



# Availability Of Pollutants Associated With Suspended Or Settled River Sediments Which Gain Access To The Great Lakes



AVAILABILITY OF POLLUTANTS ASSOCIATED WITH  
SUSPENDED OR SETTLED RIVER SEDIMENTS  
WHICH GAIN ACCESS TO THE GREAT LAKES

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## PREFACE

Efforts to control eutrophication of the Great Lakes have focused mainly on reducing the loadings of phosphorus (P) from external sources. Decisions on the reduction of phosphorus loadings require that target loadings, based on the expected response of the lakes to a given loading reduction, be established. Furthermore, decisions must be based on the expected benefit of reduced loadings as compared to the cost of loading reduction. Assessing both the cost and response for a given reduction in phosphorus loading requires an understanding of the biological availability of the different P forms entering the Great Lakes. Inorganic phosphate in solution is known to be readily available to algae and higher plants; however, the biological availability of particulate phosphorus is uncertain. Because approximately 75% of the P loadings to the Great Lakes from diffuse sources may be in particulate form, assessing the biological availability of particulate P is of considerable importance in evaluating the benefits to be accrued from a reduction in P loadings from point as compared to nonpoint sources.

The purpose of this investigation was to evaluate the availability of certain elements, mainly phosphorus, transported to the Great Lakes by suspended sediment. Nitrogen (N) was also investigated because of its importance as a nutrient element; also included were certain trace metals because of concern over their possible adverse effects in the Great Lakes.

Availability was estimated by chemical methods. For P, the chemical methods (NaOH extraction and anion exchange resin desorption) have been related to direct measurements of biologically-available P in the laboratory; for N, measurements were made of inorganic N (available) and an organic fraction which may be converted to inorganic N; for trace metals, measurements were made of the fraction readily desorbed (chelating cation exchange resin) and the fraction associated mainly with hydrous oxides (hydroxylamine hydrochloride extractable).

Samples were collected from five tributaries within the Great Lakes Basin, namely, Genesee in New York, Grand in Michigan, Maumee in Ohio, and Menomonee and Nemadji in Wisconsin. These tributaries, except the Nemadji, were also among the pilot watersheds used by the International Reference Group on Great Lakes Pollution from Land Use Activities to investigate pollutant loadings to the Great Lakes for the International Joint Commission. Samples were transported to the laboratory in Madison, Wisconsin for analysis. The suspended sediments were fractionated according to particle size, and chemical measurements were used to estimate the availability of P, N, and trace metals in the suspended sediment. Samples of recession shoreline material were also analyzed for available P.

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\*Detailed contents are presented at the beginning of each part.

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PART I

SUSPENDED SEDIMENT SAMPLING AND DISTRIBUTION

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## ABSTRACT

Suspended sediment samples were obtained from five tributaries to the Great Lakes. Samples were collected to represent each season, but the spring runoff period was emphasized. Measurements were made of the total suspended sediment concentration and the distribution among clay (0.2 - 2  $\mu\text{m}$ ), silt (2 to 20  $\mu\text{m}$ ) and sand (>20  $\mu\text{m}$ ) size fractions. Comparison of mean concentrations with concentrations reported in earlier investigations indicated the samples were representative of the sampled tributaries. Mean suspended sediment concentrations (mg/L) were 447 (Genesee), 34 (Grand), 171 (Maumee), 138 (Menomonee) and 211 (Nemadji). The concentrations varied widely in a given tributary; coefficients of variation ranged from 37% (Grand) to 165% (Genesee). Sediment distribution among the three size fractions was fairly uniform. Comparison of the mean values for the five tributaries showed the highest proportion (34 to 51%) was present in the silt fraction. The ranges for the clay and sand fractions were 21 to 42% and 14 to 35%, respectively.



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## I-1. INTRODUCTION

The approach in this investigation involved the collection of samples to reflect the possible effects of season and discharge on availability. Time-integrated samples were collected in an attempt to obtain suspended sediment representative of the tributary suspended load. However, because the number of samples collected was relatively small, evaluation of whether the samples collected were representative of the tributary is particularly important. The sampling program was not designed to evaluate the suspended sediment loading, but rather to evaluate the availability characteristics of representative samples.

## I-2. CONCLUSIONS

The mean concentrations of suspended sediment in the samples collected were representative of the respective tributaries. Even though total suspended sediment concentrations varied over a wide range, the particle size distribution was fairly uniform for a given tributary. The suspended sediment samples provided an adequate sample set for evaluation of the availability of phosphorus, nitrogen, and trace metals associated with suspended sediments in the five tributaries.

### I-3. WATERSHED CHARACTERISTICS

Characteristics of the watersheds drained by the tributaries have been described (1-4) and only a brief summary is provided for background purposes.

The Genesee River Watershed (6,420 km<sup>2</sup>) is mainly rural, except for Rochester, New York at the mouth of the Genesee River on Lake Ontario. Although Rochester is an important source of dissolved P, about 80% of the particulate P is attributed to diffuse sources (2). All samples were taken up stream from Rochester to minimize the influence of point sources on the samples.

The Grand River (watershed of 14,660 km<sup>2</sup>) is the largest single tributary to Lake Michigan and discharges at Grand Haven, Michigan. Approximately 60% of the watershed is in agricultural use (5,6). The sandy loam texture of soils in the watershed leads to high infiltration rates and relatively low erosion and particulate P loadings. The groundwater contribution to the river discharge is relatively high and constant, minimizing the fluctuations in discharge as related to storm events. About 60% of the particulate P loading is attributed to nonpoint sources.

The Maumee River Watershed (17,100 km<sup>2</sup>) is the largest watershed draining into the Great Lakes on the U.S. side. The river discharges into Lake Erie at Toledo, Ohio. About 90% of the watershed is in agricultural use; the soils tend to be fine-textured and impermeable (7). Most of the annual sediment load is attributed to soil erosion (8). Estimates of particulate P loading range from 77 to 90% of the total P loading mostly from nonpoint sources (2,3).

The Menomonee River Watershed (344 km<sup>2</sup>) is mostly urban, draining into Lake Michigan at Milwaukee, Wisconsin. The soils tend to be poorly drained (9). Particulate P represents about 80% of the annual total P loading. Samples were taken from a site reflecting the urban influence of the watershed--yet distant from the Milwaukee Sewage Treatment Plant located at Jones Island.

The Nemadji River Watershed (1,290 km<sup>2</sup>) drains the red clay region of northeastern Minnesota and northwestern Wisconsin and enters Lake Superior at Superior, Wisconsin. The fine-textured soils are subject to erosion even though the land is mostly forested (10); particulate P loading is mostly from nonpoint sources.

#### I-4. SAMPLING AND ANALYSIS

##### Collection of Suspended Sediment

Water samples were collected through the cooperation of investigators located near the tributaries. The goal was to collect samples during each season and representing events of different sizes (discharge rates). Sampling stations were located near the river mouth to obtain samples representative of the suspended sediment transported to the Great Lakes. In most cases, sampling was conducted above large urban areas located near the river-lake interface to avoid overemphasis on point sources.

On the Genesee, the main sampling station was at Avon (above Rochester, New York), a few km from Lake Ontario. Some samples also were obtained at Mt. Morris (above Avon) and on two tributaries to the Genesee, namely Oatka Creek (about 35 km above Avon) and Canaseraga Creek (about 100 km above Avon). The Maumee River was sampled at the U.S. Geological Survey Gauging station at Waterville, Ohio, about 31 km above Lake Erie. The Menomonee River was sampled at the 70th street bridge in Wauwatosa, Wisconsin, about 8.5 km above Milwaukee Harbor. This station was selected to avoid possible major influences of the Harbor on the tributary samples. The Grand River was sampled about 3 km below Grand Haven, Michigan, and these samples may reflect the influence of point sources. The Nemadji station was located about 6 km above Lake Superior (St. Louis Bay) and should reflect largely diffuse sources.

Samples were composited from several sub-samples obtained during an event. The samples were shipped in polyethylene containers by surface freight; no preservation was provided except for the Menomonee samples which were refrigerated during transit and storage. Shipment of samples generally took 1 to 4 days, and on arrival the samples were refrigerated at 4°C.

Sample identification, sampling frequency, and distribution and background information are presented in Tables I-1 and Appendix Table I-A-1. The importance of spring runoff was emphasized in the sampling program.

Table I-1. Summary of tributary samples collected for  
suspended sediment analysis

Tributary	Number of Samples			
	Spring	Summer	Fall	Winter
Genesee				
Avon	5	0	1	1
Mt. Morris	0	0	1	1
Oatka Creek	0	0	1	0
Canaseraga Creek	2	1	2	0
Grand	4	1	0	0
Maumee	2	1	0	1
Menomonee	6	3	0	1
Nemadji	7	1	2	1

## Collection of Bottom Sediment

Tributary bottom sediment dredge samples (upper few cm) were obtained from the Menomonee, Genesee, and Nemadji Rivers. These samples are described in Appendix Table I-A-2.

## Size Fractionation of Suspended Sediment

The suspended sediments were separated into size fractions of  $<0.2$ ,  $0.2$  to  $2$ ,  $2$  to  $20$ , and  $>20$   $\mu\text{m}$  by settling and centrifugation techniques. The  $<0.2$   $\mu\text{m}$  fraction was defined as the "dissolved" fraction; the other size fractions correspond to clay, silt, and sand, respectively.

The initial separation involved continuous flow centrifugation (Sorvall Model RC2-B) based on application of Stokes Law to angled-type centrifuge rotors (11) to obtain the  $<0.2$   $\mu\text{m}$  (supernatant or dissolved fraction) and  $>0.2$   $\mu\text{m}$  sized-fractions. For this separation, the samples were centrifuged at 13,000 rpm ( $20^{\circ}\text{C}$ ) at a flow rate of 314 ml/min, using the centrifuge head holding 8x50 ml centrifuge tubes. The fraction  $>0.2$   $\mu\text{m}$  was resuspended and further fractionated by quiescent settling (12). The respective settling velocities (cm/hr at  $20^{\circ}\text{C}$ ) were 0.013 to 1.3 ( $0.2$  to  $2$   $\mu\text{m}$ ), 1.3 to 130 ( $2$  to  $20$   $\mu\text{m}$ ), and 130 cm/hr ( $>20$   $\mu\text{m}$ ).

Sediment samples were analyzed without drying and subsamples were analyzed for moisture content by drying at  $105^{\circ}\text{C}$ .

## Size Fractionation of Bottom Sediment

The bottom sediment samples were suspended by shaking in distilled water for about 1 hour. The samples were then sieved ( $2000$   $\mu\text{m}$ ), and the gravel fraction ( $>2000$   $\mu\text{m}$ ) was discarded. The material  $<2000$   $\mu\text{m}$  was size fractionated into clay, silt, and sand size fractions by quiescent settling as described above for the suspended sediment samples.



## I-5. RESULTS AND DISCUSSION

To evaluate whether the samples collected were representative, comparisons were made with the tributary loading data (2). Values for mean discharge, mean total suspended sediment concentration (TSS) and, the relationship between discharge and TSS were compared (Table I-2). These comparisons indicate the samples collected were representative of the respective tributaries. The mean discharge values were higher and the TSS concentration versus flow slope values were lower for the samples collected in 1977-78 than for historical values (1,2) because the 1977-78 investigation emphasized sample collection during periods of high flow. However, the mean TSS concentrations were in the same range for the 1977-78 and earlier samples, indicating the samples collected were comparable. The correlation coefficient between TSS concentration and discharge for the 1977-78 samples indicates a high proportion (36 to 83%) of the variance in TSS concentration was due to variation in discharge.

Concentrations of TSS varied over a wide range for the samples collected (Table I-3, and Appendix I-B-1). Mean concentrations were highest for the Genesee samples and lowest for the Grand samples. Variability in concentration was particularly high for the Genesee, Menomonee, and Nemadji samples as shown by the coefficient of variation for the mean TSS concentration ( $>0.2 \mu\text{m}$ ).

The particle size distribution was fairly uniform for the samples from a given tributary. In most cases, the highest proportion (mean = 34 to 51%) was present in the 2 to 20  $\mu\text{m}$  size fraction; this fraction also exhibited the least variability (c.v. = 17 to 33%). The  $>20 \mu\text{m}$  fraction represented about 30% of the TSS for the Genesee, Grand, and Menomonee samples, but only about 15% for the Nemadji and Maumee. The 0.2 to 2  $\mu\text{m}$  fraction averaged about 20 to 40% of the TSS. The general uniformity of the particle size distribution within a given tributary sample set, in spite of the wide variation in TSS concentration, suggests the sediment types transported during periods of high loading (high flow and concentration) and low loading (low flow and concentration) may be similar.

Comparison of individual samples (see Appendix I-B-1) indicates a general tendency for lower TSS concentration and a higher proportion of fine particulates during low flow events. Similarly, the organic matter content of the suspended sediment tended to be higher for samples representing low flow and TSS concentration conditions. This was apparently related to a higher organic matter content in the finer than in the coarser size fractions (Appendix I-B-2).

Table I-2. Comparison of suspended sediment and discharge values between the observed (1977-78) samples and previous (historical) samples\*

Tributary	Discharge,** m <sup>3</sup> /sec	TSS mg/L	TSS-discharge relationship***	
			Slope x 10 <sup>3</sup>	Correlation Coefficient
Genesee				
Observed (7) <sup>+</sup>	148	430	39	0.53
Historical	78	259	57	0.48
Grand				
Observed (5)	221	34	1.7	0.83
Historical	114	19	0.5	0.06
Maumee				
Observed (4)	389	171	5.2	0.81
Historical	141	283	11.1	NA
Menomonee				
Observed (10)	8.6	138	74	0.74
Historical	2.7	NA	NA	NA
Nemadji				
Observed (7)	65	211	97	0.36
Historical	11	312	188	0.68

\*The "historical" values were obtained from the PLUARG report on U.S. Great Lakes tributary loadings (2).

\*\*Observed discharge values are instantaneous discharge for the Menomonee and Nemadji Rivers and mean daily event discharge for the other tributaries. Historical values are mean annual daily discharge.

\*\*\*Values obtained from linear regression analysis of TSS concentration against discharge.

+The numbers in parentheses are the numbers of samples. The Genesee samples include only those collected at the Avon, N.Y. station.

NA indicates data were not available.

Table I-3. Mean concentrations and size distribution of suspended sediment in tributary samples

Tributary and number of samples	Concentration of $>0.2\mu\text{m}$ fraction, mg/L	Size distribution, %			Coefficient of variation, %*			
		0.2 to $2\mu\text{m}$	2 to $20\mu\text{m}$	$>20\mu\text{m}$	0.2 to $2\mu\text{m}$	2 to $20\mu\text{m}$	$>20\mu\text{m}$	$>0.2\mu\text{m}$
Genesee (15)	447	24	44	32	44	32	30	165
Avon (7)	332	22	46	31	33	31	29	70
Tributaries (8)	546	25	42	33	52	34	32	184
Grand (5)	34	21	45	34	31	33	59	37
Maumee (4)	171	42	44	14	25	14	73	54
Menomonee (10)	138	31	34	35	92	33	68	116
Nemadji (11)	211	34	51	15	41	17	57	105

\*c.v. = standard deviation  $\div$  mean.

The particle size distribution and organic matter contents of 3 bottom sediment samples are shown in Table I-4. In contrast to the suspended sediment samples, the bottom sediment samples contained a high percentage of sand-size particulates (2 to 2000  $\mu\text{m}$ ). However, the sand fraction contained a negligible amount of organic matter, while substantial amounts (3 to 34%) were present in the silt and clay fractions.

Table I-4. Particle size distribution and organic matter content of bottom sediment samples

Tributary and sample number	Particle size distribution,%			Organic matter content,%*		
	0.2 to 2 $\mu$ m	2 to 20 $\mu$ m	20 to 2000 $\mu$ m	0.2 to 2 $\mu$ m	2 to 20 $\mu$ m	20 to 2000 $\mu$ m
Nemadji A	15	34	51	8	3	<0.5
Menomonee C	1	2	97	34	11	<0.5
Genesee B	3	10	87	11	5	<0.5

\*Organic matter was estimated by the dichromate oxidation method (13).

The analyses were conducted by the Soil and Plant Analysis Laboratory in Madison, Wisconsin.

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APPENDIX A DESCRIPTION OF SEDIMENTS

Appendix I-A-1. Identification and background information on suspended sediment samples obtained to evaluate particulate-associated pollutant availability

