0.021	265.88	0.016	359.73	<0.030	>1686.9	78	9038.9
10	0.005	12.02	<0.0007	>8.175	0.024	265.85	0.022	359.67	<0.030	>1686.9	79	9029.1
5	0.009	12.03	<0.0007	>8.179	0.023	265.97	0.026	359.76	<0.030	>1687.0	100	9318.7
5	0.010	12.02	<0.0007	>8.179	0.027	265.95	0.028	359.75	<0.030	>1687.0	97	9333.6
5	0.009	12.03	<0.0007	>8.179	0.023	265.97	0.028	359.75	<0.030	>1687.0	94	9348.7
2	0.015	12.04	<0.0007	>8.181	0.015	266.05	0.036	359.82	<0.030	>1687.1	250	9318.6
2	0.015	12.04	<0.0007	>8.181	0.021	266.04	0.042	359.81	<0.030	>1687.1	255	9308.6
2	0.014	12.05	<0.0007	>8.181	0.029	266.02	0.032	359.83	<0.030	>1687.1	260	9298.6

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H13

Desorption Isotherm Data for Fly Ash and Portland Cement

0.15 Fly Ash:0.15 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.57	<0.0007	>8.112	<0.003	>265.87	0.003	359.59	<0.030	>1684.2	12	8621.0
100	<0.005	>11.57	<0.0007	>8.112	<0.003	>265.77	0.012	358.69	<0.030	>1684.2	10	8820.6
100	<0.005	>11.57	<0.0007	>8.112	0.023	263.78	0.013	358.59	<0.030	>1684.2	11	8719.7
20	<0.005	>11.97	<0.0007	>8.168	0.035	265.37	0.019	359.51	<0.030	>1686.6	47	8879.0
20	<0.005	>11.97	<0.0007	>8.168	0.036	265.35	0.021	359.47	<0.030	>1686.6	42	8979.4
20	<0.005	>11.97	<0.0007	>8.168	0.035	265.37	0.024	359.41	<0.030	>1686.6	40	9019.1
10	0.006	12.01	<0.0007	>8.175	0.030	265.77	0.025	359.64	<0.030	>1686.9	70	9118.7
10	0.006	12.01	<0.0007	>8.175	0.033	265.74	0.010	359.79	<0.030	>1686.9	71	9108.7
10	<0.005	>12.02	<0.0007	>8.175	0.039	265.68	0.027	359.62	<0.030	>1686.9	71	9108.7
5	0.010	12.02	<0.0007	>8.179	0.015	266.00	0.019	359.80	<0.030	>1687.0	111	9263.8
5	0.010	12.02	<0.0007	>8.179	0.015	266.00	0.028	359.75	<0.030	>1687.0	111	9263.8
5	0.010	12.02	<0.0007	>8.179	0.022	265.96	0.029	359.75	<0.030	>1687.0	110	9268.7
2	0.013	12.05	<0.0007	>8.181	0.010	266.05	0.037	359.82	<0.030	>1687.1	277	9264.6
2	0.012	12.05	<0.0007	>8.181	0.015	266.04	0.034	359.82	<0.030	>1687.1	276	9266.6
2	0.014	12.05	<0.0007	>8.181	0.011	266.05	0.035	359.82	<0.030	>1687.1	280	9258.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H14

Desorption Isotherm Data for Sodium Silicate, Fly Ash, and Portland Cement Process

0.05 NaSi:0.1 Fly Ash:0.1 Cement:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>12.06	<0.0007	>8.442	0.010	276.0	0.017	372.70	<0.030	>1752.2
100	<0.005	>12.06	<0.0007	>8.442	0.012	275.8	0.014	373.00	<0.030	>1752.2
100	<0.005	>12.06	<0.0007	>8.442	0.013	275.7	0.016	372.80	<0.030	>1752.2
20	<0.005	>12.46	<0.0007	>8.498	0.008	276.7	0.094	372.52	0.040	1754.4
20	<0.005	>12.46	<0.0007	>8.498	0.008	276.7	0.091	372.58	0.047	1754.3
20	<0.005	>12.46	<0.0007	>8.498	0.008	276.7	0.087	372.66	0.043	1754.3
10	<0.005	>12.51	<0.0007	>8.505	0.009	276.7	0.120	373.20	0.035	1754.9
10	<0.005	>12.51	<0.0007	>8.505	0.009	276.7	0.096	373.44	0.045	1754.8
10	<0.005	>12.51	<0.0007	>8.505	0.011	276.7	0.111	373.29	0.067	1754.5
2	0.006	12.55	<0.0007	>8.511	0.011	276.8	0.115	374.17	0.058	1755.1
2	0.007	12.55	<0.0007	>8.511	0.011	276.8	0.010	374.38	0.070	1755.1
2	0.006	12.55	<0.0007	>8.511	0.008	276.8	0.009	374.38	0.065	1755.1

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H15

Desorption Isotherm Data for Sodium Silicate, Fly Ash, and Portland Cement Process

0.05 NaSi:0.1 Fly Ash:0.2 Cement:1 Sediment*

L/S ml/g	Arsenic C mg/ℓ	 q mg/kg	Cadmium C mg/ℓ	 q mg/kg	Chromium C mg/ℓ	 q mg/kg	Lead C mg/ℓ	 q mg/kg	Zinc C mg/ℓ	 q mg/kg
100	<0.005	>11.13	<0.0007	>7.814	0.019	254.7	0.006	346.19	<0.030	>1622.8
100	<0.005	>11.13	0.0008	7.804	0.015	255.1	0.005	346.29	<0.030	>1622.8
100	<0.005	>11.13	<0.0007	>7.814	0.016	255.0	0.007	346.09	<0.030	>1622.8
20	<0.005	>11.53	<0.0007	>7.870	0.025	255.9	0.024	346.31	<0.030	>1625.2
20	<0.005	>11.53	<0.0007	>7.870	0.022	256.0	0.023	346.33	0.039	1625.0
20	<0.005	>11.53	<0.0007	>7.870	0.021	256.0	0.024	346.31	<0.030	>1625.2
10	<0.005	>11.58	<0.0007	>7.877	0.020	256.2	0.036	346.43	<0.030	>1625.5
10	<0.005	>11.58	<0.0007	>7.877	0.018	256.2	0.042	346.37	0.040	1625.4
10	<0.005	>11.58	<0.0007	>7.877	0.018	256.2	0.018	346.61	<0.030	>1625.5
2	0.015	11.60	0.0008	7.883	0.058	256.3	0.058	346.67	0.042	1625.7
2	0.017	11.60	0.0007	7.883	0.049	256.3	0.049	346.69	0.056	1625.6
2	0.018	11.60	0.0008	7.883	0.053	256.3	0.053	346.68	0.062	1625.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H16

Desorption Isotherm Data for Sodium Silicate, Fly Ash, and Portland Cement Process

0.05 NaSi:0.25 Fly Ash:0.25 Cement:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	> 9.63	<0.0007	>6.793	0.014	221.97	0.009	300.96	<0.030	>1412.1
100	<0.005	> 9.63	<0.0007	>6.793	0.016	221.77	0.003	301.56	<0.030	>1412.1
100	<0.005	> 9.63	<0.0007	>6.793	0.013	222.07	0.004	301.46	<0.030	>1412.1
20	<0.005	>10.03	<0.0007	>6.849	0.026	222.69	0.019	301.48	<0.030	>1414.5
20	<0.005	>10.03	<0.0007	>6.849	0.022	222.77	0.012	301.62	<0.030	>1414.5
20	<0.005	>10.03	<0.0007	>6.849	0.025	222.71	0.014	301.58	<0.030	>1414.5
10	<0.005	>10.08	<0.0007	>6.856	0.022	222.97	0.020	301.66	<0.030	>1414.8
10	<0.005	>10.08	<0.0007	>6.856	0.028	222.91	0.022	301.64	<0.030	>1414.8
10	<0.005	>10.08	<0.0007	>6.856	0.028	222.91	0.020	301.66	0.036	1414.8
2	0.016	10.09	<0.0007	>6.861	0.067	223.04	0.063	301.73	0.044	1415.0
2	0.017	10.09	<0.0007	>6.861	0.072	223.03	0.050	301.76	0.036	1415.1
2	0.017	10.09	<0.0007	>6.861	0.075	223.02	0.054	301.75	0.044	1415.0

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H17

Desorption Isotherm Data for Sodium Silicate and Portland Cement Process

0.05 NaSi:0.25 Cement:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	< 0.005	> 11.57	< 0.0007	> 8.112	0.017	264.58	0.010	358.89	< 0.030	> 1684.2
100	< 0.005	> 11.57	< 0.0007	> 8.112	0.016	264.68	0.041	355.80	< 0.030	> 1684.2
100	< 0.005	> 11.57	< 0.0007	> 8.112	0.016	264.68	0.041	355.80	< 0.030	> 1684.2
20	< 0.005	> 11.97	< 0.0007	> 8.168	0.011	265.89	0.043	359.03	0.041	1686.4
20	< 0.005	> 11.97	< 0.0007	> 8.168	0.011	265.89	0.065	358.59	0.051	1686.2
20	< 0.005	> 11.97	< 0.0007	> 8.168	0.010	265.91	0.064	358.61	0.035	1686.5
10	< 0.005	> 12.02	< 0.0007	> 8.175	0.012	265.97	0.067	359.22	0.045	1686.7
10	< 0.005	> 12.02	< 0.0007	> 8.175	0.011	265.98	0.068	359.21	0.044	1686.7
10	< 0.005	> 12.02	< 0.0007	> 8.175	0.011	265.98	0.085	359.04	0.046	1686.7
2	0.007	12.06	< 0.0007	> 8.181	0.020	266.04	0.121	359.65	0.058	1687.1
2	0.007	12.06	< 0.0007	> 8.181	0.017	266.04	0.215	359.46	0.052	1687.1
2	0.006	12.06	< 0.0007	> 8.181	0.013	266.05	0.107	359.68	0.053	1687.1

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H18

Desorption Isotherm Data for Sodium Silicate and Portland Cement Process

0.05 NaSi:0.5 Cement:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	< 0.005	> 9.63	0.0008	6.783	0.015	221.87	0.012	300.66	< 0.030	> 1412.1
100	< 0.005	> 9.63	< 0.0007	> 6.793	0.012	222.17	0.013	300.56	< 0.030	> 1412.1
100	< 0.005	> 9.63	< 0.0007	> 6.793	0.012	222.17	0.014	300.46	< 0.030	> 1412.1
20	< 0.005	> 10.03	< 0.0007	> 6.849	0.016	222.89	0.064	300.58	0.052	1414.1
20	< 0.005	> 10.03	< 0.0007	> 6.849	0.008	223.05	0.061	300.64	0.041	1414.3
20	< 0.005	> 10.03	< 0.0007	> 6.849	0.010	223.01	0.072	300.42	0.037	1414.4
10	< 0.005	> 10.08	< 0.0007	> 6.856	0.006	223.13	0.088	300.98	0.036	1414.8
10	< 0.005	> 10.08	< 0.0007	> 6.856	0.010	223.09	0.079	301.07	0.044	1414.7
10	0.005	10.08	< 0.0007	> 6.856	0.008	223.11	0.063	301.23	0.042	1414.7
2	0.009	10.11	< 0.0007	> 6.861	0.010	223.15	0.021	301.82	0.043	1415.0
2	0.010	10.11	< 0.0007	> 6.861	0.013	223.15	0.023	301.81	0.043	1415.0
2	0.010	10.11	< 0.0007	> 6.861	0.014	223.15	0.008	301.84	0.049	1415.0

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H19

Desorption Isotherm Data for Firmex and Portland Cement

0.2 Firmex 0.1 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.58	<0.0007	>8.112	0.031	262.99	0.011	358.80	<0.030	>1684.2	7	9121.4
100	<0.005	>11.58	<0.0007	>8.113	0.031	262.99	0.008	359.10	<0.030	>1684.2	8	9022.6
100	<0.005	>11.57	<0.0007	>8.112	0.023	263.78	0.011	358.79	<0.030	>1684.2	7	9120.0
20	<0.005	>11.97	<0.0007	>8.168	0.045	265.17	0.017	359.55	<0.030	>1686.6	33	9158.9
20	<0.005	>11.97	<0.0007	>8.168	0.035	265.37	0.015	359.59	<0.030	>1686.6	31	9199.0
20	<0.005	>11.97	<0.0007	>8.168	0.030	265.47	0.018	359.53	<0.030	>1686.6	34	9139.0
10	<0.005	>12.02	<0.0007	>8.175	0.039	265.68	0.019	359.70	<0.030	>1686.9	53	9288.6
10	<0.005	>12.02	<0.0007	>8.175	0.044	265.63	0.021	359.68	<0.030	>1686.9	54	9278.8
10	<0.005	>12.02	<0.0007	>8.174	0.044	265.63	0.012	359.77	<0.030	>1686.9	53	9289.0
5	0.006	12.04	<0.0007	>8.179	0.024	265.95	0.015	359.82	<0.030	>1687.0	93	9353.7
5	0.008	12.03	<0.0007	>8.179	0.024	265.95	0.017	359.81	<0.030	>1687.0	88	9378.6
5	0.006	12.04	<0.0007	>8.179	0.027	265.94	0.019	359.80	<0.030	>1687.0	94	9348.7
2	0.007	12.06	<0.0007	>8.181	0.010	266.05	0.017	359.86	<0.030	>1687.1	230	9358.6
2	0.008	12.06	<0.0007	>8.181	0.008	266.06	0.022	359.85	<0.030	>1687.1	229	9360.6
2	0.008	12.06	<0.0007	>8.181	0.012	266.05	0.020	359.85	<0.030	>1687.1	227	9364.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H20

Desorption Isotherm Data for Firmex and Portland Cement

0.1 Firmex:0.2 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.58	<0.0007	>8.113	0.009	265.18	0.005	359.39	<0.030	>1684.2	12	8624.6
100	<0.005	>11.58	<0.0007	>8.113	0.014	264.68	0.007	359.20	<0.030	>1684.2	13	8526.3
100	<0.005	>11.58	<0.0007	>8.113	0.014	264.68	0.005	359.40	<0.030	>1684.2	9	8924.8
20	<0.005	>11.97	<0.0007	>8.168	0.016	265.75	0.013	359.63	<0.030	>1686.6	37	9079.9
20	<0.005	>11.97	<0.0007	>8.168	0.025	265.57	0.012	359.65	<0.030	>1686.6	37	9079.2
20	<0.005	>11.97	<0.0007	>8.168	0.020	265.67	0.013	359.63	<0.030	>1686.6	36	9098.6
10	<0.005	>12.02	<0.0007	>8.175	0.021	265.86	0.018	359.71	<0.030	>1686.9	56	9258.5
10	<0.005	>12.02	<0.0007	>8.175	0.026	265.81	0.019	359.70	<0.030	>1686.9	58	9238.4
10	<0.005	>12.02	<0.0007	>8.175	0.019	265.88	0.016	359.73	<0.030	>1686.9	59	9228.7
5	0.006	12.04	<0.0007	>8.179	0.018	265.98	0.024	359.77	<0.030	>1687.0	95	9343.7
5	0.006	12.04	<0.0007	>8.179	0.018	265.98	0.023	359.78	<0.030	>1687.0	100	9318.6
5	0.006	12.04	<0.0007	>8.179	0.018	265.98	0.028	359.75	<0.030	>1687.0	100	9318.7
2	0.009	12.06	<0.0007	>8.181	0.008	266.06	0.033	359.83	<0.030	>1687.1	251	9316.6
2	0.011	12.05	<0.0007	>8.181	0.011	266.05	0.039	359.81	<0.030	>1687.1	250	9318.6
2	0.008	12.06	<0.0007	>8.181	0.005	266.06	0.032	359.83	<0.030	>1687.1	247	9324.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H21

Desorption Isotherm Data for Firmex and Portland Cement

0.15 Firmex:0.15 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>11.57	<0.0007	>8.112	0.014	264.68	0.004	359.49	<0.030	>1684.2	4	9419.4
100	<0.005	>11.57	<0.0007	>8.112	0.022	263.88	0.003	359.59	<0.030	>1684.2	3	9518.9
100	<0.005	>11.58	<0.0007	>8.112	0.014	264.68	0.007	359.19	<0.030	>1684.2	4	9420.2
20	<0.005	>11.97	<0.0007	>8.168	0.022	265.63	0.011	359.67	<0.030	>1686.6	34	9139.1
20	<0.005	>11.97	<0.0007	>8.168	0.020	265.67	0.011	359.67	<0.030	>1686.6	35	9118.9
20	<0.005	>11.97	<0.0007	>8.168	0.021	265.65	0.009	359.71	<0.030	>1686.6	35	9119.0
10	<0.005	>12.02	<0.0007	>8.175	0.018	265.89	0.015	359.74	<0.030	>1686.9	63	9188.6
10	<0.005	>12.02	<0.0007	>8.175	0.021	265.86	0.011	359.78	<0.030	>1686.9	63	9188.7
10	<0.005	>12.02	<0.0007	>8.175	0.019	265.88	0.014	359.75	<0.030	>1686.9	62	9198.7
5	0.005	12.05	<0.0007	>8.179	0.017	265.99	0.018	359.80	<0.030	>1687.0	95	9343.7
5	0.005	12.05	<0.0007	>8.179	0.017	265.99	0.018	359.80	<0.030	>1687.0	100	9318.7
5	0.005	12.05	<0.0007	>8.179	0.016	265.99	0.018	359.80	<0.030	>1687.0	101	9313.7
2	0.008	12.06	<0.0007	>8.181	0.005	266.06	0.021	359.85	<0.030	>1687.1	248	9322.6
2	0.007	12.06	<0.0007	>8.181	0.005	266.06	0.002	359.89	<0.030	>1687.1	240	9338.6
2	0.008	12.06	<0.0007	>8.181	0.004	266.07	0.021	359.85	<0.030	>1687.1	245	9328.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H22

Desorption Isotherm Data for Lime with Fly Ash Process

0.4 Fly Ash:0.1 Lime:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	> 9.98	<0.0007	7.028	0.014	229.60	0.016	310.58	0.043	1459.2	10	7531.0
100	<0.005	> 9.98	<0.0007	7.027	0.016	229.39	0.019	310.27	0.041	1459.3	10	7523.2
100	<0.005	> 9.98	<0.0007	7.028	0.016	229.39	0.018	310.37	0.033	1460.1	9	7624.3
20	<0.005	>10.37	<0.0007	7.083	0.011	230.60	0.065	310.86	0.103	1461.3	30	7916.6
20	<0.005	>10.37	<0.0007	7.083	0.011	230.60	0.116	309.84	0.102	1461.4	33	7858.6
20	<0.005	>10.37	<0.0007	7.083	0.012	230.58	0.084	310.48	0.099	1461.4	29	7936.5
10	<0.005	>10.42	<0.0007	7.090	0.009	230.71	0.117	310.99	0.122	1462.2	53	7988.0
10	<0.005	>10.42	<0.0007	7.090	0.010	230.70	0.114	311.02	0.131	1462.1	50	8016.6
10	<0.005	>10.42	<0.0007	7.090	0.009	230.71	0.022	311.94	0.135	1462.0	49	8026.5
2	0.015	10.44	<0.0007	7.095	0.009	230.77	0.165	311.83	0.131	1463.1	167	8182.3
2	0.014	10.44	<0.0007	7.095	0.009	230.77	0.130	311.90	0.165	1463.1	178	8160.5
2	0.013	10.45	<0.0007	7.095	0.009	230.77	0.101	311.95	0.179	1463.0	176	8164.3

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H23

Desorption Isotherm Data for Lime with Fly Ash Process

0.5 Fly Ash:0.1 Lime:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	< 0.005	> 9.32	< 0.0007	> 6.581	0.009	215.56	0.006	291.91	0.071	1364.2	20	5999.8
100	< 0.005	> 9.32	< 0.0007	> 6.581	0.011	215.36	0.017	290.83	0.056	1365.7	5	7487.4
100	< 0.005	> 9.31	< 0.0007	> 6.580	0.010	215.45	0.015	291.00	0.060	1365.3	5	7481.0
20	< 0.005	> 9.71	< 0.0007	> 6.636	0.006	216.17	0.103	290.44	0.140	1368.5	23	7520.6
20	< 0.005	> 9.71	< 0.0007	> 6.636	0.004	216.21	0.127	289.96	0.125	1368.8	23	7520.4
20	< 0.005	> 9.71	< 0.0007	> 6.636	0.006	216.17	0.101	290.49	0.139	1368.5	25	7482.7
10	< 0.005	> 9.76	< 0.0007	> 6.643	0.005	216.22	0.047	290.03	0.150	1369.8	42	7560.7
10	< 0.005	> 9.76	< 0.0007	> 6.643	0.006	216.21	0.135	291.15	0.142	1369.8	42	7560.1
10	< 0.005	> 9.76	< 0.0007	> 6.643	0.007	216.20	0.116	291.34	0.161	1369.6	43	7550.4
2	0.013	9.79	< 0.0007	> 6.649	0.006	216.24	0.193	292.11	0.172	1370.9	148	7684.4
2	0.014	9.78	< 0.0007	> 6.649	0.007	216.24	0.228	292.04	0.165	1370.9	156	7668.4
2	0.014	9.78	< 0.0007	> 6.649	0.007	216.24	0.199	292.10	0.190	1370.9	154	7672.4

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H24

Desorption Isotherm Data for Lime with Fly Ash Process

0.6 Fly Ash:0.1 Lime:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>8.73	<0.0007	>6.186	0.008	202.85	0.028	272.38	0.076	1282.5	4	7107.6
100	<0.005	>8.74	<0.0007	>6.187	0.008	202.86	0.037	271.53	0.065	1283.6	5	7013.5
100	<0.005	>8.74	<0.0007	>6.187	0.007	202.96	0.034	271.83	0.069	1283.3	6	6916.5
20	<0.005	>9.13	<0.0007	>6.242	0.004	203.41	0.136	272.47	0.169	1286.7	22	7068.1
20	<0.005	>9.13	<0.0007	>6.242	0.004	203.41	0.187	271.45	0.171	1286.7	23	7047.9
20	<0.005	>9.13	<0.0007	>6.242	<0.003	>203.43	0.113	272.93	0.173	1286.6	23	7048.2
10	<0.005	>9.18	<0.0007	>6.249	0.006	203.41	0.179	273.40	0.172	1288.4	42	7088.6
10	<0.005	>9.18	<0.0007	>6.249	<0.003	>203.44	0.193	273.25	0.173	1288.3	43	7077.8
10	<0.005	>9.18	<0.0007	>6.249	0.004	203.43	0.150	273.69	0.189	1288.2	43	7078.2
2	0.017	9.20	<0.0007	>6.255	0.004	203.44	0.214	274.76	0.192	1289.7	157	7194.0
2	0.017	9.20	<0.0007	>6.255	0.005	203.44	0.349	274.49	0.185	1289.7	150	7207.7
2	0.018	9.20	<0.0007	>6.255	0.004	203.44	0.186	274.81	0.217	1289.6	146	7215.6

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H25

Desorption Isotherm Data for Firmex Process

0.4 Firmex:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	0.014	9.80	0.0017	7.426	0.006	246.44	<0.003	>333.85	<0.03	>1563.5	10	8109.3
100	0.011	10.04	0.0015	7.437	0.010	245.98	<0.003	>333.83	<0.03	>1563.3	10	8050.3
100	0.012	10.01	0.0015	7.447	0.007	246.34	<0.003	>333.85	<0.03	>1563.5	10	8116.4
20	0.017	10.87	0.0020	7.557	0.015	246.74	0.006	334.03	<0.03	>1565.9	37	8377.4
20	0.016	10.89	0.0018	7.561	0.022	246.60	0.006	334.03	<0.03	>1565.9	36	8397.2
20	0.017	10.87	0.0015	7.567	0.017	246.70	0.005	334.05	<0.03	>1565.9	36	8398.2
10	0.020	11.01	0.0050	7.547	0.028	246.76	0.006	334.09	<0.03	>1566.2	61	8508.3
10	0.020	11.01	0.0017	7.580	0.028	246.76	0.007	334.08	<0.03	>1566.2	60	8516.2
10	0.019	11.02	0.0010	7.587	0.027	246.77	0.005	334.10	<0.03	>1566.2	61	8506.2
5	0.028	11.07	0.0013	7.590	0.035	246.87	0.006	334.12	<0.03	>1566.4	84	8696.0
5	0.032	11.05	0.0007	7.593	0.036	246.86	0.006	334.12	<0.03	>1566.4	81	8711.6
5	0.033	11.04	0.0007	7.593	0.034	246.87	0.007	334.12	<0.03	>1566.4	84	8696.3
2	0.044	11.12	0.0009	7.595	0.020	247.00	0.002	334.15	<0.03	>1566.5	232	8653.0
2	0.041	11.13	0.0007	7.596	0.018	247.01	0.007	334.14	<0.03	>1566.5	237	8642.6
						247.00						

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H26

Desorption Isotherm Data for Firmex Process

0.5 Firmex:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	0.011	9.35	<0.0007	>7.026	0.006	230.17	<0.003	>311.85	<0.03	>1460.3	6	7905.9
100	0.010	9.46	<0.0007	>7.026	0.010	229.77	<0.003	>311.85	<0.03	>1460.4	7	7809.2
100	0.012	9.28	<0.0007	>7.027	0.007	230.09	0.006	311.56	<0.03	>1460.4	7	7820.4
20	0.015	10.17	<0.0007	>7.083	0.020	230.38	0.004	312.08	<0.03	>1462.8	38	7754.9
20	0.015	10.17	<0.0007	>7.083	0.017	230.44	0.004	312.08	<0.03	>1462.8	36	7795.8
20	0.015	10.17	<0.0007	>7.083	0.023	230.32	0.005	312.06	<0.03	>1462.8	34	7836.5
10	0.019	10.28	<0.0007	>7.090	0.030	230.48	0.005	312.11	<0.03	>1463.1	58	7935.8
10	0.017	10.30	<0.0007	>7.090	0.031	230.47	0.005	312.11	<0.03	>1463.1	58	7935.4
10	0.018	10.29	<0.0007	>7.090	0.025	230.53	0.005	312.11	<0.03	>1463.1	59	7926.7
5	0.023	10.36	<0.0007	>7.093	0.030	230.63	0.006	312.13	<0.03	>1463.2	94	8045.9
5	0.024	10.35	<0.0007	>7.093	0.030	230.63	0.004	312.14	<0.03	>1463.2	96	8036.4
5	0.024	10.35	<0.0007	>7.093	0.030	230.63	0.004	312.14	<0.03	>1463.2	94	8046.2
2	0.041	10.39	<0.0007	>7.095	0.028	230.73	<0.003	>312.15	<0.03	>1463.3	212	8092.1
2	0.035	10.40	<0.0007	>7.095	0.029	230.72	0.004	312.15	<0.03	>1463.3	210	8095.7
2	0.035	10.40	<0.0007	>7.095	0.028	230.73	0.004	312.15	<0.03	>1463.3	214	8088.3

