3-1-1978

Final Report Sediment Nutrient and Metal, and Water Column Heavy Metal Characterization in the Genesee River

Michael M. Reddy

Repository Citation

Reddy, Michael M., "Final Report Sediment Nutrient and Metal, and Water Column Heavy Metal Characterization in the Genesee River" (1978). *Government Documents*. 45.
http://digitalcommons.brockport.edu/wr_misc/45

FINAL REPORT

SEDIMENT NUTRIENT AND METAL, AND WATER COLUMN HEAVY METAL CHARACTERIZATION IN THE GENESEE RIVER

PART OF THE GENESEE RIVER PILOT WATERSHED STUDY FOR PLUARG TASK C

by

Michael M. Reddy

New York State Department of Health

Albany, New York 13204

This study was conducted

in cooperation with

New York State Department of Environmental Conservation

Albany, New York

and the

International Joint Commission for the Great Lakes

Windsor, Ontario, Canada

March 1, 1978

FINAL REPORT

SEDIMENT NUTRIENT AND METAL, AND WATER COLUMN HEAVY METAL CHARACTERIZATION IN THE GENESEE RIVER

PART OF THE GENESEE RIVER PILOT WATERSHED STUDY FOR PLUARG TASK C

by

Michael M. Reddy

New York State Department of Health

Albany, New York 13204

This study was conducted

in cooperation with

New York State Department of Environmental Conservation

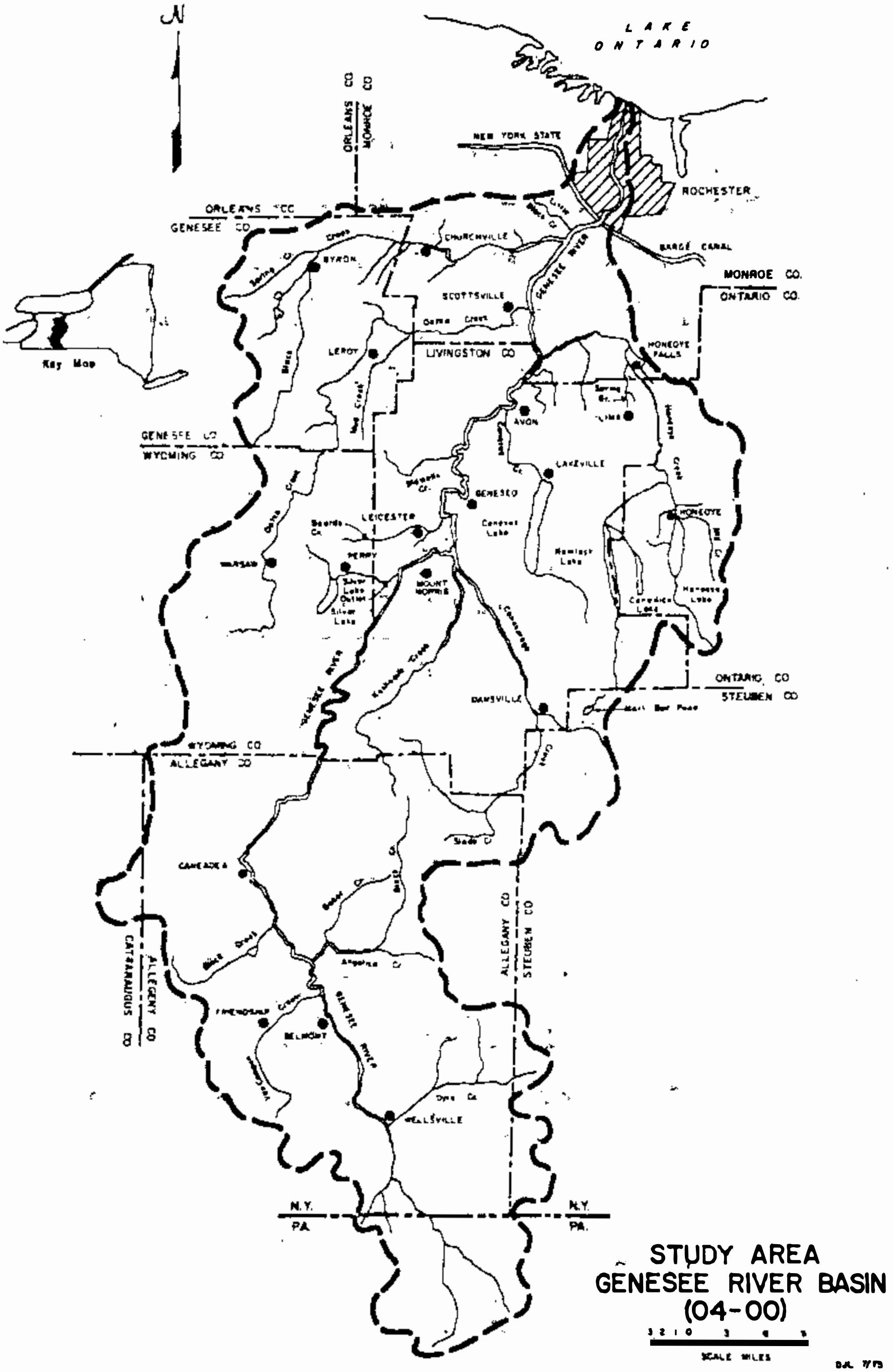
Albany, New York

and the

International Joint Commission for the Great Lakes

Windsor, Ontario, Canada

March 1, 1978



STUDY AREA
GENESEE RIVER BASIN
(04-00)

Map courtesy of the New York State Department of Environmental Conservation.

