AD-A148 321 IMPACT OF DREDGING ON WATER QUALITY AT KEWAUNEE HARBOR 1/1
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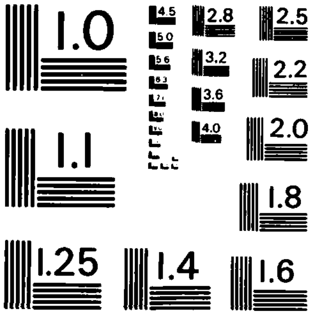

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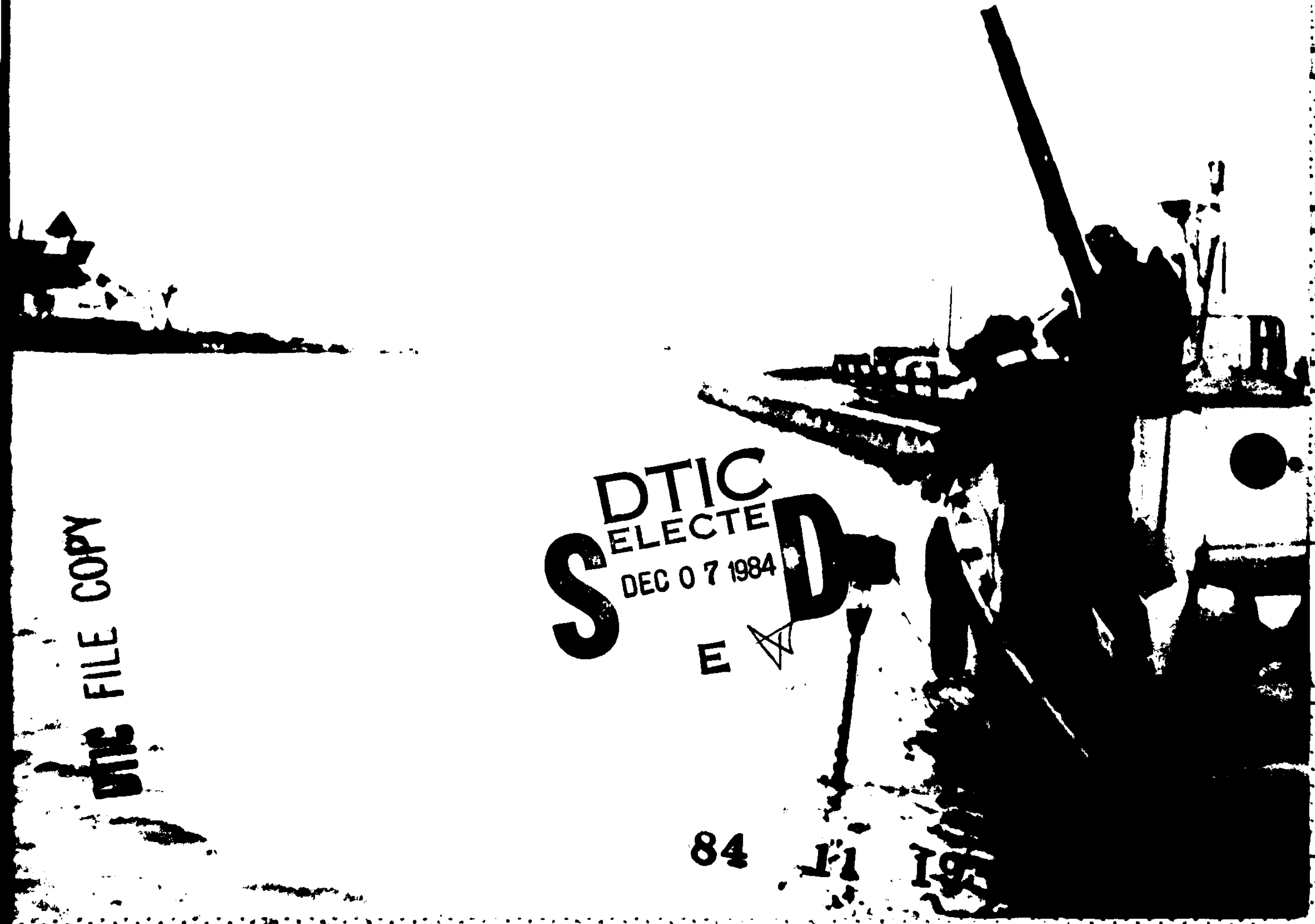
CRREL REPORT 84-21

US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

Impact of dredging on water quality at Kewaunee Harbor, Wisconsin



For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, *published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*

Cover: Sediment core collection at Kewaunee Harbor, Wisconsin.

CRREL Report 84-21

August 1984

Impact of dredging on water quality at Kewaunee Harbor, Wisconsin

I.K. Iskandar, J.H. Cragin, L.V. Parker and T.F. Jenkins

Prepared for
U.S. ARMY CORPS OF ENGINEERS, DETROIT DISTRICT

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
CRREL Report 84-21

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*
IMPACT OF DREDGING ON WATER QUALITY
AT KEWAUNEE HARBOR, WISCONSIN

5. TYPE OF REPORT & PERIOD COVERED

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
I.K. Iskandar, J.H. Cragin, L.V. Parker
and T.F. Jenkins

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, New Hampshire 03755

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Detroit District
U.S. Army Corps of Engineers
Detroit, Michigan

12. REPORT DATE
August 1984

13. NUMBER OF PAGES
19

14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*

15. SECURITY CLASS. *(of this report)*
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Dredged materials
Great Lakes
Harbors
Sediments
Wastes (industrial)
Water quality

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Six sediments and four water samples were collected from Kewaunee, Wisconsin, in 1981, prior to dredging of this Lake Michigan harbor. A modified elutrate test was used to estimate potential impact on water quality upon harbor dredging and disposal of the sediments in a confined facility. The modification of the test included a comparison between containment release under aerated vs unaerated conditions and filtered vs unfiltered elutrates. Statistical analysis showed that the differences in the chemical characteristics between the filtered and unfiltered samples were significant for soluble reactive P and all the tested metals except Cu. Significant but low amounts of heavy metals (Cd, Pb, Zn, Ni, Fe, Mn) and soluble reactive P will be released to the water if the effluent is not filtered. Under aerated conditions, COD in both the filtered and unfiltered samples was higher than under unaerated conditions. In contrast, total organic carbon was

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

20. Abstract (cont'd).

much higher under the unaerated condition than under aerated conditions. The study concluded that sediment and contaminant releases from the confined disposal facility (CDF) to the harbor water were less than those from the Kewaunee River input. Also, retention of effluent in the CDF for about four days decreased the suspended solids in the effluent to about 40 to 50 mg/L, which is similar to the concentration in the lake water. The use of sand filters should not be for routine operation but rather for emergency cases when there is not enough time for effluent retention in this CDF.

PREFACE

This report was prepared by Dr. I.K. Iskandar, Research Chemist, Earth Sciences Branch; J.H. Cragin, Research Chemist, Snow and Ice Branch; L.V. Parker, Microbiologist, Earth Sciences Branch; and T.F. Jenkins, Research Chemist, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

The study was partially funded by the Detroit District, U.S. Army Corps of Engineers, Detroit, Michigan. The authors acknowledge the assistance provided in sample collection by Frank Snitz and John Giundstroum of the Detroit District, Robert Mundelius and Richard Thibbedeau of the Kewaunee Project and Bruce Brockett of CRREL. Laboratory assistance in sample analyses was provided by Daniel Leggett, Karen Davis, Susan Ossoff and Steven Muller.

This report was technically reviewed by Daniel Leggett and Frank Snitz.