Sample No.	Location	Date	Comments	Sample No.	Location	Date	Comments
<u>GENESEE RIVER</u>				<u>GRAND RIVER</u>			
I	Canaseraga Creek at Shakers Crossing, N.Y.	19 May 77	Flow rate = 5.2 m <sup>3</sup> /sec.	I	River mouth; 3 km. down-stream from Grand Haven, MI.	15 June 77	Grand Rapids, MI. USGS Station 04119000 at km 66. Flow rate = 41 m <sup>3</sup> /sec. Water temp = 16°C.
III	Avon, N.Y.	21 June 77	Flow rate = 96.8 m <sup>3</sup> /sec.	II	River mouth, 3 km down-stream from Grand Haven, MI.	23 Aug 77	Grand Rapids, MI. USGS Station 04119000 at km 66. Flow rate = 28 m <sup>3</sup> /sec. Water temp. = 20°C
IV	Jones Bridge at Highway 20A, Mt. Morris, N.Y.	28 Sept 77	Flow rate = 205.5 m <sup>3</sup> /sec. Sampled at rising portion of hydrograph.	III	River mouth, 3 km down-stream from Grand Haven, MI.	10 Apr 78	Grand Rapids, MI. USGS Station 04119000 at km 66. Flow rate = 391 m <sup>3</sup> /sec. Water temp. = 5°C
V	Avon, N.Y.	29 Sept 77	Flow rate = 238.9 m <sup>3</sup> /sec. Sampled at rising portion of hydrograph.	IV	River mouth, 3 km down-stream from Grand Haven, MI.	12 Apr 78	Grand Rapids, MI. USGS Station 04119000 at km 66. Flow rate = 359 m <sup>3</sup> /sec.
VI	Canaseraga Creek at Shakers Crossing, N.Y.	17 Febr 78	Flow rate = 6.2 m <sup>3</sup> /sec.	V	River mouth, 3 km down-stream from Grand Haven, MI.	21 Apr 78	Grand Rapids, MI. USGS Station 04119000 at km 66. Flow rate = 161 m <sup>3</sup> /sec.
VII	Oatka Creek at Garbutt, N.Y.	17 Febr 78	Flow rate = 7.1 m <sup>3</sup> /sec.	<u>NEMADJI RIVER</u>			
VIII	Jones Bridge at Highway 20A, Mt. Morris, N.Y.	17 Febr 78	Flow rate = 22.6 m <sup>3</sup> /sec.	I	5.5 km from river mouth (St. Louis Bay) between Hwy A bridge and Soo Line RR bridge. South Superior, WI	20 May 77	Three days intermittent thunderstorm activity. Rainfall = 4.5 cm. Flow velocity = 4 cm/sec.
IX	Avon, N.Y.	17 Febr 78	Flow rate = 27.2 m <sup>3</sup> /sec.	II	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	1 June 77	Sampled at hydrograph peak. Stage = 320 cm. Rainfall = 4.5 cm. Flow velocity = 105 cm/sec.
X	Canaseraga Creek at Shakers Crossing, N.Y.	20 Sept 77	Flow rate = 101.3 m <sup>3</sup> /sec.	III	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	4 Aug 77	Thunderstorms. Stage at normal summer level.
XI	Canaseraga Creek at Shakers Crossing, N.Y.	22 Sept 77	Flow rate = 49.0 m <sup>3</sup> /sec.	IV	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	29 Sept 77	Sampled after 3-day rain (10 cm ppt). Stage = 312 cm. Discharge = 40 m <sup>3</sup> /sec. Flow velocity = 80 cm/sec, leaves present in water.
XII	Canaseraga Creek at Shakers Crossing, N.Y.	21 June 77	Flow rate = 2.4 m <sup>3</sup> /sec.	V	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	14 Nov 77	Gage height = 300 cm. Flow rate = 34 m <sup>3</sup> /sec.
XIV	Avon, N.Y.	29 Mar 78	Flow rate = 164.1 m <sup>3</sup> /sec. Water temp. = 2°C.	VI	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	25 Febr 78	Late winter, just prior to spring runoff.
XV	Avon, N.Y.	6 Apr 78	Flow rate = 152.8 m <sup>3</sup> /sec.	VII	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	30 Mar 78	Beginning of Spring runoff peak. Gage height = 370 cm and rising slowly. Ice present. Turbidity abnormally low. Not able to calculate flow rate due to ice cover.
XVI	Avon, N.Y.	18 Apr 78	Flow rate = 283 m <sup>3</sup> /sec. Water temp. = 2°C Reservoir release.	VIII	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	31 Mar 78	Peak of snow melt runoff; peak low this year. Gage height = 440 cm. Flow rate = 106 m <sup>3</sup> /sec. Flow velocity = 91 cm/sec
XVII	Avon, N.Y.	3 May 78	Flow rate = 73.6 m <sup>3</sup> /sec. Water temp. = 9°C.	IX	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	2 Apr 78	Samples obtained during decline of snow melt runoff. Gage height = 360 cm. Flow rate = 64 m <sup>3</sup> /sec. Flow velocity = 62 cm/sec. Large patches of brownish scum on water surface. River clear of ice and stage declining rapidly.
<u>MEMPHIS RIVER</u>				X	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	8 Apr 78	Samples obtained during second spring runoff peak which resulted from a spring snowfall. Sampled during hydrograph decline. Gage height = 450 cm. Flow rate = 124 m <sup>3</sup> /sec.
I	Bridge at 70th St., Wauwatosa, WI	2 Apr 77	Gage height 88 cm. Flow rate = 13.7 m <sup>3</sup> /sec.	XI	5.5 km from river mouth (St. Louis Bay), between Hwy A bridge and Soo Line RR bridge. South Superior, WI	22 Apr 78	End of spring runoff. Gage height = 340 cm. Flow rate = 45 m <sup>3</sup> /sec.
II	Bridge at 70th St., Wauwatosa, WI	28 June 77	Sampled at hydrograph peak. Gage height 83 cm. Rainfall = 1.5 cm. Flow rate = 11.3 m <sup>3</sup> /sec.				
III	Bridge at 70th St., Wauwatosa, WI	18 July 77	Gage height = 99 cm. Flow rate = 15.1 m <sup>3</sup> /sec.				
IV	Bridge at 70th St., Wauwatosa, WI	8 Aug 77	Gage height = 61 cm. Sampled during hydrograph decline. Flow rate = 3.7 m <sup>3</sup> /sec.				
V	Bridge at 70th St., Wauwatosa, WI	13 Dec 77	Gage height = 62 cm. Flow rate = 4.0 m <sup>3</sup> /sec.				
VI	Bridge at 70th St., Wauwatosa, WI	3 Febr 78	Gage height = 52 cm. Flow rate = 2.1 m <sup>3</sup> /sec. Snowmelt.				
VII	Bridge at 70th St., Wauwatosa, WI	22 Mar 78	Gage height = 79 cm. Flow rate = 9.9 m <sup>3</sup> /sec. Snowmelt.				
VIII	Bridge at 70th St., Wauwatosa, WI	30 Mar 78	Gage height = 69 cm. Flow rate = 5.7 m <sup>3</sup> /sec.				
IX	Bridge at 70th St., Wauwatosa, WI	6 Apr 78	Gage height = 75 cm. Flow rate = 8.6 m <sup>3</sup> /sec.				
X	Bridge at 70th St., Wauwatosa, WI	18 Apr 78	Gage height = 87 cm. Flow rate = 13.4 m <sup>3</sup> /sec. Rainfall = 2.3 cm				
<u>MAUMEE RIVER</u>							
I	USGS Station, Waterville, OH	26 Apr 77	Mean daily flow rate = 931 m <sup>3</sup> /sec. Normal high-flow spring runoff event.				
II	USGS Station, Waterville, OH	5 July 77	Mean daily flow rate = 116 m <sup>3</sup> /sec. Sampled at hydrograph peak.				
III	USGS Station, Waterville, OH	7 Dec 77	Mean daily flow rate = 120 m <sup>3</sup> /sec.				
IV	USGS Station, Waterville, OH	22 Mar 78	Mean daily flow rate = 2572 m <sup>3</sup> /sec. Very high flow runoff.				



## Appendix I-A-2. Identification and background information on bottom sediments

Sample No.	Location	Date	Comments
Nemadji A	South Superior, Minnesota	February 28, 1978	Sample obtained at bend in river. Depth of river = 2.5m. River bottom composed of hard, red clay with surficial deposition of coarse sand, fine gravel, and litter debris
Menomonee C	Jacobus Park Wauwatosa, Wisconsin	October 15, 1978	Runoff from urban development, light industry, and expressway development
Genesee B	Avon, New York	June 14, 1977	

APPENDIX B. PARTICLE SIZE DISTRIBUTION AND ORGANIC MATTER CONTENT  
OF SUSPENDED SEDIMENTS

Table I-B-1. Particle size distribution of suspended sediment from selected rivers at the Great Lakes Basin

Sample No.	Particles >0.2 m, mg/L	Particle size distribution, %			Sample No.	Particles >0.2 μm, mg/L	Particle size distribution, %		
		0.2 to 2 μm	2 to 20 μm	>20 μm			0.2 to 2 μm	2 to 20 μm	>20 μm
<u>GENESEE RIVER</u>					<u>MAUMEE RIVER</u>				
I	41	14	59	27	I	244	39	49	12
III	56	14	48	38	II	121	52	46	2
IV	726	30	21	49	III	66	51	35	14
V	576	32	30	38	IV	253	29	45	26
VI	16	29	56	15					
VII	11	49	27	24					
VIII	135	13	52	35					
IX	107	15	66	19	I	33	16	29	55
X	2,961	23	41	36	II	18	24	68	8
XI	394	33	30	37	III	41	17	49	44
XII	90	10	49	41	IV	51	18	39	43
XIV	473	27	45	28	V	28	32	50	18
XV	643	23	41	36					
XVI	264	29	31	40					
XVII	207	17	63	20					
<u>MENOMONEE RIVER</u>					<u>NEMADJI RIVER</u>				
					I	99	32	58	10
					II	571	22	60	18
					III	100	42	48	10
I	458	7	38	55	IV	94	29	51	20
II	306	6	30	64	V	33	39	58	3
III	310	30	51	19	VI	5	72	28	0
IV	60	8	25	67	VII	558	26	51	23
V	16	75	19	6	VIII	114	31	51	18
VI	8	82	18	1	IX	139	27	54	15
VII	77	11	44	45	X	519	22	48	29
VIII	28	16	35	49	XI	84	31	48	21
IX	28	43	39	18					
X	87	26	44	30					

Appendix I-B-2. Organic matter content of suspended sediment  
from selected rivers of the Great Lakes Basin

Sample No.	Organic matter, % in particle size fractions			
	>0.2 $\mu\text{m}$	0.2 to 2 $\mu\text{m}$	2 to 20 $\mu\text{m}$	>20 $\mu\text{m}$
<u>GENESEE RIVER</u>				
VI	28	52	15	59
VII	70	46	95	87
VIII	10	40	7	8
IX	16	27	11	21
X	4	9	4	2
XI	10	13	8	11
XII	13	24	10	16
XIV	4	7	5	2
XV	4	9	4	3
XVI	4	10	5	2
XVII	14	20	4	3
<u>MENOMONEE RIVER</u>				
VI	--	25	--	--
IX	15	13	16	15
X	19	21	20	17
<u>MAUMEE RIVER</u>				
III	19	15	18	29
IV	14	11	13	16
<u>GRAND RIVER</u>				
III	15	23	13	17
IV	20	32	18	20
V	24	26	26	19
<u>NEMADJI RIVER</u>				
V	13	15	9	75
VI	46	53	34	0
VII	5	8	5	5
VIII	10	14	10	10
IX	7	12	7	8
X	5	7	6	4
XI	7	8	6	7

PART II

AVAILABILITY OF PHOSPHORUS IN SUSPENDED SEDIMENTS  
AND RECESSIONAL SHORELINE SOILS

by

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D. E. FLATNESS  
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## ABSTRACT

The availability of inorganic phosphorus was measured in samples of suspended sediment from five tributaries to the Great Lakes (Genesee, Grand, Maumee, Menomonee, Nemadji) and in samples of recessional shoreline soils from the northeastern shore of Lake Michigan and the southern shore of Lake Erie. Two chemical methods were used to measure available inorganic P in the sediment and soil samples; extraction with 0.1M NaOH (NaOH-P) and desorption by equilibration with an anion exchange resin (resin-P). The NaOH-P was used as an estimate of the maximum available inorganic P; resin-P was a measure of a more readily available P fraction (released at higher concentrations of inorganic P in solution). For the suspended sediment, mean values of NaOH-P (as percent of sediment total P) were 14% for the Nemadji, 19% for the Genesee, and about 35% for the Grand, Maumee, and Menomonee. Mean resin P values ranged from 43 to 50% of the NaOH-P. The availability of inorganic P was fairly uniform among the clay, silt, and sand size fractions for a given tributary. Mean concentrations of available P (NaOH-P) in the suspended sediments ( $\mu\text{g P/g sediment}$ ) were 825 for the Grand, 469 for the Maumee, 460 for the Menomonee, 162 for the Genesee, and 114 for the Nemadji. Mean concentration of NaOH-P on a volume basis ( $\mu\text{g P/L of water}$ ) were 132 for the Maumee, 64 for the Menomonee, 36 for the Nemadji, 28 for the Genesee, and 16 for the Grand. For the recessional shoreline soils, available P (NaOH-P) concentrations ranged from 1 to 11  $\mu\text{g P/g sediment}$ , corresponding to 1 to 3% of the total P.

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## II-1. INTRODUCTION

The goal of the investigation was to determine the availability of phosphorus associated with suspended sediments transported to the Great Lakes. Dissolved inorganic phosphate is the biologically-available form of phosphorus. Consequently, the biological availability of phosphorus in suspended sediments (particulate P) is determined by the rate and extent of conversion to inorganic phosphate. Because conversion to dissolved inorganic phosphate is controlled in part by environmental factors, biological availability *in situ* depends on location-specific conditions.

The relationships between particulate phosphorus, dissolved inorganic phosphate, and algal phosphorus are illustrated in Fig. II-1. Particulate P in suspended sediment can be divided into non-apatite (largely Fe- and Al-associated), apatite, and organic forms (1,2). The inorganic P forms tend to control the phosphate concentration in solution through adsorption-desorption or precipitation-dissolution reactions. Particulate organic P will release dissolved organic P to solution, but dissolved organic P must also be converted to inorganic phosphate to become available. Phosphorus-limited algae can reduce the phosphate concentration to low levels ( $<0.1 \mu\text{g/L}$ ), thereby causing the release of particulate inorganic P to solution (3). The extent of availability of particulate P can be viewed as depending on the competition between the algal cell and the sediment particle for phosphate in solution. Available particulate P is the amount released from the particle at the given phosphate concentration in solution. Consequently, the factors controlling the availability of particulate P in suspended sediments include 1. the forms and amounts of phosphorus in the particulate fraction, 2. the residence time of the particle in the lake water, 3. the phosphorus status of the algal population, 4. the solution phosphate concentration maintained by the algal or other phosphorus sinks, and 5. other factors controlling the solubility of particulate phosphorus such as pH and Eh.

Assessing the actual availability of phosphorus as controlled by the above variables would require modeling the environment around the sediment particle throughout its residence time in the lake water. However, the potential availability of phosphorus can be evaluated by measuring the particulate forms of P which could be released at a low solution phosphate concentration in a realistic time period.

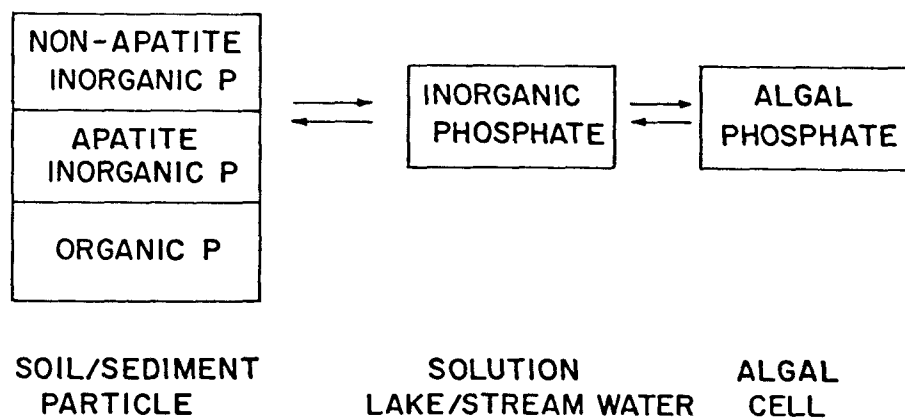


Fig. II-1. Diagram of the relationships between particulate- and algal-P.

Two main bioassay approaches have been used to estimate the potential availability of particulate phosphorus: 1. Growth response bioassay techniques (4-6), and 2. direct measurement of the conversion of sediment inorganic P to algal organic P (5, 7-9). Both approaches can be used to estimate the amount of available P in a given sample. However, the direct measurement approach can also be used to determine the availability of the different phosphorus forms.

In the direct measurement approach (7,8), uptake of sediment or soil P was measured as the decrease in particulate inorganic P or the increase in particulate organic P following incubation of a P-limited algal population (*Selenastrum capricornutum*) with the suspended soil or sediment in a growth media containing the sediment or soil as the sole source of P. This approach assumes that utilization of sediment P involves the conversion of inorganic P (sediment) to organic P in the algal cells; availability of sediment organic P is assumed to be negligible. A small correction is made for inorganic P in the algal cells. By measuring the amounts of non-apatite and apatite inorganic P before and after incubation with the test alga, the relationships between phosphorus forms and biological availability were evaluated.

A procedure involving sequential extraction with 0.1N NaOH followed by N HCl was used to measure the forms of soil or sediment inorganic P (8). Under the conditions used, the NaOH-P and HCl-P fractions correspond closely to the non-apatite and apatite inorganic P fractions, respectively (1). For a wide range of soils a high proportion (regression coefficient = 0.83) of the NaOH-P was available within 48 hr (8), while the HCl-P fraction was essentially unavailable, even over a 4-week period. Similar results were found for lake sediments (7). Consequently, NaOH-P (or non-apatite inorganic P) appears to represent the maximum amount of suspended sediment inorganic P likely to become available.

The uptake of the NaOH-P fraction from suspended sediment by algae can be viewed as a desorption reaction (Fig. II-1). The NaOH-P is desorbed because of the low solution phosphate concentration maintained by the P-deficient algae. Consequently, an alternative approach for measuring available inorganic P is to measure the amount of sediment P desorbed when a low solution phosphate concentration is maintained by an anion exchange resin (6,10,11). For several soils, it was found that the amount of inorganic P desorbed by the resin (resin-P) corresponded to approximately 50% of the NaOH-P (10). The solution phosphate concentration in the soil-resin system was near the chemical detection limit, about 1 µg/L. Apparently, P-deficient algae are able to reduce solution phosphate to a lower concentration than the resin (perhaps <0.1 µg/L), thereby resulting in a greater extent of inorganic P desorption (3). Recently, it was shown that the amount of soil inorganic P desorbed by resin-fixed aluminum corresponded closely to the NaOH-P fraction, substantiating the belief that the NaOH-P can be desorbed if the solution P concentration is sufficiently low (12).

Thus, the availability of P in suspended sediment was estimated by two methods. The non-apatite inorganic P fraction (estimated as NaOH-P) was considered to represent the maximum available inorganic P. The amount of inorganic P desorbed by equilibrating the sediment with an anion exchange resin (resin-P) was used as a measure of the more readily available fraction of the NaOH-P. These procedures do not measure the availability of sediment organic P, but the organic P in soils and sediments is apparently mineralized slowly (2,13,14) and represents a small fraction of available P in comparison to the inorganic P.

## II-2. CONCLUSIONS

Characteristic differences exist in the availability of inorganic P in suspended sediments among the tributaries to the Great Lakes. Available P (NaOH-P), expressed as a percent of total P, averaged 14% for the Nemadji, 19% for the Genesee, and about 35% for the Maumee, Menomonee, and Grand Rivers. Coefficients of variation ranged from 5 to 35%. Availability is relatively uniform among the clay, silt and sand particle size fractions. Consequently, the available P loading for each tributary can be estimated as the product of availability (NaOH-P expressed as fraction of total P) and the total P loading of the tributary.

Available P measured as NaOH-P corresponds to non-apatite inorganic P and represents the maximum amount of inorganic P expected to be made available through release of inorganic P to solution (desorption). Desorption could occur within a period of a few hours. Conversion of other forms to available P requires mineralization of organic P or weathering of apatite P. These processes occur at slow rates and are considered unimportant following deposition of suspended sediments on the lake bottom. Available P measured as resin-P represents inorganic P released to solution more readily than the total NaOH-P. Resin-P is released at solution inorganic P concentrations of about 1  $\mu\text{g/L}$ , while complete release of NaOH-P requires lower solution concentrations. Consequently, resin-P may be a better estimate than NaOH-P of the amount of P typically released in the Great Lakes. Resin-P represents 40 to 50% of the NaOH-P fraction.

While availability is relatively uniform for the different particle size fractions, particle size can be an important factor in availability through controlling the residence time of sediment in the water column. Relatively rapid settling might limit the availability of the sand ( $>20\ \mu\text{m}$ ) fraction. Conversely, the clay ( $0.2\ \text{to}\ 2\ \mu\text{m}$ ) fraction might remain permanently suspended and be subject to long term processes which increase the availability of particulate P. For a suspended sediment containing equal amounts of clay, silt and sand and 35% available P (% of total P), complete availability of inorganic P in the clay fraction would result in an available P level corresponding to 57 rather than 35% of the sediment total P.

In addition to availability (available P as a fraction of total P), suspended sediment concentration and sediment total P concentration, are major factors controlling particulate available P concentrations in tributary waters. Furthermore, tributary discharge rate is a major factor in the loading of available P from the tributary.

Depending on the tributary, available P (NaOH-P) in suspended sediments represents about 25 to 75% of the total available P loading. For the U.S. portion of the Great Lakes Basin, available P in suspended sediments is estimated to represent about 50% of the available P loading and about 25% of the total P loading.

The availability of inorganic P in the recessional shoreline samples investigated was low (<3% of total P). If these samples are representative, the contribution of shoreline erosion to available P loadings to the Great Lakes is relatively low.

## II-3. SAMPLING AND ANALYSIS

### Collection of Samples

The suspended sediment samples collected from the Genesee, Grand, Maumee, Menomonee, and Nemadji are described in Appendix I-A and I-B.

Samples of recessional shoreline material were obtained from the southern shore of Lake Erie and the northeast shore of Lake Michigan. These samples are described in Appendix II-A-1.

### Analysis of Phosphorus Forms

Dissolved reactive phosphorus (DRP) was defined as the reactive phosphorus present in the  $<0.2 \mu\text{m}$  size fraction (15). Total phosphorus was determined by the acid-persulfate digestion technique (16). Samples digested by autoclaving ( $120^{\circ}\text{C}$  at 15 psi), were neutralized and analyzed (15). Digested sediment fractions were filtered ( $0.45 \mu\text{m}$  Millipore) prior to neutralization. The total P in the sediment or sediment size fraction was termed total particulate P (TPP).

Available inorganic P in suspended sediments was estimated by two chemical methods, anion exchange resin desorption (resin-P) and dilute NaOH extractable P (NaOH-P). Following the NaOH extraction, HCl was used to extract the remaining sediment inorganic P (HCl-P). The sum of NaOH-P + HCl-P was used as an estimate of sediment "total" inorganic P.

#### NaOH-P

The sediment was extracted (18 hr) with 0.1*N* NaOH in *N* NaCl in 50 ml polypropylene centrifuge tubes using a sediment solution ratio of 1:1000 or wider, usually 1:2000 (15 mg sediment per 30 ml reagent) (8). The procedure is similar to procedures described elsewhere (e.g., 17), except for the solution:sediment ratio. Following extraction, the samples were centrifuged, filtered ( $0.45 \mu\text{m}$  Millipore), neutralized and analyzed (15).

### HCl-P

The sample previously extracted with 0.1N NaOH was extracted (1 hr) with NHCl. After centrifugation, decantation, filtration (0.45  $\mu$ m Millipore), and neutralization, the samples were analyzed (15).