CONTENTS

Page

Figures iv
Tables vi

1. Introduction 1
2. Materials and Methods 3
3. Results 12
4. Discussion 15
5. Conclusions 44

References 47
Appendices 51

1. Analytical Results for Sediment Samples from the Genesee River A1
2. Analytical Results for Water Column Samples from the Genesee River A2

FIGURES

Number Page

1 Genesee River sampling sites.................................... 5

2 A flow chart showing water column sample pretreatment procedures.. 8

3 Analysis scheme for determination of extractable metals and phosphorus in sediments.. 9

4 Frequency distribution plots of bottom sediment nutrient and metal concentrations.. 16

5 Cumulative frequency distribution plots of bottom sediment nutrient and metal concentrations on a probit scale...................... 17

6 Bottom sediment elemental concentration plotted as deviations from basin means in terms of each elements standard deviation... 22

7 Total phosphorus instantaneous unit load, percent load as dissolved phosphorus, and discharge for six stations on the Genesee River.. 33

8 Ion activity product of calcite plotted as a function of sampling point distance from Lake Ontario............................ 34

9 Plots of solution total calcium concentration and pH as a function of time for a typical calcite seeded crystallization experiment in simulated natural water.................................. 36

10 Calcite crystallization rate function $N^{-1} - N_0^{-1}$ versus time for data shown in Figure 9.................................... 37

11 Calcite crystal growth in the presence and absence of phosphate ion, as expressed by the rate function $N^{-1} - N_0^{-1}$ versus time. The symbols and the numbers beside the curves indicate the phosphate concentration multiplied by 10^4. Adapted, by permission, from the J. Crystal Growth 41 (1977) p. 294........... 39

12 Langmuir isotherm plot of $k_0/(k_0 - k)$ against the reciprocal of the phosphate concentration, where k_0 is the calcite growth rate constant in the absence of phosphate and k is the rate

FIGURES (CONTINUED)

Number Page

constant in the presence of phosphate: ( ) $k_0 = 0.824$; ( ) $k_0 = 1.205$; ( ) $k_0 = 0.790$. Adapted, by permission, from the J. Crystal Growth 41 (1977) p. 294.................... 40

13 Phosphate concentration versus time for several calcite seeded growth experiments in the presence of phosphate ion............. 41

TABLES

Number Page

1 Genesee River Sampling Sites.................................... 4

2 Sediment Sample Collection, Preservation and Pretreatment......... 7

3 Statistics for Elemental Concentrations of Bottom Sediments in the Genesee River Watershed.................................... 18

4 Estimates of Mean Elemental Concentrations of Bottom Sediments in the Genesee River Watershed.................................. 20

5 Mean Metal Concentrations (μg/g) in Genesee River Watershed Sediment Compared with Other Published Analyses.................. 23

6 Percentage of Total Metal Concentration Transported by Particulate Material.. 28

7 Statistics for Phosphorus Analyses for Sediments Collected in the Genesee River Watershed, N.Y................................. 31

8 Metal Concentrations in Sediments from the Genesee River Watershed and Four Tributaries to Chesapeake Bay......................... 46

SECTION 1

INTRODUCTION

The objectives of this study were to provide information on sediment composition as a basis for determining whether the metals and nutrients in the watershed sediments were present in high concentration and whether they were being transported in a reactive chemical form threatening to the water quality of Lake Ontario.

Freshwater sediments have a significant role in the complex interaction between pollutants and water in a river system and their analysis has been used to detect and trace pollutant inputs and to anticipate the effects of these pollutants on water quality (1-4).

In characterizing sediment transport of nutrients and trace metals in a watershed it is necessary to differentiate among the several sediment components including particulate matter, suspended sediment and bottom sediment. Each of these components has different physical properties (e.g. particle-size distribution, density and surface area), interacts in different ways with nutrients and metals in the water column and will be transported at different rates.

In addition Gibbs (5) has shown that the amount of trace metal carried by suspended sediment in a river was strongly dependent on the chemical form of the element. He used sequential chemical extractions, each corresponding to a mineralogical phase within the sediment. Gibbs distinguishes an absorbed phase consisting of ions or complexes adsorbed to sediments; an incorporated metal or phosphate phase formed by physical, chemical or biological incorporation of phosphorus or trace metals in a sediment organic matrix, metal oxide or metal hydroxide matrix; and a crystalline phase consisting of extractable phosphorus or trace metals which are part of the crystal lattice of sediment minerals. These and many other differential dissolution methods used for soil and sediment characterization, however, are largely empirical. Schwertmann (6) emphasized that the results of such procedures are best considered as a measure of the relative amount of a phase or, more generally, a measure of an elements' reactivity in a sediment under carefully controlled conditions. In the present study, these physical and chemical separation techniques are used to identify and characterize the transport phase for phosphorus and trace metals in the Genesee River Watershed.

Previous publications dealing with bottom sediment composition in the Genesee River basin include Reddy's preliminary report (7). Bannerman et al. (8) also reported on chemical analyses of bottom sediments and water column samples and a water-quality survey of the lower river has been published (9).