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INTRODUCTION

Kewaunee, Wisconsin, is located on Lake Michigan, about 40 miles northeast of Green Bay. Kewaunee Harbor has been classified as a "limited cargo port" by the Wisconsin Department of Transportation, but Kewaunee is Wisconsin's fourth largest Great Lakes port in terms of total tonnage following Superior, Milwaukee and Green Bay. The rail/car ferry service and related operations depend on keeping Kewaunee Harbor dredged to the authorized depth of 20 ft (Office of Wisconsin Coastal Management Program [WCMP] 1981). Also in this area the U.S. Army Corps of Engineers maintains a fleet of tugs, scows and derrick boats that is used in harbor maintenance and repair activities on Lake Michigan. The deepest draft required is 14 ft for one of the tugs used in stone placement.

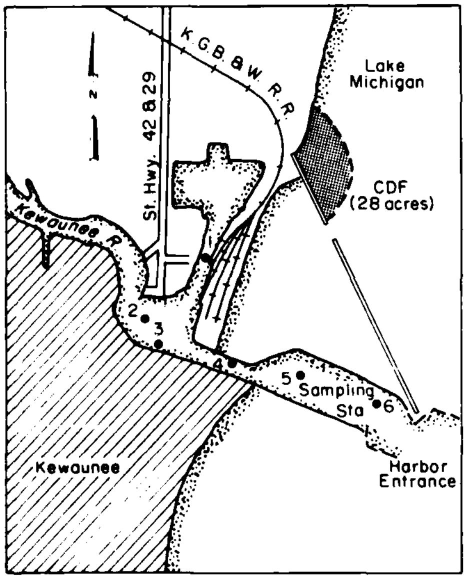

Figure 1. Kewaunee Harbor, confined disposal facility and sampling stations.

According to a report prepared by WCMP (1981), the entrance to Kewaunee Harbor contains "unpolluted" sediments to a point just inside the south breakwater (Fig. 1). This area of the harbor has accumulated 35,000 to 55,000 yd^3 of material since it was last dredged in 1977 and has an estimated annual deposition of 10,000 yd^3. The remainder of the harbor, containing 175,000 to 250,000 yd^3 of accumulated material, is either "moderately" or "highly" polluted and has an average deposition rate of about 40,000 yd^3/yr. Thus, approximately 20 to 25% of the sediment in Kewaunee Harbor requiring maintenance dredging is currently classified by EPA as "unpolluted." The Corps plans future dredgings of 50,000

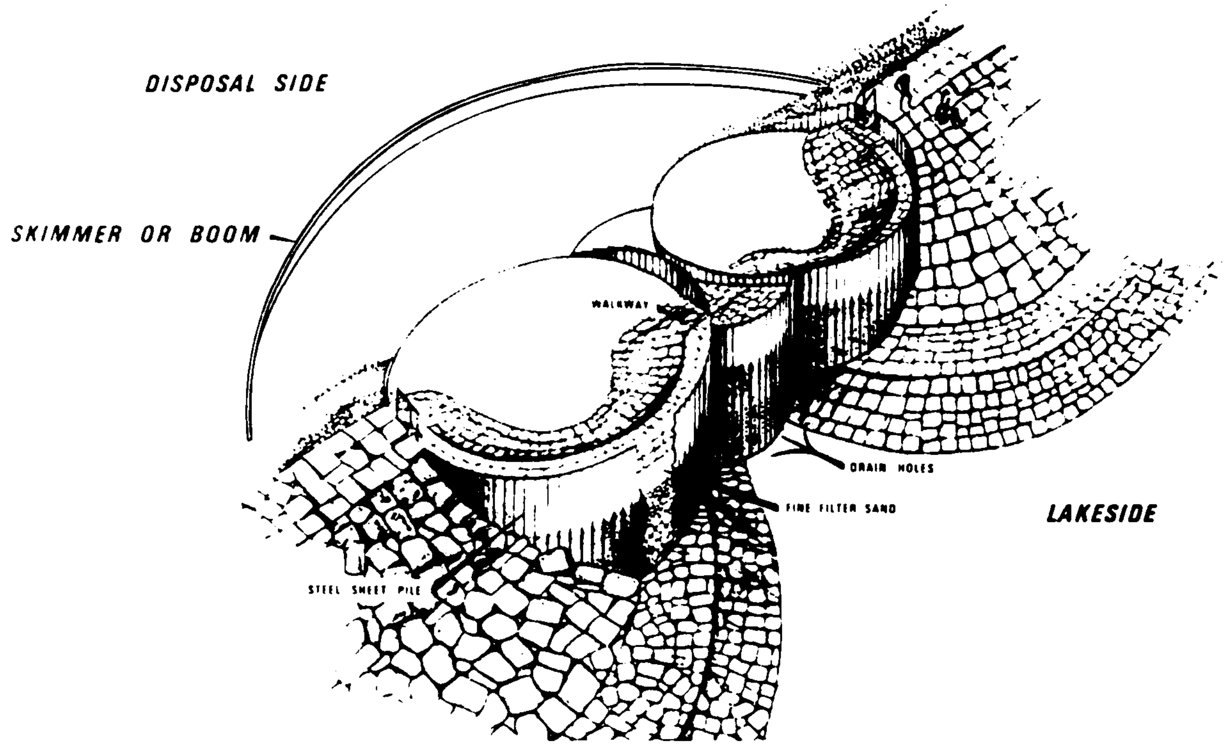

Figure 2. Conceptual drawing of a typical sand filter in Green Bay, Wisconsin.

and 100,000 yd^3 in 1985 and 1987, respectively.

In compliance with the River and Harbor Act of 1970, the city of Kewaunee has provided a 28-acre area for the construction of a confined disposal facility (CDF). The site is located on the north side of the north breakwater (Fig. 1) and has a capacity of 500,000 cubic yards of material. The cost of disposal of dredged material (WCMP 1971) using a CDF (\$5.80 to \$10.40/yd^3) is slightly higher than that of land disposal (\$5.40 to \$8.60/yd^3) and much higher than open water disposal (\$3.20/yd^3). One reason for the high cost of a CDF is the requirement that dredge effluent pass through a sand filter. Figure 2 shows a conceptual drawing of a typical sand filter recently constructed in Green Bay, Wisconsin.

In recent projects such as the one in Green Bay, Wisconsin, the cost of constructing the four filters was about \$250,000*. Maintenance and operation of these filters will add substantial costs to the initial construction cost. Furthermore no data are available for prediction of filter performance in treating the effluent. During the Dredge Material Research Program (WES 1978) attempts were made to monitor the influent and effluent in laboratory-scale lysimeters where dredge materials were placed on a 1-ft soil. Results were site specific and no general model for prediction of leachate quality was developed.

In Michigan and other states, improvement of dredge material effluent quality has been accomplished by simpler methods. Here, the effluent has been upgraded by retention behind weirs from which the liquid is allowed to overflow after some calculated period of time. During this retention time, particle settlement and coagulation occur. Although the amount of suspended solids in the final effluent from this type of purification may be higher than that of the suspended solids in the sand filter leachate, and could cause a temporary cloudy plume in the receiving water, the impact on water quality and the aquatic ecosystem may not justify the high cost associated with filtration.

To evaluate the necessity and effectiveness of CDF containment and filtration we performed elutriate tests (Lee et al. 1978) on sediments obtained from Kewaunee Harbor. Our specific objectives were 1) to physically and chemically characterize the sediments from Kewaunee Harbor

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* F. Snitz, Detroit District, Corps of Engineers, personal communication, 1982.

prior to dredging, and 2) to determine potential impact of dissolved and particulate contaminants on the receiving waters.