* PC = Portland cement
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H27

Desorption Isotherm Data for Firmex Process

0.6 Firmex:1 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	0.009	8.91	<0.0007	>6.580	0.014	214.84	0.005	292.00	<0.03	>1368.2	10	6976.0
100	0.008	9.02	<0.0007	>6.580	0.001	216.15	<0.003	>292.20	<0.03	>1368.3	11	6884.4
100	0.009	8.91	<0.0007	>6.580	0.001	216.15	0.004	292.10	<0.03	>1368.2	10	6978.0
20	0.011	9.59	<0.0007	>6.636	0.016	215.93	0.005	292.40	<0.03	>1370.6	38	7219.5
20	0.012	9.57	<0.0007	>6.636	0.017	215.91	0.005	292.40	<0.03	>1370.6	38	7219.7
20	0.012	9.57	<0.0007	>6.636	0.018	215.89	0.005	292.40	<0.03	>1370.7	37	7240.1
10	0.014	9.67	<0.0007	>6.643	0.023	216.02	0.005	292.45	<0.03	>1370.9	57	7409.8
10	0.015	9.66	<0.0007	>6.643	0.028	215.97	0.006	292.44	<0.03	>1370.9	58	7399.7
10	0.013	9.68	<0.0007	>6.643	0.024	216.01	0.006	292.44	<0.03	>1371.0	58	7400.4
5	0.018	9.72	<0.0007	>6.647	0.031	216.10	0.005	292.48	<0.03	>1371.1	97	7495.1
5	0.021	9.71	<0.0007	>6.647	0.031	216.10	0.006	292.47	<0.03	>1371.1	93	7515.0
5	0.020	9.71	<0.0007	>6.647	0.030	216.10	0.006	292.47	<0.03	>1371.1	93	7515.2
2	0.032	9.75	<0.0007	>6.649	0.017	216.22	0.009	292.48	<0.03	>1371.2	209	7562.3
2	0.028	9.76	<0.0007	>6.649	0.015	216.22	0.006	292.49	<0.03	>1371.2	218	7543.8
2	0.026	9.76	<0.0007	>6.649	0.012	216.23	0.005	292.49	<0.03	>1371.2	205	7570.2

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H28

Desorption Isotherm Data for West-P Polymer and Firmex

0.01 Polymer:0.5 Firmex:1.0 Sediment*

L/S ml/g	Arsenic C mg/ℓ	Arsenic q mg/kg	Cadmium C mg/ℓ	Cadmium q mg/kg	Chromium C mg/ℓ	Chromium q mg/kg	Lead C mg/ℓ	Lead q mg/kg	Zinc C mg/ℓ	Zinc q mg/kg	OC C mg/ℓ	OC q mg/kg
100	<0.005	> 9.89	0.0082	6.220	0.005	228.55	<0.003	>309.51	<0.030	>1449.4	10	7448.4
100	<0.005	> 9.89	<0.0007	>6.974	0.004	228.65	<0.003	>309.52	<0.030	>1449.4	10	7454.4
100	<0.005	> 9.89	<0.0007	>6.973	0.005	228.55	<0.003	>309.51	<0.030	>1449.4	10	7445.4
20	0.006	10.27	<0.0007	>7.030	0.008	228.89	0.004	309.74	<0.030	>1451.8	32	7812.0
20	0.006	10.27	<0.0007	>7.030	0.009	228.87	0.006	309.70	<0.030	>1451.8	31	7831.7
20	0.006	10.27	0.0041	6.962	0.009	228.87	0.006	309.70	<0.030	>1451.8	32	7812.4
10	0.008	10.31	0.0010	7.034	0.008	228.97	0.009	309.73	<0.030	>1452.1	57	7882.3
10	0.008	10.31	0.0008	7.036	0.008	228.97	0.006	309.76	<0.030	>1452.1	55	7902.1
10	0.008	10.31	<0.0007	>7.037	0.009	228.96	0.008	309.74	<0.030	>1452.1	54	7912.1
5	0.010	10.34	<0.0007	>7.040	0.010	229.00	0.006	309.79	<0.030	>1452.3	91	7997.3
5	0.008	10.35	<0.0007	>7.040	0.011	229.00	0.006	309.79	<0.030	>1452.3	90	8002.2
5	0.010	10.34	<0.0007	>7.040	0.011	229.00	0.007	309.78	<0.030	>1452.3	87	8017.4
2	0.012	10.37	<0.0007	>7.042	0.007	229.04	0.008	309.80	<0.030	>1452.4	219	8014.3
2	0.012	10.37	<0.0007	>7.042	0.006	229.04	0.009	309.80	<0.030	>1452.4	221	8010.6
2	0.012	10.37	<0.0007	>7.042	0.006	229.04	0.009	309.80	<0.030	>1452.4	219	8014.4

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H29

Desorption Isotherm Data for WEST-P Polymer and Firmex

0.03 Polymer:0.5 Firmex:1.0 Sediment*

	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
L/S ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	> 9.77	<0.0007	>6.889	0.005	225.79	<0.003	>305.77	<0.030	>1431.9	2	8151.5
100	<0.005	> 9.77	<0.0007	>6.889	0.009	225.39	<0.003	>305.78	<0.030	>1431.9	2	8152.4
100	<0.005	> 9.76	<0.0007	>6.887	0.011	225.17	<0.003	>305.77	<0.030	>1431.8	3	8045.7
20	0.008	10.11	<0.0007	>6.945	0.009	226.10	0.010	305.87	<0.030	>1434.3	26	7829.9
20	0.008	10.11	<0.0007	>6.945	0.012	226.04	ND		<0.030	>1434.3	25	7849.6
20	0.007	10.13	<0.0007	>6.945	0.012	226.04	ND		<0.030	>1434.3	24	7869.6
10	0.010	10.17	<0.0007	>6.952	0.013	226.15	ND		<0.030	>1434.6	45	7899.4
10	0.010	10.17	<0.0007	>6.952	0.012	226.16	ND		<0.030	>1434.6	46	7889.2
10	0.008	10.19	<0.0007	>6.952	0.012	226.16	ND		<0.030	>1434.6	45	7900.3
5	0.008	10.23	<0.0007	>6.955	0.015	226.21	ND		<0.030	>1434.7	88	7910.2
5	0.007	10.23	<0.0007	>6.955	0.013	226.22	ND		<0.030	>1434.7	95	7875.2
5	0.008	10.23	<0.0007	>6.955	0.014	226.21	ND		<0.030	>1434.7	94	7880.2
2	0.008	10.25	<0.0007	>6.957	0.009	226.27	ND		<0.030	>1434.8	234	7881.9
2	0.009	10.25	<0.0007	>6.957	0.009	226.27	ND		<0.030	>1434.8	249	7851.5
2	0.009	10.25	<0.0007	>6.957	0.008	226.27	ND		<0.030	>1434.8	244	7864.2

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H30

Desorption Isotherm Data for WEST-P Polymer and Firmex

0.05 Polymer:0.5 Firmex:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	> 9.63	<0.0007	>6.793	0.005	222.67	<0.003	>301.56	<0.030	>1412.1	6	7635.4
100	<0.005	> 9.62	<0.0007	>6.792	0.004	222.77	<0.003	>301.56	<0.030	>1412.1	6	7629.9
100	<0.005	> 9.63	<0.0007	>6.793	0.011	222.07	<0.003	>301.56	<0.030	>1412.1	5	7735.9
20	0.006	10.01	<0.0007	>6.849	0.008	223.01	0.004	301.78	<0.030	>1414.5	33	7574.3
20	0.006	10.01	<0.0007	>6.849	0.011	222.95	0.005	301.76	<0.030	>1414.5	32	7594.8
20	0.006	10.01	<0.0007	>6.849	0.011	222.95	0.005	301.76	<0.030	>1414.5	32	7593.4
10	0.009	10.04	<0.0007	>6.856	0.016	223.01	<0.003	>301.83	<0.030	>1414.8	53	7706.0
10	0.008	10.05	<0.0007	>6.856	0.013	223.04	0.006	301.80	<0.030	>1414.8	51	7725.3
10	0.009	10.04	<0.0007	>6.856	0.010	223.07	0.004	301.82	<0.030	>1414.8	49	7745.1
5	0.008	10.09	<0.0007	>6.859	0.014	223.10	0.005	301.83	<0.030	>1415.0	92	7775.2
5	0.008	10.09	<0.0007	>6.859	0.014	223.10	0.005	301.83	<0.030	>1415.0	95	7760.3
5	0.010	10.08	<0.0007	>6.859	0.011	223.11	0.006	301.83	<0.030	>1415.0	88	7795.3
2	0.010	10.11	<0.0007	>6.861	0.013	223.14	0.008	301.84	<0.030	>1415.1	232	7771.2
2	0.008	10.11	<0.0007	>6.861	0.010	223.15	0.008	301.84	<0.030	>1415.1	237	7761.3
2	0.010	10.11	<0.0007	>6.861	0.012	223.15	0.009	301.84	<0.030	>1415.1	230	7775.5

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H31

Desorption Isotherm Data for WEST-P Polymer and Portland Cement

0.01 Polymer:0.2 Cement:1.0 Sediment*

L/S	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>12.47	<0.0007	>8.719	0.010	284.80	<0.003	>386.27	<0.030	>1809.3	7	9850.5
100	<0.005	>12.47	<0.0007	>8.719	0.028	283.01	0.004	386.17	<0.030	>1809.3	8	9750.3
100	<0.005	>12.47	<0.0007	>8.719	0.026	283.21	0.005	386.07	<0.030	>1809.3	8	9750.1
20	<0.005	>12.87	<0.0007	>8.775	0.066	284.48	0.005	386.47	<0.030	>1811.6	48	9587.1
20	<0.005	>12.87	<0.0007	>8.775	0.051	284.78	0.012	386.33	<0.030	>1811.6	49	9567.9
20	<0.005	>12.87	<0.0007	>8.775	0.046	284.88	0.010	386.37	<0.030	>1811.6	46	9627.8
10	0.006	12.91	<0.0007	>8.782	0.017	285.63	0.023	386.34	<0.030	>1811.9	85	9696.4
10	0.005	12.92	<0.0007	>8.782	0.046	285.34	0.017	386.40	<0.030	>1811.9	84	9706.9
10	0.005	12.92	<0.0007	>8.782	0.043	285.37	0.017	386.40	<0.030	>1811.9	81	9737.1
5	0.010	12.92	<0.0007	>8.785	0.053	285.53	0.018	386.48	<0.030	>1812.1	135	9871.5
5	0.009	12.92	<0.0007	>8.785	0.045	285.57	0.019	386.47	<0.030	>1812.1	134	9876.6
5	0.008	12.93	<0.0007	>8.785	0.053	285.53	0.021	386.46	<0.030	>1812.1	130	9896.4
2	0.010	12.95	0.0015	8.786	0.041	285.71	0.016	386.54	<0.030	>1812.2	286	9974.4
2	0.011	12.95	0.0031	8.782	0.041	285.71	0.022	386.52	<0.030	>1812.2	271	10004.4
2	0.009	12.95	0.0011	8.786	0.038	285.72	0.028	386.51	<0.030	>1812.2	270	10006.4

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* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H32

Desorption Isotherm Data for WEST-P Polymer and Portland Cement

0.03 Polymer:0.2 Cement:1.0 Sediment*

	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
L/S ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>12.26	<0.0007	>8.580	0.023	279.00	<0.003	>380.18	<0.030	>1780.7	8	9581.2
100	<0.005	>12.27	<0.0007	>8.581	0.022	279.10	0.004	380.09	0.041	1779.6	8	9582.8
100	<0.005	>12.26	<0.0007	>8.580	0.026	278.68	0.004	380.08	<0.030	>1780.7	8	9576.4
20	<0.005	>12.66	<0.0007	>8.636	0.039	280.52	0.008	380.32	<0.030	>1783.1	49	9401.6
20	<0.005	>12.66	<0.0007	>8.636	0.038	280.54	0.011	380.26	<0.030	>1783.1	47	9440.9
20	<0.005	>12.66	<0.0007	>8.636	0.036	280.58	0.009	380.30	<0.030	>1783.1	48	9421.7
10	0.007	12.69	<0.0007	>8.643	0.043	280.87	0.017	380.31	0.048	1783.2	89	9490.1
10	0.006	12.70	<0.0007	>8.643	0.031	280.99	0.012	380.36	0.064	1783.1	85	9530.4
10	0.007	12.69	<0.0007	>8.643	0.034	280.96	0.017	380.31	<0.030	>1783.4	83	9550.3
5	0.007	12.73	<0.0007	>8.647	0.037	281.11	0.017	380.40	<0.030	>1783.6	152	9620.2
5	0.007	12.73	<0.0007	>8.647	0.030	281.15	0.018	380.39	<0.030	>1783.6	148	9640.8
5	0.007	12.73	<0.0007	>8.647	0.030	281.15	0.002	380.47	<0.030	>1783.6	145	9655.1
2	0.011	12.74	<0.0007	>8.649	0.010	281.28	0.021	380.44	<0.030	>1783.7	307	9766.8
2	0.012	12.74	<0.0007	>8.649	0.021	281.26	0.023	380.44	<0.030	>1783.7	307	9764.9
2	0.012	12.74	<0.0007	>8.649	0.018	281.26	0.020	380.44	<0.030	>1783.7	318	9744.0

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

Table H33

Desorption Isotherm Data for WEST-P Polymer and Portland Cement

0.05 Polymer:0.2 Cement:1.0 Sediment*

	Arsenic		Cadmium		Chromium		Lead		Zinc		OC	
L/S ml/g	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg	C mg/ℓ	q mg/kg
100	<0.005	>12.06	<0.0007	>8.442	0.025	274.31	0.006	373.80	<0.030	>1752.2	8	9418.4
100	<0.005	>12.06	<0.0007	>8.442	0.022	274.62	0.005	373.90	<0.030	>1752.2	8	9420.0
100	<0.005	>12.06	<0.0007	>8.442	0.021	274.71	0.007	373.70	<0.030	>1752.2	8	9420.0
20	<0.005	>12.46	<0.0007	>8.498	0.030	276.20	0.082	372.76	<0.030	>1754.6	48	9255.4
20	<0.005	>12.46	<0.0007	>8.498	0.039	276.02	0.165	371.10	<0.030	>1754.6	48	9255.6
20	<0.005	>12.46	<0.0007	>8.498	0.038	276.04	0.034	373.72	<0.030	>1754.6	46	9205.3
10	0.005	12.51	<0.0007	>8.505	0.040	276.40	0.030	374.10	<0.030	>1754.9	74	9474.7
10	0.005	12.51	<0.0007	>8.505	0.045	276.35	0.001	374.39	<0.030	>1754.9	78	9434.9
10	0.006	12.50	<0.0007	>8.505	0.038	276.42	0.005	374.35	<0.030	>1754.9	79	9425.0
5	0.007	12.53	<0.0007	>8.509	0.042	276.59	0.004	374.38	0.099	1754.7	142	9504.5
5	0.008	12.52	<0.0007	>8.509	0.048	276.61	0.006	374.37	<0.030	>1755.1	142	9504.4
5	0.008	12.52	<0.0007	>8.509	0.041	276.60	0.008	374.36	<0.030	>1755.1	144	9494.6
2	0.010	12.54	<0.0007	>8.511	0.072	276.66	0.013	374.37	<0.030	>1755.1	301	9612.4
2	0.010	12.54	<0.0007	>8.511	0.023	276.75	0.010	374.38	<0.030	>1755.1	295	9624.4
2	0.010	12.54	<0.0007	>8.511	0.025	276.75	0.009	374.38	<0.030	>1755.1	279	9656.4

* PC = Portland cement.
L/S = liquid-solids ratio.
C = contaminant concentration in leachate.
q = contaminant concentration in solidified sediment after leaching.
OC = organic carbon.

the leachate samples. Organic carbon was above the detection limit in every sample analyzed.

34. Data for 157 desorption isotherms are available in Tables H7-H33. Representative desorption isotherms are presented in Figures H4-H16. The isotherms in this set of figures illustrate the important features of the different types of isotherms that were obtained. The different isotherm types are discussed below.

35. Classification of desorption isotherms. A classification scheme was developed to provide a convenient framework for interpreting the desorption data. The data from the serial, graded batch leaching tests fall into five general classifications, depending on the liquid-solid ratios at which contaminants were detected. As previously discussed, the serial, graded batch leaching tests involved shaking solidified/stabilized sediment with water at liquid-to-solids ratios of 100:1, 20:1, 10:1, 5:1 (in selected tests), and 2:1 in order to obtain data for plotting a desorption isotherm. Table H34 is a summary of the results from the serial, graded batch leaching tests according to the classification scheme presented below.

36. For some of the isotherm data, the amount of contaminant released was below the detection limit for all of the liquid-solids ratios used in the series of tests. The leaching tests in which contaminant release was not measurable are termed "no release isotherms" (NRI). Most of the cadmium desorption isotherms for solidified Indiana Harbor sediment were classified as NRI. In general, cadmium did not leach from the solidified/stabilized sediment in concentrations significantly different from the blanks. Hence, solidified/stabilized Indiana Harbor sediment does not appear to have significant leaching potential for cadmium. The other contaminant desorption isotherms falling into this category are listed in Table H34.

37. For some of the desorption data, the amount of contaminant released was below the detection limit for all but one or two of the liquid-solids ratios in the series. When the contaminant was detected, it was usually detected in the tests conducted at the lowest liquid-solids ratios used in the series, i.e., 2:1 and 10:1. Desorption isotherms characterized by aqueous phase contaminant concentrations below the detection limit for liquid-solid ratios greater than 10:1 are termed "low release isotherms" (LRI). The arsenic desorption data for Indiana Harbor sediment solidified/stabilized with portland cement in an additive-to-sediment ratio of 0.2:1 (Table H8) is an example of a

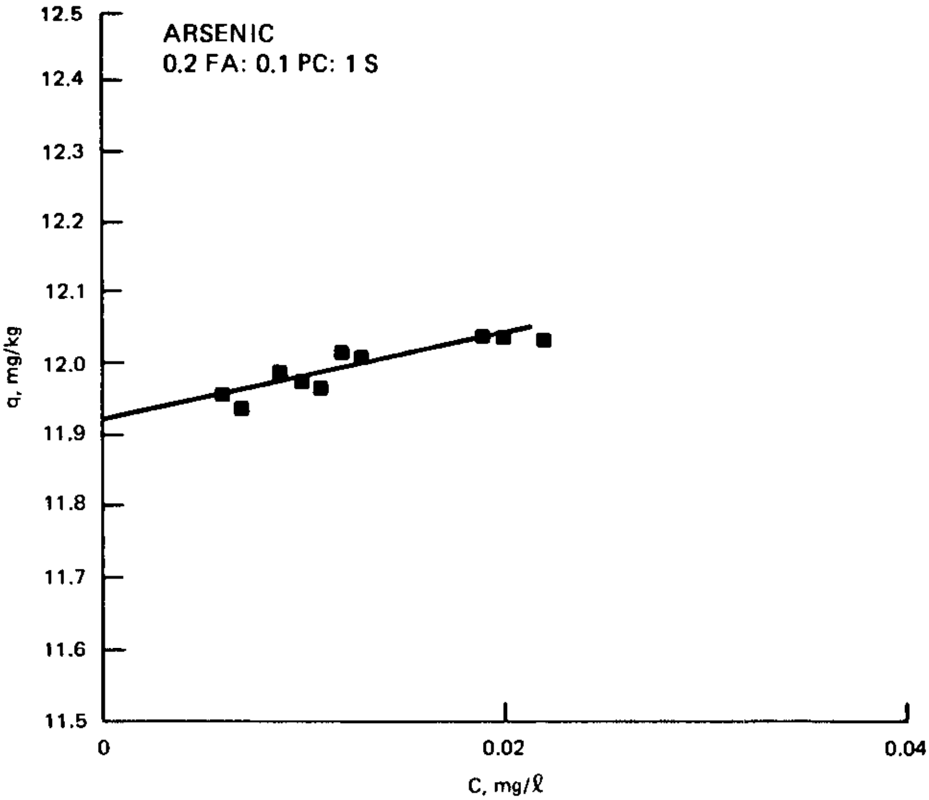

Figure H4. Arsenic desorption isotherm for 0.2 fly ash: 0.1 portland cement:1 sediment

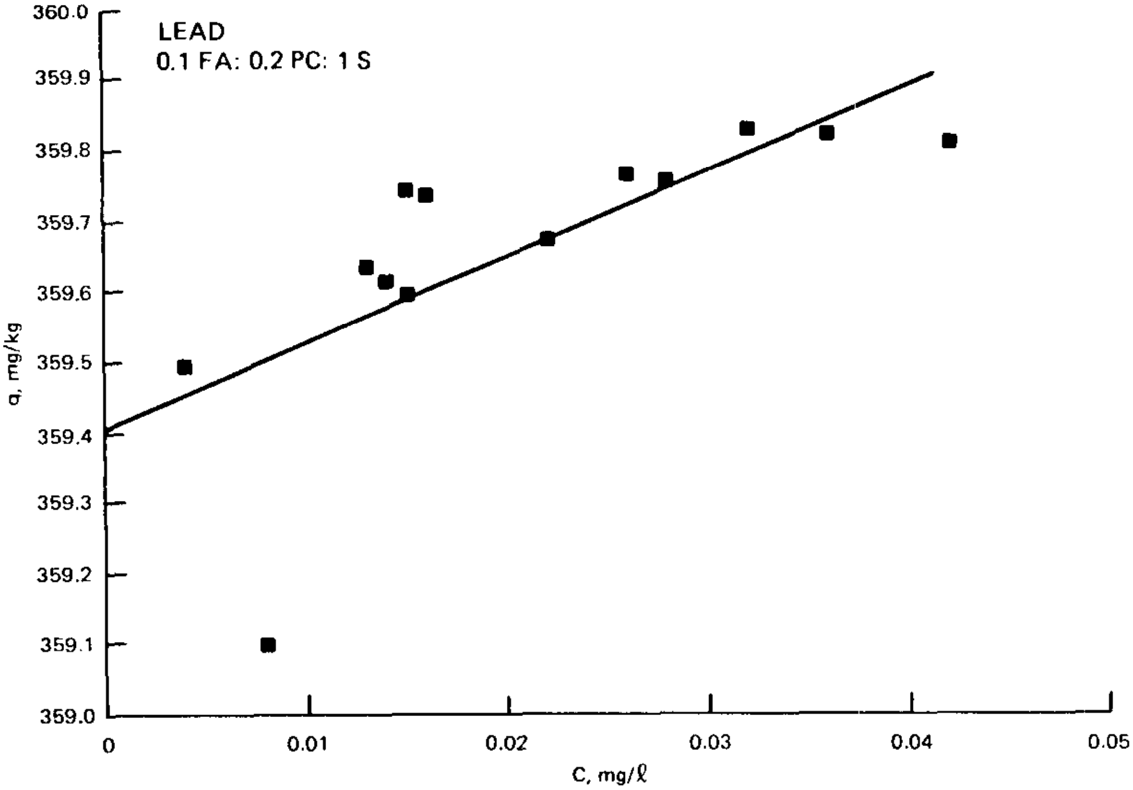

Figure H5. Lead desorption isotherm for 0.1 fly ash: 0.2 portland cement:1 sediment