### Resin-P

The method (10) was similar to previously described procedures (18, 20). Dowex 1-8X anion exchange resin (Cl form), of 20 to 50 mesh particle size, was cleaned and converted to the HCO<sub>3</sub> form by soaking in 0.1M KHCO<sub>3</sub>. The resin was acetone rinsed, air-dried, sieved (250  $\mu$ m), and the >250  $\mu$ m fraction was retained for use. The resin, 1.6 ml (1.0 g), was added to the sediment suspension (30 ml) in a 50 ml polycarbonate centrifuge tube using a sediment:solution ratio > 1:1000, usually 1:2000 (15 mg sediment per 30 ml). The resin-sediment system was equilibrated by shaking for 18 hr. After equilibration, the mixture was sieved (250  $\mu$ m) to separate the resin from the sediment. The >20  $\mu$ m sediment fractions were pre-sieved to exclude >250  $\mu$ m particles prior to the resin-P measurement. The resin was rinsed with a small amount of water and transferred to a long-neck funnel plugged with glass wool for elution. The resin was equilibrated with 0.25 N H<sub>2</sub>SO<sub>4</sub> (30 min), eluted (total acid volume of 75 ml) at <2 mL/min and an aliquot (50 ml) of the eluate was analyzed (15). The acidity of the Murphy-Riley reagent was decreased by an amount equal to the equivalents of acid in the H<sub>2</sub>SO<sub>4</sub> eluate to eliminate the neutralization step.

The relationships between resin-P, NaOH-P, phosphorus in solution and the phosphorus forms in the sediment are illustrated in Fig. II-2. As the phosphorus concentration in solution is lowered, release of phosphorus from the sediment occurs. However, until the solution concentration reaches a low level, the fraction released from the sediment is small. The phosphorus concentration maintained by the resin ( $\sim$ 1  $\mu$ gP/L) results in desorption of about 50% of the NaOH-P. However, if the concentration is lowered further ( $\sim$ 0.1  $\mu$ gP/L), desorption of the NaOH-P fraction occurs. Desorption from the HCl-P fraction is insignificant. The NaOH-P corresponds closely to the non-apatite inorganic P and the HCl-P to apatite P in the sediment. The shape of the desorption curve will vary between sediments, leading to differences in the relative proportions of resin-P and NaOH-P. Furthermore, the phosphorus concentrations corresponding to desorption of resin-P (point B) and NaOH-P (point A) are difficult to measure and are only approximate concentrations. Based on the relatively low phosphorus concentration corresponding to the desorption of resin-P, and the phosphorus concentrations in Great Lakes waters, it seems likely that *in situ* availability might correspond more closely to resin-P than to NaOH-P. However, available inorganic P should not exceed NaOH-P.



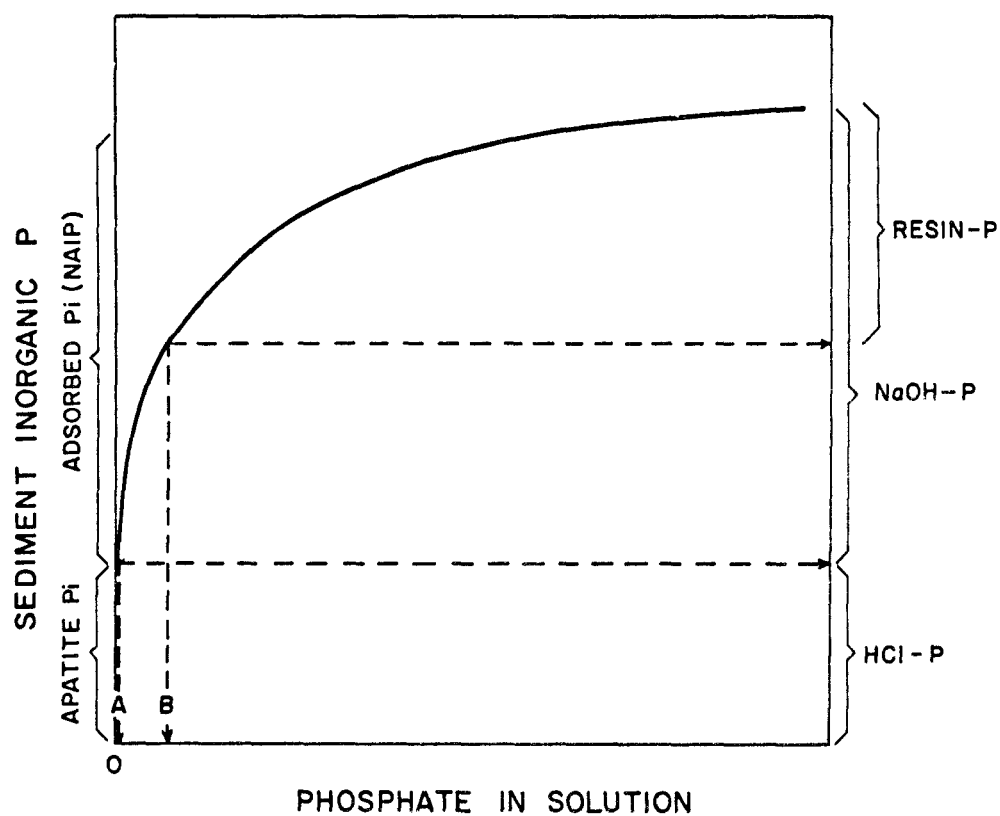


Fig. II-2. Hypothetical isotherm for inorganic P adsorption-desorption by suspended sediment illustrating the relationships between apatite and non-apatite (NAIP) and the inorganic P extracted as resin-P, NaOH-P, and HCl-P. (A  $\sim 0.1 \mu\text{g P/L}$ ; B  $\sim 1 \mu\text{g P/L}$ )

## II-4. RESULTS AND DISCUSSION

### Availability of Particulate P in Suspended Sediment

Available P in suspended sediments was measured as NaOH-P and resin-P; NaOH-P apparently represents the maximum amount of available inorganic P in suspended sediments, while resin-P may correspond more closely to the amount expected to become available from large particles with a short residence time in the lake water or for sediment suspended in lake water containing significant levels of dissolved inorganic P.

#### Proportion of available inorganic P in suspended sediment

The availability of inorganic P in suspended sediment varied appreciably among the tributaries (Table II-1). The group mean values for NaOH-P (% of total particulate P) were 14% for the Nemadji, 19% for the Genesee, and about 35% for the Grand, Maumee, and Menomonee samples. In spite of the wide variations in suspended sediment concentrations and time of sampling, the NaOH-P fraction for the samples from a given tributary was fairly constant (c.v. = 5 to 37%). This suggests some uniformity in the available P characteristics of sediments transported in a given tributary under different conditions of season, discharge and suspended sediment load.

#### Relationships between resin-P and NaOH-P

The amounts of NaOH-P and resin-P in the suspended sediments were closely related (Table II-1); the group mean values for resin-P ranged from 43 to 50% of the NaOH-P fraction. The resin-P represents a "readily desorbed" fraction of the NaOH-P. The remaining NaOH-P (NaOH-P minus resin-P) also can be desorbed if the solution inorganic phosphorus concentration is sufficiently low. Solution inorganic P concentration maintained in resin-soil suspension systems is approximately 1  $\mu\text{g/L}$  (10). However, complete desorption of the NaOH-P apparently requires the solution inorganic P concentration to be below the chemical detection limit, perhaps <0.1  $\mu\text{g/L}$  (8). Apparently, for the suspended tributary sediments, a solution concentration of about 1  $\mu\text{g/L}$  resulted in desorption of about 50% of the NaOH-P (see Fig. II-2).

Table II-1. Percentage of phosphorus in suspended sediments in available and non-available fractions\*

Tributary	n**	P as % of sediment total P			Coefficient of variation, %		
		Resin-P	NaOH-P	HCl-P	Resin-P	NaOH-P	HCl-P
Genesee	14	9	19	34	60	37	33
Grand	4	16	37	16	48	5	29
Maumee	4	17	34	20	34	14	16
Menomonee	6	16	37	27	30	12	39
Nemadji	11	7	14	49	34	37	20

\* NaOH-P + HCl-P = total inorganic P; resin-P is a part of the P in the NaOH-P fraction.

\*\* Number of samples.

Similarly, Sagher (8) found that 1/2 of the P desorbed from soils in an algal-soil suspension was desorbed when the solution inorganic P concentration had been reduced to approximately 1 µg/L. Based on these phosphorus concentration-desorption relationships, the amounts of inorganic P desorbed from suspended sediments in waters of the Great Lakes may correspond more closely to resin-P than NaOH-P.

#### Available P-particle size relationships

The distribution of available P according to suspended sediment particle size was investigated because available P might be concentrated in the fine particulates and because the residence time in the lake water column would be longer for fine than for coarse particulates. For the grouped samples, the proportion (% of particulate P in size fraction) of available P (NaOH-P or resin-P) in the three size fractions (0.2 to 2, 2 to 20, >20 µm) was fairly constant (Table II-2). The exceptions were the higher proportion of available P (resin-P or NaOH-P) in the fine (0.2 to 2 µm) size fraction of the Grand and Menomonee samples. Relatedly, in the 0.2 to 2 µm fraction, the resin-P also represented a higher proportion of the NaOH-P in the Grand (75%) and Menomonee (63%) than in the other size fractions or composite sample (about 50%; Table II-1). In the Grand samples, this was related to the high proportion of resin-P in the Grand I sample (Appendix II-B). In the Menomonee, the higher ratio of resin-P/NaOH-P was found in 5 of 8 samples collected. The high proportion of resin-P to NaOH-P indicates the inorganic P in these fractions would be released more readily than in the other fractions. Apparently, the slope of the adsorption-desorption isotherm is lower for these suspended sediments. This would result in the desorption of a higher proportion of the NaOH-P at the solution inorganic P concentration maintained in the resin-suspended sediment system (see Fig. II-2).

The high proportion of NaOH-P in the 0.2 to 2 µm size fraction of the Grand and Menomonee samples was accompanied by a decrease in the proportion of organic P (Table II-2); the proportion of HCl-P in the 0.2 to 2 µm fraction was similar to the proportion in the other size fractions. A high proportion of HCl-P was observed for the >20 µm size fraction of the Genesee samples (Table II-2). This increase in HCl-P was associated with a decrease in the proportion of organic-P.

In spite of the exceptions discussed above, the relative phosphorus composition was similar for the different size fractions (Table II-2). This similarity in composition indicates that the larger particles may be composed in part of aggregates of smaller size particles. The sediments were dispersed by shaking in water 12 to 18 hours prior to particle size fractionation. The use of chemical or vigorous physical dispersion techniques was avoided because the goal was to obtain particle size-settling velocity information representative of the suspended sediment transported to the Great Lakes. The harsh dispersion techniques would bias the results toward a higher proportion of fine

Table II-2. Distribution of phosphorus fractions among particle size fraction\*

Tributary	P fraction as % of total particulate P in size fraction			
	0.2 to 2 $\mu\text{m}$	2 to 20 $\mu\text{m}$	>20 $\mu\text{m}$	Composite, >0.2 $\mu\text{m}$
<u>Resin-P</u>				
Genesee**	6	9	5	8
Grand	40	16	17	19
Maumee	18	17	14	17
Menomonee	29	15	16	17
Nemadji	7	7	7	7
<u>NaOH-P</u>				
Genesee**	24	18	14	18
Grand	53	36	34	37
Maumee	36	32	32	34
Menomonee	46	36	37	38
Nemadji	16	14	16	15
<u>HCl-P</u>				
Genesee**	35	44	58	44
Grand	18	19	17	18
Maumee	18	20	25	20
Menomonee	28	25	26	27
Nemadji	43	61	51	51
<u>Total organic P</u>				
Genesee**	41	38	28	35
Grand	28	46	49	48
Maumee	46	48	43	47
Menomonee	26	39	37	38
Nemadji	41	25	33	32

\*Mean values for the samples collected (see Appendix I-A-1, Table I-3). Note: Because data was not obtained on all size fractions for some samples, the composite values above may differ somewhat from values calculated from the mean size distribution (Table I-3) and the mean P distribution in the size fraction (above).

\*\*Samples from Avon sampling station.

Table II-3. Concentrations of phosphorus in suspended sediments

	n*	Total particulate P	Total particulate inorganic P	NaOH-P	HCl-P	Resin P	DRP
		μg/g**					μg/L
Genesee							
All samples	15	833 (36)	429 (32)	162 (71)	284 (25)	68 (90)	23 (70)
Avon	6	597 (33)	382 (23)	110 (34)	277 (25)	50 (48)	20 (35)
Canaseraga	5	1101 (33)	549 (37)	238 (68)	324 (12)	104 (91)	32 (80)
Grand	4	2259 (47)	1184 (32)	825 (43)	359 (16)	368 (24)	43 (59)
Maumee	4	1398 (30)	742 (23)	469 (30)	273 (35)	237 (46)	149 (23)
Menomonee	6	1218 (25)	759 (21)	460 (24)	298 (32)	201 (24)	79 (42)
Nemadji	10	835 (23)	529 (15)	114 (50)	400 ( 7)	59 (41)	14 (58)

\*Total number of samples in each group; sample number is less for some analyses because insufficient sediment was available for all analyses.

\*\*Values in parentheses are coefficient of variation (cv).

particles. The relative uniformity in the proportion of available P in the three size fractions (Table II-2) combined with a similar uniformity in sediment distribution (Table I-3) indicates that the amounts of available P in the three size fractions are similar. Because of the low proportion of sediment (~15%) in the >20  $\mu\text{m}$  fraction of the Maumee and Nemadji (Table I-3), the proportion of available P in that size fraction is correspondingly lower than in the 0.2 to 2 and 2 to 20  $\mu\text{m}$  fractions.

Particle size information is of interest because availability is controlled in part by the residence time of particles in the lake water. Large particles may settle from the water column before transport to the open lake water or release phosphorus to solution. Available evidence indicates that the rate of phosphorus desorption is rapid (8,10). For example, most of the NaOH-P fraction was desorbed from soil particles within 48 hr when the soil was incubated in suspension with P-deficient algae (8). The settling velocities of the three size fractions selected in this investigation (measured directly to separate the fractions) were 0.01 to 1.1, 1.1 to 110, and > 110 cm/hr respectively, for the 0.2 to 2, 2 to 20 and >20  $\mu\text{m}$  size fractions. Using a 20 m water column as a frame of reference, the corresponding residence times would be >76 days for the 0.2 to 2  $\mu\text{m}$ , 0.76 to 76 days for the 2 to 20  $\mu\text{m}$ , and <18 hr for the >20  $\mu\text{m}$  size fraction. Considering the expected increase in residence time in the actual lake system due to turbulence, settling velocity could be a limiting factor in controlling P availability for the >20  $\mu\text{m}$  fraction, but should be relatively unimportant for the two smaller size fractions. For the suspended sediments in these size fractions, phosphorus concentration in solution will likely be more important than settling velocity in controlling the availability of the particulate inorganic P.

#### Concentrations of available P in suspended sediments

Comparison of phosphorus concentrations ( $\mu\text{g P/g}$  sediment) in suspended sediments (Table II-3) provides further insight into the available P characteristics of suspended sediments. Comparing sediments from the different tributaries, the total inorganic P concentration (Table II-3) tended to increase in the same order as the proportion of available inorganic P (Table II-1), i.e., Nemadji = Genesee < Menomonee = Maumee = Grand. This indicates that variations in suspended sediment inorganic P concentration are related more to variations in available P (NaOH-P) than non-available P (HCl-P). The NaOH-P concentration (Table II-3) increased in the same order as the proportion of NaOH-P (Table II-1), i.e., Nemadji < Genesee < Menomonee = Maumee = Grand. In contrast, the concentration of HCl-P was less variable between tributaries and relatively unimportant in accounting for variations in total inorganic P concentration (Table II-3). The total inorganic P concentration was exceptionally high in the Grand (1184  $\mu\text{g/g}$ ) as compared to the other tributaries (429 to 759  $\mu\text{g/g}$ ). This was related mainly to the high NaOH-P concentration (825  $\mu\text{g/g}$ ) as compared to the NaOH-P in suspended sediments from the other tributaries (114 to 469  $\mu\text{g/g}$ ). The high NaOH-P level in the Grand samples (1184  $\mu\text{g/g}$ ) was related in part to the high concentration in the Grand I sample (1349  $\mu\text{g/g}$ ) as

compared to the other samples (average of 650  $\mu\text{g/g}$ ). The high inorganic P concentration in the Grand samples may reflect point source contributions from the nearby urban area. The low total inorganic P concentrations in the Genesee and Nemadji sediments (429 and 529  $\mu\text{g/g}$ , respectively) are associated with correspondingly low NaOH-P concentrations (114 and 162  $\mu\text{g/g}$ ; Appendix II-A-2).

#### Comparisons with other measurements

The results obtained in this investigation are in agreement with available information from previous investigations. Bahnick (19) found P release from Nemadji River sediment suspended in Lake Superior water was about 50  $\mu\text{g P/g sediment}$ . This value is in close agreement with the average resin-P value (59  $\mu\text{g/g}$ ) found in this investigation (Table II-3). The amount released corresponded to only 44% of the NaOH-P (114  $\mu\text{g/g}$ ), probably because of the relatively high inorganic P concentration in solution in the sediment-lake water laboratory system ( $\sim 12 \mu\text{g P/L}$ ).

In sediments from the Genesee Basin, ranges of 11 to 410  $\mu\text{g/g}$  for NaOH-P and 187 to 731  $\mu\text{g/g}$  for HCl-P were reported (21). For streams in northwestern New York draining into Lake Erie reported average values of 253  $\mu\text{g/g}$  for NaOH-P + CDB-P and 265  $\mu\text{g/g}$  for HCl-P were found (22). The corresponding values from this investigation (Genesee) are 162  $\mu\text{g/g}$  and 284  $\mu\text{g/g}$  for NaOH-P and HCl-P, respectively. The combined amounts of P extracted by the NaOH and CDB reagents (22) should be approximately the same as P extracted by the NaOH reagent in this investigation because of the wider sediment:solution ratio used here (8).

For eastern Michigan tributaries draining into Lake Erie, Logan (22) found average values of 823  $\mu\text{g/g}$  for NaOH-P + CDB-P and 163  $\mu\text{g/g}$  for HCl-P. This compares with the average values of 825  $\mu\text{g/g}$  for NaOH-P and 359  $\mu\text{g/g}$  for HCl-P found in the Grand samples (Table II-3).

The results of this investigation are also in agreement with results obtained by Thomas and Williams (23) for stream and lake samples on the Canadian side of the basin. For several streams, available P (non-apatite inorganic P) ranged from 27 to 40% of total particulate P (mean is 33%). This compares to the range of 14 to 37% for the U.S. streams in this investigation (Table II-1). Similarly the Canadian values for Lake Superior (14%) and Lake Erie (37%) samples are in agreement with the corresponding tributary values (Nemadji and Maumee, respectively) from this investigation. The higher Canadian value for Lake Ontario (31 to 32%) as compared to the value for the Genesee (19%) may reflect differences in the soils on the U.S. and Canadian sides in this region.



### Available P loadings

Amounts of available inorganic P in suspended sediment expressed as a proportion of sediment total P (Table II-1) or as the concentration of P in the sediment (Table II-3) are not necessarily reflective of the relative amounts of available P transported on a unit volume or unit time basis (Table II-4). Differences between streams in suspended sediment concentration or discharge are major factors in available P loading rates. For example, because of a low average suspended sediment concentration, the Grand ranked lowest among the five tributaries in particulate available P/unit volume ( $\mu\text{g P/L}$ ) even though the Grand River ranked highest in available P concentration ( $\mu\text{g P/g}$ ) in the suspended sediment (Table II-4). However, the relative ranking for available P concentration among the other four tributaries was the same on a volume ( $\mu\text{g/L}$ ) or sediment weight ( $\mu\text{g/g}$ ) basis. The relatively high average discharge rates for the Maumee, Grand and Genesee are major factors in accounting for the relatively high annual loadings of available particulate P for these tributaries. However, the relatively low suspended sediment concentration in the Grand results in a lower available particulate P loading rate than for the Maumee in spite of the high discharge rate, and high concentration of available P in the suspended sediment of the Grand.