SAMPLING STRATEGY

Sediment and water column samples collected in this study were obtained in synoptic surveys of the Genesee River watershed. A synoptic survey, as defined by Heines et al. (10) is "a riverwide (or multireach) study invloving coordinated intensive sampling over a short time period (several days)." Velz (11) and Kittrell (12) have discussed in detail the advantages of synoptic surveys over other monitoring programs. Heines et al. have emphasized that results obtained during flow events are particularly relevant for long-range planning. In addition, sampling prior to and immediately after major basin flow events is necessary because the mobilization and deposition (i.e. transport) of sediment-associated pollutants, rather than their absolute concentrations, are often important. Therefore, attempts were made to coordinate our synoptic survey program with basin runoff events in several seasons.

Sediment samples were collected during the four seasons of the year. Field work was performed by deploying two mobile field laboratories to 28 stations in the 2400 sq. mi. basin on three consecutive days.

SECTION 2

MATERIALS AND METHODS

The 6,500 - km^2 (2,400 sq.-mi) Genesee River watershed is located in Central New York State, tributary to Lake Ontario, and has an average discharge of approximately 76 m^3/s (2,700 cfs) near Rochester, NY.

A wide variety of soil types and geochemical areas are found in the Genesee basin, which consists of three terraces separated by northward-facing escarpments. Soils in the southernmost terrace are siltstone, shale and sandstone mixed on glacial till with moderate drainage quality. The central terrace has soils composed predominantly of limestone with shale and sandstone mixed on glacial till with good drainage quality. A narrow lake plain within the city of Rochester consists of soils composed of lacustrine silt and clay deposits which are poorly drained. Sampling sites on the Genesee River used in this study are shown in Figure 1 and Table 1. The sites were selected by the U.S. Geological Survey for long-term flow and suspended sediment measurements so that pollution from any nearby point source was avoided as much as possible.

SAMPLE COLLECTION AND PRETREATMENT

Definition of Terms

Samples collected and analyzed in this investigation are defined and referred to as follows:

1. Water Column Total Concentration: The concentration of a constituent determined on an unfiltered sample.

2. Water Column Dissolved Concentration: The concentration of a constituent which will pass through a 0.45 μ membrane filter.

3. Water Column Particulate Concentration: The concentration of a constituent which is retained by a 0.45 μ membrane filter. This water column component is often termed suspended solids or suspended sediment.

4. Bottom Sediment Concentration: The concentration of a constituent of sediment wet sieved on site through a 2 mm sieve, and subsequently dried, crushed and sieved through a 100 mesh sieve before analysis.

5. Resuspended Bottom Sediment Concentration: The concentration of a constituent of bottom sediment suspended during the wet sieving of a bottom

TABLE 1. SAMPLING SITES ON THE GENESEE RIVER

Site Location	Miles from Mouth of Genesee	U.S.G.S. Station Number	Latitude	Longitide
Wellsville, N.Y.	137	04-2210-00	42° 07' 20"	77° 57' 27"
Transit Br., N.Y.	117	04-2214-23	42° 19' 46"	78° 04' 36"
Portageville, N.Y.	85	04-2230-00	42° 34' 13"	78° 02' 33"
Mt. Morris, N.Y.	62	04-2275-00	42° 44' 00"	77° 50' 21"
Avon, N.Y.	35	04-2285-00	42° 55' 50"	77° 45' 27"
Rochester, N.Y.	5	04-2320-00	43° 10' 50"	77° 37' 40"