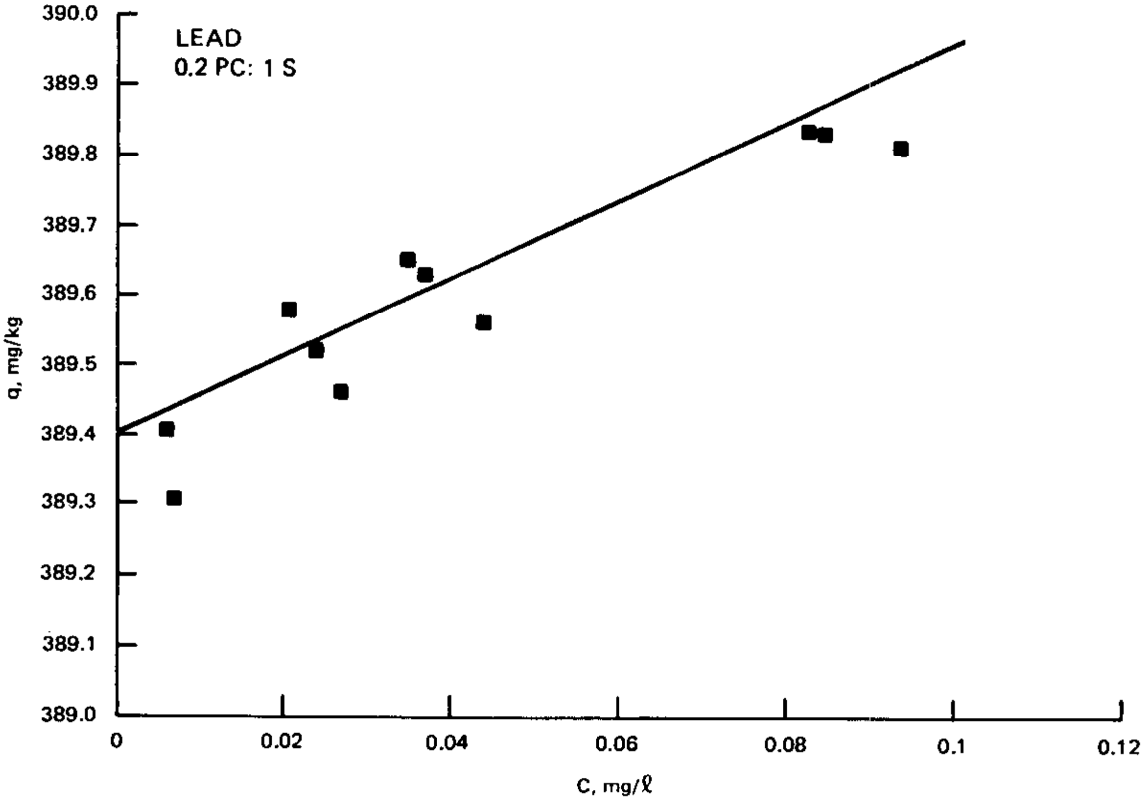

Figure H6. Lead desorption isotherm for 0.2 portland cement: 1 sediment

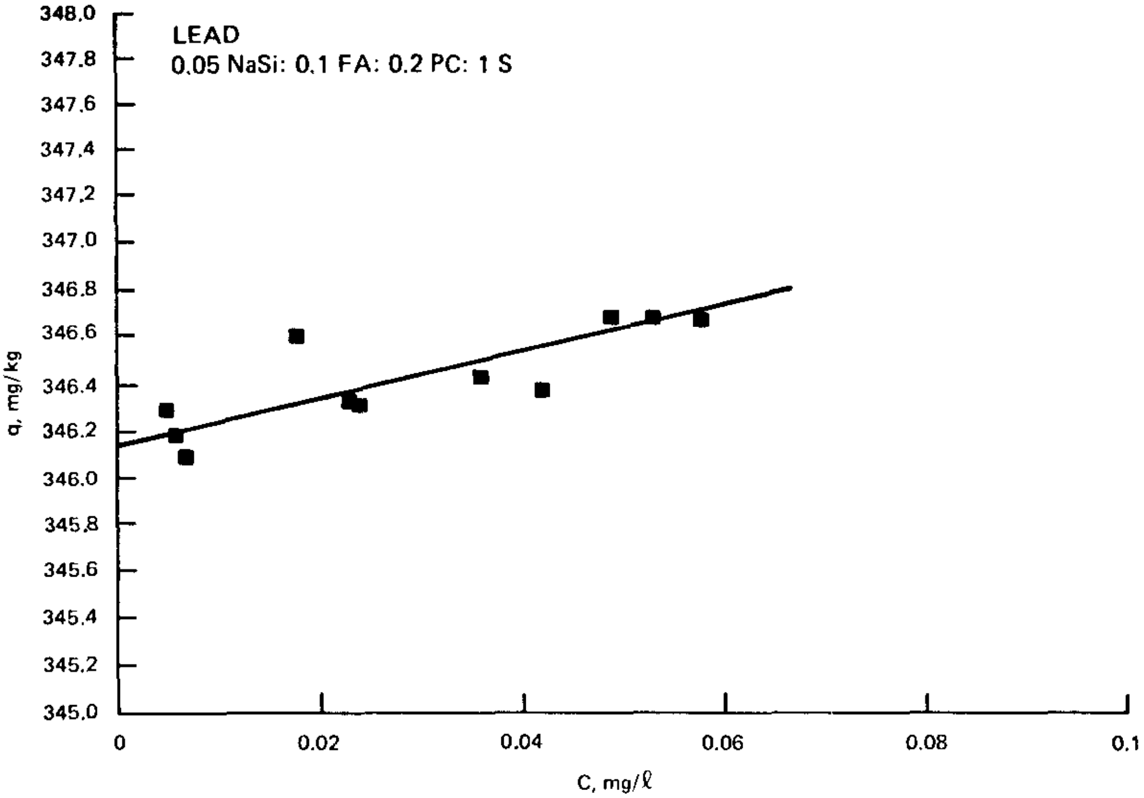

Figure H7. Lead desorption isotherm for 0.05 sodium silicate: 0.1 fly ash:0.2 portland cement:1 sediment

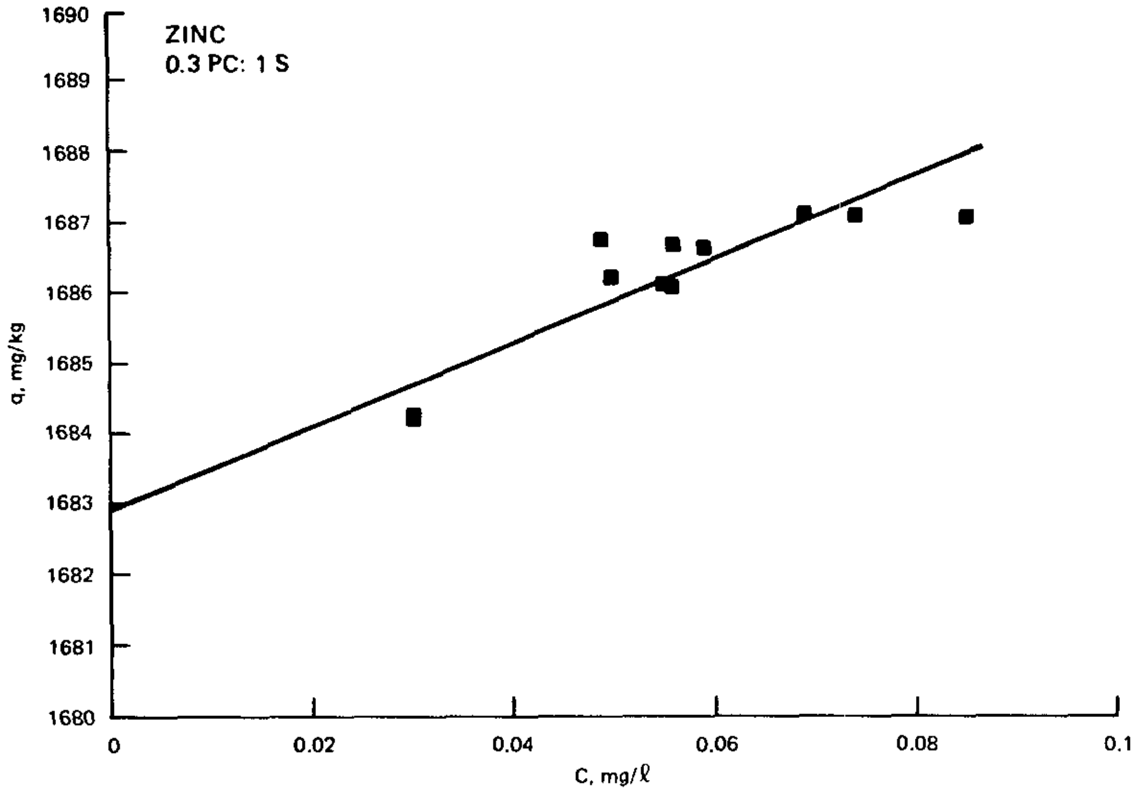

Figure H8. Zinc desorption isotherm for 0.3 portland cement: 1 sediment

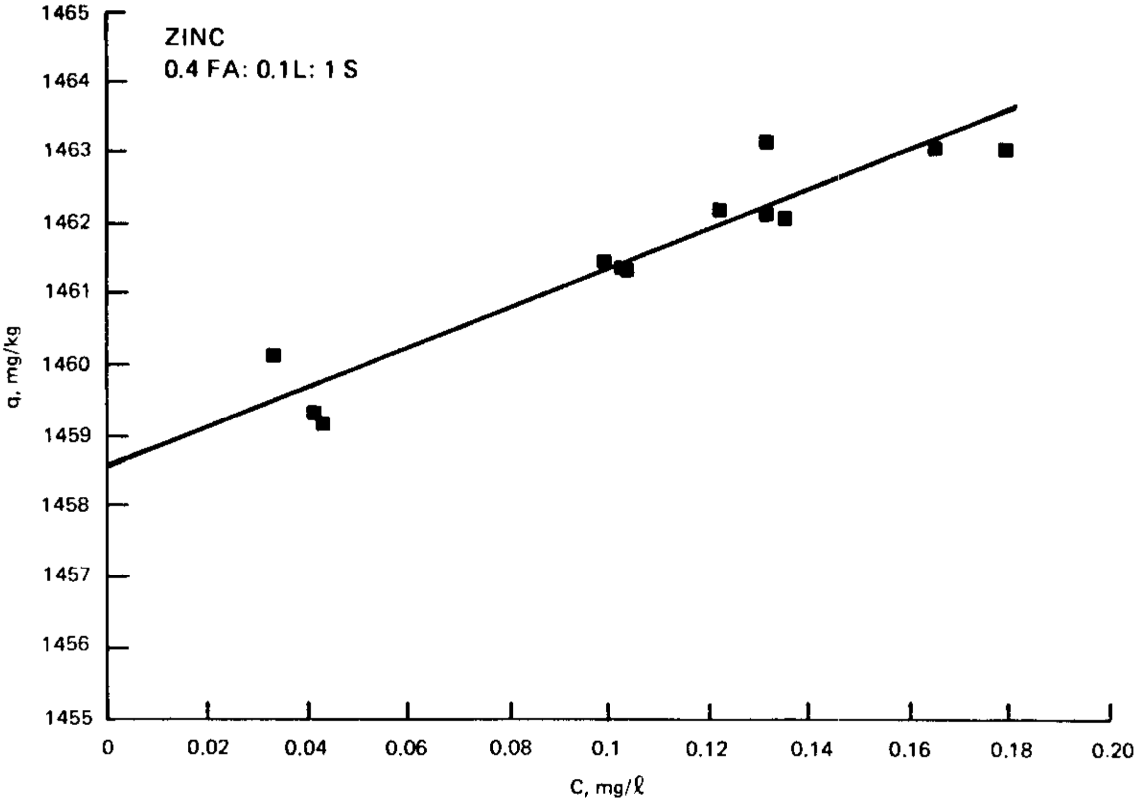

Figure H9. Zinc desorption isotherm for 0.4 fly ash: 0.1 lime:sediment

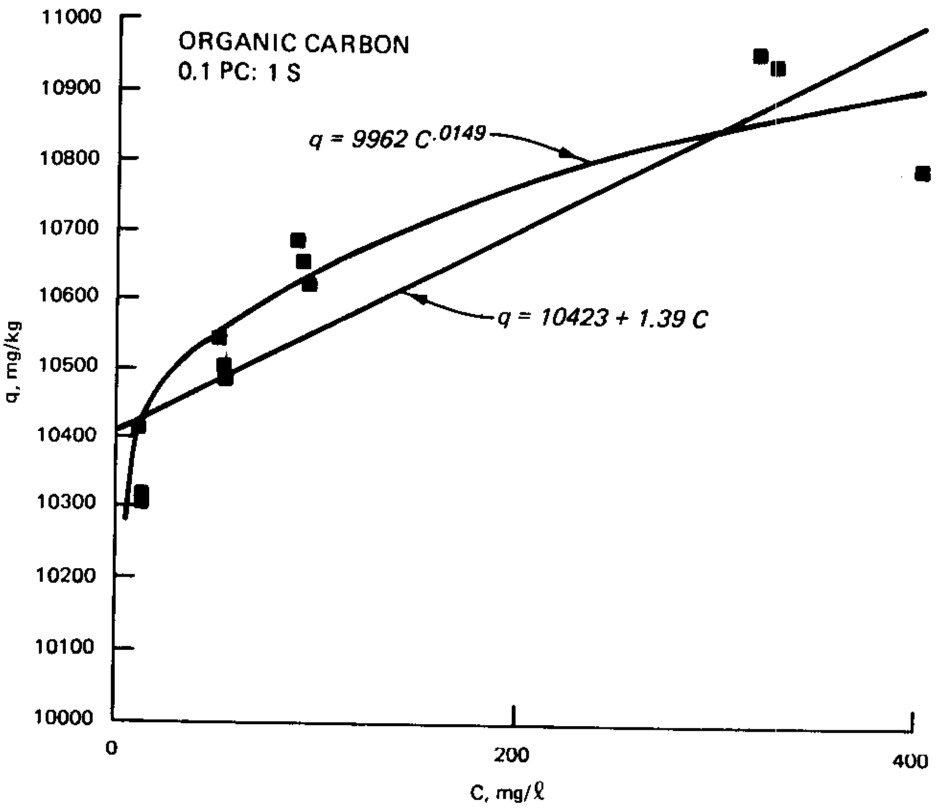

Figure H10. Organic carbon desorption isotherm for 0.1 portland cement:1 sediment

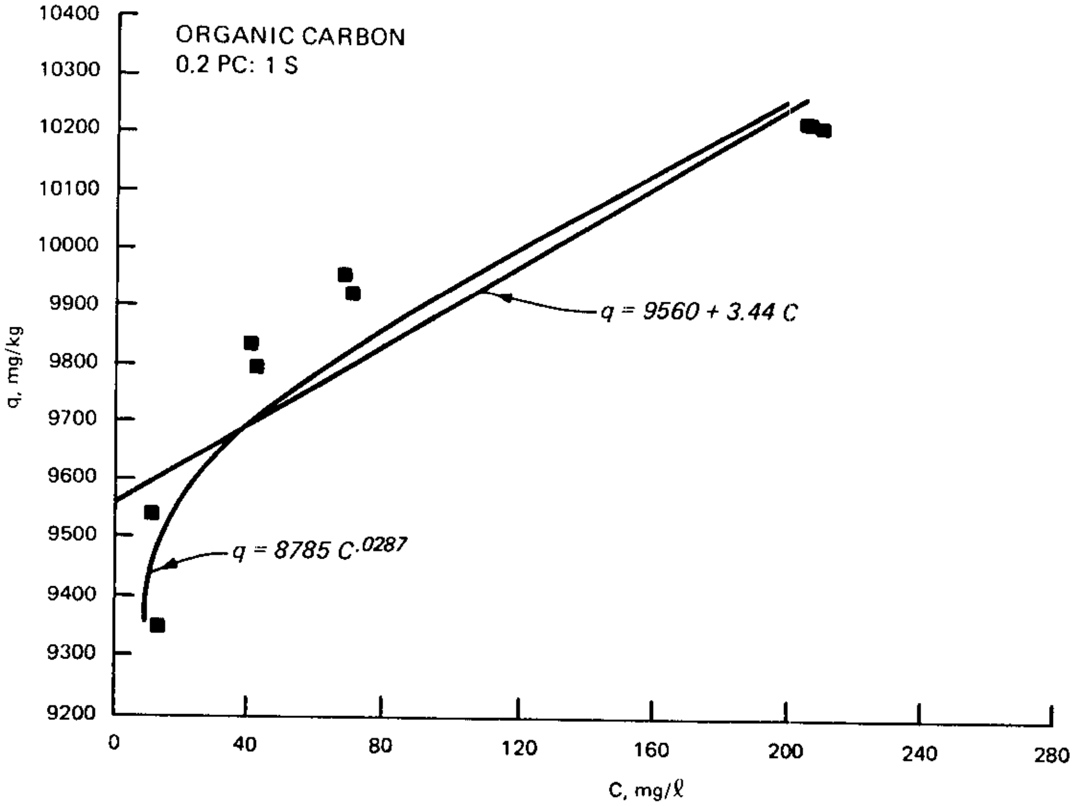

Figure H11. Organic carbon desorption isotherm for 0.2 portland cement:1 sediment

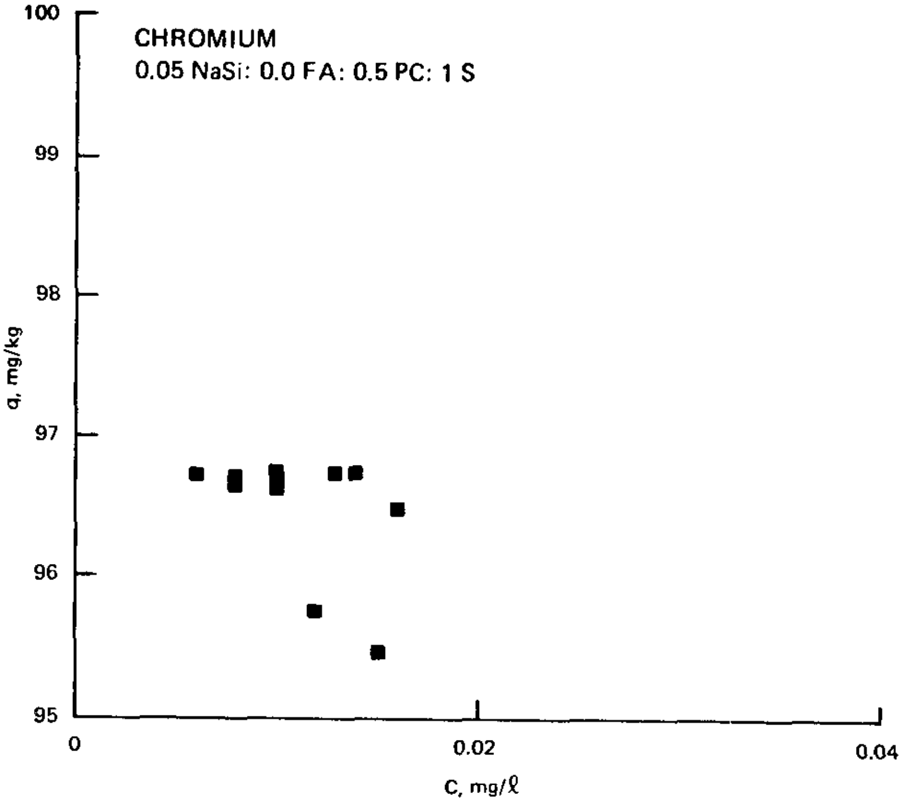

Figure H12. Chromium desorption isotherm for 0.05 sodium silicate: 0.5 portland cement:1 sediment

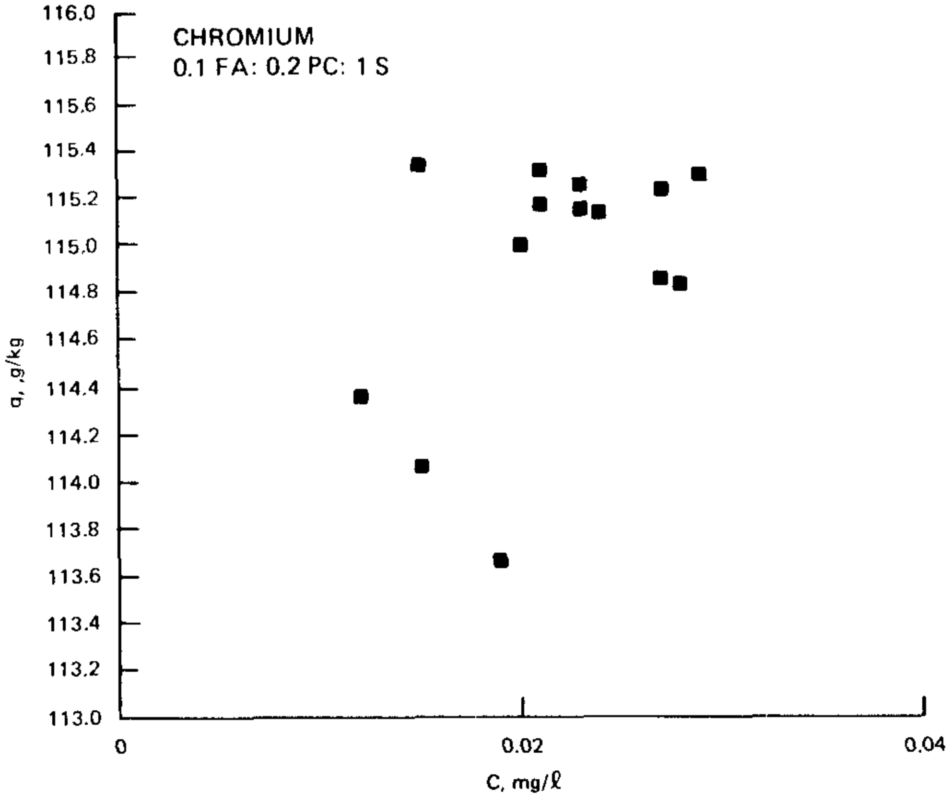

Figure H13. Chromium desorption isotherm for 0.1 fly ash:
0.2 portland cement:1 sediment

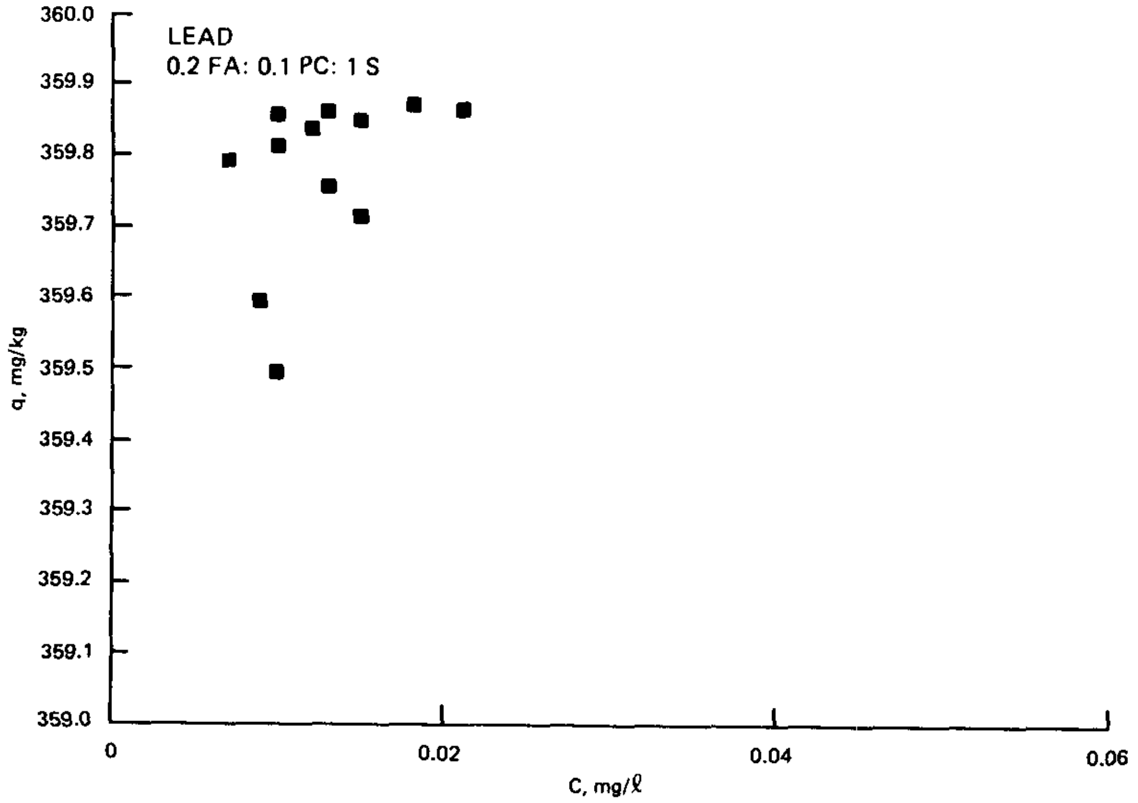

Figure H14. Lead desorption isotherm for 0.2 fly ash: 0.1 portland cement:1 sediment

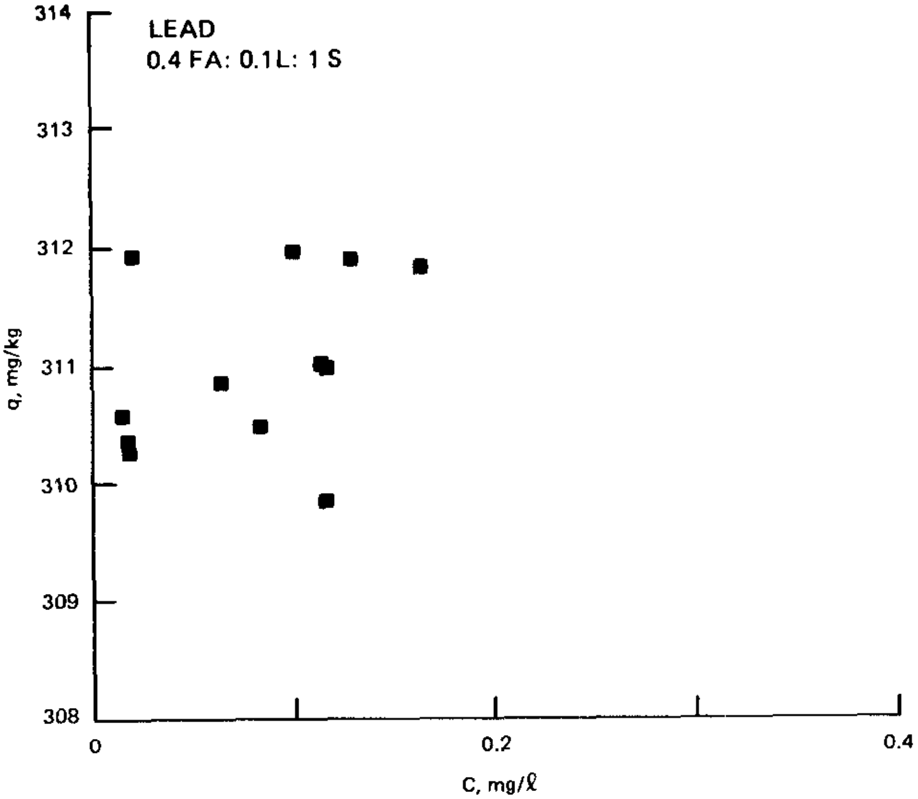

Figure H15. Lead desorption isotherm for 0.4 fly ash: 0.1 lime:1 sediment

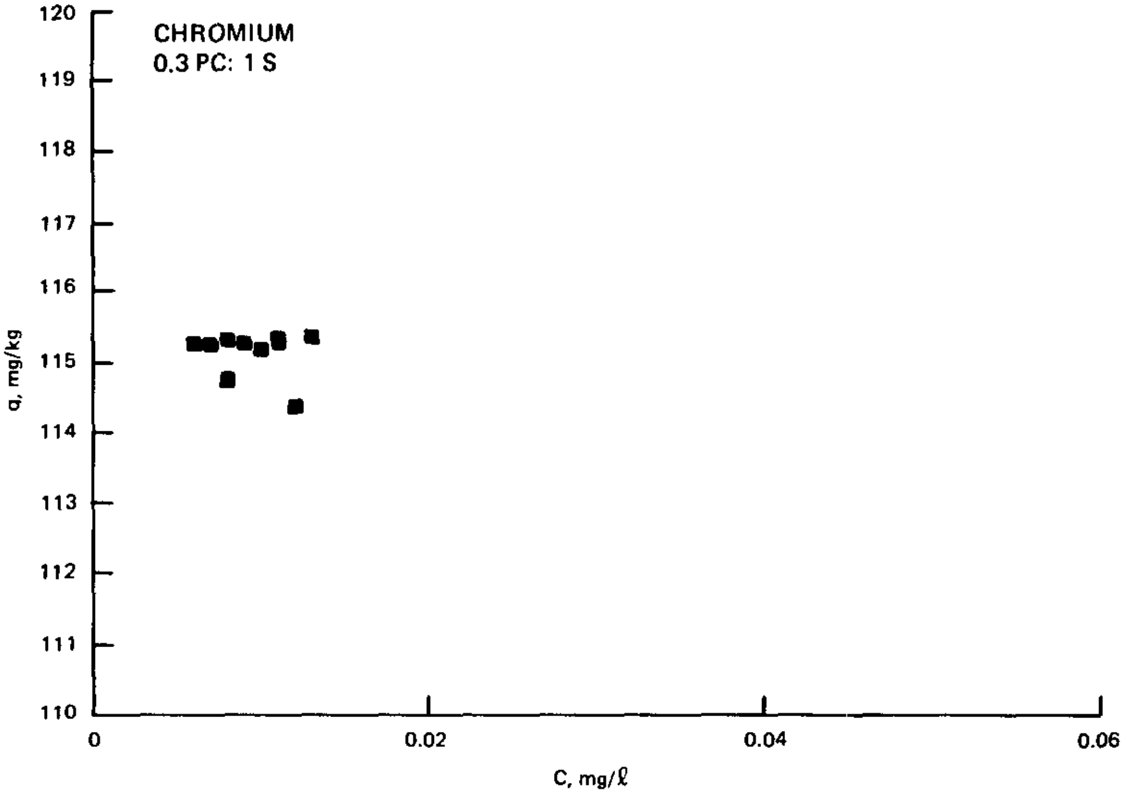

Figure H16. Chromium desorption isotherm for 0.3 portland cement: 1 sediment

Table H34

Classification of Desorption Isotherms Obtained from Serial, Graded Batch Leach Tests Conducted on Solidified/Stabilized Indiana Harbor Sediment*