EXPERIMENTAL

Field measurements and sample collection

On 21 and 22 April 1981, a team of five scientists and engineers from the Army Corps of Engineers Detroit District and the U.S. Army Cold Regions Research and Engineering Laboratory established six sampling stations (Fig. 1) in Kewaunee Harbor for sample collection. Field measurements of selected water quality parameters were conducted at all the stations using a model 8000 Hydrolab water quality monitor. These measurements included temperature, pH, dissolved oxygen, redox potential and conductivity. Also depth of the water column and turbidity were recorded. Turbidity was determined using a secchi disc on a metered rope. Measurements of all the above parameters except turbidity were conducted on samples in situ at a depth of 1 m below the water surface and at a depth of 1 m above the sediments (generally 2 to 3 m).

Sediment cores were collected from all the stations using a Wildco gravity corer. Because no physical variations were distinguishable in the sediment with depth, some cores were divided in the field into 15-cm sections and transferred to glass bottles. Triplicate grab sediment samples were also collected from all stations using a Peterson sampler. Samples were homogenized and transferred to glass containers and plastic bags for shipment back to the laboratory. Because of extreme mixing processes in the harbor, as observed during sample collection and initial water quality data acquisition, only three water samples were collected for use in the elutriate testing and three other samples for complete chemical and physical analysis. An additional water sample from the Kewaunee River near the harbor was also collected.

Table 1 summarizes the techniques used for preservation of the water samples for the various water analyses. No preservatives were added to the 50-L samples (from stations 1, 3 and 5) used for elutriate tests.

Polyethylene bottles and other labware for metal analyses were cleaned by rinsing with distilled-deionized water (DDW), leaching in 1:1 G. Frederick Smith redistilled HNO_3/DDW and finally rinsing thoroughly with DDW. All other polyethylene containers were washed with phosphate-free detergent, rinsed with tapwater and then rinsed three times with deionized water. Glass containers used for organic analyses (PCBs, chlorinated hydrocarbons, phenols, and oil and grease) were washed in a similar manner and were then rinsed three times with Baker Resi-analyzed acetone to remove any organic contaminants.

Table 1. Water sample preservation techniques.

Parameter	*Container*	*Preservative*
Total organic carbon	Polyethylene	H_2SO_4 to pH < 2
Metals (except Hg)	Linear polyethylene	HNO_3 to pH < 2
Hg	Glass	HNO_3 to pH < 2
Nitrogen forms	Polyethylene	H_2SO_4 to pH < 2
Oil and grease	Glass	H_2SO_4 to pH < 2
Chemical oxygen demand	Polyethylene	H_2SO_4 to pH < 2
PCBs	Glass	No preservatives
Chlorinated hydrocarbon	Glass	H_2SO_4 to pH < 2
Phenols	Glass	0.5 g $CuSO_4 + H_3PO_4$ to pH < 4
Ortho-P	Polyethylene	Sample filtered
Organic-P	Polyethylene	No preservatives
Total-P	Polyethylene	No preservatives
Total solids	Polyethylene	No preservatives
Volatile solids	Polyethylene	No preservatives

Elutriate testing

To evaluate potential impact of dredge material disposal and methods of effluent treatment on receiving water, a modified elutriate procedure was agreed upon after consultation with Frank Snitz of the Detroit District's Environmental Branch. To approximate the release of contaminants in effluents from the weir overflow (no sand filter), 150 g of wet sediment was placed in a graduated Erlenmeyer flask and diluted to one liter with harbor water from the nearest available station. Thus, water from station 1 was used for elutriate testing of the sediments from station 1. The water sample from station 3 was used with sediments from stations 2, 3 and 4, and the water from station 5 was used with sediments from stations 5 and 6. The mixture was stirred and then shaken for one hour on an orbital shaker. The slurry was then transferred to glass containers, allowed to settle for 20 hr, and approximately 600 mL of effluent was siphoned from the top of each sample. This effluent was then swirled to make it homogeneous and a portion (about 40 mL) filtered through Nucleopore filters with a pore size of 0.4 μm. Chemical and physical analyses were performed on both the filtered and unfiltered samples.

In addition to the above elutriates, a settling test was conducted on a separate sediment sample to determine the suspended solids as a function of settling time. Aliquots were taken at various times during a 96-hr period.

To simulate the release of contaminants in effluent fr m the CDF filters, elutriate testing was also performed on sediment subsamples as described above except that all sample preparation (shaking, settling, and filtration) was conducted under deaerated conditions in a nitrogen-filled glove box.

Analytical methods for elutriate samples

Table 2a summarizes the analytical procedures for each parameter tested. All heavy metal concentrations were determined by atomic absorption (AA) with a Perkin-Elmer model 703 AA spectrophotometer and HGA-2200 graphite atomizer. A deuterium background corrector was used to compensate for nonspecific absorption for Cu, Cd, Pb, Zn and Ni; tests showed that Fe and Mn did not require background correction. Instrumental settings were generally those recommended by the manufacturer (Perkin-Elmer 1977). Electrodeless discharge lamps (EDLs) were employed for Pb and Cd while hollow cathode lamps were used for the other metals. Because of their intense light output, EDL wattages had to be reduced to balance the D_2 background corrector energy. Mercury in sediments was determined using cold-vapor AA. Samples were analyzed in triplicate and the results reported are averages of the three determinations.

The concentration of total phosphorus was determined by persulfate digestion (Jeffries et al. 1979) followed by analysis on the Technicon Autoanalyzer II using the automated ascorbic acid reduction method (APHA-AWWA-WPCF 1980 and Technicon Industrial Method 334-74 W/B, 1977). The instrument was calibrated using six standards in the 0- to 0.5-mg/L range. Analyses were performed in triplicate and averaged.

The concentration of orthophosphate was determined by using the powder pillow technique outlined in "Water and Wastewater Analysis Procedures" (Hach Chemical Company 1978). This procedure is based on the ascorbic acid method (APHA-AWWA-WPCF 1980). A single reading was taken for each sample using a Coleman Jr. spectrophotometer. The spectrophotometer was calibrated using six standards ranging from 0 to 0.10 mg P/L.

The total nitrogen content was determined using the persulfate digestion method described previously for total phosphorus, followed by reduction of nitrogen compounds with Devarda's alloy and analysis by the automated phenate method using a Technicon Autoanalyzer II (APHA-AWWA-WPCF 1980, and described in more detail in Technicon Corp. 1973a). The instrument was calibrated using six standards in the 0- to 2-mg/L range. Analyses were performed in triplicate and averaged.

Initially we planned to determine the ammonium content of the elutriate water samples spectrophotometrically on a Technicon Autoanalyzer II using the automated phenate method (APAA-AWWA-WPCF 1980, Technicon Corp. 1977). However, because the water samples from the Kewaunee River and from sites 1, 3 and 5 contained very low concentrations of ammonium we had to measure these samples manually using the Nessler method and a UV-visible spectrophotometer (APAA-AWWA-WPCF 1980). The instrument was calibrated with standards ranging from 0 to 2.0 mg/L.

Analysis for nitrate was performed on a Technicon Autoanalyzer II using the automated cadmium reduction method (APHA-AWWA-WPCF 1980, Technicon Corp. 1973b). This method gives the sum of nitrate and nitrite. Nitrite was determined by removing the cadmium column and rerunning

Table 2. Analytical procedures for water analysis.

a. Methods used.