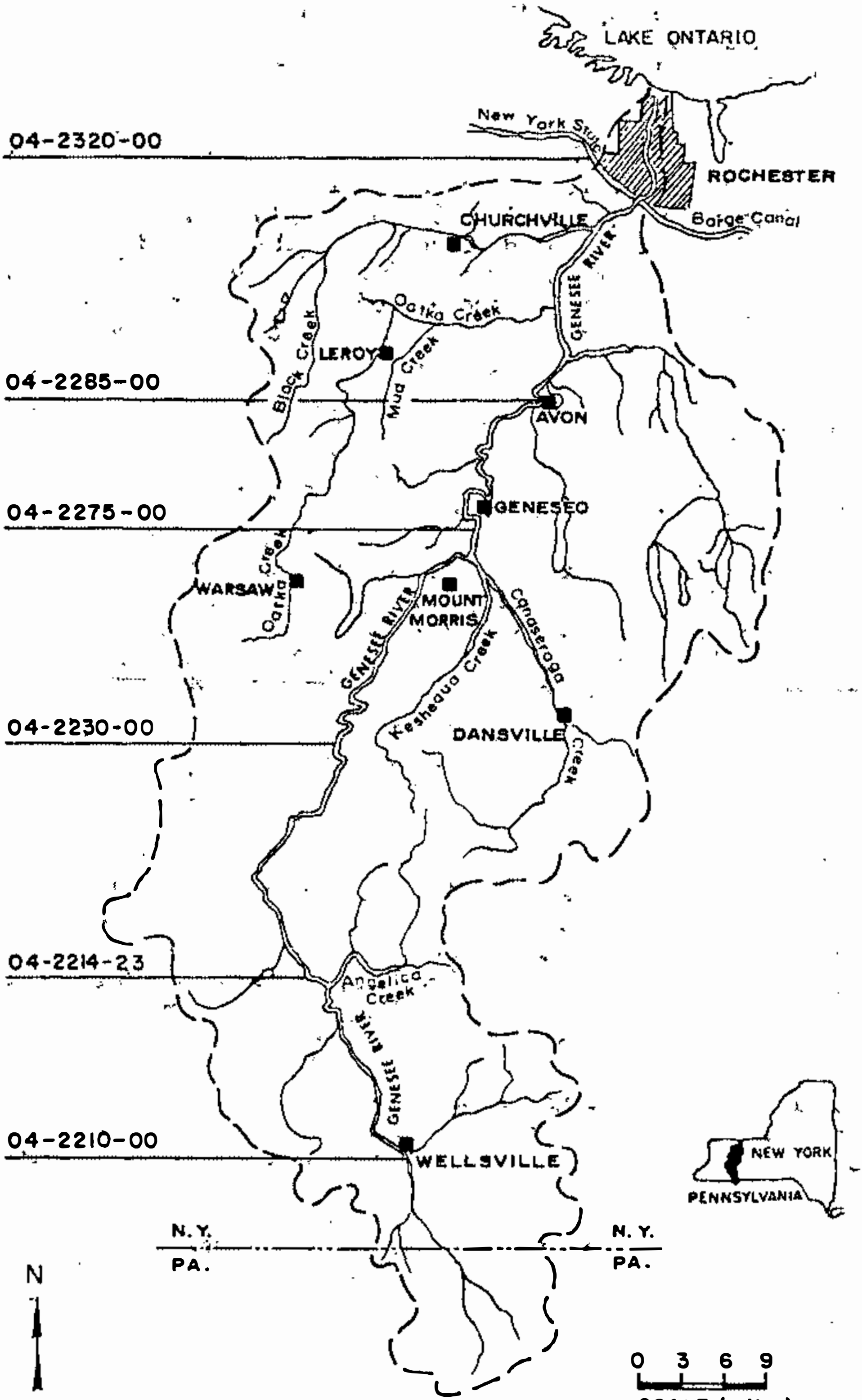


Figure 1. Genesee River sampling sites.

sediment sample. Resuspended bottom sediment consisted only of that material in suspension after standing 30 min. The resulting suspension was immediately frozen and eventually freeze-dried prior to analysis.

Sediment Samples

Sediment samples were collected in midstream and wet-sieved immediately through a 2-mm polyethylene sieve using river water. The wet sediment samples were frozen on site and stored frozen in a mobile field laboratory. Sample collection and pretreatment procedures were adapted from techniques employed by the U.S. Geological Survey and are outlined in Table 2. A summary of the analytical procedures used to characterize sediment and water column samples has also been presented elsewhere (13).

Water Column Samples

Water and suspended sediment samples were obtained using a 4 l non-metallic Van Dorn sampler at a depth of 1 m in the main channel (Fig. 2).

Unfiltered samples were acidified immediately after collection. A separate sample was filtered through a prewashed 0.45-µm Millipore filter, using compressed argon gas and Plexiglas equipment. The filtered sample was acidified immediately. The filter with particulates was dried with a brief flow of argon gas, folded and stored in a plastic Petri dish until analysis.

SAMPLE ANALYSIS

Sediment Samples

Method of Total Analysis --

Frozen bottom sediment samples were thawed for analysis, dried at 110°C, crushed, and sieved through a 100-mesh nylon sieve. After digestion with HNO_3-H_2O_2 at 100°C for 2 hours (14), metals were determined in the filtered extracts by atomic absorption spectroscopy. Silicate minerals are not solubilized in this procedure; thus the metal results are an estimate of the total extractable (environmentally available) metal content of the sediment.

Sediment total phosphorus was determined using the HNO_3-H_2O_2 digestion and/or an acid-alkaline persulfate method (15). Both digestion methods gave the same sediment phosphorus content for a series of 28 samples, one from each station in the watershed.

Total carbon, organic carbon, and total nitrogen in sediment were determined with a high-temperature (1,100°C) combustion technique, employing a Perkin-Elmer CHN analyzer (Model 240) modified to accept up to 1 g of material.

Method of Fractional Analysis --

The fractionation scheme employed in this investigation for the determination of several forms of extractable phosphorus and trace metals is shown in Figure 3. The phosphorus extraction procedure employed NaOH (with NaCl)

TABLE 2. SEDIMENT SAMPLE COLLECTION PRESERVATION AND PRETREATMENT

	Collection	Preservation	Pretreatment
Bottom Sediment	Sediments were collected in mid-stream where possible and were immediately wet-sived on site through a 2-mm polyethylene sieve using river water.	Wet sediments were frozen immediately on site and stored frozen until the start of analysis.	Frozen samples were thawed prior to ananlysis, dried at 110°C, crushed and sieved through a 100-mesh nylon sieve.
Fine-textured Sediment Washed from Bottom Sediment	Fine-textured sediment was suspended during wet-seiving. The resulting suspension was allowed to stand for 30 min, then the quiescent supernatant was carefully decanted into a 2 liter plastic bottle	Fine-textured sediment suspensions were frozen immediately on site and kept frozen until the start of analysis.	Frozen fine-textured sediment samples were thawed and centrifuged (10,000 Brrpm for 20 min.) to reduce sample volume from 2 to 0.1 liters. The resulting concentrated suspension was freeze-dried.