Process	As	Cd	Cr	Pb	Zn	OC
Portland cement						
0.1 PC:1 sediment	MRI	NRI	CI	MRI	LRI	WDI**
0.2 PC:1 sediment	LRI	CI	CI	WDI**	CI	WDI**
0.3 PC:1 sediment	LRI	NRI	CI**	CI	WDI**	WDI
0.4 PC:1 sediment	LRI	NRI	CI	WDI	CI	WDI
Portland cement with fly ash						
0.2 FA:0.1 PC:1 sediment	MRI**	NRI	CI	CI**	LRI	WDI
0.1 FA:0.2 PC:1 sediment	MRI	NRI	CI**	WDI**	NRI	WDI
0.15 FA:0.15 PC:1 sediment	MRI	NRI	CI	CI	NRI	WDI
Portland Cement with fly ash and/or sodium silicate						
0.05 NaSi:0.1 FA:0.1 PC:1 sediment	LRI	NRI	CI	CI	CI	ND
0.05 NaSi:0.1 FA:0.2 PC:1 sediment	LRI	NRI	CI	WDI**	LRI	ND
0.05 NaSi:0.25 FA:0.25 PC:1 sediment	LRI	NRI	CI	WDI	LRI	ND
0.05 NaSi:0.25 PC:1 sediment	LRI	NRI	CI	WDI	CI	ND
0.05 NaSi:0.5 PC:1 sediment	LRI	NRI	CI**	CI	CI	
Portland cement with Firmix						
0.2 FM:0.1 PC:1 sediment	LRI	NRI	CI	CI	NRI	WDI
0.1 FM:0.2 PC:1 sediment	LRI	NRI	CI	WDI	NRI	WDI
0.15 FM:0.15 PC:1 sediment	LRI	NRI	CI	WDI	NRI	WDI
Fly Ash with lime						
0.4 FA:0.1 L:1 sediment	LRI	NRI	CI	CI**	WDI**	WDI
0.5 FA:0.1 L:1 sediment	LRI	NRI	CI	CI	WDI	WDI
0.6 FA:0.1 L:1 sediment	LRI	NRI	CI	CI	WDI	WDI
Firmix						
0.4 FM:1 sediment	WDI	CI	CI	CI	NRI	WDI
0.5 FM:1 sediment	WDI	NRI	CI	LRI	NRI	WDI
0.6 FM:1 sediment	WDI	NRI	CI	LRI	NRI	WDI
Firmix with WEST-P						
0.01 WP:0.5 FM:1 sediment	MRI	NRI	CI	CI	NRI	WDI
0.03 WP:0.5 FM:1 sediment	CI	NRI	CI	ND	NRI	WDI
0.05 WP:0.5 FM:1 sediment	MRI	NRI	CI	CI	NRI	WDI
Portland cement with WEST-P						
0.01 WP:0.2 PC:1 sediment	LRI	LRI	CI	WDI	NRI	WDI
0.03 WP:0.2 PC:1 sediment	LRI	NRI	CI	WDI	NRI	WDI
0.05 WP:0.2 PC:1 sediment	LRI	NRI	CI	CI	NRI	WDI

** MRI = moderate release isotherms.
NRI = no release isotherms.
CI = cluster isotherms.
LRI = low release isotherms.
WDI = well-defined desorption isotherms.
ND = no data
** Selected for presentation as a figure.

one-point LRI. The zinc desorption data for Indiana Harbor sediment solidified with portland cement in an additive-to-sediment ratio of 0.1 portland cement: 1 sediment (Table H7) is an example of a two-point LRI. Other processes with contaminant desorption isotherms that were classified as LRI are listed in Table H34.

38. LRIs characterize contaminants that in the field situation leach in concentrations near the detection limits used in the development of the desorption isotherms. LRIs are, therefore, indicative of solidified/stabilized sediments that are not very leachable. Since most of the arsenic desorption isotherms were LRIs, solidified/stabilized Indiana Harbor sediment does not appear to have significant leaching potential for arsenic.

39. In some of the serial, graded batch leach tests, the aqueous phase concentrations were detectable in leachates from the three lower liquid-solids ratios (20:1, 10:1, and 2:1) but not in leachates from the 100:1 liquid-solids ratio. Desorption isotherms with leachate concentrations detectable at liquid-solids ratios of 20:1 and lower and that show a well-defined relationship between q and C are termed "moderate release isotherms" (MRI). A typical MRI for arsenic is shown in Figure H4. There were seven MRIs, six for arsenic and one for lead. These are listed in Table H34.

40. The next classification applies to serial, graded batch leach data in which contaminant concentrations were detectable at each liquid-solids ratio used in the series and the solid and aqueous phase concentrations follow a well-defined relationship, i.e., the points on the desorption isotherm are not clustered. The isotherm plots for this classification are termed "well-defined desorption isotherms" (WDI). Typical WDIs are shown in Figures H5-H11. Most of the WDIs fit the model presented in Appendix G, Equation G3, i.e., the aqueous phase concentration is linearly related to the solid phase concentration. Most of the organic carbon desorption isotherms were nonlinear, as shown in Figures H10 and H11. The nonlinear desorption isotherms for organic carbon are discussed later. Other contaminant desorption isotherms falling into WDI category are listed in Table H34.

41. A well-defined, linear desorption isotherm characterizes a contaminant for which the leachable solid phase concentration is high enough that the aqueous phase concentration is detectable after dilution at the highest liquid-solids ratio used in the serial, graded series. In the field situation, the dissolved concentration of such contaminants in the pore water will initially

be well above the detection limits used to develop the desorption isotherms. The initial leachate concentration is governed by the field liquid-solids ratio, the distribution coefficient K_d, and the leachable solid phase concentration. The rate at which the aqueous phase concentration decreases as clean water percolates through the solidified/stabilized sediment is in part controlled by K_d and in part by the hydraulics of the disposal site. The higher K_d, the longer the initial concentration will tend to persist, and the lower the initial concentration will be.

42. The desorption isotherm plots from some of the leaching tests were clustered, indicating that contaminant transfer from the solid phase to the aqueous phase did not follow the model in Equation G5. The leaching tests that produced clusters are termed "cluster isotherms" (CI). CIs occurred more frequently in the chromium data than for any other contaminant. All of the chromium desorption isotherms were classified as CIs. The chromium desorption isotherms shown in Figures H12 and H13 are typical CIs. Two cluster isotherms for lead are shown in Figures H14 and H15. Other contaminant desorption isotherms falling into this category are listed in Table H34.

43. Some of the CIs had a horizontal orientation (Figure H16). A CI with a horizontal orientation indicates that there is leachable contaminant in the solidified/stabilized solids and that the leaching of this contaminant is not governed by reversible ion-exchange or sorption. In this case, the distribution coefficient K_d is zero. When K_d is zero, all of the leachable contaminant concentration in the solidified/stabilized sediment is released in each test in the graded series; i.e., the leachable mass is not partitioned between solid and aqueous phases. The solid phase concentration at the end of each test approaches q_r, the concentration that is resistant to leaching. Since the solid phase concentration of leachable contaminant is constant and neither reversible exchange nor sorption occur, the aqueous phase concentration C depends only on the dilution provided by the various liquid-solids ratios used in the series. The aqueous phase concentration therefore decreases by dilution with increasing liquid-solids ratio. Theoretically, the q versus C plot should be a horizontal line that intercepts the ordinate at q_r. The CI shown in Figure H16 is an example of a q versus C plot that closely approximates the theoretical result for K_d equal to zero.

44. If the leachable solid phase concentration is small, then the differences in aqueous phase concentration provided by the change in liquid-solids

ratio will be correspondingly small. If these differences are small relative to the combined precision of the leaching tests and chemical analytical procedures, the data will be scattered about the true result, depending on the variability associated with the leaching and chemical analysis procedures. Since analytical precision is poorest near the detection limit, clustering may be due in part to the variability inherent in testing near the detection limit. The clustering or scatter shown in Figures H13-H15 is probably due to a combination of K_d equal to zero and low release relative to the testing variability. In the field situation, the combination of a leachable solid phase contaminant concentration that is low and a K_d equal to zero is characteristic of a contaminant that is initially present at low concentration and that does not persist once the initial pore water has moved out.

45. Process effectiveness for contaminant immobilization. If a process provides complete immobilization for each contaminant, all of the contaminant desorption isotherms will be NRIs. None of the processes investigated in this study completely immobilized all of the contaminants in Indiana Harbor sediment. Several of the processes in Table H34 had NRIs for two contaminants, cadmium and zinc. On the basis of the number of NRIs, however, no one process had better metal immobilization characteristics than all the others.

46. When a simple scheme such as one based on the number of NRIs does not indicate which process has the best chemical stabilization potential, a more detailed analysis is required. A contaminant specific methodology for comparing process effectiveness is outlined below that involves the distribution coefficient K_d and the amount of contaminant that is leachable q_1. The methodology is used to compare the leachability of metals from solidified/stabilized sediment to the leachability of metals from untreated sediment. A different basis, discussed later, was used to compare process effectiveness for immobilizing organic carbon.

47. The distribution coefficient K_d as previously discussed, is a contaminant-specific and solidified-sediment-specific composite coefficient that represents all equilibrium-controlled interphase transfer processes. Since it is a measurement of the relative affinity of a contaminant for the solid phase versus the aqueous phase, it is an important index of contaminant immobilization. The higher the distribution coefficient, the lower the aqueous phase concentration that a given solid phase contaminant concentration will support. The leachable contaminant concentration q_L in the solidified sediment is

also an important index of contaminant mobility since this quantity is the mass of contaminant available for partitioning between solid and aqueous phases. For a given distribution coefficient, the higher q_L, the higher the aqueous phase concentration.

48. The leachable contaminant concentration in the solidified sediment q_L is given by

$$q_L = q_o - q_r \tag{H4}$$

where

q_L = leachable contaminant concentration in the solidified/stabilized sediment, mg/kg

q_o = initial contaminant concentration in the solidified/stabilized sediment before leaching, mg/kg

q_r = contaminant concentration in the solidified/stabilized sediment that is resistant to leaching, mg/kg.

49. The leachable contaminant concentration in the solidified sediment was normalized with respect to the mass of wet sediment that was processed for solidification/stabilization. Normalized leachable solid phase concentrations can be compared directly with the untreated sediment. Comparisons between processes with different additive dosages can also be made using normalized leachable solid phase concentrations. The leachable contaminant concentration normalized with respect to the mass of sediment that was processed is given by

$$q_{nL} = q_L(1 + R)(1 + w) \tag{H5}$$

where

q_{nL} = leachable contaminant concentration with respect to the mass of sediment processed by solidification, mg/kg

q_L = leachable contaminant concentration with respect to the mass of solidified sediment, mg/kg

R = dosage of solidification/stabilization reagents, kg reagents/kg wet sediment processed

w = moisture content of the wet sediment, kg water/kg sediment solids

50. The effectiveness of solidification/stabilization as a technology for immobilizing arsenic, lead, zinc, and chromium in Indiana Harbor sediment was evaluated by using the parameters discussed above. Values for q_L, q_{nL}, and K_d for solidified/stabilized sediment were compared with those for untreated, anaerobic sediment. The data are presented in Tables H35-38, for arsenic, lead, zinc, and chromium, respectively.

51. The data showed that in most cases solidification/stabilization reduced the mass of leachable arsenic in the sediment. This is indicated in the normalized leachable arsenic concentrations presented in Table H35. The portland cement with fly ash and/or sodium silicate, portland cement with Firmix, fly ash with lime, and portland cement with WEST-P-polymer processes were particularly effective in reducing the normalized leachable arsenic concentration q_{nL}. The portland cement process was also effective when the portland cement dosage was greater than 0.1 portland cement to 1 sediment. The process formulation with the lowest q_{nL} for arsenic was the 0.03 West-P: 0.5 Firmix:1 sediment formulation. With the exception of this one formulation, the Firmix with West-P and the Firmix processes, however, did not reduce the normalized leachable arsenic concentration, although the polymer reduced q_{nL} compared with Firmix without polymer. Comparison of the q_{nL} data for the portland cement with Firmix process with the data for the 0.3 portland cement:1 sediment portland cement formulation shows that portland cement replacement with Firmix did not increase the normalized leachable arsenic concentration. Replacement with fly ash showed a slight increase.

52. As shown in Table H36, solidification/stabilization was also effective in immobilizing lead. Most of the processes reduced the mass of leachable lead in the sediment. One exception was the fly ash with lime process. Apparently the lime increased the mass of leachable lead. The other processes involving fly ash did not show a comparable increase in leachable lead. The portland cement and portland cement with fly ash processes showed increased q_{nL} with increased portland cement dosage, and the portland cement with Firmix process had higher q_{nL} than the Firmix process. In addition, the normalized leachable lead concentrations for portland cement with WEST-P were higher than those for the Firmix with WEST-P process. The process formulation with the lowest q_{nL} for lead was the 0.5 Firmix:1 sediment formulation. The other Firmix formulations and Firmix with West-P processes were also effective in reducing the normalized leachable lead concentration.

Table H35

Summary of Arsenic Leaching Indices for Solidified/Stabilized Indiana Harbor Sediment

Process	q_L mg/kg	q_{nL} mg/kg	K_d ℓ/kg
Untreated anaerobic sediment	0.41	0.41	7.46
Portland cement			
0.1 PC:1 sediment	0.29	0.60	17.7
0.2 PC:1 sediment	<0.03	<0.07	-
0.3 PC:1 sediment	<0.05	<0.13	-
0.4 PC:1 sediment	<0.05	<0.14	-
Portland cement with fly ash			
0.2 FA:0.1 PC:1 sediment	0.15	0.37	6.06
0.1 FA:0.2 PC:1 sediment	0.07	0.17	3.10
0.15 FA:0.15 PC:1 sediment	0.09	0.22	4.53
Portland cement with fly ash and/or sodium silicate			
0.05 NaSi:0.1 FA:0.1 PC:1 sediment	<0.05	<0.12	-
0.05 NaSi:0.1 FA:0.2 PC:1 sediment	<0.05	<0.13	-
0.05 NaSi:0.25 FA:0.25 PC:1 sediment	<0.05	<0.15	-
0.05 NaSi:0.25 PC:1 sediment	<0.05	<0.13	-
0.05 NaSi:0.5 PC:1 sediment	<0.05	<0.15	-
Portland cement with Firmix			
0.2 FM:0.1 PC:1 sediment	<0.05	<0.13	-
0.1 FM:0.2 PC:1 sediment	<0.05	<0.13	-
0.15 FM:0.15 PC:1 sediment	<0.05	<0.13	-
Fly ash with lime			
0.4 FA:0.1 L:1 sediment	<0.05	<0.15	-
0.5 FA:0.1 L:1 sediment	<0.05	<0.16	-
0.6 FA:0.1 L:1 sediment	<0.05	<0.16	-
Firmix			
0.4 FM:1 sediment	0.40	1.05	7.49
0.5 FM:1 sediment	0.36	1.01	8.35
0.6 FM:1 sediment	0.29	0.87	8.55

(Continued)

Table H35 (Concluded)

Process	q_L mg/kg	q_{nL} mg/kg	K_d ℓ/kg
Firmix with WEST-P			
0.01 WP:0.5 FM:1 sediment	0.21	0.60	15.87
0.03 WP:0.5 FM:1 sediment	0.02	0.06	-
0.05 WP:0.5 FM:1 sediment	0.22	0.64	19.29
Portland cement with WEST-P			
0.01 WP:0.2 PC:1 sediment	0.08	0.18	4.65
0.03 WP:0.2 PC:1 sediment	0.09	0.21	5.92
0.05 WP:0.2 PC:1 sediment	<0.06	<0.14	-

Table H36

Summary of Lead Leaching Indices for Solidified/Stabilized Indiana Harbor Sediment

Process	q_L mg/kg	q_{nL} mg/kg	K_d ℓ/kg
Untreated anaerobic sediment	2.47	2.47	2.39
Portland cement			
0.1 PC:1 sediment	0.50	1.03	2.12
0.2 PC:1 sediment	0.58	1.31	5.50
0.3 PC:1 sediment	0.98	2.44	0
0.4 PC:1 sediment	1.72	4.52	9.66
Portland cement with fly ash			
0.2 FA:0.1 PC:1 sediment	0.11	0.27	0
0.1 FA:0.2 PC:1 sediment	0.48	1.17	12.1
0.15 FA:0.15 PC:1 sediment	0.35	0.85	0
Portland cement with fly ash and/or sodium silicate			
0.05 NaSi:0.1 FA:0.1 PC:1 sediment	1.11	2.61	0
0.05 NaSi:0.1 FA:0.2 PC:1 sediment	0.63	1.60	9.39
0.05 NaSi:0.25 FA:0.25 PC:1 sediment	0.43	1.25	6.05
0.05 NaSi:0.25 PC:1 sediment	1.10	2.69	4.17
0.05 NaSi:0.5 PC:1 sediment	0.63	1.83	0
Portland cement with Firmix			
0.2 FM:0.1 PC:1 sediment	0.17	0.42	0
0.1 FM:0.2 PC:1 sediment	0.32	0.78	7.41
0.15 FM:0.15 PC:1 sediment	0.36	0.88	14.1
Fly ash with lime			
0.4 FA:0.1 L:1 sediment	1.16	3.27	0
0.5 FA:0.1 L:1 sediment	1.38	4.15	0
0.6 FA:0.1 L:1 sediment	2.10	6.71	0
Firmix			
0.4 FM:1 sediment	0.05	0.13	0
0.5 FM:1 sediment	0.04	0.11	0
0.6 FM:1 sediment	0.12	0.36	0

(Continued)

Table H36 (Concluded)

Process	q_L mg/kg	q_{nL} mg/kg	K_d ℓ/kg
Firmix with WEST-P			
0.01 WP:0.5 FM:1 sediment	0.05	0.14	0
0.03 WP:0.5 FM:1 sediment	ND	ND	ND
0.05 WP:0.5 FM:1 sediment	0.05	0.15	0
Portland cement with WEST-P			
0.01 WP:0.2 PC:1 sediment	0.35	0.80	11.5
0.03 WP:0.2 PC:1 sediment	0.27	0.62	10.9
0.05 WP:0.2 PC:1 sediment	0.36	0.85	0

Table H37

Summary of Zinc Leaching Indices for Solidified/Stabilized Indiana Harbor Sediment

Process	qL mg/kg	qnL mg/kg	Kd ℓ/kg
Untreated anaerobic sediment	9.4	9.4	-
Portland cement			
0.1 PC:1 sediment	0.1	0.2	-
0.2 PC:1 sediment	<0.1	<0.3	0
0.3 PC:1 sediment	1.7	2.2	16.5
0.4 PC:1 sediment	0.7	1.8	0
Portland cement with fly ash			
0.2 FA:0.1 PC:1 sediment	0.3	0.7	-
0.1 FA:0.2 PC:1 sediment	<0.1	<0.3	-
0.15 FA:0.15 PC:1 sediment	<0.1	<0.3	-
Portland cement with fly ash and/or sodium silicate			
0.05 NaSi:0.1 FA:0.1 PC:1 sediment	0.5	1.2	0
0.05 NaSi:0.1 FA:0.2 PC:1 sediment	0.2	0.5	-
0.05 NaSi:0.25 FA:0.25 PC:1 sediment	0.3	0.9	-
0.05 NaSi:0.25 PC:1 sediment	0.5	1.2	0
0.05 NaSi:0.5 PC:1 sediment	0.4	0.5	0
Portland cement with Firmix			
0.2 FM:0.1 PC:1 sediment	<0.1	<0.3	-
0.1 FM:0.2 PC:1 sediment	<0.1	<0.3	-
0.15 FM:0.15 PC:1 sediment	<0.1	<0.3	-
Fly ash with lime			
0.4 FA:0.1 L:1 sediment	4.8	13.5	27.3
0.5 FA:0.1 L:1 sediment	9.1	27.4	49.1
0.6 FA:0.1 L:1 sediment	10.2	32.6	45.8
Firmix			
0.4 FM:1 sediment	<0.1	<0.3	-
0.5 FM:1 sediment	<0.1	<0.3	-
0.6 FM:1 sediment	<0.1	<0.4	-

(Continued)

Table H37 (Concluded)

Process	qL mg/kg	qnL mg/kg	Kd ℓ/kg
Firmix with WEST-P			
0.01 WP:0.5 FM:1 sediment	<0.1	<0.3	-
0.03 WP:0.5 FM:1 sediment	<0.1	<0.3	-
0.05 WP:0.5 FM:1 sediment	<0.1	<0.3	-
Portland cement with WEST-P			
0.01 WP:0.2 PC:1 sediment	<0.1	<0.3	-
0.03 WP:0.2 PC:1 sediment	<0.1	<0.3	-
0.05 WP:0.2 PC:1 sediment	<0.1	<0.3	-

Table H38

Summary of Chromium Leaching Indices for Solidified/Stabilized Indiana Harbor Sediment*

Process	q_L mg/kg	q_{nL} mg/kg
Untreated anaerobic sediment	1.19	1.19
Portland cement		
0.1 PC:1 sediment	0.96	1.98
0.2 PC:1 sediment	0.18	0.41
0.3 PC:1 sediment	0.27	0.66
0.4 PC:1 sediment	0.39	1.03
Portland cement with fly ash		
0.2 FA:0.1 PC:1 sediment	0.67	1.64
0.1 FA:0.2 PC:1 sediment	0.43	1.05
0.15 FA:0.15 PC:1 sediment	0.44	1.08
Portland cement with fly ash and/or sodium silicate		
0.05 NaSi:0.1 FA:0.1 PC:1 sediment	0.30	0.70
0.05 NaSi:0.1 FA:0.2 PC:1 sediment	0.54	1.37
0.05 NaSi:0.25 FA:0.25 PC:1 sediment	0.51	1.49
0.05 NaSi:0.25 PC:1 sediment	0.43	1.05
0.05 NaSi:0.5 PC:1 sediment	0.34	0.99
Portland cement with Firmix		
0.2 FM:0.1 PC:1 sediment	0.82	2.00
0.1 FM:0.2 PC:1 sediment	0.39	0.95
0.15 FM:0.15 PC:1 sediment	0.47	1.15
Fly ash with lime		
0.4 FA:0.1 L:1 sediment	0.40	1.13
0.5 FA:0.1 L:1 sediment	0.23	0.69
0.6 FA:0.1 L:1 sediment	0.18	0.58
Firmix		
0.4 FM:1 sediment	0.33	0.87
0.5 FM:1 sediment	0.33	0.93
0.6 FM:1 sediment	0.26	0.78

(Continued)

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* Kd = 1.85 ℓ/kg.

Table H38 (Concluded)

Process	q_L mg/kg	q_{nL} mg/kg
Firmix with WEST-P		
0.01 WP:0.5 FM:1 sediment	0.16	0.45
0.03 WP:0.5 FM:1 sediment	0.25	0.72
0.05 WP:0.5 FM:1 sediment	0.23	0.67
Portland cement with WEST-P		
0.01 WP:0.2 PC:1 sediment	0.78	1.78
0.03 WP:0.2 PC:1 sediment	0.74	1.71
0.05 WP:0.2 PC:1 sediment	0.73	1.72

53. The data for zinc showed that, in general, solidification/stabilization reduced the mass of leachable zinc in the sediment. As was the case with lead, the lime in the fly ash with lime process apparently increased the leachability of zinc. The other processes involving fly ash did not show comparable increases in normalized leachable zinc. The portland cement with Firmix, Firmix, and the processes involving WEST-P were particularly effective in reducing the normalized leachable zinc concentration. The zinc desorption isotherms for all the formulations for each of these processes were NRIs.

54. Table H38 lists the leachable and normalized leachable concentrations for chromium. Since all of the chromium desorption isotherms were CIs, K_d is equal to zero in every case. Some of the solidification/stabilization processes slightly reduced the normalized leachable chromium concentration. The Firmix and Firmix with WEST-P were the only processes that consistently reduced the normalized leachable chromium concentration. All the other processes were either inconsistent in the reduction provided or increased the normalized leachable chromium concentration in some formulations. The results of these comparisons should be viewed with some caution. The lack of a well-defined relationship between solid and aqueous phase chromium concentrations makes definitive statements concerning immobilization (or the lack thereof) impossible. However, since the aqueous phase (leachate) concentrations were relatively low (<0.005 to 0.075 mg/ℓ), there does not appear to be a significant potential for release of chromium from the solidified/stabilized sediment.

55. A convenient basis for comparison of process effectiveness for overall metal immobilization potential is the total normalized leachable metal concentration, obtained by summing the normalized leachable metal concentrations for arsenic, chromium, lead, and zinc. In Table H39 the various processes are ranked according to the total normalized leachable arsenic, chromium, lead, and zinc. For reference, the total leachable metal concentration for untreated anaerobic sediment is listed at the beginning of Table H39.