The estimated annual tributary loadings of total particulate P (24) and the average proportion of total P present as available P (Table II-1) in the tributary sediments can be used to calculate the estimated annual loading of available P in suspended sediments (Table II-4). These values can be compared with the estimated dissolved P loadings (assumed to be available) to evaluate the relative importance of dissolved and particulate available P loadings. According to these estimates, available particulate P ranges from 23 to 77% of the total available P loading for the five tributaries. The low proportion in the Grand (43%) is related to the low suspended sediment concentration, while the low proportion in the Nemadji (23%) reflects the low P concentration in the sediment and the low fraction of the sediment P present as available P. In contrast, particulate available P in the Genesee represents about 77% of the total available P loading even though the available P fraction is low (19% of total particulate P), due in part to the high suspended sediment concentrations.

Based on P loadings (24) and availability of particulate P (%) found in this investigation, about 50% of the U.S. tributary loading of P to the Great Lakes is in available forms; about 50% of the available P is particulate (suspended sediment) and 50% is dissolved. The proportions are about the same for total P loading or the loading from diffuse sources. This calculation assumes that the availability of sediment P in the tributaries investigated is representative; because no tributaries to Lake Huron were measured, the proportion of suspended sediment P present as available P in Lake Huron tributaries was assumed

Table II-4. Comparison of dissolved and particulate available P loadings in tributaries.

Tributary	Discharge*	Suspended sediment*	Available particulate inorganic P**			Available P from diffuse sources***			
			Concentration in sediment	Concentration on volume basis	Of total particulate P	Annual Loading		Distribution	
			µg/g	µg/L	%	tonnes	%††	Dissolved	Particulate
	m <sup>3</sup> /sec	mg/L						%	
Genesee†	78	259	110	28	19	97	23	23	77
Grand	114	19	825	16	37	202	58	57	43
Maumee	141	283	469	132	34	1034	46	40	60
Menomonee	2.7	138†††	460	64	37	15	52	40	60
Nemadji	11	312	114	36	14	52	41	77†	23

\* Mean "historical" values (24).

\*\* NaOH-P; measured in this investigation; concentration on a volume basis was calculated from the measured concentration in sediment and the mean "historical" suspended sediment concentration.

\*\*\* Calculated from the dissolved and total particulate P loadings for 1975 (24) and the mean available P level (NaOH-P as % of total particulate P) found for each tributary in this investigation (see column 5 above). Dissolved P is considered to be completely available.

† Avon station samples only.

†† Expressed as % of the total P loading.

††† Mean value during sampling intervals in this investigation.

† Based on unit area loading (24).

to be about the same as that in Lake Michigan and Lake Erie tributaries (about 35%). However, the proportion of available P contributed by P in suspended sediments differs appreciably among tributaries, as shown in Table II-4.

#### Availability of Particulate Inorganic P in Recessional Shoreline Soils

The recessional shoreline soil samples were characterized by a low proportion of available P (resin-P or NaOH-P) and a high proportion of HCl-P (Tables II-5 and II-6). Total particulate P concentration ranges were 35 to 1086  $\mu\text{g P/g}$  for size-fractionated samples and 39 to 513  $\mu\text{g P/g}$  for composite samples. However, resin-P and NaOH-P concentration ranges were 3 to 36  $\mu\text{g P/g}$  and 1 to 33  $\mu\text{g P/g}$ , respectively, corresponding to 2 to 12% and 1 to 11% of the total particulate P. For all recessional shoreline samples, HCl-P was the dominant fraction, representing >68% of total particulate P concentration for the composite samples.

The recessional shoreline soils exhibited no clearly distinguishable trends with respect to size fraction (Table II-6); general uniformity existed for all P fractions, especially in the percentage of available particulate inorganic P (NaOH-P or resin-P). The highly siliceous sand fraction (>20  $\mu\text{m}$ ) of the Lake Michigan shoreline samples was extremely low in total P content (Table II-6).

The NaOH-P and resin-P fractions were in close agreement; consistently higher NaOH-P values, as observed for the suspended sediments, were not found. This uniformity is shown for all size fractions except the sand fractions of samples 0-1, 0-3 and Sleeping Bear 3-2 (Table II-6). The resin-P values were much higher than NaOH-P for these samples. These differences are attributed to inadequate separation of the soil from the resin during the analysis, and partial extraction of additional soil inorganic P into the resin-P<sub>i</sub> fraction as the inorganic P was eluted from the resin by acid treatment. The resin-P method requires the sand fraction to be preserved to exclude particles >250  $\mu\text{m}$  to allow subsequent separation of the resin from the resin-soil mixture prior to elution of the resin with acid. If soil particles (>250  $\mu\text{m}$ ) are retained with resin, the acid will extract P from the soil particles, resulting in an overestimation of the resin-P<sub>i</sub> fraction. For samples containing appreciable amounts of particles >250  $\mu\text{m}$ --as the case with these soils--NaOH-P results were considered more reliable estimates of particulate inorganic P.

For the non-fractionated or composited size-fractionated samples, (Tables II-5 and II-6), available P (NaOH-P) ranged from 1 to 16  $\mu\text{g P/g}$ , corresponding to 1 to 4% of the total P. The one exception was the Peterson Park 1-2 composited sample (NaOH-P is 10% of total P). However, this corresponds to only 6  $\mu\text{g P/g}$  due to the low total P content of this sample. A small variability in the NaOH-P concentration ( $\mu\text{g P/g}$ ) can result in a large percentage difference in NaOH-P for those samples exhibiting extremely low total P concentrations.

Table II-5. Inorganic phosphorus distribution in samples from recessional shoreline soils along the Great Lakes

Soil	Phosphorus Distribution				
	Total P	NaOH-P	HCl-P	NaOH-P	HCl-P
<hr/>					
<div>————— <math>\mu\text{g/g}</math> —————      — % of Total P ———</div>					
<u>NORTHEASTERN LAKE MICHIGAN SHORE</u>					
<u>Peterson Park</u>					
1-1	283	2	242	1	86
1-2	70	2	61	3	87
1-3	85	2	58	2	68
<u>Leland</u>					
2-1	282	4	249	1	88
2-2	326	8	280	2	86
2-3	339	11	292	3	86
<u>Sleeping Bear</u>					
3-1	39	1	44	3	113
3-2	81	1	66	1	81
3-3	20	5	16	3	80
3-4	471	9	425	2	90
<u>SOUTHERN LAKE ERIE SHORE</u>					
0-1	342	2	292	1	85
0-3	351	2	320	1	91
0-6	445	5	387	1	87
0-7	513	4	412	1	80

Table II-6. Inorganic phosphorus distribution in size-fractionated samples from recession shoreline soils along the Great Lakes

Soil No. and fraction	Soil in fraction	Phosphorus distribution*						
		Total P	Resin-P	NaOH-P	HCl-P	Resin-P	NaOH-P	HCl-P
<u>    μm    </u>	<u>    %    </u>	<u>    μg P/g    </u>				<u>    % of Total P    </u>		
<u>SOUTHERN LAKE ERIE SHORE</u>								
0-1								
0.2-2	1	125	3	ND	54	2	—	43
2-20	72	354	10	5	326	3	1	92
>20	27	379	33	2	343	9	1	91
>0.2	—	358	16	(4)	328	5	(1)	92
0-3								
0.2-2	1	110	5	ND	34	5	—	31
2-20	63	367	18	17	342	5	5	93
>20	35	316	34	2	332	11	1	105
>0.2	—	343	23	(11)	332	7	(3)	97
0-6								
0.2-2	1	315	13	7	243	4	2	77
2-20	65	462	7	4	377	2	1	82
>20	34	400	11	5	346	3	1	87
>0.2	—	439	8	4	365	2	1	83
0-7								
0.2-2	3	1086	32	10	853	3	1	79
2-20	50	536	11	5	410	2	1	76
>20	47	423	8	3	377	2	1	89
>0.2	—	499	10	4	408	2	1	82
<u>NORTHEASTERN LAKE MICHIGAN SHORE</u>								
Sleeping Bear 3-2								
0.2-2	0.4	174	15	8	90	9	5	52
2-20	13	496	22	33	296	4	7	60
>20	99.3	64	8	1	47	12	2	73
>0.2	—	66	8	1	48	12	2	73
Peterson Park 1-2								
0.2-2	0	—	—	—	—	—	—	—
2-20	9	329	36	38	297	11	9	90
>20	91	35	3	4	32	9	11	91
>0.2	—	61	6	6	58	10	10	92

\*Phosphorus present as Resin-P, NaOH-P and HCl-P. Parenthetic >0.2  $\mu\text{m}$  results based on incomplete data for size fractions.  
 ND indicates concentration was not distinguishable from the blank.

The low NaOH-P levels in the recessional shoreline soils apparently reflects the lack of external P inputs and soil weathering processes which increase the NaOH-P levels in surface soils. The inorganic P in these shoreline soils is apparently contained mainly in apatite, as shown by the HCl-P values. Apatite P is considered to be unavailable.

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# APPENDIX A. RECESSIONAL SHORELINE SOILS AND TRIBUTARY SEDIMENTS

Appendix II-A-1. Description of recessional shoreline soil samples\*

Sample No.	Location	Material	Comments
<u>Southern Lake Erie Shore, Ohio</u>			
01	Ashtabula	Till	Recession rate 30 to 90 cm/yr
03	Bratenahl	Till	Recession rate 30 to 90 cm/yr
06	Vermilion	Till	Recession rate 30 to 90 cm/yr
07	Huron	Glaciolacustrine clay	Recession rate 30 to 90 cm/yr
<u>Peterson Park, Michigan</u>			
1-1	Leelanau Co. (T32N,R11W,Sec.29)	Light brown sandy clay	Sampled 10m above beach
1-2	Leelanau Co. (T32N,R11W,Sec.29)	Light brown clayey sand with few pebbles	Sampled 15m above beach
1-3	Leelanau Co. (T32N,R11W,Sec.29)	Light brown clayey sand with few pebbles	Sampled 20m above beach
<u>Leland, Michigan</u>			
2-1	Bluff 1.6km north of harbor	Light brown clay	Sampled in active slump 6m above water.
2-2	Bluff 1.6km north of harbor	Light brown clay	Sampled 15m above water
2-3	Bluff 1.6km north of harbor	Brown and blue-gray clay	Sampled 20m above water, 4m below noneroded portion
<u>Sleeping Bear Dune, Michigan</u>			
3-1	T29N,R15W,Sec.25	Sand	Sampled 30m above beach
3-2	T29N,R15W,Sec.25	Sand	Sampled 45m above beach
3-3	T29N,R15W,Sec.25	Sand	Sampled 60m above beach
3-4	T29N,R15W,Sec.25	Hard clay layer	Sampled 42m above beach

\*Sampled 6/29/77 except samples 01,03,06 and 07 for which dates are unknown.

Appendix II-A-2. Inorganic P distribution in size-fractionated suspended sediments

Sample No.	Sediment Fraction	Phosphorus distribution								Sample No.	Sediment Fraction	Phosphorus distribution																			
		TPP	Resin-P	NaOH-P	HCl-P	Resin-P	NaOH-P	HCl-P				TPP	Resin-P	NaOH-P	HCl-P	Resin-P	NaOH-P	HCl-P													
		µg P/g				% of TPP						µg P/g				% of TPP															
GENESEE RIVER																MAUMEE RIVER															
I	0.2-2	656	211	438	209	32	67	32		I	0.2-2	2905	653	1070	619	22	37	21													
	2-20	1104	248	314	335	22	28	30			2-20	1100	222	370	252	20	34	23													
	>20	737	131	160	296	18	22	40			>20	941	263	310	313	28	33	33													
	>0.2	942	211	290	307	22	31	33			>0.2	1785	396	636	402	22	36	23													
III	0.2-2	800	146	227	173	18	28	22		II	0.2-2	726	191	348	187	26	48	26													
	2-20	762	94	176	278	12	23	36			2-20	1072	208	367	210	19	34	20													
	>20	834	69	119	241	8	14	29			>20	755	91	193	195	12	26	26													
	>0.2	795	92	161	249	12	20	31			>0.2	886	197	354	198	22	40	22													
IV	0.2-2	354	60	160	316	7	19	37		III	0.2-2	572	88	182	68	15	32	12													
	2-20	621	30	84	300	5	14	48			2-20	1821	223	476	345	12	26	19													
	>20	522	14	42	420	3	8	80			>20	2039	120	629	323	6	31	16													
	>0.2	658	34	92	351	5	14	53			>0.2	1215	140	347	201	12	29	17													
V	0.2-2	805	64	154	308	8	19	38		IV	0.2-2	2329	234	658	288	10	28	13													
	2-20	453	30	74	290	7	16	64			2-20	1561	244	502	282	15	32	18													
	>20	335	8	26	252	2	8	75			>20	1265	143	468	302	11	37	24													
	>0.2	494	29	74	278	6	15	56			>0.2	1707	213	538	291	12	32	17													
VI	0.2-2	1271	196	579	219	15	46	17		GRAND RIVER																					
	2-20	1346	232	409	403	17	30	30		I	0.2-2	1039	849	698	194	82	67	19													
	>20	1314	86	286	527	7	22	40			2-20	1902	400	564	317	21	30	17													
	>0.2	1319	200	440	368	15	33	28			>20	1428	386	487	284	27	34	20													
VII	0.2-2	420	65	103	53	15	25	12			>0.2	1503	464	543	279	31	36	19													
	2-20	1816	172	405	227	9	22	13		II	0.2-2	4968	541	2652	392	9	53	8													
	>20	1580	80	316	196	8	20	12			2-20	3571	372	973	378	10	27	11													
	>0.2	1070	97	236	134	9	22	12			>20	2812	---	850	312	---	30	11													
VIII	0.2-2	689	29	157	61	4	23	23			>0.2	3832	392	1349	376	10	35	10													
	2-20	714	29	97	296	4	14	41		III	0.2-2	1173	246	443	257	21	38	22													
	>20	665	16	61	309	2	9	47			2-20	1738	276	769	402	16	44	23													
	>0.2	694	25	93	283	4	13	41			>20	2121	240	755	385	11	36	18													
IX	0.2-2	846	59	217	---	7	26	---			>0.2	1810	256	707	370	14	39	20													
	2-20	671	42	117	289	6	17	44		IV	0.2-2	1344	403	600	320	30	45	23													
	>20	944	21	125	520	2	13	55			2-20	1974	458	719	458	23	36	24													
	>0.2	749	41	134	---	5	18	---			>20	2041	252	729	404	12	36	20													
X	0.2-2	809	28	122	312	3	15	39			>0.2	1889	360	702	410	19	37	32													
	2-20	560	10	40	320	2	7	57		V	0.2-2	1110	637	715	233	57	64	21													
	>20	391	35	15	257	9	4	66			2-20	4445	402	1924	559	9	43	15													
	>0.2	562	23	50	299	4	9	53			>20	4760	---	---	---	---	---	---													
XII	0.2-2	1390	52	433	257	4	31	19			>0.2	3435	---	---	---	---	---	---													
	2-20	1249	78	301	---	6	24	---		NEMADJI RIVER																					
	>20	1436	58	302	517	4	21	36		I	0.2-2	978	49	34	140	5	3	14													
	>0.2	1340	67	315	---	5	23	---			2-20	775	71	108	459	9	14	59													
XIV	0.2-2	770	72	195	307	9	25	40			>20	633	85	71	370	13	11	58													
	2-20	630	74	117	283	12	19	44			>0.2	816	65	70	347	8	9	42													
	>20	419	56	71	299	13	17	71		II	0.2-2	936	41	81	475	4	9	51													
	>0.2	609	68	125	394	11	21	48			2-20	608	25	46	430	4	8	71													
XV	0.2-2	720	52	151	287	7	21	40			>20	600	26	50	---	4	8	---													
	2-20	595	21	34	177	4	6	29			>0.2	679	29	54	---	4	8	---													
	>20	332	11	43	239	3	13	72		III	0.2-2	701	67	116	420	10	17	60													
	>0.2	529	25	64	225	5	12	42			2-20	931	49	76	462	5	8	50													
XVI	0.2-2	757	76	183	271	10	24	36			>20	741	54	151	436	7	20	59													
	2-20	603	34	122	270	6	20	45			>0.2	806	57	100	437	7	12	54													
	>20	383	12	26	186	3	7	48		IV	0.2-2	685	25	98	286	4	14	42													
	>0.2	560	37	101	237	7	18	42			2-20	622	31	70	440	5	11	71													
XVII	0.2-2	512	---	---	---	---	---	---			>20	689	19	50	392	3	7	57													
	2-20	564	41	122	261	7	22	46			>0.2	647	27	73	381	4	11	59													
	>20	---	10	50	212	---	---	---		V	0.2-2	948	31	130	315	3	14	36													
	>0.2	---	58	---	---	---	---	---			2-20	983	57	125	468	6	13	47													
I	0.2-2	923	353	386	234	38	42	25			>20	1309	156	151	504	12	12	38													
	2-20	1103	210	399	278	19	36	25			>0.2	963	47	126	416	5	13	43													
	>20	981	228	414	257	23	42	26		VI	0.2-2	1095	73	244	354	7	22	33													
	>0.2	1023	231	406	263	23	40	26			2-20	1768	99	245	619	6	14	35													
II	0.2-2	1748	507	1055	290	29	60	17			0.2-20	1310	81	245	428	6	19	33													
	2-20	915	133	279	360	15	30	39			VII	0.2-2	834	74	131	401	9	16	48												
	>20	978	174	345	381	18	35	39		2-20		694	47	64	445	7	9	64													
	>0.2	958	165	300	377	17	31	39		>20		598	33	51	350	6	9	58													
III	0.2-2	1018	214	306	404	21	30	40		>0.2		708	51	78	412	7	11	58													
	2-20	915	133	279	360	15	30	39		VIII	0.2-2	812	106	256	311	13	32	38													
	>20	978	174	345	381	18	35	39			2-20	998	90	244	442	9	24	45													
	>0.2	958	165	300	377	17	31	39			>20	848	65	198	270	8	23	32													
IV	0.2-2	2212	452	1172	360	20	53	16			>0.2	913	90	239	371	10	26	41													
	2-20	1606	244	591	372	14	37	23		IX	0.2-2	898	67	161	402	7	18	45													
	>20	1800	222	598	410	12	33	23			2-20	893	85	170	---	10	19	---													
	>0.2	1784	241	642	397	14	36	22			>20	814	69	140	5	8	17														
V	0.2-2	129	40	90	32	31	70	25			>0.2	883	78	163	---	9	18	---													
	2-20	4217	825	1755	463	20	42	11		X	0.2-2	848	47	126	476	6	15	56													
	>20	2609	---	1051	408	---	40	16			2-20	671	33	66	393	5	10	58													
	>0.2	1054	---	464	136	---	44	13			>20	471	12	86	314	3	18	67													
VI	0.2-2	608	119	172	221	20	28	37			>0.2	652	30	85	388	5	13	60													
	IX	0.2-2	423	148	188	200	35	44	48		XI	0.2-2	884	103	159	425	12	17	49												
		2-20	1968	201	828	446	10	42	23			2-20	472	50	122	420	11	26	89												
		X	0.2-2	827	281	365	160	34	44	19			>20	462	24	132	194	5	29	42											
2-20			1526	63	537	357	4	35	24			>0.2	809	92	149	417	11	18	52												
>20	1360		115	481	272	8	35	20																							
>0.2	1290		135	475	281	10	37	21																							

PART III

AVAILABILITY OF NITROGEN IN SUSPENDED  
AND BOTTOM SEDIMENTS

by

J. J. PERRY  
D. E. ARMSTRONG

## Abstract

Nitrogen availability was evaluated for size-fractionated suspended sediments obtained from selected Great Lakes tributaries. Suspended sediment samples were obtained near river mouths and separated by centrifugation and quiescent gravity settling into 0.2 to 2, 2 to 20 and >20  $\mu\text{m}$  size-fractions.

Nitrogen analyses were performed on the individual particulate fractions to determine the amounts and proportions of the various forms of nitrogen.

The available nitrogen included readily available inorganic nitrogen, (i.e., exchangeable ammonium, and nitrite and nitrate) and the acid hydrolyzable portion of the organic nitrogen that is susceptible to preferential mineralization. Available organic nitrogen in suspended sediments was defined as the hydrolyzable ammonium, amino acid, and hexosamine nitrogen.