Figure 2. TRACE METAL FLOW CHART

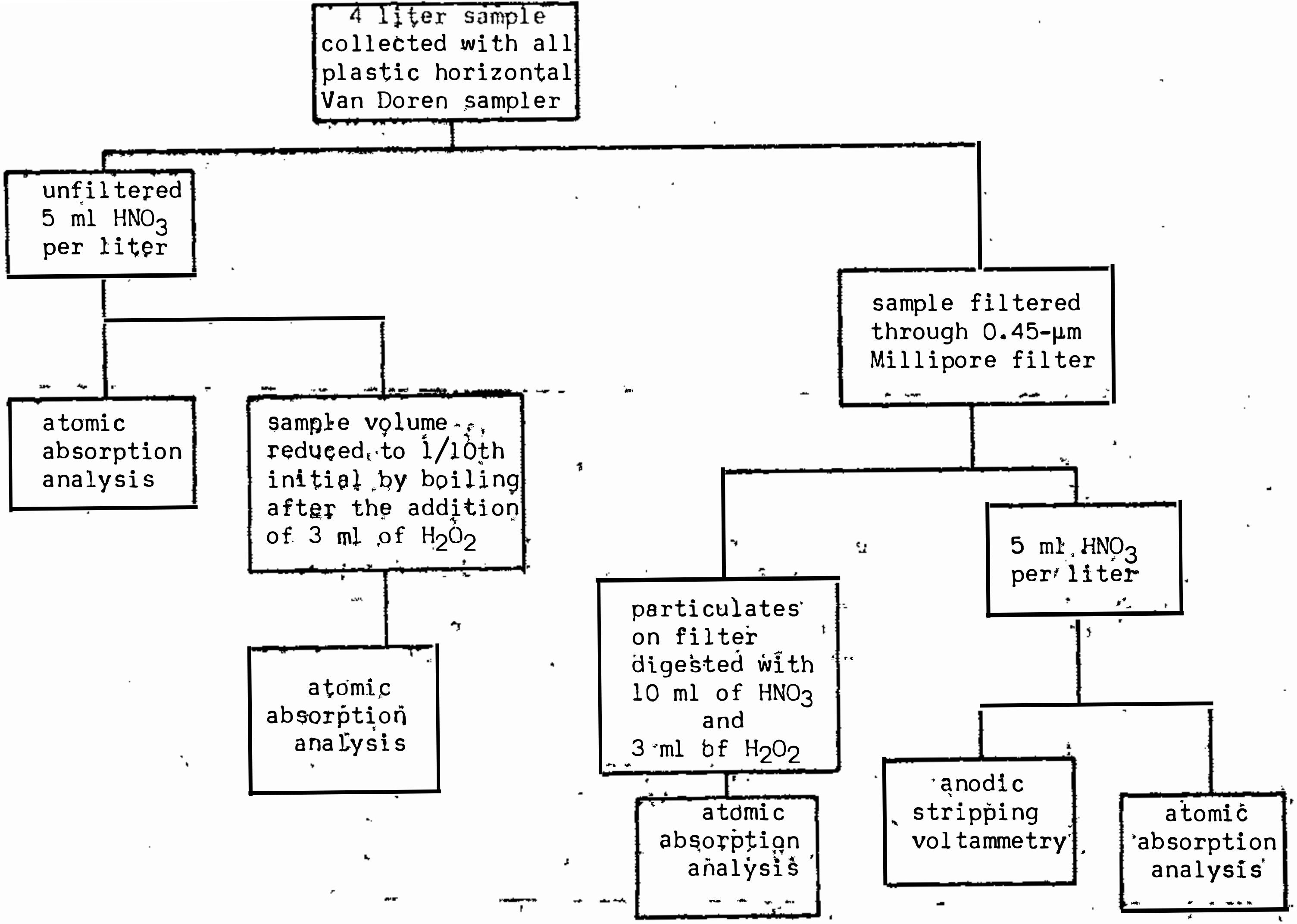
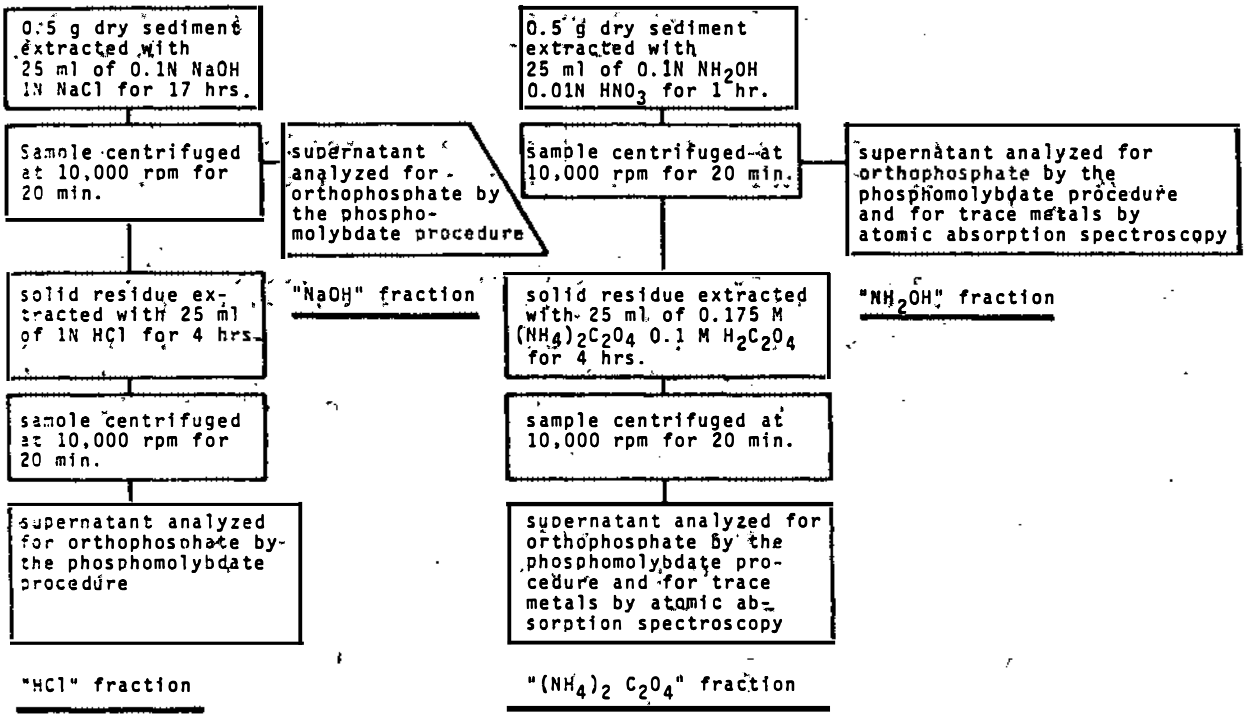