56. With the exception of the fly ash with lime process, all the processes reduced the leachability of the metals in Indiana Harbor sediment. The process formulations ranked number 1 and 2 were the 0.01 WEST-P:0.5 Firmix:1 sediment and the 0.05 WEST-P:0.5 Firmix:1 sediment formulations. Because the leachates from the 0.03 WEST-P:0.5 Firmix:1 sediment were not analyzed for lead, this process formulation was not included in the ranking. However, the data for the other metals suggests that had the lead data been available, the

Table H39

Process Effectiveness for Metal Immobilization Ranked According to the Sum of the Nomalized Leachable Metal Concentrations

Ranking	Process	q_{nL}* (mg/ℓ)
-	Untreated anaerobic sediment	13.47
1	0.01 WEST-P:0.5 Firmix:1 sediment	1.49
2	0.05 WEST-P:0.5 Firmix:1 sediment	1.76
3	0.2 portland cement:1 sediment	2.09
4	0.1 Firmix:0.2 portland cement:1 sediment	2.16
5	0.4 Firmix:1 sediment	2.35
6	0.5 Firmix:1 sediment	2.35
7	0.6 Firmix:1 sediment	2.41
8	0.15 fly ash:0.15 portland cement:1 sediment	2.45
9	0.15 Firmix:0.15 portland cement:1 sediment	2.46
10	0.1 Fly Ash:0.2 portland cement:1 sediment	2.69
11	0.03 WEST-P:0.2 portland cement:1 sediment	2.84
12	0.2 Firmix:0.1 portland cement:1 sediment	2.85
13	0.2 Fly ash:0.1 portland cement:1 sediment	2.98
14	0.05 WEST-P:0.2 portland cement:1 sediment	3.01
15	0.01 WEST-P:0.2 portland cement:1 sediment	3.06
16	0.05 Sodium silicate:0.5 portland cement:1 sediment	3.47
17	0.05 Sodium silicate:0.1 fly ash:0.2 portland cement:1 sediment	3.60
18	0.05 Sodium silicate:0.25 fly ash:0.25 portland cement:1 sediment	3.79
19	0.1 Portland cement:1 sediment	3.81
20	0.05 Sodium silicate:0.1 fly ash:0.1 portland cement:1 sediment	4.63
21	0.05 Sodium silicate:0.25 portland cement:1 sediment	5.07
22	0.3 Portland cement:1 sediment	5.43

(Continued)

$q_{nL} = q_{nL,As} + q_{nL,Cr} + q_{nL,Pb} + q_{nL,Zn}$

Table H39 (Concluded)

Ranking	Process	q_{nL} (mg/ℓ)
23	0.4 Portland cement:1 sediment	7.49
24	0.4 Fly ash:0.1 lime:1 sediment	18.05
25	0.5 Fly ash:0.1 lime:1 sediment	32.40
26	0.6 Fly ash:0.1 lime:1 sediment	40.05

top three process formulations probably would have been Firmix with WEST-P formulations. The second best process for metal immobilization was the Firmix process. The three Firmix formulations ranked fourth, fifth, and sixth. The 0.2 portland cement:1 sediment process formulation ranked number 3. The other portland cement formulations, however, ranked at the other end of the scale, numbers 19, 22, and 23. Thus, with the exception of one formulation, the portland cement process was not as effective as the other processes.

57. As previously noted, the desorption isotherms for organic carbon showed a curvilinear relationship between solid and aqueous phase organic carbon concentrations. Figures H10 and H11 are typical of the curvilinear plots obtained from most of the organic carbon desorption data. Curvilinear plots usually occur in adsorption studies involving organic chemicals. Three adsorption isotherms are well known, the BET, the Langmuir, and the Freundlich isotherms. Hill, Myers, and Brannon (1986) have discussed the potential application of these isotherms to desorption data from contaminated sediment.

58. The Langmuir equation was chosen for application to the organic carbon desorption isotherm data. The Langmuir equation is given below:

$$q = \frac{QbC}{(1 + bC)} \qquad \text{(H6)}$$

where

q = solid phase contaminant concentration, mg/kg

Q = sorption capacity of the solid phase, mg/kg

b = Langmuir distribution coefficient, ℓ/mg

C = aqueous phase contaminant concentration, mg/kg

Equation H6 models a contaminant that is totally leachable, i.e., q_r is equal to zero.

59. By fitting data to the linearized form of the Langmuir equation given below, the Langmuir coefficients, Q and b, can be obtained.

$$\frac{C}{q} = \frac{1}{Qb} + \frac{1C}{Q} \qquad \text{(H7)}$$

For comparison, Equation G3 and equation H7 were fitted to the organic carbon desorption isotherm data for untreated anaerobic sediment and solidified/ stabilized Indiana Harbor sediment. The coefficients of determination, r^2 values, are presented in Table H40. As the r^2 value approaches unity, the regressed equation fits the data better.

60. The fit of the linear desorption model, Equation G3, was good for some data and poor for other data. The fit of the nonlinear desorption model provided by the Langmuir equation was good for all of the data and was better than the linear desorption model in every case. However, since fitting Equation H7 involves regressing C against itself, comparison of r^2 values for Equations G3 and H7 has limited meaning. An inspection of the desorption plots showed the nonlinearity of the process controlling organic carbon desorption to be unmistakable. Thus, a nonlinear model, such as the Langmuir equation, is more appropriate. In addition, the consistency of the r^2 values for the Langmuir equation furnished a consistent basis for comparing the effectiveness of different solidification/stabilization processes that the linear desorption model could not provide.

61. The Langmuir coefficients determined by regression of Equation H7 onto the organic carbon desorption data are presented in Table H40. The values for the sorption capacity of the solids Q were normalized with respect to the mass of wet sediment solidified using the same approach previously described for normalized leachable metal concentrations, Equation H5. The normalized sorption capacity Q_n represents the maximum organic carbon concentration that the solid phase can sorb. Hence, the higher Q_n, the greater the capacity of the solids for holding organic carbon.

62. The Q_n values for the solidified, stabilized sediment were slightly less than the Q_n of the untreated anaerobic sediment. This is not unexpected since the setting agents compete with sorbed materials for reaction sites on the sediment solids. The normalized sorption capacities for the solidified sediment were lower because solidification utilizes some of the sorption sites on the sediment solids, and, apparently, the setting agents add little or no additional sorption capacity. The reduction in Q_n, however, was not particularly significant. The Q_n for the solidified sediment ranged from 95.6 to 99.6 percent of Q_n of the untreated anaerobic sediment.

63. Since the organic carbon analysis consisted of determining total organic carbon in filtered leachate, the analysis included naturally occurring

Table H40

Langmuir Coefficients For Organic Carbon in Leachates From Solidified/Stabilized Indiana Harbor Sediment

Process	r^2 (Eq G5)	r^2 (Eq H7)	b ℓ/kg	Q mg/kg	Q_N mg/kg
Untreated sediment	0.9175	0.9999	0.95	23400	23400
Portland cement					
0.1 PC:1 sediment	0.7799	0.9999	0.64	10900	22600
0.2 PC:1 sediment	0.7712	0.9999	0.52	10300	23200
0.3 PC:1 sediment	0.8269	0.9999	0.80	9440	23100
0.4 PC:1 sediment	0.4346	0.9999	1.21	8770	23100
Portland cement with fly ash					
0.2 FA:0.1 PC:1 sediment	0.6729	0.9999	0.46	9260	22600
0.1 FA:0.2 PC:1 sediment	0.5607	0.9999	0.52	9380	22900
0.15 FA:0.15 PC:1 sediment	0.5417	0.9999	0.90	9300	22700
Portland cement with Firmix					
0.2 FM:0.1 PC:1 sediment	0.5595	0.9999	2.25	9380	22900
0.1 FM:0.2 PC:1 sediment	0.3801	0.9999	1.27	9360	22900
0.15 FM:0.15 PC:1 sediment	0.0069	0.9999	2.01	9350	22800
Fly ash with lime					
0.4 FA:0.1 L:1 sediment	0.6428	0.9999	0.91	8220	23200
0.5 FA:0.1 L:1 sediment	0.1233	0.9994	0.80	7740	23300
0.6 FA:0.1 L:1 sediment	0.7445	0.9999	2.09	7220	23100
Firmix					
0.4 FM:1 sediment	0.4520	0.9999	1.22	8690	22900
0.5 FM:1 sediment	0.7216	0.9999	1.02	8120	22900
0.6 FM:1 sediment	0.6266	0.9999	0.69	7610	22900
Firmix with WEST-P					
0.01 WP:0.5 FM:1 sediment	0.4713	0.9999	1.22	8050	22800
0.03 WP:0.5 FM:1 sediment	0.2111	0.9999	-8.6	7860	22600
0.05 WP:0.5 FM:1 sediment	0.3765	0.9999	2.88	7780	22700
Portland Cement with WEST-P					
0.01 WP:0.2 PC:1 sediment	0.6314	0.9998	0.61	10000	22800
0.03 WP:0.2 PC:1 sediment	0.6574	0.9999	0.66	9790	22600
0.05 WP:0.2 PC:1 sediment	0.6868	0.9999	0.71	9660	22700

organic compounds such as humic and fluvic acids that are normally found in high concentration in sediments. Hence, the organic carbon desorption isotherms may reflect primarily the desorption characteristics of these substances. The ability of special solidification/stabilization agents, such as WEST-P, to reduce the leachability of specific organic contaminants such as PCBs could not be evaluated on the basis of the data available.

Limitations of laboratory evaluations.

64. Several important aspects of field application were not addressed in this laboratory study. Topics beyond the scope of this investigation include scale-up factors, long-term stability of the solidified/stabilized sediment, and engineering economy. In the field, strengths may be lower than those obtained in the laboratory due to lower mixing efficiency and/or dosage control. The implementation strategy (see body of report) will affect mixing efficiency and dosage control. For this reason, these factors are best evaluated in a field demonstration. Temperature is another processing variable that was not investigated that can be important in the field.

65. Caution must also be exercised in extrapolating the desorption data to the field. The surface area for leaching in the field may be different from that in the serial, graded batch leach tests. Since the solidified/stabilized sediment samples were ground, the surface-area-to-mass ratio in the laboratory tests is probably higher than that in the field. However, the laboratory leach data are not necessarily conservative since the impact of grinding on contaminant mobility is poorly understood.

66. Chemical leach data from serial, graded batch leach tests and the methods of data analysis presented in this report were designed to provide a basis for evaluating the source term in permeant-porous media equations. Permeant-porous media equations are mass transport equations that describe the generation of leachate as water percolates through a porous medium, such as solidified/stabilized sediment. Mass transport models with other assumptions and equations, such as the solid-phase diffusion approach (Cote and Isabel 1984), might also be applied to solidified/stabilized sediment and give reasonable results. The permeant-porous media model is probably a worst-case model, and the solid-phase diffusion model is probably a best-case model (Myers and Hill 1986). The lack of detailed field records, however, makes definitive statements concerning the relative merits of the two approaches impossible.

Conclusions

67. The range in 28-day UCS was 48.5 psi (334 kPa) to 682 psi (4700 kPa), depending of the agent(s) used for solidification and the dosage applied. This range in product strength is indicative of the versatility of solidification as a physical stabilization process for Indiana Harbor sediment. The technology has the flexibility to meet specifications for physical stability ranging from primarily immobilizing sediment solids in a low strength product to producing a material suitable for end uses typical of soft concrete.

68. Solidification/stabilization reduced the leachability of arsenic, cadmium, chromium, lead, and zinc. Cadmium and zinc were completely immobilized by some processes. Because some solidification/stabilization tend to increase the leachable metal concentration, careful process selection is needed to maximize chemical stabilization. The most effective processes for metal immobilization were Firmix with WEST-polymer and Firmix.

69. Solidification/stabilization did not significantly alter the sorption capacity of the sediment for total organic carbon. Data were not available to evaluate the potential of solidification/stabilization technology to reduce the leachability of specific organic compounds.

APPENDIX I: FEASIBILITY STUDY OF CONTAINED AQUATIC DISPOSAL IN INDIANA HARBOR CANAL AND ENTRANCE CHANNEL

Background

1. The proposed maintenance dredging of Indiana Harbor and Canal includes about 200,000 cu yd of highly contaminated material located in the canal portion of the project (Figure I1). One of the alternatives being considered for disposal of this material is capped aquatic disposal (CAD). Possible sites for the CAD include Lake Michigan, Indiana Harbor proper, the entrance channel to Indiana Harbor, and the Indiana Harbor Canal. If the CAD is determined to be feasible and subsequently selected for further study, a demonstration site will first be tested to demonstrate that the CAD is an acceptable approach. A small fraction of the contaminated material will be dredged and placed in the demonstration CAD site to be monitored. If the demonstration site proves acceptable, the same procedure can then be used to dispose of the estimated 200,000 cu yd of contaminated material.

Objectives of the Hydraulics Laboratory Effort

2. The objectives of this effort are to:

a. Determine the feasibility of CAD in the Indiana Harbor Canal and Entrance Channel.

b. If CAD is feasible, make specific siting and configuration recommendations for both the demonstration and full volume sites.

c. Evaluate cap stability based on available data to include vessel traffic.

d. Design a long-term program to monitor cap stability.

Approach

3. The first step was to evaluate the feasibility of CAD in the canal and entrance channel with respect to excavation constraints in these areas. Maximum allowable depths of excavation, impact of excavation on structural integrity of nearby harbor structures, and the existence of buried cables or other conduits were established.

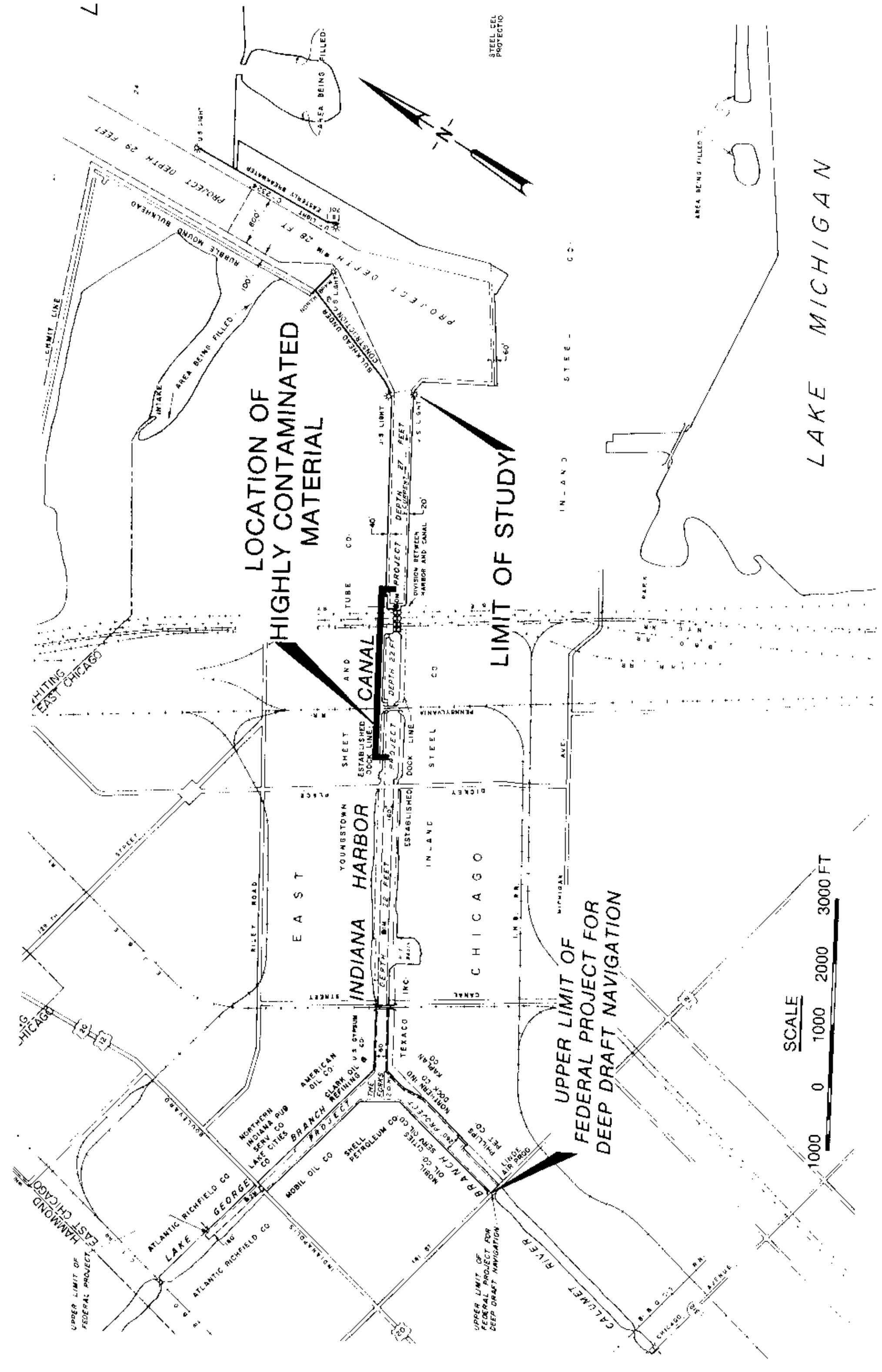

Figure I1. Site map

4. The second step was to site and size the required excavation for the full-volume site and to design the cap. Based on available current data (both normal and extreme environments), the stability of the proposed sand cap was evaluated. Due to the negative results of the study, the long-term monitoring was not addressed. In addition to the references cited, a general bibliography containing several related subjects is included at the end of the main text.

Area of Concern

5. The areas for potential CAD sites included the entrance channel, the Indiana Harbor Canal, and the branches of the Federal project beyond the Forks (Figure I1). The two areas within the Canal having PCB contaminated sediments were not considered for potential CAD sites.

6. Another area that was not considered was the Forks area since it is actively used as a turning basin and vessels' propeller wash strongly agitates bottom sediments. Other constraints considered were buried pipeline and cable crossings near the various bridges and the two fixed bridges near the Federal project limits (B&OCT railroad on the Lake George Branch with a vertical clearance of 5 ft, and the 141st Street bridge with a vertical clearance of 8 ft (National Ocean Survey Charts)).

CAD Design Considerations

7. The volume of highly contaminated material to be dredged has been estimated to be 200,000 cu yd at in-situ density. Depending on the dredge and dredge operation method, this volume may increase severalfold. For this effort, it was assumed that 220,000 to 400,000 cu yd must be contained in the CAD site.

8. In order to estimate the area required for the CAD site, a cross section was developed for the smaller and less used branches of the canal. By incorporating a 3-ft sand cap, the area available for the contaminated material was reduced and would require over 1-1/2 miles of uninterrupted channel for a CAD site, which because of obstructions is not available. The maximum containment capacity in these areas is approximately 50,000 cu yd without encroaching into the Forks area. Therefore, the areas chosen for further

study were the US turning basin and adjacent canal and the entrance channel (Figure I1).

9. There is a very limited amount of flow information available for these areas. The velocity and direction of flow is apparently related to conditions in Lake Michigan. From various sources, we found that the flow may be either in or out of the entrance channel and velocities may range from 0 to 1 fps.* A criterion of 3 fps was selected as the flow speed for incipient motion of the cap.

10. Another consideration was the physical characteristics of dredging equipment to be used. The depth of the design cross section was limited to approximately 50 ft so that most dredge types could be used.

11. The disposal location for the materials dredged to create the disposal trench was not addressed in this effort.

12. A literature search revealed that typical vessels could have a length over all of 600 to 800 ft and greater. These tankers and freighters have drafts up to 30 ft and propeller diameters in the range of 20 ft. Some of these vessels already operate in the entrance channel area.

Cap Stability

Natural flows

13. To address grain-size requirements for capping materials under natural flows, the Ackers-White Method was utilized (Ackers and White 1973). This method uses the various parameters of particle diameter, velocity, bed shear stress, etc., to arrive at the critical flow condition for initiation of sediment motion. By varying the average grain size (D_{50}), the method indicates that at project depths a mixture of coarse sands and fine gravels will withstand velocities of over 3 fps under normal conditions. A cap thickness of 3 ft was chosen as protection against major storm events, so that some erosion of the cap could occur without exposing the contaminated material. It also provides flexibility in replacement time whereas a thinner cap would require additional materials immediately. A thicker cap would be more costly and reduce the available containment area even more. At the Duwamish Waterway

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* Personal communications, Howard A. Benson and Robert F. Athow, 1985, and US Army Engineer Waterways Experiment Station (1959) Northwest Bulkhead studies.

contaminated dredge disposal site (Seattle, Wash.), a sand cap of approximately 2 ft was used (Sumeri 1984). However, the site was located in an existing 75-ft-deep depression, and the final elevation of the cap surface was 55 to 60 ft mllw. There are no design criteria for cap thickness, but the 3-ft cap thickness was selected as reasonable for a shallow channel.

Ackers-White

14. In the development of the Ackers-White formulation (Ackers and White 1973), coarse sediment is considered to be transported as bed load and fine sediment as suspended load. Sediment mobility is described by the ratio of the appropriate shear force on a unit area of the bed to the immersed weight of a layer of grains. The mobility number is denoted F_{gr}, and is defined as:

$$F_{gr} = \frac{v_*^{\,n}}{gD(s - 1)} \quad {\frac{V}{32 \log \frac{\alpha d}{D}}}^{1-n} \qquad \text{(I1)}$$

where

$v*$ = shear velocity based on energy grade line slope

D = sediment diameter

g = acceleration of gravity

s = mass density of sediment relative to that of water

V = mean velocity of flow

α = coefficient in rough turbulent equation

d = mean depth of flow

n = transition exponent depending on sediment size

A dimensionless grain diameter D_{gr} is defined as:

$$D_{gr} = D \, {\frac{g(s - 1)}{v^2}}^{1/3} \qquad \text{(I2)}$$

where

v = kinematic viscosity of fluid.

15. Once the value of D_{gr} has been derived, the value of n, the transport exponent, can be determined as follows:

$$\begin{aligned}
&\text{for } D_{gr} \leq 1.0 \quad n = 1 \\
&\text{for } 1.0 < D_{gr} \leq 60 \quad n = 1.0 - 0.56 \log D_{gr} \\
&\text{for } D_{gr} > 60 \quad n = 0
\end{aligned}$$

and the value of the sediment mobility number calculated from Equation I1.

16. The Ackers-White approach uses dimensionless expressions for sediment transport based on the stream power concept. In the case of coarse sediments, it uses the product of net grain shear stress and stream velocity as the power per unit area of bed; and for fine sediments, it uses the product of the total shear stress and velocity. The dimensionless sediment transport rate G_{gr} is described by the equation

$$G_{gr} = C \frac{F_{gr}}{A} - 1^{m} \qquad \text{(I3)}$$

where

C = coefficient in sediment transport function

A = value of F_{gr} at nominal initial motion

m = exponent in sediment transport function

The values of C, A, and m can be derived as follows:

$$\begin{aligned}
&\text{for } 1 < D_{gr} \leq 60 \quad && \log C = 2.86 \log D_{gr} - (\log D_{gr})^2 - 3.53 \\
& && A = (0.23/ D_{gr}) + 0.14 \\
& && m = (9.66/D_{gr}) + 1.34 \\
&\text{for } D_{gr} > 60 \quad && C = 0.025 \\
& && A = 0.17 \\
& && m = 1.50
\end{aligned}$$

17. Once the dimensionless sediment transport rate has been derived from Equation I3, the sediment transport in mass flux per unit mass flow rate X can be determined from the equation

$$X = \frac{G_{gr}SD}{d} \; {\frac{V}{v^{*}}}^{n} \qquad (I4)$$

18. By reworking the Ackers-White formulation with the variables of both grain size and depth as functions of flow speed, the initiation of motion, or, conversely, the cap stability was determined for capping materials. Figure I2 illustrates these results graphically as a family of curves, each curve representing a different depth. The graph indicates the velocity, in feet per second, at which the median sediment grain (D_{50}) begins movement at the channel depth indicated. Coarse sand mixed with fine gravel will resist natural bottom velocities and most storm events in the channel and canal within the 3-fps criterion.

Ship traffic

19. Two mathematical methods were compared to address the effects of ship traffic directly over the cap. The first method, Liou and Herbich (1976), is fairly involved mathematically and the authors developed a computer program to solve it. Also presented are the data of several case studies based on Corpus Christi ship channel traffic. The results appear excessively conservative (stone size of several feet in diameter); however, the method is again described in Herbich et al. (1984) and includes correction for boundary layer and relative velocity effects.

20. The second method reviewed, Blaauw and van de Kaa (1978), is based on empirical, laboratory, and field observations. Since actual case studies were not provided, it was decided to use this method and then compare the results with those of Herbich et al.

21. The Blaauw and van de Kaa method addresses the design of bottom protection from the scour produced by a vessel with a single propeller at constant speed. The following is a brief explanation of the various equations.