The available nitrogen in the suspended sediments ranged from 5 to 21% and 42 to 62% of the total nitrogen for the inorganic and hydrolyzable organic nitrogen, respectively.

Higher concentrations of available nitrogen occurred in the fine particulate fractions except for the Maumee River suspended sediment which contained higher concentrations of available nitrogen in the sand fraction. This was consistent with an increased proportion of organic matter in the sand.

The annual available nitrogen loading for the rivers--from lowest to highest--was Menomonee < Nemadji << Genesee < Grand << Maumee. Annual loadings were strongly influenced by river discharge.

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### III-1. INTRODUCTION

Information on the amounts, forms and distribution of nitrogen compounds associated with size-fractionated suspended sediments is lacking. However, the status of nitrogen compounds has been investigated in bottom sediments (1-6), soils (7-9) and wastewater systems (10,11). These systems are related closely to the suspended sediment system and offer insight into evaluation of the nitrogen status of suspended sediments.

The quantities of nitrogen in suspended sediments range between 0.02 and 10%, representing nitrogen from eroded subsoils and sewage outfalls, respectively. Other nitrogen sources include precipitation, fertilizers, septic tank effluent, runoff, nitrogen fixation, organic matter decomposition and sediment release.

The type of nitrogen present depends on the nitrogen source, sediment geochemistry, internal transformations and environmental conditions. Up to 50% of the organic nitrogen in soil is not characterized as being among known compounds (8,12,13).

Available nitrogen is defined as that fraction of the total nitrogen that is readily to moderately assimilable by either phytoplankton or macrophytes. The most important of these are the inorganic nitrogen and simple hydrolyzable organic compounds containing free amino or amide groups. The inorganic nitrogen forms in solution (ammonium and nitrate) are considered directly available, while organic forms are made available through conversion to inorganic nitrogen (mineralization). The inorganic nitrogen compounds occur as either fixed or exchangeable ammonium and nitrite or nitrate. Exchangeable ammonium is adsorbed to particles, especially in alkaline systems. Fixed ammonium is held within the lattices of clay minerals and is the only form of inorganic nitrogen considered unavailable (14). Nitrite and nitrate are associated with the anion exchange sites and water held in the interstitial spaces of the particulates.

Naturally occurring organic nitrogen compounds are primarily in the form of free and condensed amino acids, amino sugars, purines and pyrimidines and comprise the major form of nitrogen associated with particulates in aqueous systems. These compounds, with the exception of some of the refractory components, are mineralized fairly rapidly and are considered to be available sources of nitrogen in aquatic systems. In soils more than 95% of the nitrogen is organically combined and from 1 to 3% of this is mineralized during the growing season. Much (40%) of the organic nitrogen also is in the form of amino acids, amino sugars and nucleic acids. These compounds have been shown to undergo rapid mineralization when added to soils (15,16). However, mineralization of soil organic nitrogen is retarded by association with soil organic and mineral components.

Numerous attempts have been made to develop a nitrogen availability index. However, the biological stability inherent in various nitrogen

fractions still remains a matter of conjecture. This biological stability may be due to the formation of lignoprotein complexes involving reaction of carbonyl groups in lignin with amino groups in proteins. These complexes may be highly resistant to mineralization (8,17). Organic nitrogen compounds are also known to be adsorbed on and within clay minerals, thereby retarding enzymatic hydrolysis (18-20). Also, inorganic ammonia and nitrite have been shown to react with organic matter, resulting in conversion to unavailable forms (21). However, these more recalcitrant nitrogen associations and complexes may not exist for extended periods of time (17), and generally have not been found in soil in appreciable amounts (22).

Some of the more accepted nitrogen availability indices involve quantifying those selected nitrogen fractions which have been shown to be preferentially mineralized during incubation experiments (14,23-25). It should be noted, however, that the types of organic matter found to be readily mineralized are highly variable (26). Consequently, implication of availability for a specific nitrogen fraction is a relative distinction, and differences in availability between different organic nitrogen fractions may be only moderately significant.

The amino acid-N fraction is generally accepted as the fraction preferentially mineralized during incubation; this has been demonstrated for soils and sediments. For example, evaluation of the changes in the mineralizable N distribution in soils during incubation (24) and extensive cultivation (14) indicated that the greatest nitrogen loss was associated with decreases in amino acid-N and hydroxy amino acid-N. Similarly, greater nitrogen losses were observed to occur in the nondistillable acid-soluble-N (amino acid-N) fraction than that of other nitrogen fractions during cultivation and cropping (7). Relatedly, it was concluded that nondistillable acid soluble-N was decomposed to a greater extent than other fractions (27-32).

In lake sediments, amino acid-N tends to be more abundant and hexosamine-N is less abundant in eutrophic than in oligotrophic lakes, apparently because the sediment organic matter has undergone less microbial turnover in eutrophic lakes as a result of lower dissolved oxygen concentrations. This suggests that under favorable environmental conditions the amino acid-N fraction is mineralized preferentially (1).

The data of Kemp and Mudrochova (3) suggest preferential mineralization of amino acid-N in Lake Ontario sediments. They observed varying organic C:organic N ratios throughout the sediment profiles. The higher C:N ratios occurred in horizons having very low sedimentation rates. A sharp decline in amino acid-N was observed in these horizons. It was concluded that nonhydrolyzable nitrogen is associated with sediments that have undergone extensive humification. The nitrogen associated with humified organic matter is known to be more biologically stable (8). Similarly, the proportion of amino acid nitrogen to total nitrogen was found to decrease with age in most soils (33).

Chichester (25) evaluated the nitrogen status of size-fractionated organo-mineral soil particulates. It was found that greater biological mineralization of organic-N occurred within the finer than the coarser particulates. The amount of mineralizable N in each particle size fraction



varied directly with the concentration of total N and inversely with the corresponding C:N ratios. Higher C:N ratios resulted from greater amounts of undecomposed plant residues in the coarser particulates than in the finer particles. Nitrogen mineralization in the fine particulates was 3 to 4 times greater than in the coarse particles.

### III-2. CONCLUSIONS

The available nitrogen, consisting of the inorganic nitrogen (except fixed ammonium) and a portion of the hydrolyzable organic nitrogen, ranged from 52 to 73% (mean values) of the total nitrogen in the suspended sediments. The highest and lowest percentage of available nitrogen occurred in the Maumee and Nemadji sediments, respectively. An intermediate percentage (mean of 65 to 67%) of available nitrogen occurred in the Genesee, Grand and Menomonee sediments. High proportions (mean of 16 to 21%) of the available nitrogen consisted of available inorganic nitrogen in the Grand, Maumee and Menomonee sediments. Conversely, the percentage inorganic nitrogen was lower (mean of 5 to 10%) in the Genesee and Nemadji sediment.

Mean concentrations of available nitrogen were 8.3, 4.1, 3.7, 2.0 and 1.6 mg/g in the Grand, Maumee, Menomonee, Nemadji and Genesee sediments, respectively. Those rivers containing high available nitrogen concentrations (mg/g) also had high concentrations (mg/L) of dissolved inorganic nitrogen and a large portion of the total sediment nitrogen occurred as available inorganic nitrogen. The concentration of all forms of nitrogen usually increased during low flow events. This resulted from an increased proportion of fine particulates and an increased nitrogen concentration in the fine particulates. The Nemadji and Genesee Rivers contained low concentrations (mg/g) of all forms of nitrogen. This was related to the forested character of the Nemadji Watershed and the high proportion of nitrogen-poor sand in the Genesee sediment.

The annual available nitrogen loading from different sources was calculated using historical values for suspended sediment concentrations, discharge and dissolved nitrogen, and the measured concentrations of particulate available nitrogen. The annual loads were 180, 220, 3,800, 6,500 and 44,200 metric tons for the Menomonee, Nemadji, Genesee, Grand and Maumee Rivers. These values represent 66 to 96% of the total nitrogen load. The annual available nitrogen loadings were influenced most strongly by discharge rate and concentration of dissolved inorganic nitrogen. The dissolved inorganic nitrogen contributed 55 to 91% of the annual available N load. The low loadings in the Menomonee and Nemadji reflected the low discharge and moderate concentration (mg/L) of particulate available nitrogen. The Genesee and Grand Rivers had intermediate available nitrogen loads. This resulted from high discharge even though the particulate available nitrogen concentration (mg/L) was relatively low. The Maumee River exhibited the highest annual loading which was due to a high discharge rate and a high particulate and dissolved available nitrogen concentration (mg/L).

### III-3. METHODS AND PROCEDURES

#### Sample Collection

The suspended and bottom sediment samples collected from tributaries to the Great Lakes and analyzed for available nitrogen are described in Appendix I-A.

#### Nitrogen Analyses

Two chemical fractions were used as estimates of available nitrogen (N). Inorganic-N [ $\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$ ]-N, except fixed  $\text{NH}_4^+$ -N, was considered readily available. A fraction of the organic N, consisting of hydrolyzable  $\text{NH}_4$ -N, amino acid-N and hexosamine-N released into solution during acid hydrolysis, was considered more available than the remaining organic-N.

Inorganic-N (not including fixed  $\text{NH}_4^+$ ) was measured by a steam distillation procedure (12). Total N was measured by a semimicro-Kjeldahl method (12,34). Hydrolyzable forms of organic N were determined by Kjeldahl steam distillation procedures (12). The procedure involved refluxing the sample with HCL (6 ), reaction of the hydrolysate with ninhydrin to cleave amino groups, and measurement of the  $\text{NH}_4^+$  liberated by steam distillation. The ninhydrin reaction is specific for  $\alpha$ -amino groups. The sum of hydrolyzable  $\text{NH}_4$ -N (AN) + amino acid-N (AAN) + hexosamine-N (HN) was measured directly, i.e., the procedure converted these forms to  $\text{NH}_4$ -N. Non-hydrolyzable N (NHN) + unidentified hydrolyzable N (UHN) were calculated as the difference between total organic-N and (AN + AAN + HN). The total hydrolyzable-N (THN) is [(AN + AAN + HN) + UHN]. The (AN + AAN + HN) fraction is comparable to the nondistillable and soluble N fraction (28,30) which in turn is analogous to the amino acid-N fraction of Stevenson (33). Dissillable acid soluble N is comparable to (AN + HN).

#### III-4. RESULTS AND DISCUSSION

##### Availability of N in Suspended Sediments

Nitrogen in suspended sediments is evaluated according to the following relationships: 1. the concentrations of the different forms of nitrogen, 2. relative proportions of the nitrogen forms and 3. distribution of the different forms of nitrogen in size-fractionated suspended sediments.

##### Genesee River

Relatively low, but variable concentrations of nitrogen were observed in the Genesee River (Avon) suspended sediments (Table III-1). The mean concentrations of inorganic N, (AN + AAN + HN) and total N in the Avon sediment were 0.25, 1.42 and 2.42 mg/g, respectively. The range of values for sediment total-N was similar to values observed by Reddy (35) for bottom sediments collected in Lake Ontario at the mouth of the Genesee River. In contrast, the bottom sediment total N was more variable and substantially higher in samples obtained throughout the Genesee Watershed (35). Values for these samples agree with total N values for the suspended sediments from tributaries to the Genesee. The inorganic N concentration (0.25 mg N/g) in the Genesee-Avon sediments was low in comparison to sediments from tributaries to the Genesee or the other rivers evaluated in this study. However, the concentrations at the Avon station were more consistent with values observed for bottom sediments than for soils. Relatedly, the mean dissolved inorganic-N concentration of 1.1 mg/L (Table III-2) was also low and similar to values reported for the Genesee River plume in Lake Ontario (36).

The mean concentrations of AN + AAN + HN for the Genesee-Avon sediments (Table III-1) are lower than those observed for Lake Ontario bottom sediments (3) or suspended sediments for Genesee River tributaries. Higher nitrogen concentrations in the bottom sediments may result from the selective sorting of nitrogen-rich finer particulates in the far-shore depositional areas. The higher nitrogen concentrations in the suspended sediments may be related to the high gradients and greater sediment heterogeneity in the Genesee tributaries. A similar trend was observed by Reddy (37) for phosphorus concentrations.

The proportion of nitrogen as (AN + AAN + HN)--with a mean of 59%--was slightly higher for the Genesee than for the other river sediments (Table III-2). This slightly elevated distribution was offset by a lower proportion of inorganic-N (5%), thereby maintaining the (NHN + UHN) distribution (35%) similar to those of the other river sediments. In comparison to the Avon station, the Genesee tributary sediments had a slightly increased proportion of organic N in the (AN + AAN + HN) fraction.

Table III-1. Mean concentrations of the different nitrogen forms in size-fractionated suspended sediments

Sediment size fraction	Suspended sediment	Particulate-N distribution			Total-N
		Inorganic	(AN+AAN+HN)	(NHN+UHN)	
μm	%*	mg/g**			
<u>GENESEE</u>					
0.2-2	22	0.78 (11)	4.76 (68)	1.62 (23)	7.00
2-20	46	0.17 (12)	0.84 (61)	0.40 (29)	1.37
>20	32	0.14 (7)	1.18 (58)	0.75 (37)	2.04
>0.2	332	0.25 (10)	1.42 (59)	0.80 (33)	2.42
0.2-2	26	2.73 (13)	17.11 (80)	1.71 (8)	21.09
2-20	44	0.50 (10)	3.80 (74)	0.87 (17)	5.11
>20	30	0.34 (5)	2.19 (32)	4.31 (64)	6.77
>0.2	546	0.57 (7)	4.73 (59)	2.86 (35)	8.08
<u>MENOMONEE</u>					
0.2-2	31	3.08 (27)	4.82 (42)	4.95 (43)	11.40
2-20	34	1.03 (18)	3.17 (56)	1.80 (32)	5.71
>20	35	0.39 (8)	3.01 (16)	1.70 (35)	4.91
>0.2	138	0.80 (16)	3.11 (55)	2.01 (35)	5.65
<u>MAUMEE</u>					
0.2-2	42	1.93 (33)	2.05 (35)	2.23 (38)	5.90
2-20	44	0.36 (8)	2.94 (63)	1.44 (31)	4.69
>20	14	1.50 (20)	4.52 (61)	2.15 (29)	7.41
>0.2	171	1.17 (21)	3.13 (55)	1.55 (27)	5.64
<u>GRAND</u>					
0.2-2	21	7.59 (44)	6.74 (39)	6.07 (35)	17.26
2-20	45	1.00 (8)	6.94 (55)	4.82 (38)	12.58
>20	34	1.48 (16)	5.37 (57)	2.89 (31)	9.42
>0.2	34	2.29 (18)	6.74 (54)	4.21 (34)	12.49
<u>NEMADJI</u>					
0.2-2	34	0.82 (15)	2.12 (40)	2.54 (48)	5.33
2-20	51	0.19 (6)	2.41 (42)	1.81 (54)	3.36
>20	15	0.40 (17)	1.36 (57)	0.77 (32)	2.40
>0.2	211	0.38 (10)	1.73 (43)	1.87 (48)	3.87

\*Values for composite (>0.2  $\mu\text{m}$ ) fraction expressed in mg/L.

\*\*Values in parentheses are percentages of total-N in size fraction.

Table III-2. Nitrogen distribution (mean values) in tributary suspended sediment and water

Nitrogen distribution					
Dissolved Inorganic	Particulate associated-N				
	Inorganic*	Hydrolyzable**	Available***	Nonavailable†	Total
mg/L	±††				
<u>GENESEE</u>					
1.1 (0.6-1.5)	5 (2-10)	59 (37-80)	67 (36-88)	33 (12-64)	0.24 (0.12-0.64)
<u>MENOMONEE</u>					
2.2 (1.3-2.8)	16 (7-19)	55 (49-67)	65 (61-72)	35 (28-43)	0.57 (0.39-0.98)
<u>MAUMEE</u>					
5.3 (0.8-10.0)	21 (5-29)	55 (44-58)	73 (63-93)	27 (27-37)	0.56 (0.46-0.65)
<u>GRAND</u>					
2.1 (0.7-3.7)	18 (6-22)	54 (45-70)	66 (63-73)	34 (27-37)	1.25 (0.72-1.82)
<u>NEMADJI</u>					
1.0 (0.4-2.3)	10 (6-20)	49 (37-59)	52 (51-70)	48 (30-53)	0.39 (0.09-0.48)

\* Includes  $\text{NO}_2$ ,  $\text{NO}_3$  and exchangeable  $\text{NH}_4$ .

\*\* Includes ammonium, amino acid and hexosamine nitrogen.

\*\*\* Includes hydrolyzable-N and  $(\text{NO}_2 + \text{NO}_3)\text{-N}$ .

† Includes total-N minus available-N.

†† Expressed as % of total-N, except total-N which is % of suspended particulates.

### Grand River

High concentrations of all forms of particulate-associated nitrogen were found in the Grand River suspended sediments. The mean inorganic-N, (AN + AAN + HN) and total-N concentrations in the combined sediments were 2.3, 6.7 and 12.5 mg N/g, respectively (Table III-1). Similar values for the Grand River have been reported (38,39). These very high concentrations are atypical for most mineral soils, particularly the sandy soils common in the Grand watershed. The high values probably reflect the influence of urban point sources (Grand Haven). Relatedly, the dissolved inorganic-N concentration also was quite high, averaging 2.1 mg N/L (Table III-2). Most of particulate inorganic N (86%) was in the form of (NO<sub>2</sub> + NO<sub>3</sub>)-N. However, the concentration of exchangeable NH<sub>4</sub>-N was high (mean of 0.30 mg/L), compared with previously reported values (38). This high concentration of exchangeable NH<sub>4</sub>-N may also reflect the influence of point sources.

The distribution of the various nitrogen forms was essentially uniform among the different Grand River samples (Table III-3). Hydrolyzable-N averaged 54% of the total particulate-N (Table III-2). Most of the nitrogen (48%) was present in the form of hydrolyzable amino acid-N and hexosamine-N (data not shown). Amino acid-N (AAN) constituted most of the nitrogen in this fraction and is considered to be a readily mineralizable form of organic-N, particularly under aerobic conditions. The nonhydrolyzable-N and unidentifiable hydrolyzable-N fractions accounted for 34% of the total-N and are considered to be less available forms of nitrogen (Table III-2). The readily available inorganic N comprised 18% of the total N.

The nitrogen distribution in the size-fractionated particulates varied with type of nitrogen (Table III-1). The nitrogen concentration was highest in the finer particulates, resulting from increased concentrations of inorganic-N and (UHN + NHN). The concentration in the (AN + AAN + HN) fraction was relatively uniform among the three size fractions.

### Maumee River

Interpretation of the data from the Maumee sediments is somewhat restricted due to the limited number of samples. However, some complementary information is available (40).