Parameter	Method	Estimated precision (%)
Heavy metals	Furnace atomic absorption	20
Total-P	UV-vis spectrophotometry	15
Ortho-P	UV-vis spectrophotometry	10
Total-N	UV-vis spectrophotometry	10
Nitrate and nitrite	UV-vis spectrophotometry	10
Chemical oxygen demand	UV-vis spectrophotometry	10
Total organic-C	Infrared spectrophotometry	10
Total suspended solids	Gravimetry	10
Volatile suspended solids	Gravimetry	10
Oil and grease	UV-vis spectrophotometry	5

b. Accuracy of inorganic analyses.

	Accepted values (mg/L)	Observed values (mg/L)	Deviation	Average error (%)
Ammonium	1.91	1.91	0	+ 1.6
	6.5	6.7	+ 3.1	
Nitrate	3.1	2.9	− 6.4	− 4.6
	0.80	0.76	− 5.0	
	8.0	8.2	+ 2.5	
Ortho-P	0.31	0.31	0	2
	0.31	0.31	0	
Total P	0.93	0.81	− 12.9	− 11.3
	0.93	0.84	− 9.7	
COD	119.9	116.6	− 2.8	− 2.8

c. Accuracy of heavy metal analysis.

Metal	Trace metal standard	Concentration (μg/L) Expected	Concentration (μg/L) Measured
Cu	EPA #1	8.7	9.5 ± 0.4
	NBS #1	18 ± 2	17 ± 1
Fe	EPA #1	16	18.4 ± 0.4
	EPA #2	796	752 ± 17
Mn	EPA #3	47	49 ± 1
	EPA #2	478	476 ± 6
Pb	EPA #1	30	33 ± 1
	NBS #1	27 ± 1	28 ± 1
Cd	NBS #1	10 ± 1	7.5 ± 1.0
Zn	EPA #1	6.1	5.7 ± 0.3
	EPA #3	26	20 ± 2
Ni	EPA #1	8.7	8.6 ± 0.1

d. Standard additions recoveries.

	Amount spiked (mg/L)	Amount recovered (mg/L)	Recovery	Average error (%)
Ortho-P	0.064	0.062	97	
	0.064	0.063	98	+ 7.0
	0.062	0.071	114	
	0.062	0.064	103	
	0.064	0.072	112	
	0.063	0.068	108	
	0.060	0.063	105	
	0.061	0.063	103	
	0.063	0.067	106	
	0.063	0.072	114	
Nitrate-N	3.0	3.2	107	+ 7.8
	3.0	3.5	117	
	3.0	3.2	107	
	3.0	3.0	100	

the samples. The instrument was calibrated using six standards in the 0- to 2.0-mg/L range. Triplicate analyses were performed and averaged.

Organic carbon was determined by persulfate oxidation using an ampule modification (described in the operations manual for the Oceanography International Corp. 0524 B Total Carbon System) followed by infrared analysis on the OIC Horiba PIR 2000 detector (APHA-AWWA-WPCF 1980). The instrument was calibrated with 10 standards in the 0- to 100-mg/L range. Duplicates of each sample were analyzed, and if in good agreement they were averaged. A third replicate was analyzed when the two duplicates did not agree within 10%.

Chemical oxygen demand was determined by a semi-micro spectrophotometric method developed by Knechtel (1978) using a Baush and Lomb Spectronic 20 spectrophotometer. The instrument was calibrated with 10 standards in the 0 to 80 μg/L range.

Total suspended solids and total volatile suspended solids concentrations were determined gravimetrically (APHA-AWWA-WPCF 1980). Reported values are from a single determination. Oil and grease concentrations were determined with the trichlorotrifluoroethane extraction method (APHA-AWWA-WPCF 1980).

Accuracy of the laboratory analyses for elutriate samples

Analysis accuracy was estimated by two criteria. The first involved comparing analyses of EPA and NBS standards with the known concentration to give a relative deviation. The concentrations of the standards were in the range of samples tested. This method was employed to determine the accuracy of the total P, total N, ammonium, nitrate, ortho-P and COD analyses (Table 2b). EPA and NBS samples were also tested for the metal analyses and are reported in Table 2c.

The second method to evaluate accuracy involved spiking actual samples with a known amount of analyte to determine the percentage recovery. This method can determine whether matrix interferences are in the actual samples. This method was followed for the ortho-P and nitrate determinations (Table 2d).

From these analyses it appears that the accuracy of the trace metal, ammonium, nitrate, ortho-P, total P, and COD analyses are within the limits given in Table 2.

Sediment analyses

Techniques used for analysis of sediment samples were generally similar to those described for the elutriate samples except for the differences listed below. Subsamples from the grab sediments were used for determination of water content, organic carbon, particle size, heavy metals, oil and grease, COD, total and volatile solids, soluble NH_4, NO_3 total and soluble NH_4 and PO_4, PCBs and chlorinated hydrocarbons. The water content of the sediment was determined gravimetrically by drying the sediment at 105°C in a conventional oven overnight (Black et al. 1965). Organic carbon was determined with two different methods: the first method by wet oxidation of carbon with potassium dichromate (Bremner and Jenkinson 1960) and the second method by persulfate oxidation and infrared analysis as described before for organic carbon analysis in water. The sediment COD was determined by oxidation with $K_2Cr_2O_7$ in the presence of $HgSO_4$ and $H_2SO_4 + Ag_2SO_4$, and back titrating with $Fe(NH_4)_2(SO_4)$ as described by Plumb (1981). Soluble NH_4, NO_3 and PO_4 were determined in a water extract of wet sediments (1:5 *w/w** sediment to water) and analyses were conducted using spectrophotometer methods for P, and distillation titration for NH_4 and NO_3. PCBs and chlorinated hydrocarbons were determined in dry sediment samples using electron capture gas chromatography with a glass capillary column. Arochlor 1016 and 1254 were quantified from representative peaks and compared to EPA standards. The very low quantities preclude meaningful estimation of isomer class distribution. The limit of detection for Arochlors was 0.02 $\mu g/g$ dry sediment. The limit of detection for the chlorinated pesticides was 0.05 $\mu g/g$ dry sediment.

Particle size analyses were conducted twice on each sample: at first on the untreated sample and then when it had been treated with H_2O_2 to destroy the organic matter. Comparison between the results from the two methods gives an idea of the amount of clay size fraction held together with organic matter.

Oil and grease content was determined using the trichlorotrifluoroethane extraction method (APHA-AWWA-WPCF 1980).

For total heavy metal analyses, sediments were first digested with $HNO_3/HClO_4$ at 220° C as described by Iskandar and Keeney (1974). A separate subsample was digested with concentrated HNO_3 at a lower temperature (60°C) for Hg, which was determined using cold-vapor atomic adsorption spectrophotometry. Lead was determined with a graphite furnace AA spectrophotometer, according to the manufacturer's recommended instrumental settings (Perkin-Elmer 1973).

RESULTS AND DISCUSSION

In-situ measurements

The weather during the sampling period was windy and cloudy with air temperatures of 12° to 14°C. Table 3 summarizes the data obtained from in-situ measurement of selected water quality parameters at the six sampling stations. In general, only slight variations were observed in measured water quality values among stations 1, 2, 3 and 4. However, temperature, conductivity and Eh at those four stations were somewhat higher than those at stations 5 and 6. Dissolved oxygen (DO) at the six stations ranged from 8.9 to 11.4 mg/L. The DO at stations 1, 2, 3 and 4 was about 2 mg/L lower than at stations 5 and 6. The water quality parameters at stations 1 through 4 compared to those at stations 5 and 6 probably differ because the water at stations 5 and 6 is well-mixed with water from Lake Michigan, while that from stations 1 through 4 essentially represents Kewaunee River water. The pH of the water throughout the harbor was 8.0 or greater while the Eh ranged from 185 to 232 mV.