22. The value of the axial efflux velocity of propeller V_o may be determined by:

$$V_o \sim 1.60 \; n \; D_p \; K_T(\text{prop}) \qquad (I5)$$

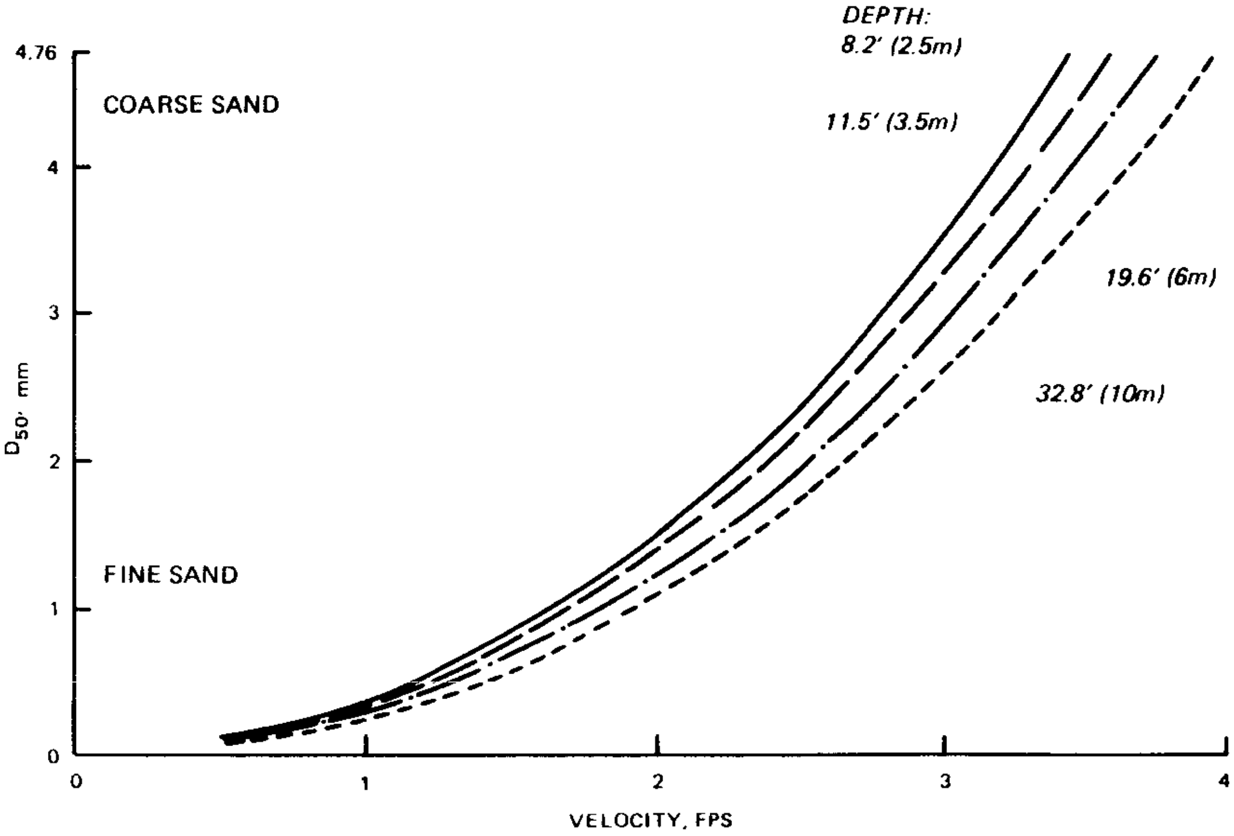


Figure 12. Particle movement predictions by Ackers-White method (Mannings n = 0.03)

where

n = number of revolutions per second of propeller

D_p = diameter of propeller

$K_T(\text{prop})$ = propeller thrust coefficient

23. The next value to be calculated is the initial diameter of slipstream behind the propeller D_0 :

$$D_0 = \frac{D_p}{2} \tag{I6}$$

24. Laboratory tests indicated that the area in which maximum scour of the channel bottom occurs is $0.10 < Z/X < 0.25$, where Z is the vertical distance from the propeller axis to the bottom, and X is the axial distance from the propeller plane behind the vessel. Using the theory of a submerged jet, the next equation was developed to calculate the velocity distribution within the maximum scour zone:

$$\frac{V_x}{V_0} = 2.78 \frac{D_0}{X} e^{-15.43 \frac{Z^2}{X^2}} \tag{I7}$$

where

V_x = axial velocity at a point

e = 2.718 (the base of the natural logarithm system)

25. Since the axial velocity V_x has been calculated, the bottom shear stress can be determined with Equation I8:

$$T = \frac{1}{2} C_f \rho V_x{}^2 \tag{I8}$$

where

T = bottom shear stress

c_f = bottom friction factor which in general is $0.06 < c_f < 0.11$

ρ = density of water

26. The median size (D_{50}) of bottom protection can be computed by:

$$\Delta D_{50} \geq \frac{T}{(\rho g \psi)} \tag{I9}$$

where

Δ = relative density of bottom material = $\frac{\rho_s - \rho}{\rho}$

ψ = shear stress parameter (given, between 0.02 and 0.06)

ρ_s = density of bottom protection

27. It was decided to analyze the entrance channel area first since it would be the major containment site.

28. Tugs are not used in the canal. Current practice in the Indiana Harbor Canal by commercial vessel operators is to "coast" through the canal, then move through the bridges under power. However, should a vessel be in an emergency situation such as possible collision or an extreme storm event, a vessel may use full power, forward or reverse, and perhaps even drag the vessel's anchor(s). An emergency situation must be considered since this CAD site lifetime will be many years and, as the length of time increases, so does the probability of a potential problem.

29. The entrance channel was chosen as a realistic case since there is more traffic in and around the harbor area. At this location, project depth is 27 ft plus 2 ft overdepth, or 29 ft, which was rounded to 30 ft. A realistic 20-ft-diam propeller was selected with rotation at 50 rpm. Based on these parameters, the Blaauw and van de Kaa method indicated that 6-in.-diam rock would be required to protect the cap from scour due to propeller wash. At 100 rpm, still a realistic possibility, the rock size increases to just over 2 ft (Figure I3).

30. A method to determine the effects of a pressure gradient beneath a passing vessel (coasting and not under power) on a channel bottom has not been considered. The dropping of an anchor or dragging anchor cannot be easily addressed but will have a major impact on any cap material. These effects were not considered further since the simple calculation showed the cap to be infeasible.

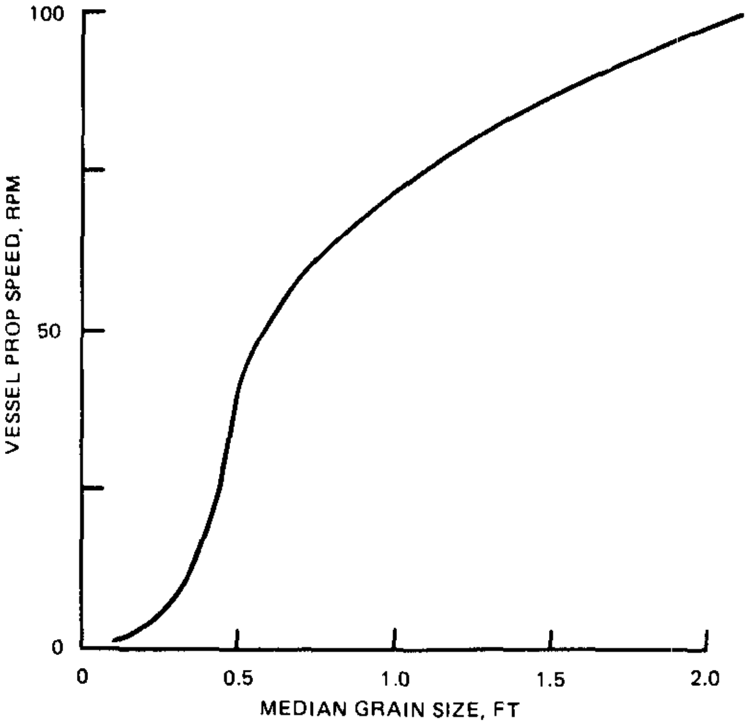


Figure I3. Armor stone size as a function of vessel speed

31. A comparison of these results to those of Liou and Herbich (1976) and Herbich et al. (1984) indicate reasonable agreement. Although vessels using the Corpus Christi ship channel analyzed by Herbich are larger, the channel is also deeper (45 ft). Their results show 1-1/2- to 2-ft stone sizes as needed for bottom protection. This agrees with our upper range of values. As another check, several flood control channel design handbooks dealing with bottom velocities were reviewed. Using 15 fps, these works indicate a 1.5-ft-diam or 250-lb stone would be required.

Volumetric Design with Cap and Armor

32. A second cross section was developed from the first (Figure I4) which also included a 3-ft-deep sand cap with the top of the sand 2 ft below the authorized channel depth. Note that Figure I4 is the entrance channel cross section whereas the cross section for the canal is not as wide nor deep.

33. Figure I5 shows the third cross section which includes a 3- to 6-ft armor layer. The required cap area decreases the lower containment area by almost 50 percent. This means that 120,000 to 150,000 cu yd maximum of the 220,000 to 400,000 cu yd can be placed and another site must be located for the remainder. Beneath the armor layer, a gradation of sands and gravels prevents contaminated material movement through the armor layer. As with the cap thickness, there is no design criterion for stone armor layer thickness. As the median stone diameter increases, the relative void ratio also increases. A narrow band or "veneer" of armor would be unacceptable since the finer cap material would migrate or be forced through the voids thus escaping and leaving less protection for the materials below. A minimum of 3 ft was selected for armor thickness to ensure the sand cap integrity.

34. Aside from propeller wash, this channel bottom armor could, especially at periods of low water, become a hazard to navigation. A laden vessel during low water might strike the armor layer, damaging both the ship and armor. Maintenance dredging above the armor will have to be accomplished more cautiously, causing increased costs. Should a dredge accidentally pick up some of the armor material, there would be additional expenses in pump and equipment repair plus down time. Placement of the armor layer presents additional problems. Aside from handling problems, placement would require techniques of placing rather than dumping and the installation of some type of

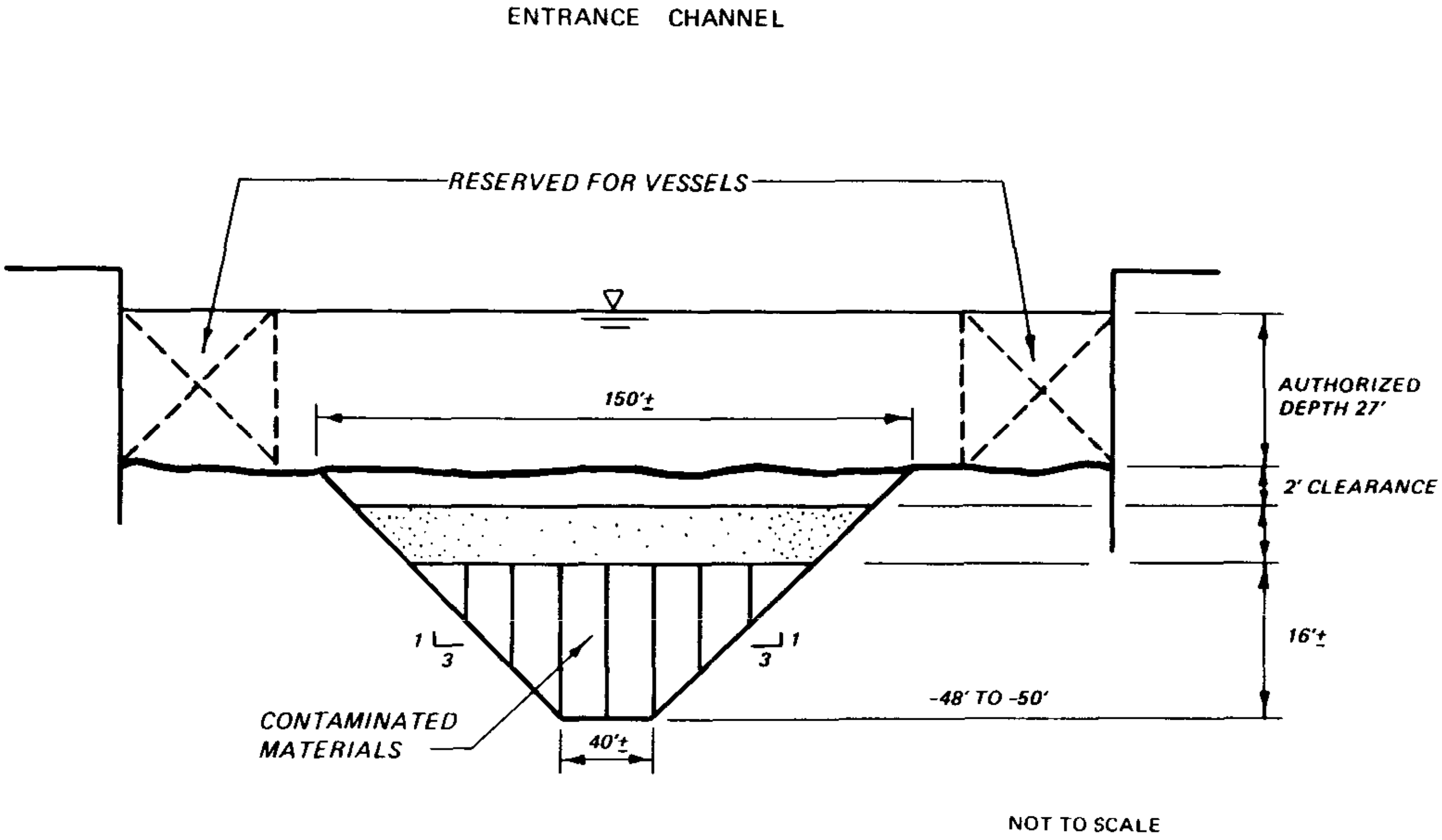


Figure I4. Trench cross section with 3-ft cap

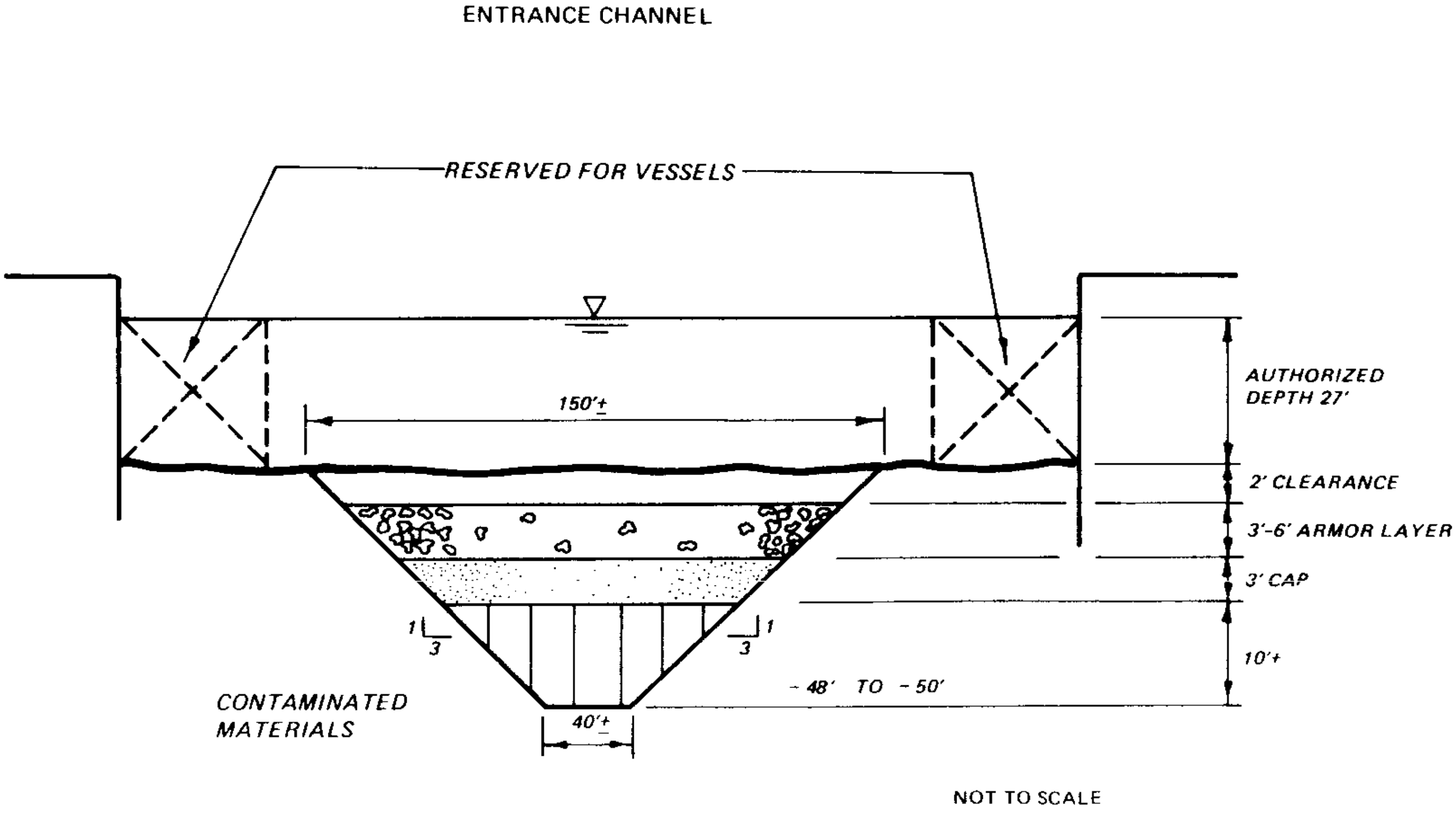


Figure 15. Trench cross section with 3-ft cap and 6-ft armor layer

filter cloth or netting prior to its placement over the unconsolidated or "liquefied" dredged material. These factors together with the cost of a stone armor layer greatly reduce the viability of CAD in the entrance channel and canal.

Monitoring

35. The best method of monitoring the armor layer would be side scan sonar combined with regular echo sounding. The layer would be mapped when placed and then remapped and compared periodically. Depending upon turbidity levels in the area, closed circuit television is a possibility. Due to the results of this limited study, a detailed monitoring program was not addressed pending further decision on the CAD.

Conclusions

36. Storage volume in the amount of 220,000 to 400,000 cu yd is needed for contaminated materials. There is 150,000 to 170,000 cu yd of storage volume available in the entrance channel and canal areas with a 3-ft sand cap and 3- to 6-ft stone armor layer. Protection of the cap against erosion by natural currents will require a median grain size of 0.14 in. in the cap. Protection of the cap against erosion by vessel propwash will require an armor layer 3 to 6 ft thick of minimum 6-in.-diam stone. Use of the stone armor layer will cause operational difficulties and reduce the storage space available. Alternate sites for a CAD appear more favorable than the entrance channel and canal.

APPENDIX J: CONTAINED AQUATIC DISPOSAL: SITE LOCATION AND CAP MATERIAL INVESTIGATIONS FOR OUTER INDIANA HARBOR AND SOUTHERN LAKE MICHIGAN

Introduction

1. The investigations described in this appendix are part of a study performed for the Chicago District of the US Army Corps of Engineers of alternative methods for disposing of approximately 200,000 cu yd of highly contaminated dredged sediments from the Indiana Harbor Canal. This canal connects Indiana Harbor, Indiana, with the Grand Calumet River. In these investigations, regions in and around Indiana Harbor were evaluated for their potential as contained aquatic disposal (CAD) sites. CAD involves placing contaminated material in an existing or dredged depression, then covering it with a layer of clean sediment (primary cap) to prevent contaminants from escaping into the overlying water column. A protective cover layer or armor cap may be placed over the primary cap to protect it from erosion by wave action or currents.

Problem Statement

2. The investigations described in this report were performed in response to a study need to identify potential CAD sites and develop design guidance for erosion-resistant armor caps. Locations in southern Lake Michigan and Outer Indiana Harbor were evaluated for potential CAD usage. Bottom currents arising from a variety of forcing functions (waves, winds, seiching, and propeller wash) were calculated, and stable armor cap material was selected based on the magnitude of the bottom currents.

Potential CAD Sites

Southern Lake Michigan

3. The investigation in southern Lake Michigan was limited to those areas between 30 and 70 ft below Low Water Datum (LWD) within an 11-mile radius of Indiana Harbor (Figure J1). Based upon discussion with District personnel, 70 ft was selected as the maximum practical depth for CAD in this study. The shortest distance from Indiana Harbor to the 70-ft contour, 11 statue miles, was then used to define the maximum practical haul distance.

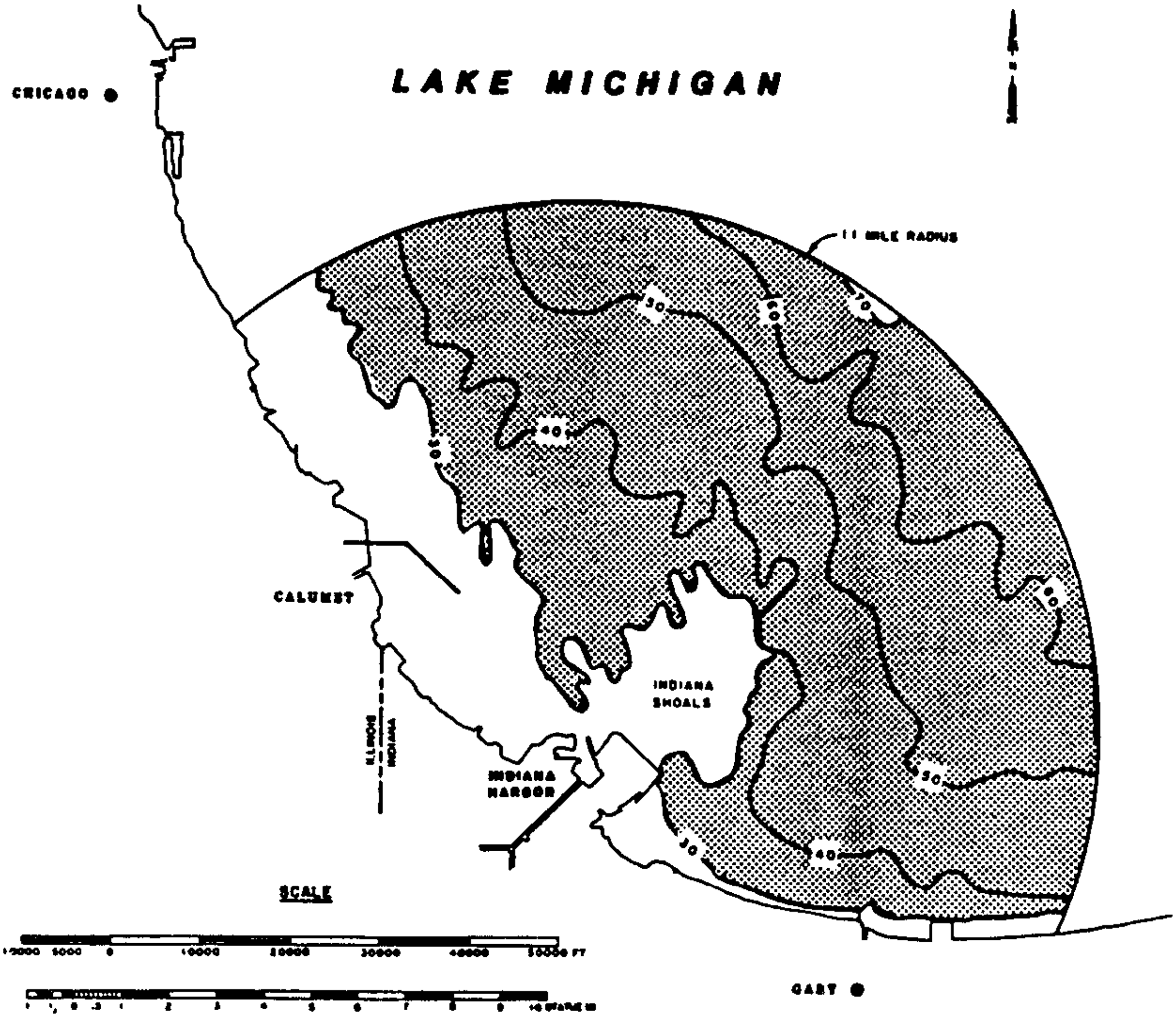


Figure J1. Eleven-mile radius of Indiana Harbor

The minimum depth was selected so as to limit the possibility of a large ship running aground on the CAD site and cutting through the primary cap. Based on recommendations in Engineer Manual (EM) 1110-2-1603 (Office, Chief of Engineers 1983) a minimum study depth of 30 ft was selected to allow for squat, pitch, roll, and heave of the 26-ft draft vessels that use Indiana Harbor. This minimum depth excludes Indiana Shoals, which is a large area of convoluted bathymetry extending 4 miles to the northeast of Indiana Harbor. Although large ships usually avoid this area, the shoals are regularly subjected to breaking waves, making the area unsuitable for CAD consideration.

Outer Indiana Harbor

4. The southern half of the Outer Harbor of Indiana Harbor (Figure J2) was also considered as a potential site for CAD. The trapezoidal area shown allows 200 ft of clearance between the navigation project boundaries and the edge of the potential CAD site. Calculations show that a dredged hole in this area, 15 ft deep below the authorized project depth of 28 ft with side slopes of 4 to 1, would have to capacity to hold 580,000 cu yd of contaminated sediments. This volume should be adequate to hold 200,000 cu yd of contaminated sediment with a conservative bulking factor, the primary cap, and an armor cap. Therefore, this site was initially considered as a potential site for CAD.

Ice Gouging

5. The term "ice gouging" refers to moving ice cutting furrows or tracks in the bottom of a body of water. The potential for ice gouging was examined in this study because of the possibility of damaging a CAD armor or primary cap. Discussions with NCD, the Fleet Operations Office of Inland Steel Corporation, and the US Coast Guard indicated that drifting ice reaches maximum thicknesses of 6 to 8 ft along the breakwaters outside the harbor and that ice thickness within the harbor usually does not exceed 1 ft. Fast ice along the shore usually does not exceed 1.5 ft in thickness (National Oceanic and Atmospheric Administration (NOAA) 1983). Based upon this initial information, ice gouging was not considered to present a serious threat to CAD caps in the study area. Therefore, no further study of ice gouging was conducted.

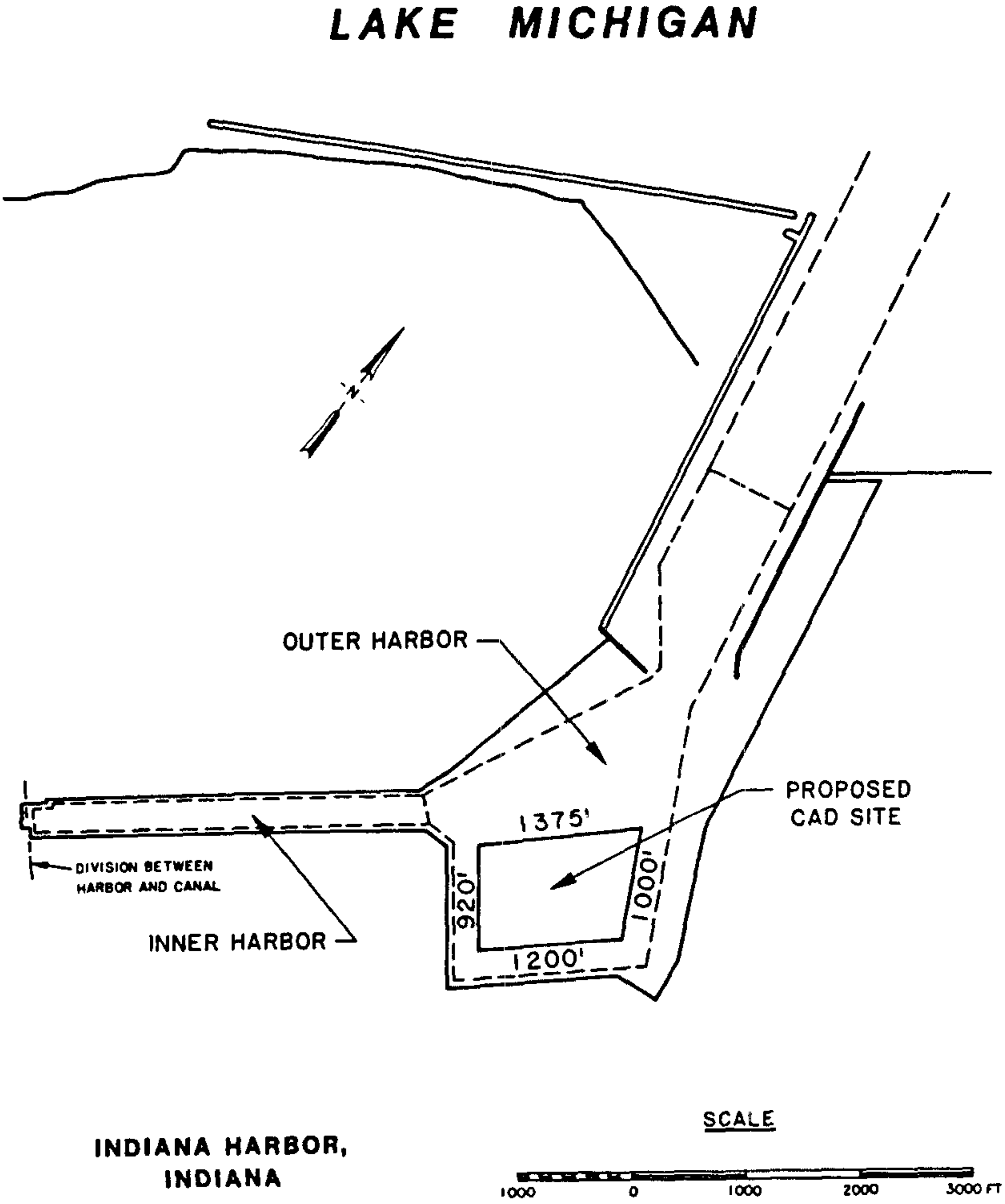


Figure J2. Indiana Harbor, Indiana

Forcing Functions

6. To initially select a stable CAD armor cap material, the maximum anticipated total bottom shear stress must be known. Bottom shear stress is a function of the bottom current; consequently, those factors capable of producing significant bottom currents were examined. These included waves, winds, seiches, and propeller wash.