Figure 2. A flow chart showing water column sample pretreatment procedures.

Figure 3. Analysis scheme for determination of several forms of extractable phosphorus and trace metals in fluvial bottom sediments and suspended bottom sediments



for the extraction of non-occluded phosphorus and HCl for occluded phosphorus (adopted from Williams et al., (16,17). Work performed in this laboratory (18) and elsewhere (19) indicates that the NaOH extractable phosphorus is a measure of biologically available phosphorus. Hydrochloric acid extractable phosphorus reflects apatite phosphorus and phosphorus incorporated in iron oxides.

Methods used to measure extractable metals were chosen so that some information could be obtained on the association of phosphorus with hydrous metal oxides.

A hydroxylamine extraction procedure (20) (see Figure 3) for extraction of manganese under acidic, mildly reducing conditions was used to examine the manganese-phosphorus relationship. Subsequent extraction with ammonium oxalate-oxalic acid solution was used to remove amorphous iron oxides and organic iron, and phosphorus associated with these constituents (6).

Water Column Samples

Water column analysis was performed as described by Krishnamurty and Reddy (13, 21). Filters, with particulates, were digested employing a HNO_3-H_2O_2 procedure prior to analysis.

QUALITY CONTROL PROCEDURES

During each analysis replicates of actual sediments were run as quality-control check samples. Precision and accuracy of the total sediment digestion procedure for metal analyses were published (14). The coefficient of variation (CV) of metal analyses for each of these samples was 0.10 or less.

For phosphorus, in addition to the sediment quality-control samples, a National Bureau of Standards standard reference material (No. 1571, Orchard Leaves) was analyzed with each batch of samples. The total phosphorus content of this reference material by the acid-alkaline persulfate method was 2,038 µg/g (certified value, 2,100 ± 100 µg/g) with a CV of 0.05 ($\underline{n}$ = 21). The CV for total phosphorus analysis of three actual sediments used as quality-control check samples were 0.12 ($\underline{n}$ = 12), 0.16 ($\underline{n}$ = 11), and 0.13 ($\underline{n}$ = 11), with means of 412, 487, and 758 µg P/g respectively.

In a quality-control sediment sample analyzed for total carbon (mean 0.5%) and total nitrogen (mean 0.06%) the CV were 0.20 ($\underline{n}$ = 9) and 0.23 ($\underline{n}$ = 9) respectively.

Precision for replicate phosphorus fractional analysis on actual sediment samples used for quality control checks shows a CV of about 0.10 for all extraction procedures for samples containing more than 100 µg P/g extractable phosphorus. Precision for metal extraction analysis is similar to that for phosphorus.

SEEDED CRYSTALLIZATION EXPERIMENTS

A detailed description of the seeded growth technique has been published recently (22). The following summarizes the experimental procedure employed. Reagent grade chemicals; distilled, deionized, filtered (0.22-um Millipore filter) water; and grade A glassware were used in all experiments. Supersaturated calcium carbonate solutions were prepared by drop-wise addition of 200 ml of 5×10^{-4} M calcium chloride solution to 200 ml of 8×10^{-3} M sodium bicarbonate solution in a thermostated double-walled Pyrex glass reaction vessel. Stability of the supersaturated solution was verified by the constancy of pH for at least one hour before the start of each experiment. Solution pH changes accompanying calcite growth after inoculation of the stable supersaturated solution with seed crystal were monitored with a Corning pH Meter and a strip chart recorder. Calcium concentration in solution was followed during crystallization by analysis of solution filtrates. An EDTA titration procedure employing calcein indicator (23) with a micrometer burette was used to determine calcium concentration in the filtered solution. Total carbonate concentration was calculated from a titrimetric analysis of the filtrate using 0.01 N sulfuric acid and methyl purple indicator (pH range 4.8 - 5.4). A Quantachrome Monosorb surface area analyzer was used to measure seed crystal surface area; a Phillips powder diffraction apparatus with copper K_a radiation and a nickel filter was employed for X-ray powder diffraction verification of seed crystal composition. Calcite seed crystals were prepared by rapidly adding 0.5 M $CaCl_2$ solution to 0.5 M Na_2CO_3 solution at 5° C. The viscous suspension formed was gradually warmed to 25° C, stirred overnight, then washed with distilled water. Seed was aged in distilled, deionized water 6 months before use. The seed consisted of uniform aggregates of flat crystals shown to be calcite by X-ray diffraction, with a surface area of 1.71 m^2/g. Seeded crystal growth experiments were performed in solutions resembling natural waters. Ionic species concentrations were calculated from measured solution pH and from total calcium and carbonate concentrations, using the mass action and mass balance equations (24). Calculations were performed using successive approximations for ionic strength, I, (24) with a Wang 720 C programmable calculator. Ion activity coefficients were obtained from the modified Debye - Hückel equation proposed by Davies (25). Bicarbonate ion was the predominant carbonate species in the experimental solutions comprising more than 95% of the total carbonate concentration. Calcium carbonate and bicarbonate ion-pair concentrations were considered in solubility calculations. The influence of phosphate ion-pair formation on the crystallization reaction was examined and found to be negligible (22) at the phosphate concentration levels employed.