All stations exhibited shallow water depth ranging from 1.1 m (station 3) to 4.7 m (station 4). The water from all stations was turbid with point of visual extinction readings of about 1 m, indicating high suspended solids and color due to the presence of colloidal particles and organic matter.

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* Weight/weight.

Table 3. In-situ measurement of selected water quality parameters, April 1981.

Station	*Location*	*Date*	*Water depth (m)*	*Temperature (°C)*	*Conductivity (mmhos/cm)*	*D.O. (mg/L)*	*pH*	*Eh (mV)*
1	S*	21 Apr	1.0	8.8	0.53	8.9	7.96	187
	D†	21 Apr	3.7	8.8	0.53	9.0	7.98	185
2	S	21 Apr	0.5	9.0	0.57	9.9	8.13	232
	D	21 Apr	1.3	9.2	0.56	9.7	8.13	227
3	S	22 Apr	0.4	8.7	0.55	9.7	8.12	217
	D	22 Apr	1.1	8.7	0.55	9.9	8.07	220
4	S	22 Apr	0.6	8.6	0.53	9.8	8.17	229
	D	22 Apr	4.7	8.6	0.53	9.8	8.17	230
5	S	22 Apr	0.7	7.6	0.31	11.4	8.44	162
	D	22 Apr	2.3	7.6	0.31	11.3	8.42	147
6	S	22 Apr	0.5	7.6	0.30	11.3	8.31	217
	D	22 Apr	3.9	7.6	0.31	11.4	8.28	218

* Surface measurement at 1-m depth.

† Deep measurement at a depth of 1 m above sediments.

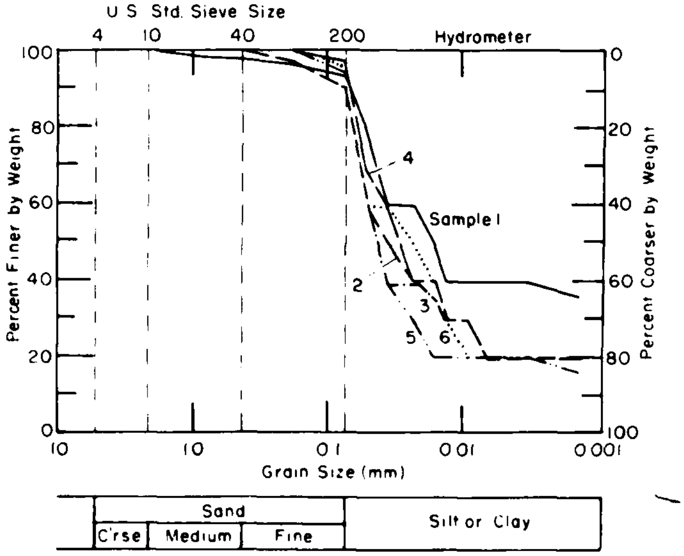

Figure 3. Grain size distribution of samples with no organic matter included.

Sediment characteristics

Figure 3 shows the particle size distribution in the sediments from stations 1-6 using the sieving and hydrometer methods after digesting the organic matter. The data indicate that the sediments have similar texture, with the silt and fine sand fractions forming the major portions. The clay content (< 0.005 mm) was about 20% in all the samples except in that from station 1 where it was about 40%. The silt and fine sand fraction (0.005 to 0.05 mm) was about 40-50%. When the analyses were repeated without destroying the organic matter (Fig. 4) the sediment from station 1 showed only 20% clay. The remaining 20% apparently consisted of aggregated clay particles held together by organic material or polyvalent cations that appeared in the silt fraction. This is important because the clay size fraction is the portion of the sediment in natural systems that will remain suspended the longest and also is the fraction that

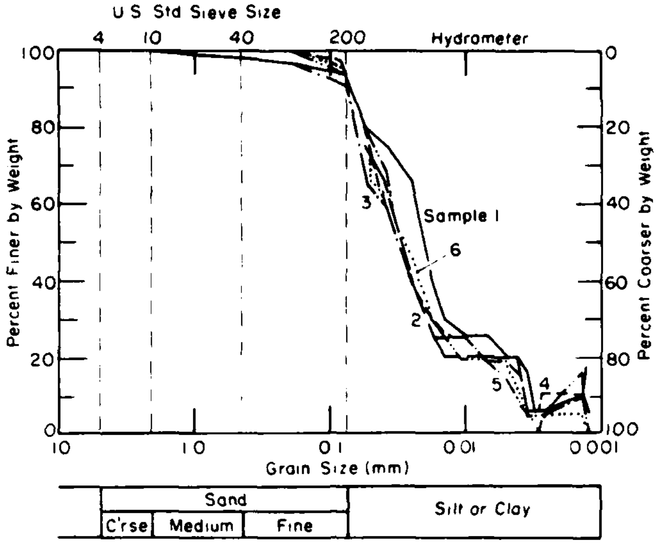

Figure 4. Grain size distribution of samples with organic matter included.

Table 4. Organic carbon in sediments from Kewaunee Harbor.

Station	Moisture content (%)	Organic-C content (%) Wet oxidation method	Organic-C content (%) Carbon analyzer method
1	181	4.06	4.19
2	121	3.29	3.36
3	129	2.63	2.78
4	121	2.09	2.43
5	59	1.15	1.42
6	95	1.58	1.76

Table 5. Percent of total and volatile solids in sediments from Kewaunee, Wisconsin.

Station/ sample	Total solids	Volatile solids	Fixed residue
1	36.08	9.02	90.98
2	44.16	7.62	92.38
3	46.36	7.51	92.49
4	52.21	4.96	95.04
5	35.91	7.92	92.08
6	60.41	2.70	97.30

Table 6. Heavy metals in sediments from Kewaunee, Wisconsin.
Concentrations in μg/g of dry sediment.

Station	Cd	Cu	Cr	Fe	Mn	Ni	Zn	Pb	Hg
1	2.6	24.8	20.1	12500	230	24.1	69.8	16.0	<0.005
2	1.9	15.0	11.4	8420	164	15.2	96.5	7.5	<0.005
3	2.6	16.3	12.1	8550	165	22.0	85.5	12.3	<0.005
4	2.7	19.7	15.0	9640	209	22.5	69.0	7.5	<0.005
5	3.01	12.9	11.9	7490	192	19.1	30.4	6.0	<0.005
6	2.6	17.9	12.9	9170	201	19.6	42.7	5.2	<0.005

contains most of the heavy metals and other contaminants. Based on analysis of sediments without destroying the organic matter, these sediments could be texturally classified as silty loam.

Moisture content (Table 4) in the sediments varied from 59 to 181%. The moisture content was highest in stations near the Kewaunee River and lower near the harbor's south entrance and is probably related to sediment texture and the percentage of organic carbon. Results for organic carbon (Table 4) obtained by the two methods compare well (Table 4) with a correlation coefficient of 0.997. Organic carbon ranged from 1.1% (station 5) to 4.1% (station 1). The high value in the sample from station 1 is probably due to the Kewaunee River's input of high suspended solids

Table 7. Oil and grease in sediments from Kewaunee, Wisconsin.

Station	Oil & grease (% dry weight)	Oil & grease (% wet weight)
1	0.054	0.019
2	0.037	0.016
3	0.026	0.012
4	0.023	0.012
5	0.010	0.003
6	0.009	0.006

containing organic matter. Total solids (Table 5) ranged from 36 to 60% of which 2.7 to 9% is volatile solids.