7. To assist the Chicago District in developing economic design alternatives, the wave- and wind-generated currents and the corresponding armor cap material sizes were calculated for return periods of 20, 50, and 100 years. The design lake levels on which to base these predictions is also important. The Shore Protection Manual (SPM) (US Army Engineer Waterways Experiment Station (WES) 1984) lists the record low monthly mean over the past 77 years as 1.4 ft below LWD. Seiches and/or wind setdown have resulted in short-term lake levels of 4.9 ft below LWD at Calumet Harbor, 6 miles northeast of Indiana Harbor. After considering this information and discussing the problem with the North Central Division (NCD) Coastal Section, of the US Army Corps of Engineers, it was decided to use a design lake level of 2.0 ft below LWD for this study.

Waves - Deep Water

Specification of wave conditions

8. For the purposes of this study, the term "wave conditions" means a significant wave height and period with an associated frequency of reoccurrence. Numerical computations were performed which treat the significant wave as monochromatic. The process of specifying wave conditions at all points of interest to the present study consisted of three steps:

- a. Obtain deep-water wave conditions appropriate to southern Lake Michigan for design return intervals of 20, 50, and 100 years.
- b. Transform these wave conditions shoreward, taking into account refraction, diffraction, dissipation, and breaking.
- c. Use the transformed wave characteristics at the entrance channel of Indiana Harbor to deduce wave conditions for selected locations over the potential CAD site in the outer harbor area.

Deep-water design waves were developed in a hindcast study done by Resio and Vincent (1976). They computed design wave characteristics for 64 locations on the perimeter of Lake Michigan. Site number 29 (Burns Harbor, Indiana) was selected for use in this study. It is the nearest site to Indiana Harbor and is subjected to the longest fetch in southern Lake Michigan (approximately 250 miles). Maximum deep-water wave heights for all return intervals which occurred during the winter period (January-March) were selected as most appropriate for this study. Table J1 summarizes each design deep-water wave used for subsequent calculations.

Transformation of deep-water waves to shore

9. A strict interpretation of the concept "deep-water wave" for the longest period (12.1 sec) requires that the above wave conditions be applied in a water depth of about 380 ft. This corresponds to an offshore distance of about 45 miles, thus necessitating a fairly large computational domain for the refraction-diffraction wave transformation model. The bounds of this domain are shown in Figure J3. The point labeled "IH" is the computational site at which boundary conditions for the Outer Harbor model were obtained.

10. The computational domain contains a square grid system of 5,000-ft spacing. There are 47 steps in the offshore direction (44.5 miles in length) and 41 steps in the alongshore direction (38.8 miles in length). Bathymetry data were obtained from US Lake Survey Chart No. 75 (Lake Michigan, Waukegan, Ill., to South Haven, Mich.). These data were then adjusted to the design lake level of 2.0 ft below LWD.

11. The computational model used is the Regional Coastal Processes Wave Refraction-Diffraction (RCPWAVE) model, developed by Ebersole et al. (1985). The governing equations are the "mild-slope" velocity potential equations for monochromatic waves. They are valid when applied to regions with bottom slopes less than approximately 1:10. Combined refraction and diffraction effects caused by bathymetric variations are accurately modeled as long as the mild-slope constraint is satisfied. Waves can be taken to the breaking limit. Beyond breaking, computations are continued by using standard depth-limited criteria, coupled with dissipation as a function of propagation distance.

12. The wave conditions from Table J1 were applied uniformly on the deep water edge of the computational domain. Computed wave heights in the interior of the domain are used in estimating CAD armor cap material sizes for potential disposal sites lying in the shaded area shown in Figure J1.

Wave characteristics in the Outer Harbor

13. Estimation of wave conditions in a harbor requires a carefully designed computational procedure. Account must be taken of cross-harbor

Table J1

Design Deep-Water Wave Conditions

Return Interval years	Sig. Wave Height ft	Sig. Wave Period sec	Direction deg true*
20	19.7	10.6	180
50	22.0	11.5	180
100	23.9	12.1	180

* Degrees relative to true north.

reflections, absorption of wave energy from reflection off nonperfect wall boundaries such as rubble-mound revetments and breakwaters, and wave dissipation from bottom friction. Traditional potential theory methods almost always overestimate amplification factors through inadequately describing these effects. An acceptable model must also allow waves reflected back to the harbor entrance to freely leave the modeled area. These considerations led to selection of a linear wave theory, hybrid element model (HARBS) recently developed by Dr. H.S. Chen at WES. Preliminary description of this model is provided in US Army Engineer Waterways Experiment Station (1985). An expanded technical report is in preparation.

14. The computational domain of this hybrid element model is depicted in Figure J4. The model boundaries are the physical boundaries, seawalls, bulkheads, etc., of the entire water body of the Outer Harbor. Wave energy was allowed to radiate into the Inner Harbor. Also shown are 16 points at which wave conditions were obtained for the Outer Harbor potential CAD site. The semicircular radiation boundary of the model where waves enter the model is approximately 4,500 ft down-channel from the point where the offshore refraction-diffraction computations ended. Design wave characteristics used at the channel entrance are summarized in Table J2. The 50-year significant wave height is slightly smaller than the 20- and 100-year heights. This is probably due to the coarse representation of Indiana Shoals, which is the principal site of wave breaking near the harbor entrance. The coarse representation caused wave breaking at a greater distance from shore for this particular combination of height, period, and incident angle, resulting in the reduced height.

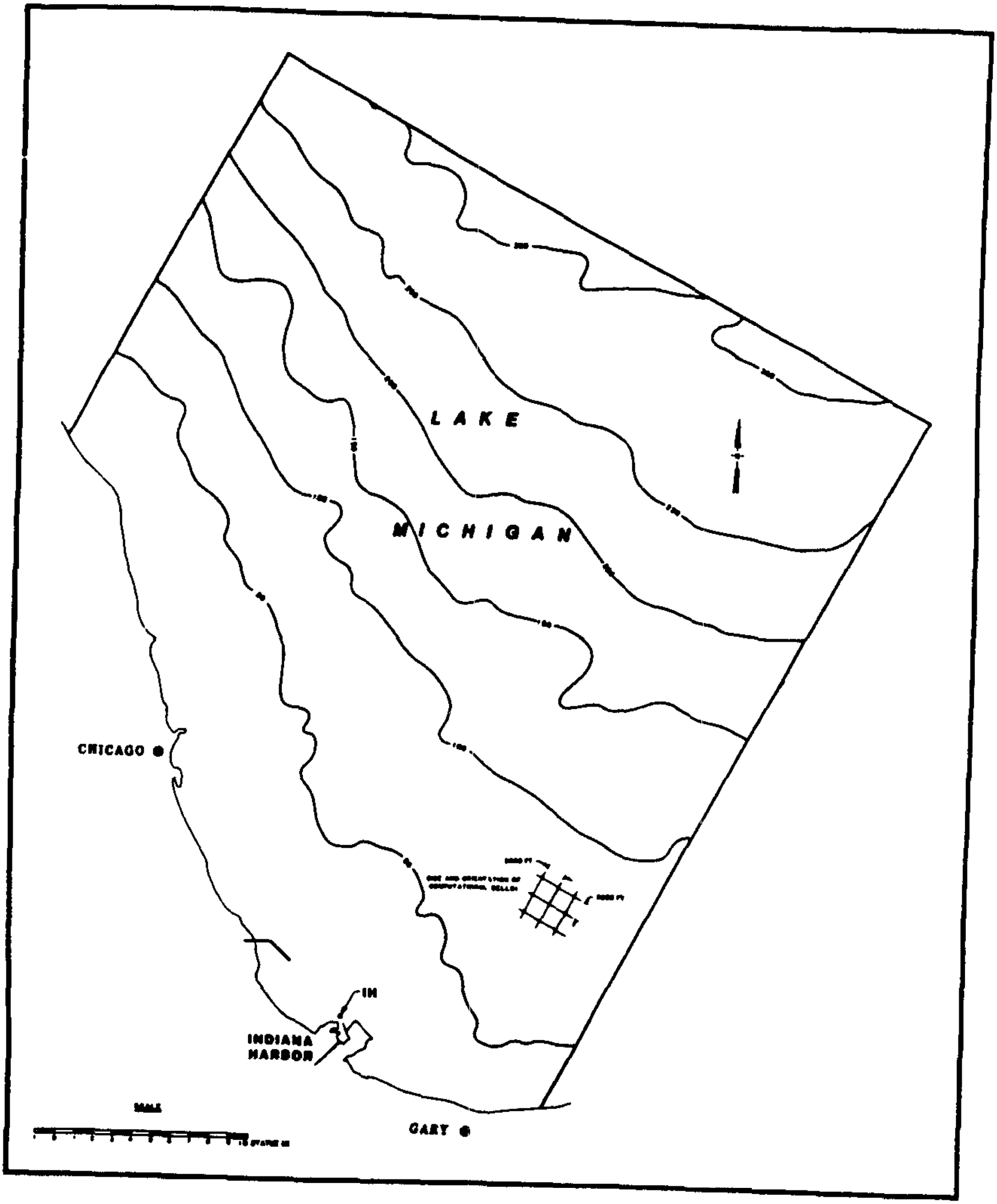


Figure J3. Wave transformation computational boundaries

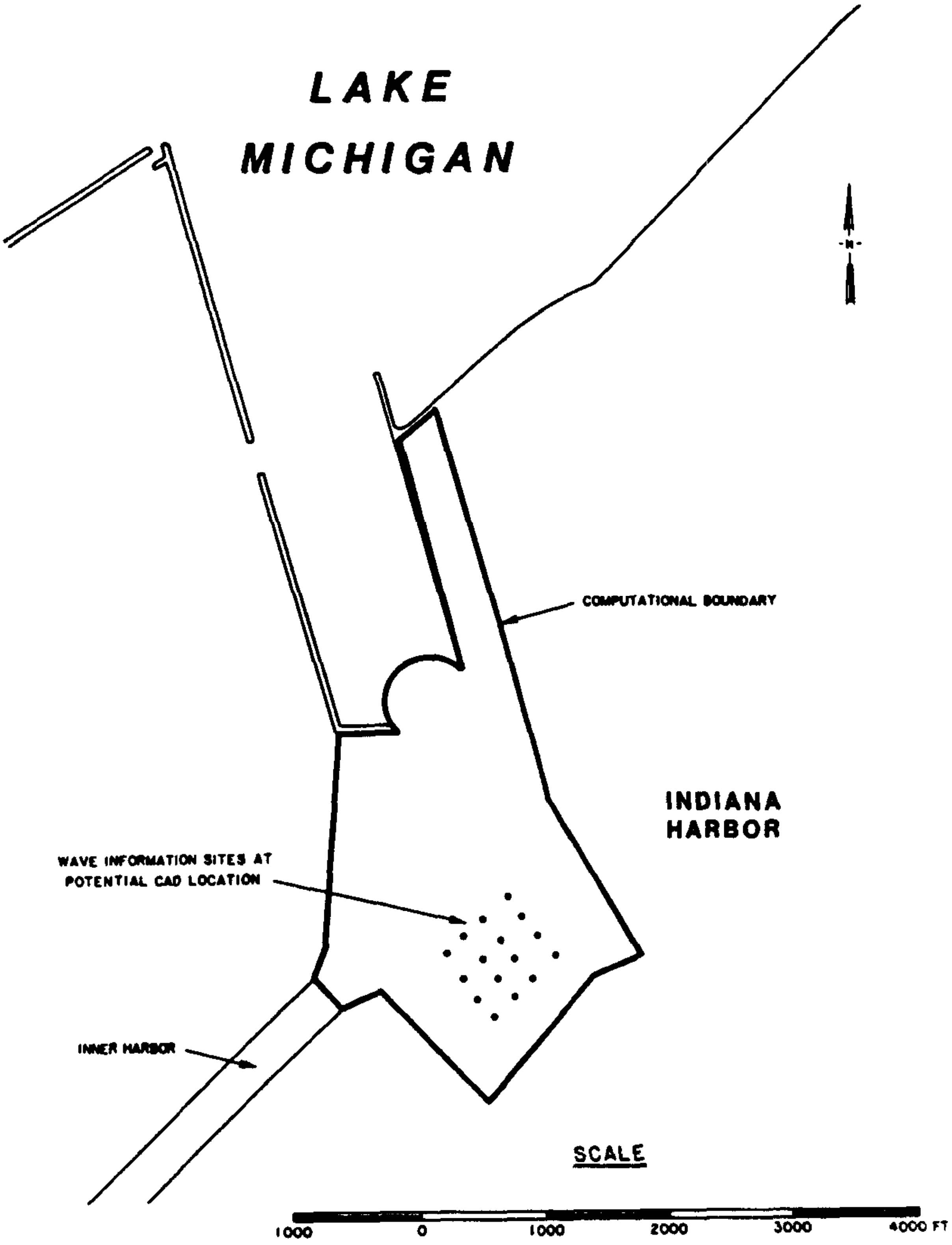


Figure J4. Outer Harbor wave model computational boundaries

Table J2

Design Wave Conditions at Channel Entrance

Return Interval years	Sig. Wave Height ft	Sig. Wave Period sec	Direction deg true *
20	13.5	10.6	193
50	12.7	11.5	194
100	13.6	12.1	195

* Degrees relative to true north.

15. A mean direction of 194 deg true was adopted for all three cases. Reflections off the western breakwater cause the waves to arrive essentially normal to the radiation boundary of the computational region, corresponding to a propagation direction of 130 deg true. Frictional losses in propagation from the channel entrance to the model boundary were not considered.

16. The finite element model for the interior region requires at least four or five points per wavelength. The shortest period wave at the harbor entrance has a wavelength of approximately 300 ft. Thus, a maximum spatial element size of 70 to 90 ft is required. The selected network is shown in Figure J5. It consists of 1,351 nodes and 2,521 computational elements. Depth at all points within the navigation project boundaries was assumed to be authorized project depth. Data from a 1984 bathymetric survey by Chicago District were used for points outside the project. All depths were corrected for design lake level before computations were made. A reflection coefficient of 0.95 was used for solid vertical walls, and a reflection coefficient of 0.60 was used for rubble-mound structures.

17. Model output consists of an amplification factor (wave height at an interior point divided by input wave height at the radiation boundary). Values at the points indicated in Figure J4 were converted to their corresponding significant height for use in armor cap material size determinations. Wave heights at the 16 points were all less than 0.2 ft. These long period waves should produce no appreciable bottom stresses at the potential CAD site. These waves are considered in Part V of this appendix.

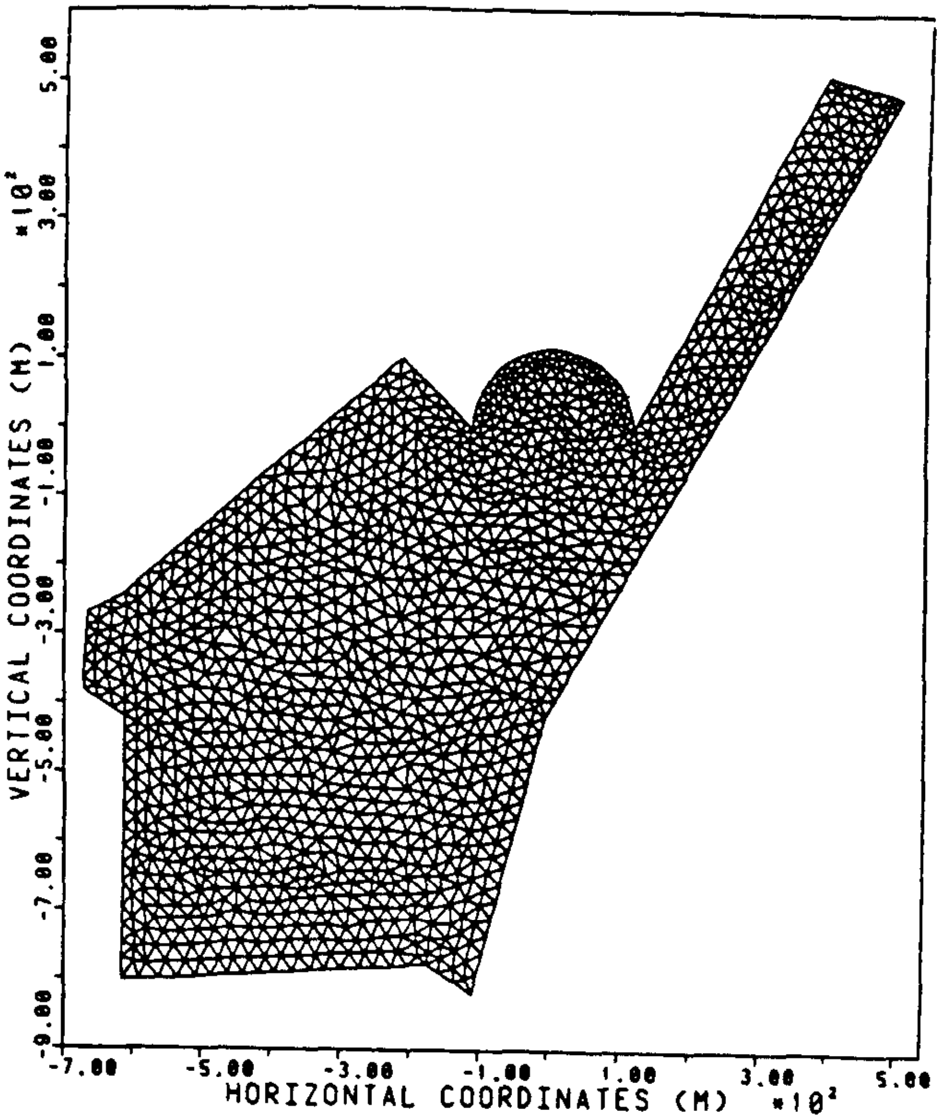


Figure J5. Outer Harbor finite element computational network

Potential seiche modes in the Outer Harbor

18. The hybrid element Outer Harbor model was run in a resonant-period search mode. Waves of unit amplitude were applied at the radiation boundary for a wide range of periods, and amplification factors were recorded at sites throughout the Outer Harbor region. No resonances were detected for periods less than 2,300 sec. Since there is essentially no energy in wind wave spectra at such long periods, wind waves appear incapable of exciting seiche modes in the Outer Harbor. Mechanisms such as atmospheric pressure

fluctuations associated with frontal passage can supply energy at low frequencies, but the HARBS model cannot be used for such an investigation.

Maximum bottom currents due to waves

19. Bottom currents due to waves result from the orbital motion of the water particles as the waves pass overhead. In deep water these water particle orbits are circular. As the waves move into shallow water, the orbits become elliptical, and near the bottom they approach horizontal.

20. Linear wave theory predicts that the maximum horizontal velocity u at the bottom is:

$$u = \frac{H\pi}{T} \frac{1}{\sinh \frac{2\pi d}{L}} \qquad \text{(J1)}$$

where

H = wave height

T = wave period

d = water depth

L = wavelength

21. To calculate maximum bottom orbital velocities due to waves in the southern Lake Michigan study area, the wave height and length calculated by RCPWAVE were used in Equation J1 together with the depth and wave period.

Currents Due to Wind

22. Bottom currents due to winds were calculated using the following methods and assumptions. First, wind data were determined from fetch-limited wave forecasting curves. These data were then used as input to standard physical oceanography equations (Neumann and Pierson 1966) for drift and slope currents. Drift currents result from the transfer of wind stress on the water surface through the water column. Slope currents flow along the bottom away from areas where wind has caused an increase in water levels. Values for drift and slope currents were calculated at depths from 30 to 70 ft at 10-ft increments. Values for the two currents were added together vectorially to give a maximum current at each depth. These total values were plotted, and a

curve drawn between points. Maximum wind-induced bottom current velocities were read off the curve for specific locations in southern Lake Michigan.

23. Vincent's (1983) report on fetch-limited wave predictions was used to determine wind velocities and durations. The fetch and the wave period and height predicted by WIS data for Lake Michigan (Resio and Vincent 1976), determined the wind velocity and duration. For the 20-year return period, winds were 55 knots for 8.7 hr; for the 50-year return period, winds were 55 knots for 10.5 hr; and for the 100-year return period, winds were 55 knots for 11.5 hr.

24. The time limits of this study did not allow running the three-dimensional numerical model needed to accurately calculate the site-specific bottom currents due to winds associated with the 20-, 50-, and 100-year conditions. There are no quicker, less costly methods for accurately simulating the wind field-generated bottom currents. Consequently, physical oceanography theory was used to estimate these currents. The assumptions made in applying this theory were selected to result in conservative answers.

Drift currents

25. The following discussion is based on information found in Neumann and Pierson's (1966) text on physical oceanography. The frictional drag of wind passing over water produces a surface, or drift, current. With time, due to the viscosity of water, momentum will be transferred vertically and produce currents to significant depths. Because of the Coriolis force, the current in each succeedingly deeper layer of moving water is directed slightly to the right (in the northern hemisphere) of the one above it. A necessary assumption to use Eckman's equations for the velocity of these drift currents is that the wind field is uniform, constant in speed and direction everywhere, and has been blowing for a sufficient length of time to allow the currents to reach a steady-state.

26. These assumptions are conservative for the shallow depths at the southern end of Lake Michigan, where land and bathymetry modify current direction and speed. The actual wind field is not uniform in direction, speed, or duration. Since duration cannot be included in the Eckman equations, the currents associated with the various return periods are all assumed to be equal and based on a 55-knot wind. This will make the answers for the 20- and 50-year return periods even more conservative. Current forecasting curves for the open ocean (Gaythwaite 1981) predict surface currents that vary

± 15 percent when going from the 50- to 20- and 50- to 100-year return period wind durations.

27. The depth of the basin used in these equations is the mean depth of Lake Michigan, 280 ft. The southern basin of Lake Michigan has an average depth of 390 ft, and would allow larger currents. However, since the currents of interest are actually occurring at much shallower depths, the shallower average depth of the lake was used.

28. Eckman's equations for a drift current in an ocean of finite depth are:

$$U_d = \alpha A - \beta B \tag{J2}$$

$$V_d = \alpha B + \beta A \tag{J3}$$

where

U_d = drift current velocity component in the direction the wind is blowing (assumed positive in the wind direction)

V_d = drift current velocity component at right angles to the direction the wind is blowing

$$\alpha = \frac{\tau_w}{\pi\nu}\left(\frac{C+E}{R}\right)$$

$$\beta = \frac{\tau_w}{\pi\nu}\left(\frac{C-E}{R}\right)$$

τ_w = shear stress, taken from standard tables

ν = eddy viscosity = $9.5 \ \tau_w + 9$ (estimated linear fit to observed data)

$C = \cosh p \cos p$

$E = \sinh p \sin p$

$R = \cosh 2p + \cos 2p$

$p = \frac{ad}{\sqrt{2}}$

$a = (f\ \rho/\nu)^{1/2}$

d = average basin depth

f = Coriolis force

ρ = density of seawater

and

$B = \cosh q \sin q$

$A = \sinh q \cos q$

$D = \pi \sqrt{\frac{2\nu}{\rho f}}$

$q = p - \frac{az}{\sqrt{2}}$

z = depth of the current

Slope currents

29. In addition to causing a drift current, the wind can eventually pile water up against the coast. This increase in height will produce a flow away from the high area and counteract to some degree the drift current. The slope current can be treated separately from a pure drift current.

30. Eckman's equations for slope currents assume there is no wind at the sea surface. The wind duration factor is not a significant problem for the calculation of slope currents. Once the slope is set up nearshore, the currents start almost immediately.

31. Eckman's equations for slope currents are:

$$U_s = \frac{-g^S}{f} \left[\left(\frac{\cosh m \cos n + \cosh n \cos m}{R}\right) -1\right] \tag{J4}$$

$$V_s = \frac{+g^S}{f} \left(\frac{\sinh m \sin n + \sinh n \sin m}{R}\right) \tag{J5}$$

where

U_s = slope current velocity component offshore (positive to the north)

S (surface slope) = $\frac{\tau_w}{gd}$

$m = p + \frac{az}{2}$

$n = p - \frac{az}{2}$

$R = \cosh \frac{2a}{2} d + \cos \frac{2ad}{2}$

V_s = slope current velocity component parallel to shore (positive to the west)

32. The results of the wind current calculations are presented in Table J3. Drift and slope currents were combined vectorially to give a total wind current. The vector direction of the total wind current deviates from north-south due to the V-component of the drift current. However, since the refracted wave directions are not consistent throughout the grid, the absolute value of the total wind current was added to the wave-induced bottom current. This produced a conservative estimate of total bottom current, with an accuracy consistent with the time limits of this study.