SECTION 3

RESULTS

SEDIMENT COMPOSITION AND ITS VARIATION AT SITES ON THE GENESEE RIVER

Bottom Sediments

Total Analysis --

Bottom sediment nutrient and metal concentrations at six sites on the main stem of the Genesee River are shown in Appendix 1 A. These samples were collected after the spring snow-melt runoff, the major hydrological sediment-mixing and transport event in the basin. The samples were obtained from slightly different locations at each site to determine sediment homogeniety.

Fractional Analysis --

Fractional extractional analytical results for bottom sediments discussed in the previous section are shown in Appendix 1 B (for phosphorus analysis) and 1 C (for metal analysis).

Resuspended Bottom Sediment, Total Analysis

Resuspended sediment samples collected from the Genesee River during March and July 1976 were analyzed to determine the composition of fine sediment in the river. These results are shown in Appendix 1 D and are discussed in Section 4.

WATER COLUMN METAL CONCENTRATION AND ITS VARIATION

Preliminary basin-wide surveys

Total Water Column Analysis --

A preliminary survey was conducted on April 14 and 15, 1975 to determine the total concentration of several metals in surface waters of the Genesee River basin. The metals analyzed for in several or all samples included arsenic, cadmium, chromium, copper, iron, lead, mercury, potassium, sodium, zinc, calcium, magnesium and nickel.

Samples from five sites were analyzed for arsenic and mercury. All results were less than the minimum reportable concentration (0.02 mg/l for arsenic and 0.0004 mg/l for mercury). Further work on these two elements was not performed in this special study.

Total water column cadmium concentrations were determined at 20 sampling sites. All results from these analyses were less than the minimum reportable concentration for cadmium (0.020 mg/l).

Copper, chromium, lead, nickel and zinc were also determined for samples collected at each of twenty sites. All results were equal to, or less than the minimum reportable metal concentration. Significant total water column concentrations were observed for iron, potassium, sodium magnesium, calcium and manganese.

Total Water Column Analysis (with evaporative preconcentration) -- Evaporative preconcentration was used to increase metal analysis sensitivity for total water column concentrations. Results of evaporative preconcentration for total water column analysis for representative samples collected at 6 sites on the Genesee River December 14, 1975 are presented in Appendix 2 A.

Dissolved Heavy Metal Analysis (by Differential Pulse Anodic Stripping Voltammetry, DPASV)

In order to achieve analytical sensitivity compatible with low concentrations of dissolved cadmium, copper, lead and zinc the DPASV procedure was used. Filtered samples from twenty stations in the Genesee River Watershed were collected on December 12 to December 15, 1975 and analyzed for lead, cadmium, copper and zinc using DPASV. On March 12 to March 15, 1976 filtered water column samples were collected at each of twenty-eight stations in the watershed and analyzed for lead and cadmium by DPASV. Results of these analyses for six stations on the Genesee River are shown in Appendix 2 B. These results show very low but measurable concentrations of dissolved cadmium, lead, zinc and copper.

Total Water Column Metal Concentrations at Six Sites on March 13, 1976

Total metal analyses were done on water column samples collected at six sites on the Genesee River during a peak flow period in March 1976 to monitor the metal concentration along the Genesee River. Results for analysis of total water column samples collected on this date are shown in Appendix 2 C. Aluminum, copper, chromium, lead, nickel and zinc concentrations, determined by atomic absorption spectroscopy, were at or below the minimum reportable concentration. Elements which showed significant concentrations in the samples, iron and manganese, demonstrated good reproducibility between duplicates.

Dissolved Water Column Metal Concentrations at Six Sites on March 13, 1976

Dissolved metal concentrations are often the water column parameter with greatest potential inpact on water quality. For this reason dissolved metal concentrations and their variation were determined along the length of the Genesee River during a peak flow period during March 1976. The results are shown in Appendix 2 C. As found for the total water column concentrations discussed in the preceding section, aluminum, copper, chromium, lead, nickel and zinc concentrations (determined by atomic absorption spectroscopy) were at or below the minimum reportable concentration. As shown previously for total concentrations, iron and manganese usually show measurable values at each station.

Particulate Metal Water Column Concentrations at Six Sites on March 13, 1976

Analytical results for the determination of particulate metal concentrations in water column samples from six sites on the Genesee River, March 13, 1976 are shown in Appendix 2 D. In contrast to the total and dissolved analyses, the particulate determination shows measurable metal concentrations for nearly all metals at each station.

SECTION 4

DISCUSSION

DATA ANALYSIS

Bottom Sediment Composition

Statistics --

In order to discuss the chemical composition of basin sediments most conveniently, statistical procedures are usually employed. The basis for evaluating the pollutional impact of point and nonpoint sources of individual nutrients and metals in a basin is the frequency histogram, the statistical distribution of the concentrations. In natural materials the concentrations sometimes follow a Gaussian (normal) distribution (26), while in other cases the distribution may not be amenable to a simple description (27). As Siegel (28) and Miesch (29) have emphasized, the distribution of chemical elements in rocks, soils, sediments, water, and a variety of other natural materials most often approximates a logarithimically transformed Gsussian (lognormal) distribution which exhibits a positive asymmetry.