Table 6 summarizes the heavy metal data at the six stations. With the exception of Fe and Mn, the level of heavy metals in these sediments is low and within the range of nonpolluted sediments. The concentration of Hg was very low (<0.005 μg/g). The concentrations of other selected metals in these sediments (μg/g dry weight basis) were Cd (1.9-3.1), Cu (12.9-24.8), Cr (11.4-20), Ni (15-24), Zn (30-96), and Pb (5.2-16.0). In general sediments from station 1 exhibited the highest concentration of heavy metals and those from station 6 showed the lowest concentrations.

Table 7 summarizes the data for oil and grease. Oil and grease ranged from 0.003% (wet weight) at station 5 to 0.19% at station 1. The high level in stations 1 and 2 is probably due to shipping activities.

Table 8 contains the nitrogen and phosphorus data of Kewaunee sediments. The NH_4 plus NO_3 (soluble N) concentrations were low and ranged from 0.39 (station 5) to 2.11 meq-N/100 g sediments (station 2). Most of the total N in the sediment was in a form of organic N (>92%). Total N ranged from 11.1 to 30.8 meq/100 g dry sediments. Soluble P ranged from 0.24 (station 6) to 0.71 μg P/g sediments (station 1). Total P, however, ranged from 154 to 314 μg P/g sediments. Although no efforts were made to fractionate P, it is likely that most of P is bound with organic matter, hydrous Fe and Al oxides and calcium carbonates.

Table 9 summarizes the data on PCB's and chlorinated pesticides in sediment samples from

Table 8. Concentration of N and P in Kewaunee sediments.

	Nitrogen (meq/100 g)			Phosphorus (μg P/g dry sediment)	
Station	NH_4+NO_3	Organic N	Total N	Soluble P	Total P
1	1.37	29.4	30.8	0.71	216
2	2.11	26.3	28.4	0.25	248
3	0.93	27.3	28.2	0.54	314
4	0.79	22.3	22.9	0.25	266
5	0.31	10.7	11.1	0.41	154
6	0.49	11.9	12.4	0.24	268

Table 9. PCBs and chlorinated hydrocarbons in sediments from Kewaunee, Wisconsin.

	Station					
Compound	1	2	3	4	5	6
Arochlor 1016 (μg/g)	<0.02	<0.02	0.06	<0.02	<0.02	0.04
Arochlor 1254 (μg/g)	<0.02	0.06	0.03	<0.02	<0.02	0.03
Alpha BHC (ng/g)	12.7	1.4	12.5	1.7	1.7	1.7
Lindane (ng/g)	8.9	2.2	7.8	2.3	1.5	1.2
Heptachlor (ng/g)	14.0	13.3	17.1	ND*	ND	9.5
Aldrin (ng/g)	ND	ND	ND	ND	ND	3.4
Heptachlor epoxide (ng/g)	ND	ND	ND	ND	ND	0.46
p,p' DDE (ng/g)	3.7	1.7	2.3	ND	3.0	1.9
Dieldrin (ng/g)	ND	ND	ND	ND	ND	1.3
p,p' DDT (ng/g)	ND	36.2	ND	1.6	ND	ND

* ND indicates no detector response in the region of the pesticide peak. Values are referred to, therefore, as not detected, rather than below detection limit.

Kewaunee Harbor. The concentration of Arochlor 1016 was below 0.02 μg/g at stations 1, 2, 4 and 5 and was 0.06 and 0.04 μg/g at stations 3 and 6 respectively. The concentration of Arochlor 1254 was below 0.02 μg/g at stations 1, 4 and 5 and was 0.06, 0.03 and 0.03 μg/g at stations 2, 3, and 6 respectively. These levels, however, are low. The maximum pesticide level observed was 17.1 ng/g of heptachlor at station 3. Again, this level is still quite low.

Settling test

To determine the effect of detention time on effluent suspended solids, a settling test was performed by mixing 150 g of undried sediment with enough harbor water to make a liter of solution and then shaking it for 1 hour. The suspension was transferred to a graduated cylinder and suspended solids were determined gravimetrically over time (1 to 96 hr) by withdrawing 25 mL from a depth of 10 cm. Sediment samples from the six stations showed similar results (Table 10). Figure 5 shows the decrease in suspended solids with time for station 3. More than 96% of the solids settled out within the first hour and approximately 99% of the solids settled within the first 8 hours. Very little additional settling occurred during the period from 8 to 48 hours. After 96 hours, suspended solids were less than 40 mg/L.

Table 10. Changes in suspended solids with time at 10-cm depth in graduated cylinder.

Time (hours)	*Station*					
	1	*2*	*3*	*4*	*5*	*6*
0	51,200	48,000	61,200	67,600	82,400	86,800
1	2,400	2,000	2,000	1,600	1,200	1,600
4	2,400	1,600	1,600	1,600	1,200	1,200
8	1,600	1,200	800	800	800	1,200
16	1,600	800	800	800	800	800
24	800	400	800	400	800	400
48	400	400	400	400	400	400
96	<40	<40	<40	<40	<40	<40

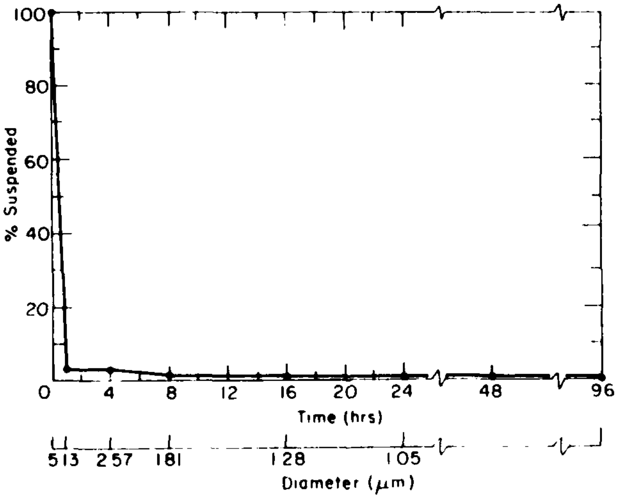

Figure 5. Percentage of suspended solids in sediments from station 3 as a function of settling time and particle diameter.

Chemical characteristics of Kewaunee water

Table 11 summarizes the chemical analyses of the four water samples collected from the mouth of the Kewaunee River and from stations 1, 3 and 5 (see Fig. 1). Since total suspended solids, total volatile suspended solids, and metals were determined on the unfiltered samples, the data represent total concentrations. Total organic carbon was determined for both the filtered and unfiltered samples. COD, total N, total P, ammonium, nitrate and soluble reactive P were determined on the filtered samples.

Total suspended solids ranged from 34 to 60 mg/L; the high values of 50 and 60 mg/L were found in the samples from stations 3 and 5, respectively, and could be due to mixing processes by wind action and ship activities within this shallow harbor. Volatile suspended solids constituted about 18 to 30% of the total suspended solids. The chemical oxygen demand ranged from 78 to 105 mg/L. Total organic carbon, nitrogen and phosphorus forms were present in normal levels. Heavy metals (Cu, Fe, Mn, Pb, Cd, Zn, Ni) are all present in low levels (μg/L) and are below the maximum allowable concentrations for water supply and agricultural irrigation waters. Therefore the effects of industrial input are minimal.

All water samples and elutriates contained less than 50 μg/L of phenols. The concentration of oil and grease in the water samples from the Kewaunee River and at stations 1, 3 and 5 are 0.6, 0.9, 6.6, and 3.5 mg/L respectively. No analyses were performed on the elutriates due to the low levels present and high volumes required for analysis.