The Maumee River sediments contained high mean concentrations of all forms of nitrogen (Table III-1). The mean inorganic-N, (AN + AAN + HN) and total-N concentrations were 1.2, 3.1 and 5.6 mg N/g, respectively. These high concentrations are more consistent with values observed for bottom sediments (1,3) than for soils. The inorganic-N is particularly high and variable and occurred primarily in the form of (NO<sub>2</sub> + NO<sub>3</sub>)-N. Relatedly, the high sediment (NO<sub>2</sub> + NO<sub>3</sub>)-N concentrations were directly proportional to the dissolved (NO<sub>2</sub> + NO<sub>3</sub>)-N concentrations. The amount of inorganic N in the sediment, particularly (NO<sub>2</sub> + NO<sub>3</sub>)-N, was inversely proportional to the river flow rate

Table III-3. Concentrations of the different nitrogen forms in individual composite (>0.2  $\mu$ m) suspended samples

Sample no.	Flow rate	Exchangeable $\text{NH}_4+\text{NO}_2+\text{NO}_3$	Hydrolyzable	Non available**	Available***	Total
	$\text{m}^3/\text{sec}$			$\text{mg N/g}^+$		
<u>GENESEE</u>						
I	5.2	0.92	--	--	--	--
III	97	0.74	1.92	--	2.42	--
IV	206	0.03 (2)	1.18 (87)	0.16 (12)	1.19 (88)	1.35
V	239	0.15 (8)	0.82 (46)	0.88 (49)	0.92 (51)	1.80
VI <sup>++</sup>	6.2	--	4.43 (73)	--	--	6.04
VII	7.1	--	7.72 (55)	--	--	14.09
VIII	23	0.46 (15)	0.75 (24)	2.02 (64)	1.14 (36)	3.16
IX	27	0.61 (10)	2.38 (37)	3.38 (53)	2.98 (47)	6.36
X	101	0.08 (3)	2.05 (78)	0.52 (20)	2.12 (80)	2.64
XI	49	0.36 (8)	2.91 (63)	1.40 (30)	3.22 (70)	4.62
XII	2.4	0.91 (7)	10.52 (81)	1.67 (13)	11.36 (87)	13.03
XIV	164	0.05 (3)	1.41 (76)	0.41 (22)	1.44 (78)	1.85
XV	153	0.04 (3)	0.93 (80)	0.20 (17)	0.96 (83)	1.16
XVI	283	0.17 (9)	1.43 (73)	0.37 (19)	1.58 (81)	1.95
XVII	74	0.03 (2)	1.10 (80)	0.26 (19)	1.11 (81)	1.37
Composite	96	0.49 (8)	2.70 (62)	1.02 (29)	2.54 (71)	4.45
<u>MENOMONEE</u>						
I	13.7	0.21	--	--	--	--
II	11.3	0.84 (16)	3.50 (65)	1.78 (33)	3.61 (67)	5.39
III	15.1	0.68 (17)	1.80 (46)	1.70 (43)	2.22 (57)	3.92
IV	3.7	0.62 (14)	2.26 (52)	1.60 (37)	2.74 (63)	4.34
XI <sup>++</sup>	2.1	4.71 (48)	1.74 (18)	3.84 (39)	6.00 (61)	9.84
VII	9.9	0.36 (7)	3.25 (67)	1.35 (28)	3.50 (72)	4.85
VIII	5.7	0.89 (14)	3.48 (54)	2.24 (35)	4.17 (65)	6.41
IX	8.6	1.66 (19)	4.26 (49)	3.05 (35)	5.69 (65)	8.74
X	13.4	1.10 (19)	3.20 (54)	2.32 (39)	3.60 (61)	5.92
Composite	8.6	0.80 (16)	3.11 (55)	2.01 (35)	3.65 (65)	5.65
<u>MAUMEE</u>						
I	931	0.31	--	--	--	--
II	116	2.19	1.70 (84) <sup>+++</sup>	0.15 (7) <sup>+++</sup>	1.88 (93) <sup>+++</sup>	4.62 <sup>++</sup>
III	120	1.88 (29)	2.87 (44)	1.78 (27)	4.71 (73)	6.49
IV	2572	0.29 (5)	3.38 (58)	2.15 (37)	3.65 (63)	5.80
Composite	389	1.17 (21)	3.13 (55)	1.97 (35)	4.10 (73)	5.64
<u>GRAND</u>						
I <sup>++</sup>	41	3.73 (22)	9.69 (57)	6.15 (36)	10.76 (64)	16.91
II <sup>++</sup>	28	3.89 (21)	8.19 (45)	6.75 (37)	11.48 (63)	18.23
III	391	1.22 (7)	3.51 (49)	2.49 (35)	4.70 (65)	7.19
IV	359	1.94 (21)	4.60 (51)	2.62 (29)	6.45 (71)	9.07
V	161	0.65 (6)	7.70 (70)	3.03 (27)	8.01 (73)	11.04
Composite	221	2.29 (18)	6.74 (54)	4.21 (34)	8.28 (66)	12.49
<u>NEMADJI</u>						
I	--	0.49	--	--	--	--
II	43	0.29 (12)	1.04 (44)	1.20 (50)	1.18 (50)	2.38
III	--	0.20 (10)	0.95 (49)	0.86 (44)	1.09 (56)	1.95
IV	40	0.21 (11)	0.78 (40)	1.01 (52)	0.92 (48)	1.93
V <sup>++</sup>	34	1.18 (24)	1.71 (34)	2.31 (46)	2.69 (54)	5.00
VI <sup>++</sup>	--	--	5.61 (42)	--	--	13.31
VII	--	0.09 (6)	0.89 (59)	0.57 (38)	0.94 (62)	1.51
VIII	106	0.62 (20)	1.77 (58)	0.91 (30)	2.14 (70)	3.05
IX	64	0.26 (7)	2.10 (53)	1.72 (43)	2.24 (53)	4.22
X	124	0.10 (11)	0.33 (37)	0.47 (53)	0.41 (47)	0.88
XI	45	0.35 (7)	2.11 (44)	2.35 (49)	2.40 (51)	4.75
Composite	65	0.29 (10)	1.25 (49)	1.14 (45)	2.00 (52)	3.90

\*Includes (ammonium + amino acid + hexosamine)-N.

\*\*Includes (non hydrolyzable + unidentifiable hydrolyzable)-N.

\*\*\*Includes hydrolyzable-N and  $(\text{NO}_2+\text{NO}_3)_4$ .

+Values in parentheses are percentage of total-N.

++0.2-20  $\mu$ m size fraction.

+++2-20  $\mu$ m size fraction.



which, in turn, was related to the granulometric configuration (see Appendix Table I-A-2 and Tables III-1 and III-3). Apparently, as the river flow rate decreased, the proportion of fine particulates increased and there was an increase in the proportion of fine (nitrogen rich) particulates as well as an increase in the nitrogen concentration in all particulate fractions. Therefore, the flow rate had a qualitative influence on inorganic-N loading. Probably the dynamics of the inorganic-N loading are influenced strongly by the high proportion (50%) of tile drained agricultural land (40).

The distribution of the nitrogen species was similar to that of the Grand sediments (Table III-2). The proportions of the total-N occurring as (AN + AAN + HN), and inorganic-N were 55 and 21%, respectively. The less available nitrogen (NHN and UHN) accounted for 28% of the total N.

The similarities in the distribution of the N species between the Grand and Maumee sediments is of interest since the nature, amount and particle size distribution of the sediments was so dissimilar. In the Maumee, the highest N concentration was found in the sand fraction in the form of (AN + AAN + HN) (Table III-A-1). Conversely, the clay fraction contained the lowest concentration of total-N and (AN + AAN + HN). However, the proportion and concentration of inorganic-N in this fraction were higher than in either the silt or sand fractions. The concentration of sand-associated N was largely a function of the concentration of AAN and HN, whereas the clay-associated N was influenced more strongly by the concentration of inorganic-N.

Changes were observed in the concentrations of dissolved and particulate inorganic-N in relation to varying flow rates (see Appendix Table I-A-2 and Table III-3). During high flow periods, the particulate and dissolved inorganic-N concentrations decreased; increased concentrations were observed during low discharge periods. Thus, the possibility of an equilibrium relationship between dissolved and particulate inorganic-N exists. The high and low N concentrations may result from the selective erosion and transport of particulates during different runoff events or possibly from the dilution-concentration effect of different river discharge volumes.

#### Menomonee River

The Menomonee River sediments contained moderately high concentrations of inorganic-N (AN + AAN + HN) and total-N (Table III-1). The respective mean concentrations of 0.8, 3.1 and 5.7 mg/g were similar to values for the Maumee River sediments. Little variability was observed in the concentrations between composite samples and values are similar to those reported for the Menomonee River (41).

The dissolved inorganic-N concentration was relatively uniform for all events, averaging 2.2 mg N/L (Table III-2); the form was primarily ( $\text{NO}_2 + \text{NO}_3$ )-N.

The distribution of the various N species was similar between samples (Table III-3). One exception was a spring snowmelt event (Sample VI) which contained a high proportion of N in the inorganic-N fraction and a low amount of (AN + AAN + HN). This resulted from an increased proportion of inorganic-

N-rich silt and clay during a low flow event which contained high amounts of organic matter. The proportion of the mean total particulate N in the composite samples occurring as inorganic-N and (AN + AAN + HN) was 16 and 55%, respectively (Table III-2). This is similar to the distribution in the Grand and Maumee sediments.

Approximately 50% of the total-N was contained in the clay fraction (Table III-1). The remaining N was distributed equally between silt and sand fractions. The increased amount of N in the clay fraction resulted in part from the high concentrations of inorganic-N and (UHN + NHN) in this fraction. The (AN + AAN + HN) tended to be distributed equally between the size separates.

There was a slight seasonal trend in the concentration and distribution of N (Tables III-3 and Appendix I-A-1). During the summer months (Samples II, III and IV) the concentrations of all forms of N were reduced equally. This resulted from a decrease in the N concentration in the clay fraction and/or decrease in the proportion of N-rich clay (Appendix III-A-1 and I-A-2). The reduced amount of N may be more a reflection of the distribution and nature of the particulates during different runoff events than a seasonal trend. The Menomonee particulates contained both variable and high amounts of organic matter which affected the particle size-distribution and concentrations of N.

#### Nemadji River

The Nemadji River generally contained low amounts of particulate-associated N; however, higher N concentrations were observed during the late fall and winter months when the amount of sand was low and the organic matter content was higher (Samples V and VI; Table III-3; Appendix I-A-2). During the spring snowmelt the proportion of (AN + AAN + HN) increased.

The mean concentrations of inorganic-N (AN + AAN + HN) and total-N in the composite sediments were 0.4, 1.7 and 3.9 mg N/g (Table III-1). These are similar to concentrations reported for Genesee sediments. Much lower total Kjeldahl N concentrations (<0.05%) were reported for suspended and bottom sediment (<0.05%) from the Nemadji River and bottom sediment from the Lake Superior entry (42).

The average dissolved-N concentration was 1 mg N/L (Table III-2). About 60% of the dissolved inorganic-N was present as (NO<sub>3</sub> + NO<sub>2</sub>)-N. The dissolved (NO<sub>3</sub> + NO<sub>2</sub>)-N concentration in Nemadji tributaries was reported to be 10 to 60% of that present in the Nemadji River (43).

The relative proportion of the various nitrogen forms between samples was similar, except for an increase in the (AAN + HN) during the spring snowmelt events (Samples VII, VIII, and IX, Table III-3). The mean inorganic-N and (AN + AAN + HN) concentrations were 10 and 49% of the total-N (Table III-2). These values are somewhat low in comparison to other river sediments. During snowmelt events, (AN + AAN + HN) increased to 57% (Table III-3) of the total-N as a result of decreases in the amounts of (UHN + NHN) and inorganic-N. This coincided with the observation of brown patches of scum on the water surface. During the winter a greater portion of total-N was distributed in

the inorganic-N fraction. Most of the inorganic-N was in the form of  $\text{NO}_3\text{-N}$ , probably indicating diffuse source inputs. The high amounts of total-N during this period resulted from the increased organic matter content of the sediment. This organic matter may have originated from bedload in view of the reduced possibility of erosion of organic debris from frozen soils.

The highest concentration of all N forms occurred in the clay fraction (Table III-1). The concentration of total-N was 1.4 times greater in the clay than in the composite sediment. This was due to a higher concentration of inorganic-N and (UHN + NHN) in the clay. Conversely, the sand contained the lowest amount of total-N due to lower concentrations of (UHN + NHN). The silt fraction contained low amounts of inorganic-N and moderate amounts of organic-N. During winter, the particle size distribution changed substantially due to lower discharge rates (Appendix I-A-2). This resulted in an increased proportion of N-rich fine particulates (Appendix III-A-1). However, the flow rates and suspended sediment concentrations during the winter were so low that the amounts of N entering Lake Superior were reduced.

#### Factors Controlling Particulate Available N Concentrations in Tributary Waters

The concentrations of particulate available-N in the tributaries to the Great Lakes are influenced by 1. tributary discharge, 2. sediment delivery ratio, 3. sediment particle size distribution and 4. the available-N concentration and distribution among sediment particle size fractions.

Considerable variation exists in the importance of these factors for the different tributaries. This section is concerned with the importance of these factors in controlling the particulate available N concentrations (amount/unit volume) in the different tributaries.

In the Genesee, Menomonee and Nemadji Rivers (event response tributaries), the sediment delivery ratio increases sharply with flow. The total suspended solids (TSS) versus discharge slope values (Table I-2) clearly indicate this trend. The Maumee River is also an event response tributary, but the slope value is much lower because the Maumee Watershed is large and a runoff event occurring in one portion of the Watershed may be moderated elsewhere by baseflow.

Generally, the sediment load for the Genesee, Menomonee, and Nemadji Rivers consists mostly of suspended sediment rather than bedload from channel erosion. In addition, the particle size distribution and the concentration of available-N in the suspended sediment depends more on intensity and location of rainfall in the watershed, cover conditions or other factors, than on tributary discharge rate. These factors are particularly apparent in the Nemadji River. For example, during high flow periods (i.e., spring snowmelt, intense runoff events), the available nitrogen concentration in sediment was low, but because of the very high sediment concentration the particulate available-N concentration in the water was quite high. Conversely, during low discharge periods (i.e., winter, summer), the concentration (mg/g) of particulate available-N increased. However, the available-N concentration was reduced because the suspended sediment concentration was low. The fluctuating

concentrations of suspended sediment (mg/L) and available-N (mg/g) during high and low discharges, were moderating influences on the variability in particulate available-N concentrations. As a result, the particulate available-N concentrations tended to be related to discharge rate.

Variations in the particulate available-N concentration in the Menomonee River were related closely to suspended sediment load. In turn, the sediment load was related closely to discharge rate (Table I-2). Therefore, these two factors largely controlled the annual available-N load from the Menomonee River--due to the uniform concentration (mg N/g) of available-N during moderate to high discharges. The concentration was more variable during low discharge events as a result of increased amounts of organic matter. However, this was insignificant because these events accounted for a very small portion of the annual available-N loading.

The proportional relationship between sediment concentration and available-N concentration may be due in part to the homogeneous nature of the suspended sediment. The particulates contained a high portion of organic matter which may act as an aggregating agent. It is possible that the fractionation scheme did not disperse the sediments completely, and the intrinsic nature of the particulates may not be reflected in the three size fractions obtained (Part I). As a result, the available N distribution among the size fractions was relatively uniform.

The particulate available-N concentration in the Genesee River was variable and controlled by several factors, the most important being the sediment size-distribution and concentration. Discharge rate was not an important factor in determining the amount of available-N in the water column because of the rather poor relationship between TSS and discharge (Table I-2). Also, the high mean concentration of available-N in the clay, though several times greater than in the silt and sand (Table III-1), was too variable to be an indicator of amount of available-N in the water (Appendix III-A-1). However, the amount of available N (mg/L) was significantly higher during runoff events with high suspended sediment concentrations (Samples V, XIV, XV, Table III-3). These events occurred generally during moderate to high discharge periods. Concentrations of clay, silt and total sediment were the controlling factors during periods of reduced available-N concentrations. Generally, the concentration of available-N in the sediment had a minor effect on particulate available-N concentration in the water. Lower concentrations of available-N resulted from reduced TSS and more specifically from reduction in the amount of silt and clay. Though the available-N concentration in the sediment (mg/g) varied considerably during these events (Samples III and XVII), the actual amount of particulate available-N in the water was controlled by the amount of suspended sediment.

Particulate available-N concentration in the Maumee River--like that of Nemadji River--was primarily influenced by flow rate. Sediment concentration was not proportional to flow rate especially at high flow rates. This is indicated by the low value for TSS against discharge relationship (Table I-2). Also, the sediment size-distribution was quite stable (Table I-3) and the concentration (mg/L) of particulate available-N was controlled almost exclusively by silt and clay particulates which comprised some 86% of the sediment. The sand fraction had little influence on available-N loadings, even though it contained the highest available-N concentration (mg/g).

Particulate available-N concentrations in the Grand River were relatively constant. This was due to the degree of uniformity of available-N distribution among clay, silt, and sand fractions, and the low variability in suspended concentrations.

#### Annual Loadings of Available-Nitrogen

The available-N from diffuse sources represented 66 to 96% of the total-N entering the Great Lakes from the tributaries (Table III-4). Most of this occurred in the form of dissolved-N, although the relative distribution between tributaries was quite variable (55 to 91%). The impact of the dissolved N was most apparent in the Maumee Watershed. A very high proportion (91%) of the annual available N load occurred as dissolved N, probably as a result of the extensive agricultural tile drainage systems in the Maumee Watershed. In contrast, the Nemadji River had the lowest proportion of dissolved N (55%), probably reflecting the heavily forested character of the watershed. The dissolved available-N fraction also was relatively significant in the Grand and Genesee Rivers, but for different reasons. In the Genesee River, this reflected the low available-N concentration (1.62 mg/g) in the suspended sediment. In the Grand River, the low suspended sediment concentration effectively reduced the relative significance of the particulate available-N loading.

The relative loadings of particulate available-N from the different tributaries were strongly influenced by wide differences in suspended sediment concentration and tributary discharge rates. For example, the Maumee and Menomonee Rivers both contained similar moderate concentrations of particulate available-N. However, the annual particulate available-N load varied by a factor of 100 (Maumee, 4,000 MT/yr; Menomonee, 39 MT/yr) because the discharge from the Maumee River is 50 times greater than that of the Menomonee River. Likewise, relatively low loadings of particulate available-N occurred from the Nemadji River because discharge was very low, even though the suspended sediment concentration was higher than that in the other rivers. The Grand River particulate available-N concentration (mg/L) was low, but because of high discharge, the annual available-N loading was moderately high.

The major factor controlling annual particulate available-N loading was the tributary discharge. The Menomonee and Nemadji Rivers had low discharge rates and consequently the annual particulate available-N loading was very low. Conversely, high annual loads occurred in the Genesee, Grand and Maumee Rivers which had high discharge rates.

Table III-4. Comparison of dissolved and particulate available N loadings

Discharge***	Suspended Sediment***	Available Particulate N*			Available N from diffuse sources**			
		Concentration	Total particulate N		Annual Loading	Distribution		
m <sup>3</sup> /sec	mg/L	mg/L	mg/g	%	Tonnes	%†	Dissolved Particulate	
							—	—
<u>GENESEE††</u>								
78	259	0.42	1.62	67	3,836	82	69	31
<u>MENOMONEE</u>								
2.7	138	0.50	3.65	65	177	90	78	22
<u>MAUMEE</u>								
141	283	1.16	4.10	73	44,175	96	91	9
<u>GRAND</u>								
114	19	0.16	8.28	66	6,468	81	66	34
<u>NEMADJI</u>								
11	312	0.62	2.00	52	222	66	55	45

\*Includes particulate NO<sub>2</sub>+ NO<sub>3</sub>+NH<sub>4</sub>+ AAN + HN measured in this investigation. Concentration (Vol) was calculated from the observed nitrogen concentration (wt) in the sediment and the mean historical suspended sediment concentration.

\*\*Genesee, Grand and Maumee values are calculated from the dissolved and particulate diffuse N loadings for 1975, reported by Sonzogni et al. (44) and the mean available N distribution (available N as % of the total particulate N) found for each tributary in this investigation (see column 6). Menomonee and Nemadji values based on unit area loadings (44). The amount of dissolved organic N is considered relatively insignificant.

\*\*\*Mean historical values from Sonzogni et al. (44), except Menomonee River values which are from Bannerman et al. (41).