Bottom Currents Due to Propeller Wash

33. Ships perform docking maneuvers in Indiana Harbor using the combined action of their main propeller and bow thrusters. The main propellers of these large (up to 1,000 ft long) ships generate high velocities, which have the potential to cause significant disruption and erosion of the bottom. These effects could seriously impact on the capability of the Outer Harbor to serve as a successful CAD site. Consequently, a preliminary investigation was

Table J3

South Lake Michigan Bottom Currents Due to Winds

Depth ft	U drift* ft/sec	V drift ft/sec	U slope** ft/sec	V slope ft/sec	U total ft/sec
30	3.4	1.4	1.1	0	2.7
40	3.1	0.8	1.1	0	2.2
50	2.6	0.3	1.1	0	1.6
60	2.5	0	1.1	0	1.4
70	2.2	-0.3	1.1	0	1.1

* U drift is onshore.
** U slope is offshore.

made into expected propeller wash velocities and the armor cap material required to withstand them.

Probability of maximum velocities

34. Docking maneuvers are usually done at very low speeds, 1 knot or less, and corresponding low propeller speeds. However, in extreme cases, such as high winds, loss of rudder control, avoidance of obstacles, etc., ships will use full throttle for short periods. Therefore, the possibility of large ships using full throttle in the Outer Harbor should be planned for within the life of a CAD site. Economics force ship owners to operate their vessels at maximum safe drafts, which means even though lake level varies, the actual minimum keel clearance should remain approximately the same.

Propeller jet theory

35. The flow field generated by a propeller is complicated because the velocity field has axial, radial, and tangential components. Most theoretical work on propeller jets is based on diffusion of submerged jets.

36. Application of submerged jet theory to propeller wash has not been fully successful due to the complicated flow components. For this preliminary investigation, model testing done in Europe and limited prototype measurements provide the necessary information. Significant damage to channels and harbor structures caused by propeller-wash-generated erosion has prompted European research (Berg and Cederwall 1981).

37. The flow behind a propeller is generally divided into two zones, the zone of flow establishment immediately behind the propeller and the zone of

established flow which begins within a distance of 7 to 10 propeller diameters. Because the highest bottom velocities occur in the zone of flow establishment and because the Outer Harbor CAD site could be immediately below a large vessel, the remaining discussion is restricted to velocities in that region.

38. The velocities produced by a propeller are a function of the diameter D, the speed at which the propeller revolves n, and the thrust coefficient of the propeller K_T. Based on information from the Fleet Operations Office at Inland Steel Corporation, the largest ships now using Indiana Harbor have propellers 20 ft in diameter turning at up to 105 rpm (1.75 rps) and driven by 14,000-hp engines. Thrust and thrust coefficients of these propellers were not available, but Blaauw and Van de Kaa (1978) present typical values for similar propellers. They also give several different equations for determining the maximum axial velocity behind the propeller V_o.

$$V_o = 1.6nD \left(K_T\right)^{1/2} \tag{J6}$$

39. Blaauw and Van de Kaa show a K_T value of 0.265 for a single nonducted propeller 20 ft in diameter. Using Equation J7, this corresponds to a V_o of 29 fps. They also present another equation for determining V_o,

$$V_o = 1.47 \left(\frac{Pd}{D^2}\right)^{1/3} \tag{J7}$$

where Pd is the installed horsepower.

40. For a ship with 14,000 hp, V_o equals 39 fps. Model tests conducted by Blaauw and Van de Kaa using ships similar to those using Indiana Harbor produced prototype maximum propeller wash velocities of 33 fps. Berg and Cederwall (1981) used the equation

$$V_o = 0.95nD \tag{J8}$$

to calculate maximum propeller wash velocity. This equation results in a V of 33 fps. For further calculations using maximum axial propeller wash velocities, the average value of these four methods, 34 fps, will be used.

Bottom Stresses

41. Shear stresses are exerted on the bottom material by currents, increasing in proportion to the current velocity squared. For a conservative CAD armor cap design, the armor cap material should be able to resist the design current-induced shear stress without any motion.

42. When the bottom shear stress exceeds a critical value, movement of the bottom material will begin. Initiation of motion is a complex phenomenon, a function of the current's vertical velocity profile, fluid viscosity, and the size, shape, density, and exposure of the bottom material. At the point of initial motion, the combined lift and drag forces produced by the fluid become large enough to counteract the gravity and frictional forces that hold the material particles in place.

43. A more detailed discussion of initiation of motion theory is beyond the scope of this report. For additional explanation of initiation of motion theory relevant to this study see Ackers and White (1973), Madsen and Grant (1976), and Hammond, Heathershaw, and Langhorne (1984). For the bottom velocities associated with the 20-, 50-, and 100-year design waves and the expected maximum propeller wash velocities, the information in the Shore Protection Manual (SPM) on "Velocity Forces - Stability of Channel Revetments and EM 1110-2-1601 (US Army Engineer Waterways Experiment Station 1984) (Office, Chief of Engineers 1970) is sufficient for the purposes of this study.

44. The equation for stable particle weight as a function of bottom stresses can be simplified by assuming a level bottom. Since the bottom slope in southern Lake Michigan averages 1 on 1,000, this is a reasonable assumption.

45. The theory discussed in the SPM explains how the stable particle weight for a given velocity can be calculated directly. When the stresses caused by the bottom current are set equal to maximum stress a given size particle can resist, which occurs at initiation of motion, the stresses are eliminated from the equation. The resulting equation, 7-142 from the SPM, equates a stable particle weight for a given bottom velocity:

$$W = 0.0219\ V^6\ \frac{W_r}{g^3} \left(\frac{W_w}{W_r - W_w} \right)^3 \qquad \text{(J9)}$$

where

W = stable particle weight

V = bottom velocity

W_r = unit weight of particle

g = acceleration of gravity

W_w = unit weight of water

46. For fresh water and particle with a unit weight of 165.4 pcf, Equation J9 reduces to

$$W = 2.44 \times 10^{-5} V^6 \tag{J10}$$

This is also the empirical equation recommended by EM 1110-2-1601. This equation was used with the wave, wind, and propeller wash velocities calculated in this study. Prototype tests used to derive this equation included particles over 1.5 ft in diameter and velocities over 17 fps, which are in the range of velocities found in this study.

Results - Translation of Velocities into Stable Material Sizes

Southern Lake Michigan

47. In the southern Lake Michigan area, the maximum bottom currents due to waves and wind were combined to give a conservative estimate of the total maximum bottom velocity at a specific point. Total velocity magnitudes ranged from a low of 6.0 fps for a 17.7-ft wave with a 10.5-sec period at a depth of 64 ft (20-year wave) to a high of 12.9 fps for a 22.8-ft wave with a 12.1-sec period at a depth of 34 ft. Using Equation J10, these velocities were converted into stable material sizes for the 20-, 50-, and 100-year design waves.

48. It was not necessary to compute the particle weights at each of the 172 grid points falling within the boundaries of the study area. Instead,

stable weights were calculated at a sufficient number of selected points to allow the drawing of weight contours. This involved calculating the stable particle weights at 52 points for the 20-year design wave, 46 points for the 50-year wave, and 89 points for the 100-year wave.

49. 20-year design wave. Figure J6 shows that areas requiring the smallest stable particle weights closest to Indiana Harbor for the 20-year wave are east of Indiana Harbor. Areas requiring stable weights of 5 to 20 lb are less than 5 miles away, 2- to 5-lb areas are 6 miles away, and 1- to 2-lb areas can be found just over 8 miles away.

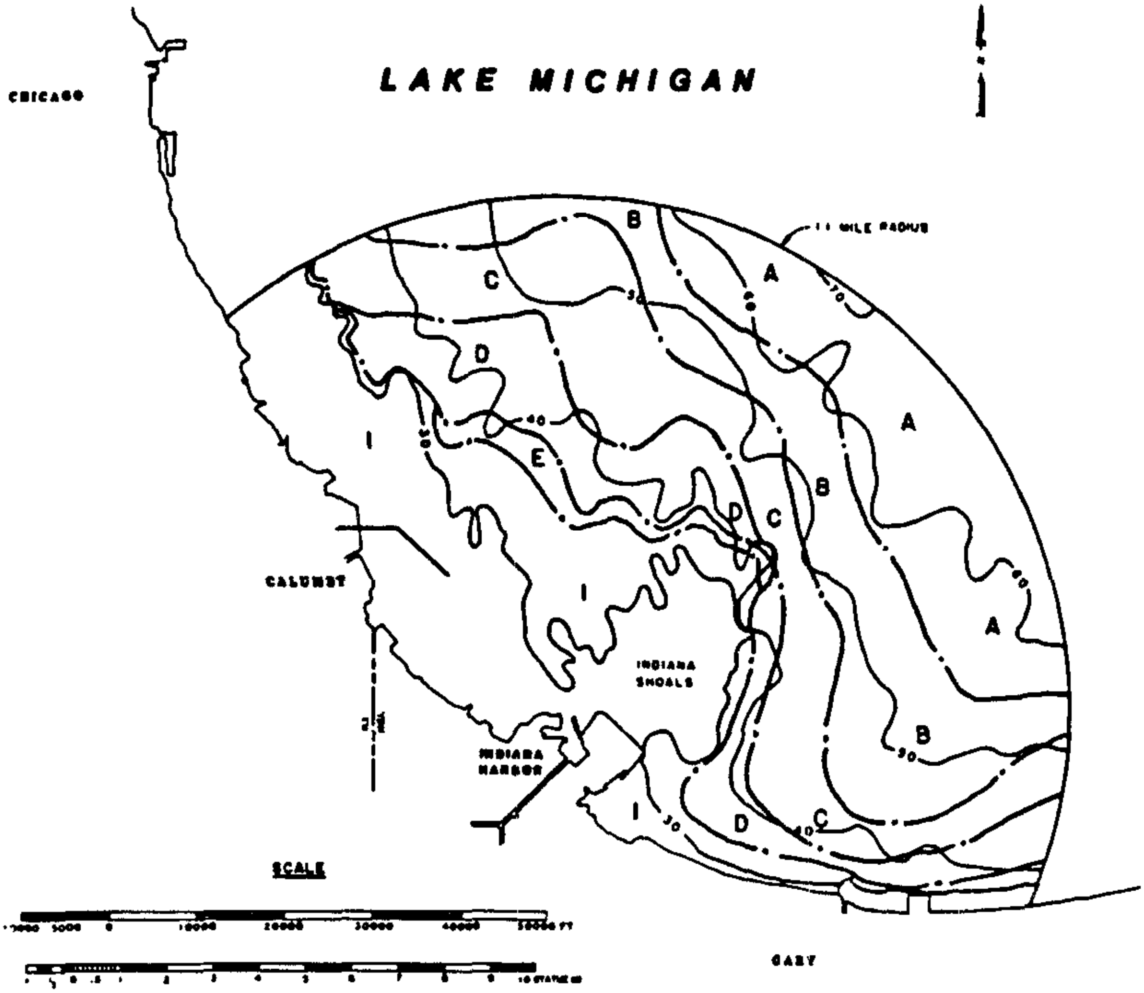
50. 50-year design wave. Figure J7 shows stable weights for the 50-year design wave. It exhibits the same pattern as Figure J1, with the smallest stable material east of Indiana Harbor. Areas requiring stable particle weights of 5 to 10 lb are 5 miles away, and 2- to 5-lb areas can be found 8 miles away.

51. 100-year design wave. The pattern of stable particle weights remains consistent for the 100-year design wave (Figure J8). Rapid shoaling of the 100-year wave conditions produces high bottom velocities and correspondingly large particle sizes in depths of less than 50 ft to the north of Indiana Harbor and immediately east of Indiana Shoals. The best potential sites for CAD continue to be the relatively deep areas to the east of Indiana Harbor. Areas requiring stable particle weights of 10 to 20 lb are 5 miles away, areas needing 5 to 10 lb material are less than 7 miles away, and areas requiring 2- to 5-lb material are over 10 miles away.

Outer Harbor - wave-induced currents

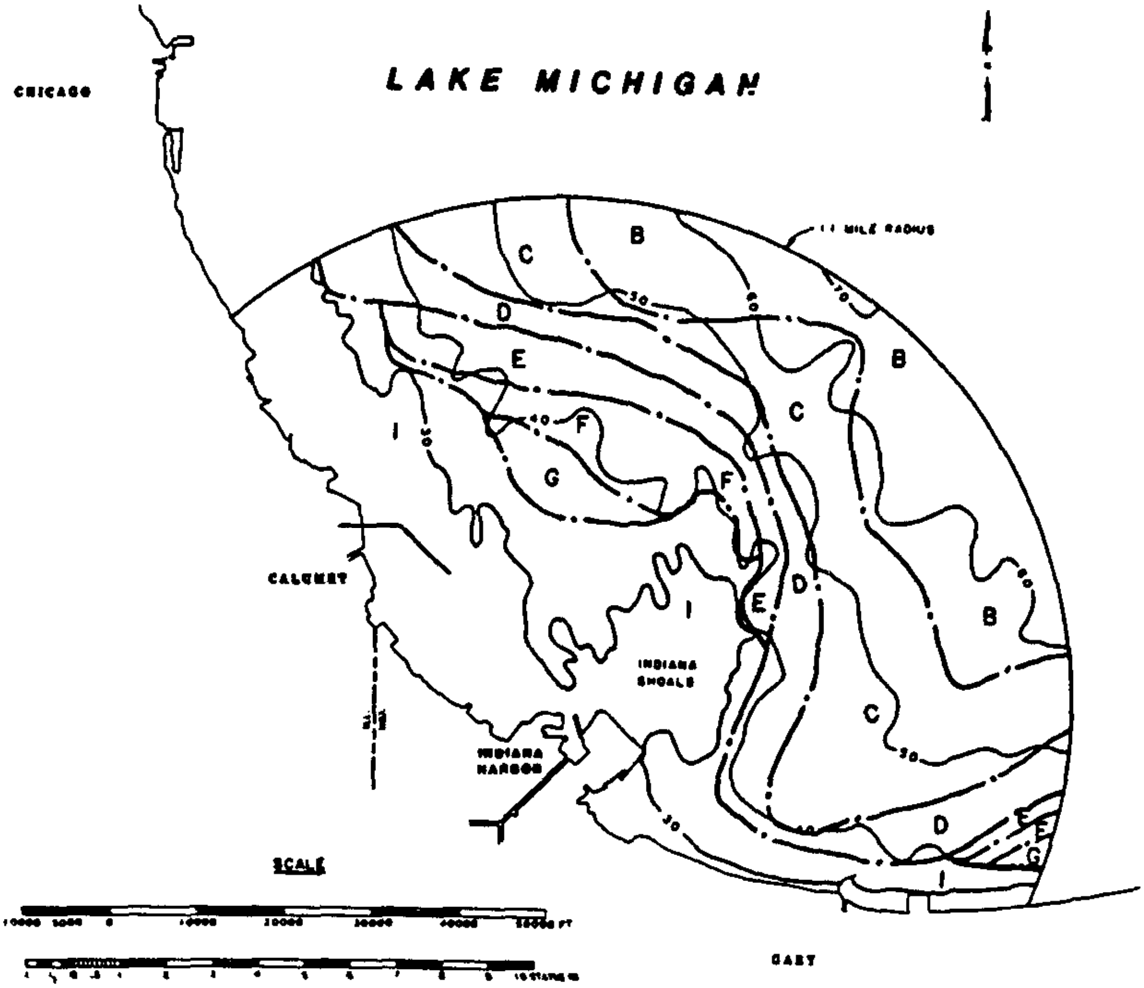
52. As discussed earlier, the amount of wave energy reaching the potential CAD site in the Outer Harbor for the 20-, 50-, and 100-year design waves was very low due to their long periods and sheltering by harbor structures. Other data indicate that significant waves are possible in the Outer Harbor under less severe lake conditions.

53. Earlier model studies (US Army Engineer Waterways Experiment Station 1959) with a slightly different structural configuration of the jetties and breakwaters outside Indiana Harbor showed that short period waves produced maximum waves inside the harbor. The maximum waves predicted by the model tests were a good indicator of the maximum possible waves inside the harbor. These waves are expected to occur fairly often, perhaps every few years, since they are locally generated. The "worst case" wave from the model tests, a



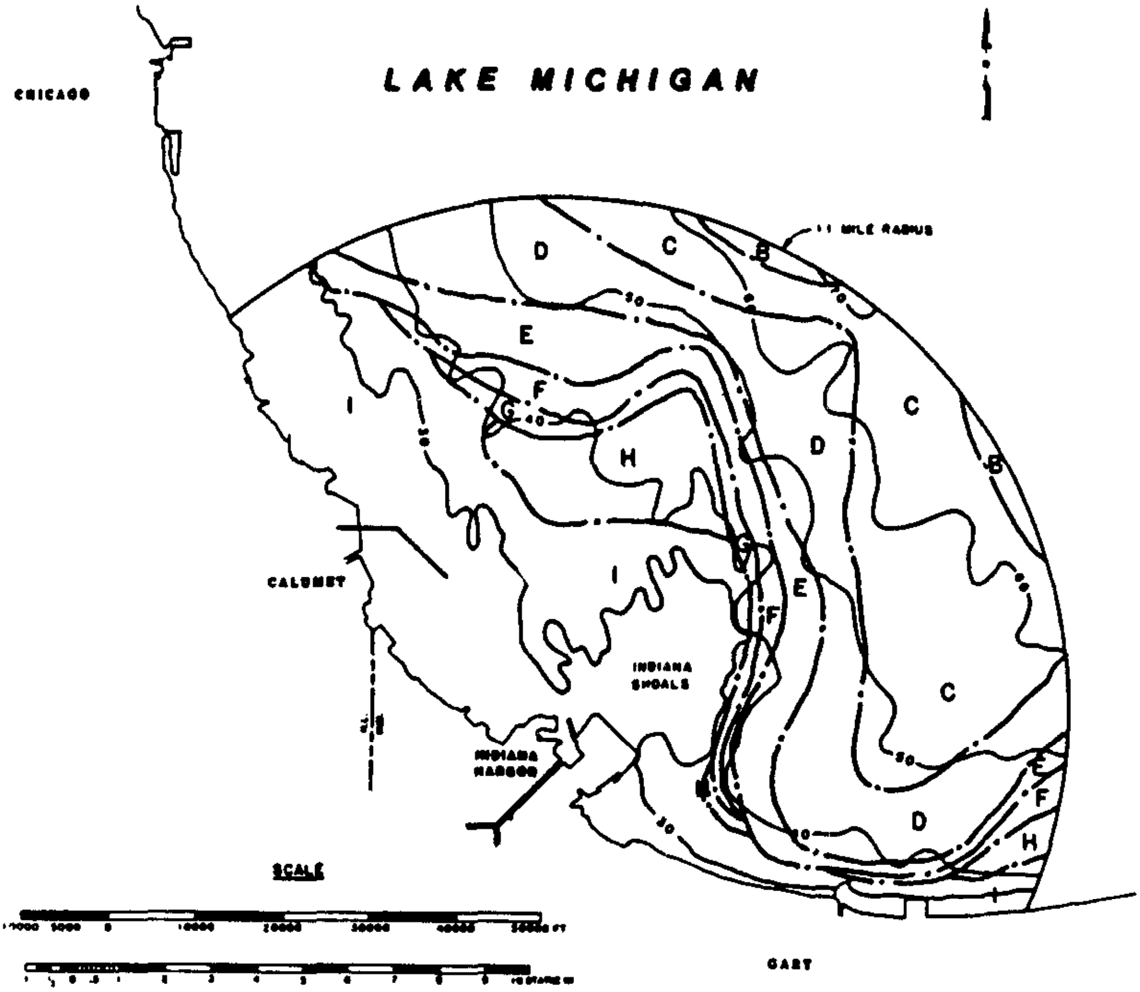
AREA	PARTICLE WEIGHT (LB)
A	1-2
B	2-5
C	5-10
D	10-20
E	20-30
I	AREAS OF BREAKING WAVES, SHOALS, AND SHALLOW WATER, NOT RECOMMENDED AS SITES FOR CAD

Figure J6. Armor cap material sizes based on 20-year design wave



AREA	PARTICLE WEIGHT (LB)
B	2-5
C	5-10
D	10-20
E	20-30
F	30-40
G	40-60
I	AREAS OF BREAKING WAVES, SHOALS, AND SHALLOW WATER, NOT RECOMMENDED AS SITES FOR CAD

Figure J7. Armor cap material sizes based on 50-year design wave



AREA	PARTICLE WEIGHT (LB)
B	2-5
C	5-10
D	10-20
E	20-30
F	30-40
G	40-50
H	50-112
I	AREAS OF BREAKING WAVES, SHOALS, AND SHALLOW WATER, NOT RECOMMENDED AS SITES FOR CAD

Figure J8. Armor cap material sizes based on 100-year design wave

17-ft, 7.5-sec wave at the entrance channel, produced a wave 4 ft high in the potential CAD location. Experienced Inland Steel fleet operations personnel have reported approximately 3-ft waves inside the harbor, which is in reasonable agreement with the model tests.

54. A 7.5-sec period wave, 4 ft high in 26 ft of water produces a maximum bottom velocity of 1.8 fps. The studies of Hallermeier (1980) and Hammond, Heathershaw, and Langhorne (1984) predict that a medium coarse sand, with a mean diameter of just over 2 mm, would be stable under these conditions.

Outer Harbor - propeller wash

55. The velocity at the bottom is strongly influenced by the depth of water between the propeller and the bottom. From model test results (Blaauw and van de Kaa 1978, Berg and Cederwall 1981), bottom velocities of 0.5 to 0.7 times the maximum axial propeller wash velocities were found when the clearance between the propeller and the bottom was small. Blaauw and van de Kaa derived the following equation from their measurements:

$$V_x = V_o \; 2.78 \; D/X \; \exp \; (-15.43 \; Z^2/X^2) \qquad \text{(J11)}$$

where

V_x = bottom velocity at x distance behind the propeller

V_o = maximum axial velocity

D = effective propeller diameter, 0.707 D

X = distance behind the propeller

Z = distance from the propeller axis to the bottom

56. The maximum scour occurred at Z/X ratios of 0.25. To calculate design velocities in the Outer Harbor, a 2-ft distance between the keel and lowest portion of the propeller was assumed. Based on these parameters, design bottom velocities and corresponding stable particle weights were calculated (Table J4).

57. Since the weights shown in Table J4 are based totally on vessel emergencies, a CAD armor cap using smaller material could probably be used in the Outer Harbor in conjunction with multiple layers of bedding/filter stone and monitoring of the cover with side scan sonar and fathometer surveys on a yearly basis or after a significant ship incident. A responsive maintenance plan would be necessary to ensure the integrity of such an armor cap.

Table J4

Stable Particle Weights for Design Propeller Wash Velocities as a Function of Keel Clearance

Keel Clearance ft	Bottom Velocity fps	Particle Weight lb	Particle Diameter ft
1	19.8	1,470	2.6
3	17.1	610	1.9
5	15.2	300	1.5

Discussion

58. Interpretation of the location and stable material sizes required for potential CAD sites in southern Lake Michigan was relatively straightforward and requires no additional discussion. However, results of the Outer Harbor CAD site investigation require some expansion.

59. Although the Outer Harbor CAD armor cap design described in Part V is possible, ship operators using Indiana Harbor may object to having a large portion of the Outer Harbor covered with armor stones. Ships occasionally must use their anchors as emergency brakes in critical situations, and anchors are not as effective for that purpose in a stone bottom. In addition, ships now enter and exit Indiana Harbor with minimum keel clearance due to the soft bottom. A stone bottom may force ship operators to increase keel clearance, thereby reducing their cargo load. The armor cap will also increase the potential for damage to a ship if it hits bottom.

60. Future dredging considerations may also affect an Outer Harbor CAD site design. The area now under consideration as a potential CAD site has experienced shoaling in the past. If a CAD site were constructed in the Outer

Harbor, maintenance dredging would need to be done with good control on maximum digging depth. Recessing the CAD armor cap below authorized project depth would reduce the potential for dredge disturbance and could also make the use of smaller armor material more feasible. Recessing would also eliminate the need for ship operators to reduce vessel draft to allow for a "hard" versus "soft" bottom.

Summary

61. Potential CAD sites were identified for the approximately 200,000 cu yd of highly contaminated sediments located in Indiana Harbor Canal. One potential site is located in the Outer Harbor of Indiana Harbor, and the remainder comprise a large area in southern Lake Michigan within an 11-mile radius of Indiana Harbor at depths between 30 and 70 ft.

Southern Lake Michigan

62. The most promising areas for CAD sites appear to be 4 to 8 miles to the east of Indiana Harbor in water depths of 40 to 60 ft. Depending on the depth, location, and design wave return period, armor cap particle weights of 1 to 20 lb are required for stability. The stable cap weights increase with decreasing depth and longer design wave return periods.

Outer Harbor

63. Currents due to waves and seiching were found not to be limiting factors in the design of stable armor cap material for the Outer Harbor. For complete stability against the high propeller velocities possible from large ships during emergency maneuvers, armor cap material of 300-lb stone or larger may be needed for the Outer Harbor site. However, it should be feasible to reduce the required material armor material size considerably by employing techniques such as recessing the cap, periodic monitoring, and repair if needed. There is the possibility of objections to the Outer Harbor CAD site from ship operators due to potential for damage to ships if they hit bottom and lack of anchor holding capacity in the CAD site which would not allow ships to use their anchors during emergencies.

Recommendations

64. The studies described in this report are limited in scope. Site investigations and more detailed analyses would be needed to properly design a CAD armor cap and its underlayers for physical stability. Such analyses should also optimize the armor cap design by assessing the possibility of limited motion versus repair cost. Should the Outer Harbor or southern Lake Michigan potential CAD sites be considered for actual disposal, several steps should be taken during more detailed investigation of these sites.

Southern Lake Michigan

65. By making additional runs of RCPWAVE at a grid spacing of 2,500 ft or 1,250 ft, the stable material size at a given location could be determined more accurately. Improved bathymetric data may show existing bottom depressions that could be used to reduce the required armor material size. By running a wind-driven circulation model; e.g., the WES Implicit Flooding Model (WIFM), a direct estimate of wind-driven currents could be obtained. The computed depth mean current could then be used with a simplified Eckman model to estimate bottom currents.

Outer Harbor

66. Earlier physical model tests with a slightly different configuration of Indiana Harbor showed that locally generated, short period waves produced maximum waves inside the harbor. Since these types of events occur regularly, it may be worthwhile running the HARBS model under a variety of short period wave conditions. Also, a more thorough investigation into propeller wash effects would give more project-specific results. Calculations of the amount of sediment transport associated with typical velocities and durations of emergency ship maneuvers should reduce the size of the presently recommended armor material. A thicker cover layer of smaller size that allows for partial removal under extreme conditions may be more economical.