Table 11. Chemical analysis of water samples from Kewaunee, Wisconsin (mg/L except as indicated).

			Station							
	River water		*1*		*3*		*5*		*Water supply*	*Agriculture irrigation*
Parameter	*F**	*UF†*	*F*	*UF*	*F*	*UF*	*F*	*UF*		
Chemical oxygendemand	92	—	92	—	105	—	78	—	—	—
Total organic C	11	14.6	11.3	14.2	8.7	12.4	2.0	7.6	—	—
Total nitrogen	7.3	—	4.9	—	2.7	—	1.2	—	0.1	—
Total phosphorus	<0.2	—	<0.2	—	<0.2	—	<0.2	—	—	—
NH_4-N	0.98	—	0.93	—	1.51	—	0.25	—	0.5	—
NO_3-N	2.0	—	2.4	—	2.2	—	0.5	—	10.0	—
Reactive soluble P	0.053	—	0.052	—	0.047	—	0.005	—	—	—
Total suspended solids	—	33.9	—	36.5	—	50.4	—	60.0	—	—
Volatile suspended solids	—	9.9	—	9.5	—	10.5	—	11.2	—	—
Cu (μg/L)	—	5.4	—	5.3	—	8.5	—	2.0	—	20-5,000
Fe (μg/L)	—	23.0	—	62.0	—	30.0	—	42.0	300	5,000-20,000
Mn (μg/L)	—	4.1	—	3.9	—	8.5	—	0.70	50	200-10,000
Pb (μg/L)	—	<0.2	—	<0.2	—	<0.2	—	<0.2	50	5,000-10,000
Cd (ng/L)	—	0.058	—	0.037	—	0.045	—	0.012	10	10-50
Zn (μg/L)	—	7.9	—	4.4	—	6.4	—	1.0	5000	—
Ni (μg/L)	—	1.2	—	1.6	—	1.6	—	0.9	No standard	200-2,000

* Filtered.
† Unfiltered.

Chemical characteristics of sediment elutriates under aerobic conditions

The aerobic procedure simulates the release of contaminants from weirs. Table 12 summarizes the data obtained from the analysis of filtered (F) and unfiltered (UF) elutriate samples obtained under aerobic conditions. As might be expected, the unfiltered samples have a higher COD (chemical oxygen demand) and contain higher concentrations of total organic carbon, nutrients and trace metals. Suspended solids in the unfiltered samples ranged from 100 to 150 mg/L, about three times higher than the harbor water. Volatile suspended solids ranged from 23 to 31 mg/L, about 20% of which is organic matter. Total phosphorus was below 0.2 mg/L in the unfiltered samples and less than 0.08 mg/L in the filtered samples.

Table 12. Chemical analysis of filtered and unfiltered elutriate samples from Kewaunee sediments under aerated conditions (mg/L except as indicated).

	Station											
	1		2		3		4		5		6	
Parameter	F*	UF†	F	UF	F	UF	F	UF	F	UF	F	UF
Chemical oxygen demand	52	87	59	112	66	99	72	100	51	68	52	79
Total organic carbon	10.3	17.3	9.4	19.1	9.5	18.7	8.8	12.5	4.0	8.0	4.2	7.7
Total N	15.0	21.3	14.8	17.3	12.0	16.8	7.0	13.7	5.0	9.8	5.6	10.0
NH_4-N	8.2	8.6	8.8	9.3	7.4	8.3	4.6	5.1	4.0	4.8	4.6	5.0
NO_3-N	1.50	1.43	1.05	0.98	1.3	1.20	1.16	1.10	0.46	0.38	0.30	0.23
Total P	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Reactive soluble P	0.022	0.022	0.037	0.031	0.036	0.050	0.055	0.072	0.035	0.095	0.019	0.043
Total suspended solids	—	146.5	—	99.3	—	134.1	—	100.6	150.2	—	137.0	
Volatile suspended solids	—	31.1	—	23.9	—	25.1	—	22.3	—	27.6	—	22.6
Cu (μg/L)	6.6	8.8	6.2	6.5	7.8	12.3	7.4	9.7	6.2	11.0	10.7	13.2
Fe (μg/L)	27	3880	20	3500	17	4000	23	3800	23	6300	33	4300
Mn (μg/L)	159	255	74	215	34	220	8.9	130	1.8	115	3.8	145
Pb (μg/L)	<0.2	2.6	<0.2	2.0	<0.2	2.9	<0.2	1.9	<0.2	2.6	<0.2	2.1
Cd (ng/L)	12	156	13	84	17	185	69	127	12	294	<5	148
Zn (μg/L)	5.2	25.8	0.8	13	4.4	21.2	0.9	11.8	4.9	25.9	0.7	16.6
Ni (μg/L)	1.3	5.6	1.4	4.7	1.1	5.1	2.0	4.3	1.2	6.9	15	5.5

* Filtered.

† Unfiltered.

Table 13. Chemical analysis of filtered and unfiltered elutriate samples from Kewaunee sediments under unaerated conditions (mg/L except as indicated).

	Station											
	1		2		3		4		5		6	
Parameter	F*	UF†	F	UF	F	UF	F	UF	F	UF	F	UF
Chemical oxygen demand	443	200	54	111	120	87	476	231	372	172	535	229
Total organic carbon	92.5	44.4	12.3	28.0	24.9	19.2	94.5	53.6	46.5	25.2	96.3	50.0
Total N	11.3	15.0	12.5	16.0	10.8	13.8	6.5	8.0	14.5	6.5	11.8	7.5
NH_4-N	9.1	8.4	9.3	10.0	7.8	8.3	4.8	4.6	4.3	3.7	5.1	5.2
NO_3-N	0.08	0.33	2.4	2.3	2.0	1.7	0.08	0.08	0.11	0.07	1.18	1.15
Total P	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Reactive soluble P	0.07	0.13	0.08	0.15	0.06	0.12	0.05	0.06	0.06	0.14	0.08	0.09
Total suspended solids	—	173.5	—	72.5	—	132.1	—	121.2	—	141.5	—	136.9
Volatile suspended solids	—	34.5	—	19.7	—	26.8	—	22.3	—	23.2	—	28.2
Cu (μg/L)	7.0	8.8	6.3	5.5	6.8	9.7	8.5	8.0	7.9	9.5	9.4	7.1
Fe (μg/L)	19	4200	36	2900	21	4100	41	3500	13	6300	52	3900
Mn (μg/L)	196	290	148	220	171	265	8.9	195	1.8	135	318	205
Pb (μg/L)	<0.2	2.8	<0.2	1.98	<0.2	2.37	<0.2	1.76	<0.2	2.37	<0.2	1.7
Cd (ng/L)	16	222	31	120	160	885	125	415	74	237	74	212
Zn (μg/L)	3	18.7	5.6	15.1	3.4	22.1	2.6	13.9	4.4	23.8	6.5	19.8
Ni (μg/L)	1.4	5.4	1.3	3.9	1.3	5.8	2.0	6.5	1.4	7.4	1.9	5.6

* Filtered.

† Unfiltered.

Chemical characteristics of sediment elutriates under nonaerated conditions

Table 13 shows the chemical analysis of the elutriate water samples processed under a nitrogen atmosphere (anaerobic conditions). The filtered water under this condition simulates the leachate from CDF sand filters. Chemical oxygen demand (COD) for most samples was higher than that obtained under aerobic conditions, ranging from 87 to 231 in the unfiltered samples and 54 to 476 in the filtered samples. There was no consistent trend with sample location, and in 5 of the 6 samples the filtered samples contained higher COD values than did the unfiltered ones. Total organic carbon was also much higher under nonaerated conditions than under aerated conditions. This could be due to aerobic degradation of organic matter in the sediments. Total and volatile suspended solids concentrations were similar under aerated and unaerated conditions.