†Expressed as a % of the diffuse total N

††Avon station only

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# APPENDIX III-A. NITROGEN DISTRIBUTION IN SUSPENDED SEDIMENTS

Table III-A-1. Nitrogen distribution in size fractionated suspended sediments of samples from selected rivers in the Great Lakes Basin

Nitrogen distribution										Nitrogen distribution									
Sample No.	Sediment size fraction $\mu\text{m}$	Exchangeable $\text{NH}_4$ mg/g	mg/L	$\text{NO}_2 + \text{NO}_3$ mg/g	mg/L	Hydrolyzable* mg/g	mg/L	Total mg/g	$\mu\text{g/L}$	Sample No.	Sediment size fraction $\mu\text{m}$	Exchangeable $\text{NH}_4$ mg/g	mg/L	$\text{NO}_2 + \text{NO}_3$ mg/g	mg/L	Hydrolyzable* mg/g	mg/L	Total mg/g	$\mu\text{g/L}$
GENESEE RIVER										GENESEE (CONTINUED)									
I	diss	--	0	0.49	--	--	--	--	--	XV	diss	--	0.14	--	1.26	--	--	--	--
	0.2-2	0.51	<0.01	2.73	0.02	--	--	--	--		0.2-2	0	0	0.12	0.02	1.38	0.21	1.65	0.23
	2-20	0.14	<0.01	0.40	0.01	--	--	--	--		2-20	0.01	<0.01	0.02	0.01	1.37	0.29	1.32	0.36
	>20	0.16	<0.01	0.31	<0.01	--	--	--	--		>20	<0.01	<0.01	0	0	0.50	0.11	0.66	0.15
	>0.2	0.20	0.01	0.72	0.03	--	--	--	--		>0.2	<0.01	<0.01	0.03	0.02	0.93	0.61	1.16	0.76
III	diss	--	0.32	0.88	--	0.52	--	--	--	XVI	diss	--	0.07	--	1.05	--	--	--	--
	0.2-2	1.01	0.01	2.65	0.02	5.64	0.05	--	--		0.2-2	0	0	0.15	0.01	3.12	0.24	3.28	0.25
	2-20	0.11	<0.01	0.09	<0.01	1.47	0.04	--	--		2-20	0.04	<0.01	0.13	0.01	1.08	0.09	1.62	0.13
	>20	0.11	<0.01	0.22	0.01	1.07	0.02	--	--		>20	0.01	<0.01	0.17	0.02	0.44	0.05	1.22	0.13
	>0.2	0.24	0.01	0.50	0.03	1.92	0.11	--	--		>0.2	0.02	<0.01	0.15	0.04	1.43	0.38	1.95	0.51
IV	diss	--	1.12	1.40	--	--	--	--	--	XVII	diss	--	0.14	--	0.98	--	--	--	--
	0.2-2	0.02	<0.01	0.01	<0.01	0.16	0.24	1.25	0.27		0.2-2	0.01	<0.01	0.01	<0.01	1.93	0.67	2.22	0.77
	2-20	0.05	0.01	0.01	<0.01	0.71	0.11	1.02	0.16		2-20	0.06	0.01	0	0	0.95	0.13	1.40	0.18
	>20	0.02	0.01	0.01	<0.01	1.39	0.50	1.56	0.55		>20	<0.01	<0.01	<0.01	<0.01	3.46	0.19	0.66	0.27
	>0.2	0.02	0.02	0.01	0.01	1.18	0.86	1.35	0.98		>0.2	0.02	0.01	0.01	<0.01	1.10	0.99	1.37	1.22
V	diss	--	0.07	0.49	--	--	--	--	--	MENOMONEE RIVER									
	0.2-2	0.11	0.02	0.22	0.04	1.55	0.28	2.19	0.40	I	diss	--	0.14	--	2.66	--	--	--	--
	2-20	0.02	<0.01	0.07	0.01	0.76	0.13	1.43	0.25		0.2-2	0.17	0.01	0.51	0.02	--	--	--	--
	>20	0.02	0.01	0.03	0.01	0.27	0.06	1.79	0.40		2-20	0.06	0.01	0.13	0.02	--	--	--	--
	>0.2	0.05	0.03	0.10	0.06	0.82	0.47	1.80	1.04		>20	0.04	0.01	0.11	0.03	--	--	--	--
VI	diss	--	0.14	1.40	--	--	--	--	--		>0.2	0.06	0.03	0.15	0.07	--	--	--	--
	0.2-2	0.45	<0.01	3.59	0.02	10.84	0.05	14.43	0.07	II	diss	--	0.39	--	1.05	--	--	--	--
	2-20	--	--	--	--	2.29	0.02	3.30	0.03		0.2-2	8.31	0.14	0.58	0.01	15.16	0.26	33.25	0.57
	0.2-20	--	--	--	--	4.43	0.07	6.04	0.10		2-20	0.31	0.03	0.08	0.01	2.80	0.26	4.41	0.41
VII	diss	--	0.28	1.96	--	--	--	--	--		>20	0.27	0.05	0.08	0.02	2.81	0.55	4.46	0.68
	0.2-2	1.80	0.01	3.57	0.02	11.20	0.06	14.77	0.08		>0.2	0.73	0.22	0.11	0.03	3.50	1.07	5.39	1.63
	2-20	--	--	--	--	7.18	0.02	10.05	0.03	III	diss	--	0.27	--	0.88	--	--	--	--
	>20	--	--	--	--	1.12	<0.01	16.93	0.05		0.2-2	0.40	0.04	1.04	0.10	2.11	0.20	6.84	0.66
	>0.2	--	--	--	--	7.72	0.08	14.09	0.16		2-20	0.13	0.02	0.12	0.02	1.52	0.24	2.33	0.36
VIII	diss	--	0.35	1.40	--	--	--	--	--		>20	0.37	0.02	0.20	0.01	2.03	0.12	3.62	0.21
	0.2-2	0.50	0.01	2.06	0.04	0	0	16.54	0.29		>0.2	0.26	0.08	0.42	0.13	1.80	0.56	3.92	1.23
	2-20	0.02	<0.01	0.16	0.01	0.96	0.07	1.78	0.12	IV	diss	--	0.63	--	1.40	--	--	--	--
	>20	0	0	0.11	<0.01	0.73	0.03	1.16	0.05		0.2-2	1.00	0.01	3.09	0.02	1.60	0.01	5.09	0.03
	>0.2	0.07	0.01	0.39	0.05	0.75	0.10	3.16	0.46		2-20	0.10	<0.01	0.63	0.01	1.69	0.03	3.23	0.05
IX	diss	--	0.07	1.40	--	--	--	--	--		>20	0.04	<0.01	0.08	<0.01	2.54	0.10	4.65	0.19
	0.2-2	0	0	1.15	0.02	16.88	0.27	28.76	0.46		>0.2	0.14	0.01	0.48	0.03	2.26	0.14	4.34	0.26
	2-20	0	0	0.56	0.04	0.15	0.01	1.10	0.08	V	diss	--	0.70	--	2.24	--	--	--	--
	>20	0.06	<0.01	0.28	0.01	5.10	0.11	7.31	0.15		0.2-2	0.24	<0.01	4.26	0.03	0.64	<0.01	8.77	0.06
	>0.2	0.01	0.07	0.60	0.07	2.38	0.39	6.36	0.69		2-20	1.29	<0.01	4.25	<0.01	6.74	0.01	14.62	0.16
X	diss	--	0.07	0.98	--	--	--	--	--		>20	0.45	0.01	4.26	0.03	1.74	0.01	9.84	0.22
	0.2-2	0.03	0.02	0.23	0.16	5.22	3.50	6.75	4.53	VI	diss	--	2.03	--	0.91	--	--	--	--
	2-20	0	0	0.03	0.04	1.07	1.33	1.48	1.82		0.2-2	0.24	<0.01	4.26	0.03	0.64	<0.01	8.77	0.06
	>20	0	0	0.01	0.01	1.19	1.26	1.40	1.48		2-20	1.29	<0.01	4.25	<0.01	6.74	0.01	14.62	0.16
	>0.2	0.01	0.02	0.07	0.21	2.05	6.09	2.64	7.83		>20	0.45	0.01	4.26	0.03	1.74	0.01	9.84	0.22
XI	diss	--	0.07	--	1.12	--	--	--	--	VII	diss	--	0.35	--	1.26	--	--	--	--
	0.2-2	0	0	0.05	0.01	4.79	0.61	7.30	0.94		0.2-2	0.64	0.01	1.79	0.02	5.09	0.04	10.95	0.10
	2-20	0	0	0.85	0.10	1.56	0.19	3.55	0.42		2-20	0.05	<0.01	0.07	<0.01	3.20	0.11	4.24	0.14
	>20	0.04	0.01	0.15	0.02	2.34	0.34	3.18	0.46		>20	0.05	<0.01	0.07	<0.01	2.88	0.10	3.99	0.14
	>0.2	0.02	0.01	0.33	0.13	2.91	1.14	4.62	2.16		>0.2	0.11	0.01	0.25	0.03	3.25	0.25	4.85	0.38
XII	diss	--	0.21	0.12	--	--	--	--	--	VIII	diss	--	0.28	--	2.52	--	--	--	--
	0.2-2	0	0	3.43	0.03	53.51	0.49	62.22	0.60		0.2-2	0.67	<0.01	0.35	0.02	5.23	0.02	9.24	0.06
	2-20	0.08	<0.01	0.49	0.02	6.88	0.30	7.20	0.34		2-20	0.13	<0.01	0.10	<0.01	2.38	0.02	3.83	0.04
	>20	0.09	<0.01	0.61	0.02	4.13	0.15	5.70	0.23		>20	0.08	0.01	0.18	<0.01	3.49	0.05	5.97	0.08
	>0.2	0.07	0.01	0.84	0.07	10.52	0.94	13.03	1.17		>0.2	0.20	0.01	0.69	0.02	3.43	0.09	6.41	0.18
XIV	diss	--	0	0.91	--	--	--	--	--	IX	diss	--	0	--	2.10	--	--	--	--
	0.2-2	0	0	0.09	0.01	2.79	0.35	3.90	0.50		0.2-2	0.39	<0.01	2.17	0.03	5.60	0.07	10.97	0.14
	>20	0.02	<0.01	0.03	0.01	0.43	0.06	0.63	0.08		2-20	0.14	<0.01	1.09	0.01	3.81	0.04	7.50	0.08
	>0.2	0.02	<0.01	0.03	0.01	1.41	0.67	1.85	0.88		>20	0.07	<0.01	0.50	<0.01	3.97	0.02	6.82	0.32
											>0.2	0.23	0.01	1.43	0.04	4.26	0.13	8.74	0.25
										X	diss	--	0.14	--	1.89	--	--	--	--
											0.2-2	1.23	0.03	0.84	0.02	3.04	0.07	6.93	0.16
											2-20	0.46	0.02	0.11	<0.01	3.16	0.12	5.64	0.21
											>20	0.57	0.02	0.41	0.01	3.32	0.09	5.30	0.14
											>0.2	0.70	0.07	0.40	0.03	2.20	0.28	5.86	0.51

Table III-A-1 (continued)

Sample No.	Sediment size fraction $\mu\text{m}$	Nitrogen distribution						Sample No.	Sediment size fraction $\mu\text{m}$	Nitrogen distribution								
		Exchangeable $\text{NH}_4$ mg/g	mg/L	$\text{NO}_2 + \text{NO}_3$ mg/g	mg/L	Hydrolyzable* mg/g	mg/L			Total mg/g	mg/L	Exchangeable $\text{NH}_4$ mg/g	mg/L	$\text{NO}_2 + \text{NO}_3$ mg/g	mg/L	Hydrolyzable* mg/g	mg/L	Total mg/g
MAUMEE RIVER																		
I	diss	--	0	--	0.82	--	--	--	I	diss	--	0.18	--	0.21	--	--	--	--
	0.2-2	0.09	0.01	0.50	0.05	--	--	--		0.2-2	0.04	<0.01	0.61	0.02	--	--	--	
	2-20	0.05	0.01	0.05	0.01	--	--	--		2-20	0.16	0.01	0.29	0.02	--	--	--	
	>20	0.04	<0.01	0.19	0.01	--	--	--		>20	0.05	<0.01	0.19	<0.01	--	--	--	
	>0.2	0.07	0.02	0.24	0.06	--	--	--		>0.2	0.11	0.01	0.38	0.04	--	--	--	
II	diss	--	0.35	--	6.06	--	--	--	II	diss	--	0.21	--	0.32	--	--	--	
	0.2-2	1.13	0.07	2.66	0.17	--	--	7.10		0.2-2	0.43	0.06	0.43	0.06	1.43	0.18	5.45	
	2-20	0.08	<0.01	0.16	0.01	1.70	0.09	2.03		2-20	0.04	0.01	0.02	0.01	0.68	0.23	1.14	
	>20	2.83	0.01	1.49	<0.01	--	--	--		>20	0.16	0.02	0.16	0.02	1.73	0.18	2.66	
	>0.2	0.69	0.08	1.50	0.18	--	--	--		>0.2	0.15	0.09	0.14	0.08	1.34	0.59	2.38	
III	diss	--	0.21	--	8.82	--	--	--	III	diss	--	0.77	--	0.61	--	--	--	
	0.2-2	0	0	2.70	0.09	1.38	0.05	5.45		0.2-2	0.09	<0.01	0.15	0.01	1.17	0.05	2.25	
	2-20	0.07	<0.01	0.87	0.02	3.81	0.09	6.75		2-20	0.03	<0.01	0.14	0.01	0.71	0.03	1.74	
	>20	0.14	<0.01	1.12	0.01	4.58	0.04	7.31		>20	0.04	<0.01	0.12	<0.01	1.18	0.01	1.60	
	>0.2	0.04	<0.01	1.84	0.12	2.87	0.18	6.49		>0.2	0.06	0.01	0.14	0.01	0.95	0.09	1.95	
IV	diss	--	0.07	--	3.92	--	--	--	IV	diss	--	0.98	--	1.33	--	--	--	
	0.2-2	0.03	<0.01	0.60	0.05	2.70	0.20	5.16		0.2-2	0.22	0.01	0.11	<0.01	0.87	0.02	2.42	
	2-20	0.02	<0.01	0.12	0.01	3.30	0.37	5.29		2-20	0.02	<0.01	0.17	0.01	0.74	0.04	1.28	
	>20	0.03	<0.01	0.16	0.01	4.40	0.28	7.51		>20	0.02	<0.01	0.07	<0.01	0.75	0.01	2.90	
	>0.2	0.02	0.01	0.27	0.07	3.38	0.85	5.80		>0.2	0.07	0.01	0.14	0.01	0.78	0.07	1.93	
GRAND RIVER																		
I	diss	--	0.53	--	0.21	--	0	--	V	diss	--	0.28	--	0.35	--	--	--	
	0.2-2	13.45	0.07	2.92	0.02	21.84	0.12	30.22		0.2-2	0.47	0.01	1.52	0.02	2.27	0.03	9.09	
	2-20	0.32	<0.01	0.76	0.01	5.76	0.06	18.41		2-20	0.02	<0.01	0.65	0.01	1.33	0.03	3.94	
	>20	0.32	0.01	0.51	0.01	6.60	0.12	12.66		0.2-20	0.20	0.01	0.98	0.03	1.71	0.06	5.00	
	>0.2	2.66	0.06	1.07	0.04	9.69	0.29	16.91		VI	diss	--	0.07	--	0.42	--	--	
II	diss	--	0.56	--	0.42	--	--	--		0.2-2	0	0	2.76	0.01	6.00	0.02	12.76	
	0.2-2	1.73	0.01	9.09	0.04	7.34	0.03	33.68		2-20	--	--	--	--	4.38	0.01	14.21	
	2-20	0.16	<0.01	1.26	0.02	8.56	0.11	13.03		0.2-20	--	--	--	--	5.61	0.03	13.31	
	>20	1.13	<0.01	3.04	<0.01	--	--	--	VII	diss	--	0.07	--	0.49	--	--	--	
	>0.2	0.61	0.01	3.26	0.06	--	--	--		0.2-2	0.03	0.01	0.15	0.02	1.14	0.17	1.99	
	<20	0.60	0.01	3.29	0.06	8.19	0.14	18.23		2-20	0.05	0.01	0	<0.01	0.87	0.25	1.40	
III	diss	--	0.35	--	3.36	--	--	--		>20	0.03	0.01	0.04	<0.01	0.56	0.09	1.24	
	0.2-2	0	0	5.49	0.04	1.14	0.01	10.06		>0.2	0.04	0.02	0.05	0.03	0.89	0.51	1.51	
	2-20	0	0	0.32	0.01	3.20	0.05	6.22		VIII	diss	--	0.14	--	0.70	--	--	
	>20	0.03	0.01	0.26	<0.01	4.70	0.08	6.86		0.2-2	0.08	<0.01	0.43	0.02	1.87	0.07	2.49	
	>0.2	0.03	0.01	1.19	0.05	3.51	0.13	7.19		2-20	0.14	0.01	0.03	<0.01	1.79	0.10	3.00	
IV	diss	--	0.07	--	3.22	--	--	--		>20	0.86	0.02	1.30	0.03	1.78	0.04	2.55	
	0.2-2	0	0	4.77	0.04	2.40	0.02	9.34		>0.2	0.25	0.03	0.37	0.05	1.77	0.21	3.05	
	2-20	0.07	<0.01	1.55	0.03	5.10	0.10	9.34		IX	diss	--	0.21	--	0.63	--	--	
	>20	0.03	<0.01	9.85	0.02	4.81	0.11	8.69		0.2-2	0.30	0.01	0.33	0.01	3.43	0.13	7.20	
	>0.2	0.09	<0.01	1.85	0.09	4.60	0.23	9.07		2-20	0.05	<0.01	0.03	<0.01	1.34	0.11	2.75	
V	diss	--	0	--	1.96	--	--	--		>20	0.01	<0.01	0.21	<0.01	2.80	0.06	4.59	
	0.2-2	0.47	<0.01	0	0	1.00	0.01	2.94		>0.2	0.12	0.01	0.14	0.01	2.10	0.30	3.96	
	2-20	0.33	<0.01	0.22	<0.01	12.10	0.17	15.97		X	diss	--	0.28	--	0.63	--	--	
	>20	0.06	<0.01	1.16	0.01	--	--	--		0.2-2	0.01	<0.01	0.25	0.03	0.53	0.07	2.07	
	>0.2	0.34	0.01	0.31	0.01	7.70	0.18	11.04		2-20	0.02	<0.01	0.01	<0.01	0.31	0.08	0.54	
										>20	0.01	<0.01	0.05	0.01	0.20	0.03	0.40	
										>0.2	0.02	0.01	0.08	0.04	0.33	0.18	0.88	
										XI	diss	--	0.49	--	0.70	--	--	
	0.2-2	0.01	0.05	0.64	0.02	2.55	0.07	7.53		0.2-2	0.01	<0.01	0.10	<0.01	1.97	0.08	3.60	
	2-20	0.01	<0.01	0.20	<0.01	1.80	0.03	3.28		>20	0.01	<0.01	0.02	<0.01	1.80	0.03	3.28	
	>0.2	0.06	0.05	0.29	0.03	2.11	0.18	4.75		>0.2	0.06	0.05	0.29	0.03	2.11	0.18	4.75	

\*Hydrolyzable N = hydrolyzable  $[\text{NH}_4\text{-N} + \text{Amino Acid - N} + \text{Hexoseamine-N}]$

PART IV

AVAILABILITY OF THE TRACE METALS, COPPER, LEAD  
AND ZINC IN SUSPENDED AND BOTTOM SEDIMENTS

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## ABSTRACT

The availability of trace metals (Cu, Pb, and Zn) was measured in suspended and bottom sediments from five tributaries to the Great Lakes. Availability was estimated as the fraction extracted by a hydroxylamine hydrochloride reagent (HH-metal) or a chelating cation exchange resin (resin-metal). The amount of sediment remaining following analyses for phosphorus and nitrogen limited the number of samples available for trace metal analysis. Mean values of the available metal fraction (HH-metal) for the individual tributaries ranged from 25 to 45% of the sediment total metal. Exceptions were the Menomonee samples where mean values for the three metals ranged from 46 to 76% and Pb in the Genesee samples (mean = 60%). Differences in availability among the clay, silt, and sand size fractions were not significant. Resin-metal was less than HH-metal (mean values), with the exception of Pb in the Menomonee samples. However, the relative proportions of resin-metal and HH-metal varied among the different metals and tributaries.

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#### IV-1. INTRODUCTION

The availability of trace metals associated with suspended tributary sediments is of importance in determining whether trace metals will be transported to the bottom sediments through particle sedimentation or whether the trace metals will be released into the lake water and possibly accumulated by aquatic organisms. This investigation focused on Cu, Pb, and Zn. In addition to total metal concentrations, available metal concentrations were estimated using hydroxylamine hydrochloride extraction (HH-metal) and resin desorption (resin-metal) techniques. The hydroxylamine hydrochloride reagent solubilizes surface-bound metal associated with metal (e.g., Fe, Mn) hydrous oxides (1). The resin desorption method is comparable in principle to the method used for estimating available P involving equilibration with an anion exchange resin (see Part II). In the case of the trace metals, a metal chelating resin was used. By removing dissolved metals from solution, the resin will promote metal desorption from the sediment particles until an equilibrium is reached between the sediment and the metal concentration maintained in solution by the resin.

#### IV-2. CONCLUSIONS

Available metal concentrations in sediments generally represents an average of 25 to 45% of the total metal. Availability may be higher in sediments influenced by local sources of metals. For example, mean available metal (HH-metal) levels ranged from 46 to 76% of the total metal for Cu, Pb, and Zn in the Menomonee River samples. Other exceptions may also occur, such as Pb in the Genesee which averaged 60% of the sediment total Pb.

Differences in availability among the different particle size fractions may exist, but were not significant in the samples investigated. The resin-metal fraction generally represents a smaller fraction than the HH-metal of the total metal concentration. However, a consistent relationship between HH-metal and resin-metal was not found.

### IV-3. SAMPLING AND ANALYSIS

#### Collection of Samples

The suspended and bottom sediments collected for analysis of trace metal availability are described in Part I of this report.

#### Analysis for Trace Metals

Total metal (Cu, Pb, Zn) concentrations were measured by digestion with a HCl-HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> reagent (2 hr) at 70°C, followed by analysis by atomic absorption spectroscopy (2).

#### Analysis for Available Metals

Available metals were estimated by two chemical methods, a chelating cation exchange resin desorption technique (resin-metal) and by extraction with a hydroxylamine hydrochloride reagent (HH-metal).

##### Resin-metal

Cation exchange resin (Chelex 100, 50 to 100 mesh size) in the sodium acetate form was equilibrated at pH 7.0 for 18 hr with the sediment suspension. The resin was separated by sieving and eluted with 2*N* HNO<sub>3</sub> to remove adsorbed metals (3). The eluate was analyzed by atomic absorption spectroscopy (AAS).

##### HH-metal

The sediment was extracted with 1.0 *M* hydroxylamine hydrochloride in 25% acetic acid (1) and the extracted metals were analyzed by atomic absorption spectroscopy.

#### IV-4. RESULTS AND DISCUSSION

The concentrations of total metal, HH-metal, and resin-metal were measured on size-fractionated sediments (0.2 to 2, 2 to 20, and > 20  $\mu\text{m}$ ) obtained from the Genesee, Grand, Maumee, Menomonee and Nemadji Rivers which discharge to the Great Lakes. The metals investigated were Cu (Table IV-1), Pb (Table IV-2) and Zn (Table IV-3). Analysis of metal concentrations and distribution was limited to some extent by the number of samples available. Because priority was given to analysis of phosphorus and nitrogen in the suspended sediment samples collected, the amount remaining for trace metal analysis was frequently insufficient, especially where the suspended sediment concentrations were low. For the Grand and Maumee, only two samples were analyzed and, with a few exceptions, only total metal concentrations in the three particle size fractions were measured. However, the sample number/size fraction ranged from 6 to 8 for the Genesee, 4 to 6 for the Menomonee, and 3 to 5 for the Nemadji. A few bottom sediments and intact suspended sediment samples also were analyzed. Details of individual sample analyses are given in Appendix IV-A-1 and IV-A-2.

The expected tendency for higher total metal concentrations (mean values) in the fine (0.2 to 2  $\mu\text{m}$ ) particulate fraction was observed for Cu and Pb in the Genesee, Maumee, and Nemadji and for Zn in the Genesee and Maumee samples (Tables IV-1, IV-2, IV-3). However, as shown by the high coefficient of variation for the mean values ( $\sim$  20 to 80%), there were exceptions to this trend for individual samples. For the other sample groups (Cu, Pb and Zn in the Grand and Menomonee, and Zn in the Nemadji), mean total metal concentrations were either fairly uniform among the size fractions or highest in one of the larger size fractions.

The proportion of the total metal present as available metal (HH-metal or resin-metal) did not differ appreciably among the three particle size fractions (Tables IV-1, IV-2, IV-3). While some differences were noted in mean values, the differences were not considered significant in view of the relatively higher coefficients of variation and the small sample size.

The concentrations and distribution of total and available metals in intact suspended sediment samples were calculated by summing the individual size-fraction sediment-weighted metal concentrations (Table IV-4). The highest concentrations of Cu, Pb, and Zn occurred in the Menomonee sediments. This likely reflects the numerous sources of trace metals in the urbanized Menomonee Watershed. Intermediate concentrations were observed in the Grand and Maumee suspended sediments, while concentrations of all three metals were appreciably lower in the Genesee and the Nemadji than in the suspended sediments of the other three tributaries.

Table IV-1. Copper distribution in size-fractionated suspended sediments

Sediment size fraction	Cu			Coefficient of variation		
	Total	HH-Cu	Resin-Cu	Total	HH-Cu	Resin-Cu
	$\mu\text{g/g}$		%			
<u>GENESEE RIVER</u>						
0.2 to 2 $\mu\text{m}$	82	35	32	35(7)	46(6)*	60(4)
2 to 20 $\mu\text{m}$	61	36	28	41(8)	38(5)	106(4)
>20 $\mu\text{m}$	46	53	14	77(6)	61(4)	49(3)
>0.2 $\mu\text{m}$	64	49	14	29(2)	0(2)	16(2)
<u>MENOMONEE RIVER</u>						
0.2 to 2 $\mu\text{m}$	124	64	61	41(6)	14(4)	19(4)
2 to 20 $\mu\text{m}$	168	35	25	54(5)	42(4)	39(3)
>20 $\mu\text{m}$	144	42	28	57(4)	21(4)	64(3)
>0.2 $\mu\text{m}$	187	40	25	23(3)	3(2)	45(2)
<u>MAUMEE RIVER</u>						
0.2 to 2 $\mu\text{m}$	88	34	32	72(2)	42(2)	-(1)
2 to 20 $\mu\text{m}$	51	20	19	11(2)	-(1)	12(2)
>20 $\mu\text{m}$	49	--	--	-(1)	--	--
>0.2 $\mu\text{m}$	84	--	--	-(1)	--	--
<u>GRAND RIVER</u>						
0 to 2 $\mu\text{m}$	92	--	8	35(2)	--	-(1)
2 to 20 $\mu\text{m}$	87	--	--	41(2)	--	--
>20 $\mu\text{m}$	64	--	--	-(1)	--	--
>0.2 $\mu\text{m}$	64	--	--	-(1)	--	--
<u>NEMADJI RIVER</u>						
0.2 to 2 $\mu\text{m}$	57	29	22	35(5)	27(3)	35(4)
2 to 20 $\mu\text{m}$	39	23	10	37(4)	24(3)	50(2)
>20 $\mu\text{m}$	35	18	16	49(3)	0(2)	-(1)
>0.2 $\mu\text{m}$	50	22	13	3(2)	-(1)	-(1)

\*Number of samples analyzed.

Table IV-2. Lead distribution in size-fractionated suspended sediments

Sediment size fraction	Pb			Coefficient of variation		
	Total	HH-Pb	Resin-Pb	Total Pb	HH-Pb	Resin-Pb
	μg/g	%				
<u>GENESEE RIVER</u>						
0.2 to 2 μm	86	52	49	29(7)*	20(5)	(1)
2 to 20 μm	48	68	89	64(8)	32(3)	(1)
>20 μm	28	54	64	53(6)	38(3)	(1)
>0.2 μm	38	52	--	19(2)	2(3)	--
<u>MENOMONEE RIVER</u>						
0.2 to 2 μm	569	76	22	47(5)	11(4)	50(4)
2 to 20 μm	666	71	9	60(5)	26(4)	72(3)
>20 μm	643	81	18	64(4)	17(4)	44(3)
>0.2 μm	847	68	13	31(3)	12(2)	11(2)
<u>MAUMEE RIVER</u>						
0.2 to 2 μm	117	33	7	64(2)	66(2)	(1)
2 to 20 μm	81	40	--	26(2)	-(1)	--
>20 μm	87	--	--	-(1)	--	--
>0.2 μm	124	--	--	-(1)	--	--
<u>GRAND RIVER</u>						
0 to 2 μm	97	--	--	10(2)	--	--
2 to 20 μm	177	--	--	17(2)	--	--
>20 μm	117	--	--	(1)	--	--
>0.2 μm	126	--	--	(1)	--	--
<u>NEMADJI RIVER</u>						
0.2 to 2 μm	39	13	5	27(5)	11(2)	(1)
2 to 20 μm	28	30	--	40(4)	26(2)	--
>20 μm	33	29	3	71(3)	(1)	(1)
>0.2 μm	34	25	--	17(2)	(1)	--

\*Number of samples analyzed.

Table IV-3. Zinc distribution in size-fractionated suspended sediments

Sediment size fraction	Zn			Coefficient of variation		
	Total	HH-Zn	Resin-Zn	Total	HH-Zn	Resin-Zn
	µg/g	%				
<u>GENESEE RIVER</u>						
0.2 to 2 µm	203	35	13	33(7)*	23(6)	35(3)
2 to 20 µm	159	26	8	35(8)	39(5)	63(3)
>20 µm	96	26	4	73(6)	64(3)	26(4)
>0.2 µm	124	32	10	6(2)	33(2)	10(2)
<u>MENOMONEE RIVER</u>						
0.2 to 2 µm	376	62	23	53(5)	16(4)	14(4)
2 to 20 µm	598	48	13	47(5)	29(4)	12(3)
>20 µm	431	58	21	45(4)	23(4)	17(3)
>0.2 µm	593	46	18	18(3)	11(2)	12(2)
<u>MAUMEE RIVER</u>						
0.2 to 2 µm	386	20	13	74(2)	25(2)	44(2)
2 to 20 µm	214	23	10	1(2)	-(1)	28(2)
>20 µm	161	--	--	-(1)	--	--
>0.2 µm	354	--	--	-(1)	--	--
<u>GRAND RIVER</u>						
0.2 to 2 µm	221	--	--	28(2)	--	--
2 to 20 µm	336	--	--	20(2)	--	--
>20 µm	198	--	--	-(1)	--	--
>0.2 µm	221	--	--	-(1)	--	--
<u>NEMADJI RIVER</u>						
0.2 to 2 µm	150	22	13	26(5)	46(3)	54(4)
2 to 20 µm	116	21	7	46(4)	53(3)	81(2)
>20 µm	262	43	--	57(3)	87(2)	--
>0.2 µm	138	26	7	8(2)	-(1)	-(1)

\*Number of samples analyzed.

Table IV-4. Mean concentrations of total and available Cu, Pb, and Zn in tributary suspended sediments.\*

Tributary	Total Metal		HH-Metal	Resin-metal
	µg/L	µg/g	— % —	
<u>Copper</u>				
Genesee	27	61	41	25
Menomonee	25	146	46	37
Maumee	11	66	26	25
Grand	3	80	--	--
Nemadji	10	45	24	15
<u>Lead</u>				
Genesee	23	51	60	71
Menomonee	87	628	76	16
Maumee	17	97	37	7**
Grand	5	140	--	--
Nemadji	7	32	24	5
<u>Zinc</u>				
Genesee	67	150	25	8
Menomonee	65	471	56	19
Maumee	48	279	22	12
Grand	9	265	--	--
Nemadji	32	150	25	10

\* Calculated from the mean concentrations in the three particle size fractions (Tables IV-1, IV-2, IV-3) and the average size distribution and concentrations of the suspended sediments (Table I-3).

\*\* Based on one sample.



Available metal concentrations, measured as HH-metal, ranged from 24 to 41% of the total Cu, 24 to 76% of the total Pb, and 22 to 56% of the total Zn. For resin-metal, concentrations ranged from 15 to 37% for Cu, 5 to 71% for Pb, and 8 to 19% for Zn. The expected lower proportion of resin-metal (as compared to HH-metal) was observed in most of the sample groups, but Pb in the Genesee samples was an exception. These samples also exhibited a high degree of availability (60 and 71% for HH-Pb and resin-Pb, respectively). Only Pb in the Menomonee samples exhibited a higher degree of availability (76%).

The fraction of the total metal present as HH-metal was higher in the Menomonee samples than in samples from the other tributaries. Relatedly, total metal concentrations were also highest in the Menomonee samples. This likely reflects the local sources of trace metals in the urban/industrial Menomonee Watershed.

The trace metal concentrations expressed on a volume basis did not follow the same order as concentrations expressed on a sediment basis (Table IV-4). These differences result from the large differences in mean suspended sediment concentration among the five tributaries. For example, the Genesee samples exhibited the highest concentrations of Cu and Zn expressed on a  $\mu\text{g/L}$  basis even though concentrations on a  $\mu\text{g/g}$  basis were relatively low compared to the other tributaries.

The HH-metal is considered the best estimate of the available fraction of the total trace metal in the sediment. With the exception of the Menomonee samples and Pb in the Genesee samples, mean HH-metal concentrations were in the range 22 to 46% of the total metal concentration. The reason for the high proportion of HH-Pb in the Genesee samples (60%) as compared to Cu and Zn (41 and 25%, respectively) is uncertain.

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Appendix IV-A-1. Trace metals in suspended sediments

Sample No.	Sediment fraction	Cu			Pb			Zn		
		Total	Resin	HHV*	Total	Resin	HHV	Total	Resin	HHV
µm										
µg/g**										
GENESEE										
I	0.2 to 2	--	--	--	--	--	--	--	--	--
	2 to 20	90	--	--	94	--	--	232	--	--
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
III	0.2 to 2	--	--	--	--	--	--	--	--	--
	2 to 20	56	--	--	67	--	--	259	--	--
	>20	46	--	--	52	--	--	212	--	--
	>0.2	--	--	--	--	--	--	--	--	--
IV	0.2 to 2	91	17(19)	50(55)	60	ND	31(52)	188	15(8)	50(27)
	2 to 20	67	4(6)	33(49)	23	ND	16(70)	131	17(13)	27(21)
	>20	74	12(15)	32(43)	19	ND	6(30)	67	3(4)	14(21)
	>0.2	77	11(15)	38(49)	33	ND	17(52)	125	11(9)	29(24)
V	0.2 to 2	95	15(16)	49(52)	73	ND	37(51)	230	39(17)	105(46)
	2 to 20	61	5(8)	30(49)	39	ND	18(46)	137	4(3)	35(26)
	>20	17	1(6)	7(39)	27	ND	18(67)	46	1(2)	15(33)
	>0.2	51	6(12)	25(49)	43	ND	29(53)	122	12(10)	47(39)
VIII	0.2 to 2	121	ND	24(20)	80	--	--	151	--	50(33)
	2 to 20	72	ND	--	31	--	--	123	--	--
	>20	102	ND	--	39	--	--	151	--	--
	>0.2	--	ND	--	--	--	--	--	--	--
IX	0.2 to 2	81	27(33)	18(27)	104	51(49)	51(49)	182	--	46(25)
	2 to 20	10	7(70)	4(40)	36	32(89)	32(89)	112	--	17(15)
	>20	21	4(19)	22	14	9(64)	9(64)	42	--	8(19)
	>0.2	--	--	--	--	--	--	--	--	--
X	0.2 to 2	84	--	17(20)	86	--	--	166	--	65(42)
	2 to 20	--	--	29	--	--	--	--	--	29
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
XI	0.2 to 2	27	--	46(>100)	132	--	--	53(40)	344	139(40)
MONONGAHELI RIVER										
I	0.2 to 2	107	63(59)	65(61)	720	260(26)	513(71)	530	120(23)	289(55)
	2 to 20	134	48(36)	57(43)	1062	166(16)	800(75)	787	100(13)	311(40)
	>20	162	46(28)	62(38)	1223	145(12)	873(71)	626	111(18)	265(42)
	>0.2	147	48(33)	60(41)	1122	162(14)	816(73)	680	108(16)	284(42)
II	0.2 to 2	229	148(65)	159(69)	904	79(9)	680(75)	725	154(21)	480(66)
	2 to 20	327	58(18)	99(30)	1112	101(9)	521(47)	1011	124(12)	336(34)
	>20	191	20(10)	85(45)	666	98(15)	480(72)	439	109(25)	274(62)
	>0.2	234	39(17)	94(40)	814	98(12)	504(62)	625	116(19)	305(49)
III	0.2 to 2	116	54(47)	61(53)	198	35(18)	141(71)	418	111(27)	208(50)
	2 to 20	126	26(21)	60(48)	233	8(3)	166(71)	341	50(15)	172(50)
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
IV	0.2 to 2	165	--	121(73)	467	--	409(88)	428	--	330(77)
	2 to 20	150	--	--	475	--	--	438	--	--
	>20	200	--	106(53)	668	--	535(80)	493	--	359(73)
	>0.2	185	--	--	604	--	--	474	--	--
MAUMET RIVER										
I	0.2 to 2	132	42(32)	32(24)	170	12(7)	82(48)	588	50(9)	96(26)
	2 to 20	55	11(20)	11(20)	96	ND	38(40)	214	18(8)	50(23)
	>20	49	--	--	87	--	--	161	--	--
	>0.2	84	--	--	124	--	--	354	--	--
II	0.2 to 2	43	--	19(44)	64	ND	11(17)	184	32(17)	42(23)
	2 to 20	47	8(17)	--	66	ND	--	213	25(12)	--
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
GRAND RIVER										
I	0.2 to 2	69	--	--	103	--	--	177	--	--
	2 to 20	61	--	--	156	--	--	289	--	--
	>20	64	--	--	117	--	--	198	--	--
	>0.2	64	--	--	126	--	--	221	--	--
II	0.2 to 2	114	9(8)	--	90	ND	--	265	132(50)	--
	2 to 20	112	--	--	198	--	--	382	--	--
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
MAUMET RIVER										
I	0.2 to 2	26	8(31)	10(38)	21	ND	3(14)	93	20(22)	25(31)
	2 to 20	45	6(13)	13(29)	41	ND	10(24)	161	18(11)	47(29)
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
II	0.2 to 2	51	13(25)	12(24)	42	2(5)	5(12)	157	20(13)	36(23)
	2 to 20	48	3(6)	11(23)	31	ND	11(35)	144	5(3)	36(25)
	>20	51	8(16)	9(18)	59	2(3)	17(29)	139	17(12)	48(35)
	>0.2	49	7(13)	11(22)	38	ND	10(25)	146	11(7)	38(26)
III	0.2 to 2	75	12(16)	--	38	ND	--	180	17(9)	--
	2 to 20	51	3(6)	--	23	ND	--	133	12(9)	--
	>20	--	--	--	--	--	--	--	--	--
	>0.2	--	--	--	--	--	--	--	--	--
IV	0.2 to 2	71	11(15)	--	48	ND	--	187	12(6)	--
	2 to 20	44	--	--	23	--	--	118	--	--
	>20	38	--	--	24	--	--	83	--	--
	>0.2	50	--	--	30	--	--	130	--	--

\*HHV is hydroxylamine hydrochloride extraction.

\*\*Values in parentheses expressed as percentage of total.

ND is sample below detection limit.

Appendix IV-A-2. Trace metals in bottom sediments

Sample No.	Sediment size fraction	Cu			Pb			Zn		
		Total	Resin	HHX*	Total	Resin	HHX	Total	Resin	HHX
μm		ug/g								
<u>GENESEE</u>										
B	0.2-2	73	42 (58)**	28 (38)	68	ND	46 (68)	160	22 (14)	28 (38)
	2-20	50	13 (26)	12 (24)	10	ND	25 ( )	114	9 (8)	12 (24)
	>20	17	ND	5 (29)	16	ND	ND	55	4 (7)	5 (29)
	>0.2	--	--	--	--	--	--	--	--	--
<u>MENOMONEE</u>										
C	0.2-2	128	95 (74)	--	554	130 (23)	--	479	124 (20)	--
	2-20	104	--	20 (19)	456	--	419 (92)	423	--	274 (66)
	>20	24	11 (46)	8 (33)	116	31 (27)	310 (>100)	164	35 (21)	87 (53)
<u>NEMADJI</u>										
A	0.2-2	63	--	16 (25)	45	--	--	133	--	14 (11)
	2-20	29	--	5 (17)	5	--	--	58	--	6 (10)
	>20	17	--	3 (18)	15	--	--	40	--	3 (8)

\* HHX is hydroxylamine hydrochloride extraction.

\*\* Values in parentheses expressed as percentage of total

ND is sample below detection limit.

<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT The purpose of this investigation was to evaluate the availability of certain elements, mainly phosphorus, transported to the Great Lakes by suspended sediment. Nitrogen (N) was also investigated because of its importance as a nutrient element; also included were certain trace metals because of concern over their possible adverse effects in the Great Lakes. Rivers investigated include: Genesee River, N.Y.; Grand River, Michigan; Maumee River, Indiana and Ohio; Menomonee River, Wisconsin; Nemadji River, Minnesota and Wisconsin.		
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