Statistical analysis showed that the differences in the chemical characteristics between the filtered and the unfiltered samples were significant for soluble reactive P and all the metals except Cu (Table 14). Significant but low amounts of heavy metals and soluble reactive P will be released to the water if the effluent is not filtered (Tables 12 and 13). Of the seven trace metals analyzed, both Cd and Mn were significantly higher statistically in the anaerobic samples (both filtered and unfiltered) than in those prepared in the aerobic samples (Table 14). Soluble reactive P was also significantly higher statistically in the samples prepared under anaerobic conditions than in those prepared under aerobic conditions (Table 14). This difference could be due to release of iron and aluminum-sorbed P when sediments were allowed to exhibit reducing conditions.

Table 14 also shows a significant difference among the station locations in the concentrations of Cu, Mn, total N, NH_4-N and suspended solids. No consistent trend with location was observed, however.

Table 14. Summary of statistically significant correlations by analysis of variance.

Parameter/factor	*Aeration* *A*	*Filtration* *F*	*AF*	*Location* *L*	*AL*	*FL*	*AFL*
Total N	—	—	—	0.05	—	—	—
NH_4-N	—	—	0.05	0.001	—	—	—
NO_3-N	—	—	—	—	0.001	—	—
PO_4-P	0.01	0.001	—	—	—	—	—
Organic carbon	—	—	0.025	—	0.05	—	—
Chem. ox. dem.	—	—	0.025	—	—	—	—
Volatile susp. sol.	—	—	—	—	—	—	—
Total susp. sol.	—	—	—	0.025	—	—	—
Metals							
Cu	—	—	0.025	0.01	—	—	—
Cd	0.05	0.01	—	—	—	—	—
Pb	—	0.001	—	—	—	0.025	—
Mn	0.001	0.001	—	0.001	—	—	—
Fe	—	0.001	—	—	—	0.001	—
Zn	—	0.001	—	—	0.025	—	—
Ni	—	0.001	—	—	—	—	—

Table 15. Average net release of contaminants in aerated and nonaerated unfiltered elutriates compared with Kewaunee River water.

Parameter	River water	Avg net release (elutriate) Aerobic	Avg net release (elutriate) Anaerobic	Ratio to river water Aerobic	Ratio to river water Anaerobic
Total organic C (mg/L)	14.6	14.7	25.6	1.0	1.7
Total suspended solids (mg/L)	33.9	76.7	78.3	2.3	2.3
Volatile solids (mg/L)	9.9	16.5	15.2	1.7	1.5
Cu (μg/L)	5.4	5.7	2.9	1.1	0.5
Fe (μg/L)	28.0	4257	4110	152	147
Mn (μg/L)	4.1	158	213	38.6	52
Pb (μg/L)	<0.2	<1.9	<2.2	19	22
Cd (ng/L)	0.06	0.133	0.385	2.2	6.4
Zn (μg/L)	7.9	16.1	7.9	2.0	1
Ni (μg/L)	1.2	4.0	4.0	3.3	3.3

Table 16. Calculated annual input of selected parameters by Kewaunee River and CDF effluent.

Parameter	Kewaunee River	CDF effluent	CDF: river
	10^3 kg/yr		
Total organic-C	1062	1.48	0.004
Total suspended solids	1012	7.74	0.008
Volatile solids	721	1.6	0.002
	kg/yr		
Cu	393	0.580	0.001
Fe	2037	429	0.21
Mn	298	15.9	0.06
Pb	< 14	< 0.2	0.001
Cd	4.37	0.013	0.003
Zn	575	1.62	0.003
Ni	87	0.40	0.005

Potential impact of effluent disposal on Kewaunee Harbor water

To assess the potential impact of the dredge effluent disposal to the Kewaunee water, the net release (or uptake) of elements in elutriates was calculated by subtracting the concentrations of elements present in the harbor water used for elutriations from the concentrations of these elements in the elutriates. An average for the six stations was then calculated and compared with the concentration in the river water. Table 15 shows that under aerobic conditions the most significant impact will be in the increase of Fe, Mn and Pb and to some extent Ni, Cd, Zn and suspended solids. This degradation in water quality parameters could be better described by the amounts and volume discharged rather than concentrations. On an annual basis, the total volume to be dredged is 165,000 yd^3 of which 132,000 yd^3 is water and 33,000 yd^3 is solids. The average water flow of the Kewaunee River for 10 years is 81.5 in.-ft/s*. Based on these assumptions the annual input from the CDF effluent compared to that from the Kewaunee River is calculated for each parameter and summarized in Table 16. This table shows that the amount of contaminants released from CDF effluent discharge to Kewaunee water in most cases would be less than 1% of that discharged by the Kewaunee River into the harbor. Exceptions were Fe and Mn but, in natural water such as Lake Michigan, the DO and pH are high enough to permit Fe and Mn to precipitate as oxides and hydrous oxides which settle and become a part of the sediments. During precipitation, other metals and suspended solids may be coprecipitated, resulting in a further improvement in water quality.

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* Roy Campbell, USGS, Madison, Wis., personal communication.

SUMMARY AND CONCLUSIONS

A field and laboratory study was conducted to evaluate the water and sediment characteristics in Kewaunee Harbor prior to dredging and to assess potential impact of effluent disposal on water quality parameters. The field tests consisted of in-situ water quality analyses, and the laboratory tests were conducted by elutrating sediment samples with harbor water under aerated and nonaerated conditions and then determining levels of contaminants released. The study also included an assessment of the necessity of filtration on the removal of contaminants.

The results indicated that the harbor water contains high levels of suspended solids (34-60 mg/L), has DO ranging from 8.9 to 11.4 mg/L, a pH above 7.5 and an Eh ranging from 185 to 232 mV. The sediment is a silty loam and contains from 1.1 to 4.1% organic carbon. Settling tests simulating dredge material disposal operations showed that more than 96% of the sediments will be settled to a depth of 10 cm within 1 hr and 99% will be settled within 8 hr. To obtain a reduction to less than 50 mg/L of suspended sediments in the effluent, 96 hr of settling time is necessary.

Chemical analysis of filtered and unfiltered effluents obtained from elutrating the sediments with harbor water in a ratio of 3:17 (wet sediment to water) showed that filtration significantly reduced suspended solids, total-P and all trace metals except Cu. However, total-P and trace metal levels in the unfiltered elutriates were too low to cause any significant impact on water quality. Suspended solids ranged from 100 to 150 mg/L, but if sufficient settling time is allowed (48 hr), it is likely that a significant reduction in suspended solids will occur.

Analyses for phenols, oil and grease, PCBs and chlorinated hydrocarbons were conducted but the concentrations were low.

A comparison was also made between potential input of contaminants from unfiltered CDF effluent and Kewaunee River water. Based on net release of contaminants (after subtracting contaminants in water used for elutriation), the input from the CDF effluent is generally less than 1% of that from the river on an annual basis.

Based on this study we conclude that discharging the effluent from the CDF without filtration will not cause a significant impact on water quality. Filtration of effluent will decrease the suspended solids to a very low concentration (about 5 mg/L) but this is not necessary because the receiving water itself contains 36 to 60 mg/L of suspended solids. Settling time in the CDF on the order of 48 to 96 hr should be sufficient to produce effluent with 40 mg/L of suspended solids, which make it comparable to the receiving water. If sand filters are already available they may be used when time for settling is not sufficient or during the last year or two of operation when the CDF is nearly full of solids.

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