Frequency distribution plots of the bottom sediment nutrient and metal concentrations are shown in Figure 4. The bell-shaped, symmetrical plots for Al, Fe, and P are typical of a normal distribution. Plots for Cu, Mn, Ni, Pb, Zn, total and organic C, and total N show a positive asymmetry. The Cr distribution is strongly influenced by the frequency of results at or near the detection limit. No sediment constituent examined in this study had a negatively asymmetric frequency distribution plot. Figure 5 shows the corresponding cumulative frequency distributions.

An essential statistical tool for measuring background, local, and regional pollutant inputs and for identifying possible and probable sites of point and nonpoint source pollution is the standard deviation (SD) of a series of basin bottom sediment concentrations. In a geochemical analysis sites having a concentration 2 SD greater than the basin mean are considered anomalous.

A statistical summary of the bottom sediment concentrations for the entire basin is presented in Table 3. This includes the arithmetic mean, SD, and coefficient of variation (CV) (statistics of a normally distributed population) and the log-transformed, or geometric, mean and SD (statistics for a log-normally distributed population). The choice of whether to use a normal or a log-normal statistical analysis depends on the actual

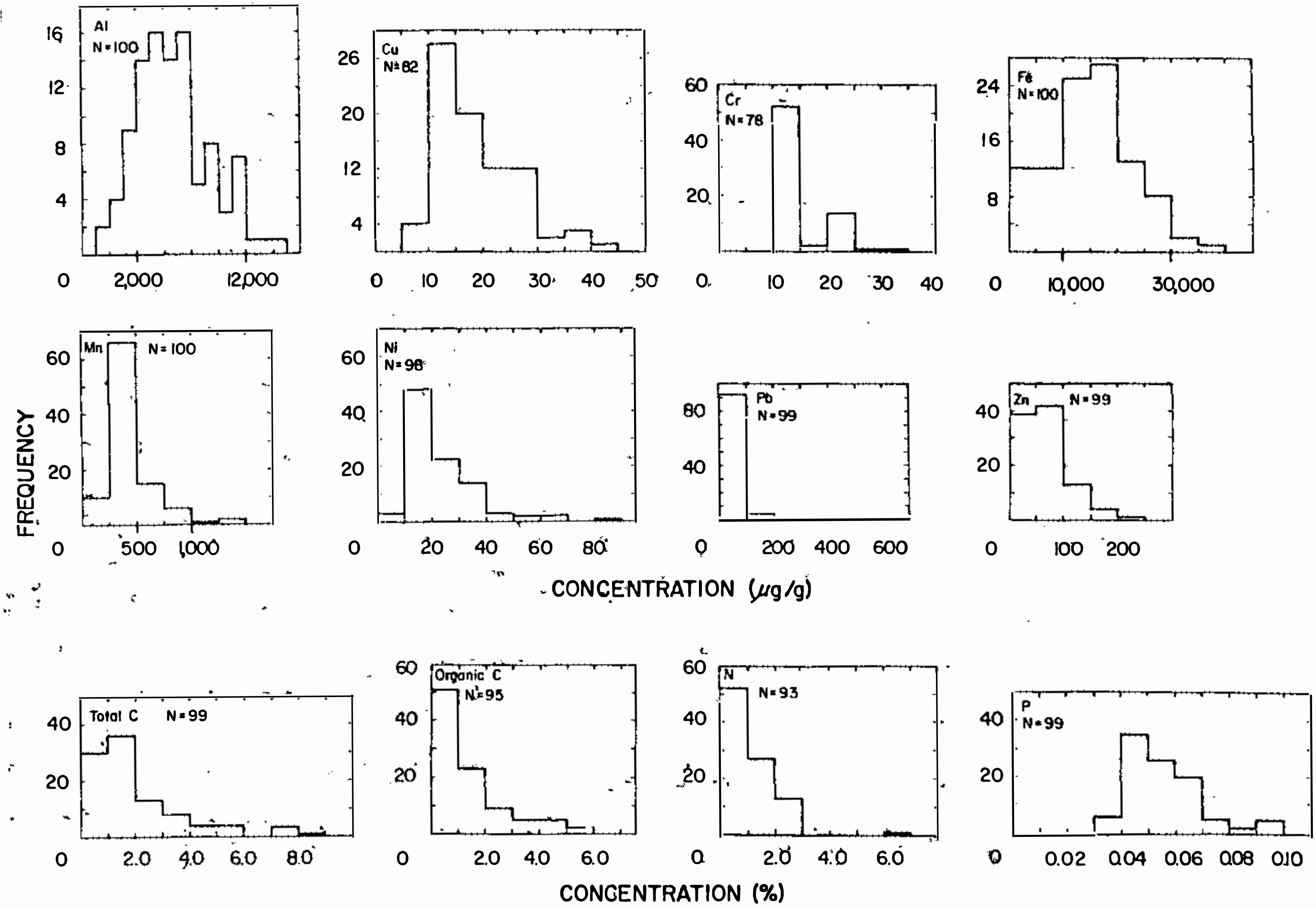


Figure 4. Frequency distribution plots of bottom sediment nutrient and metal concentrations.

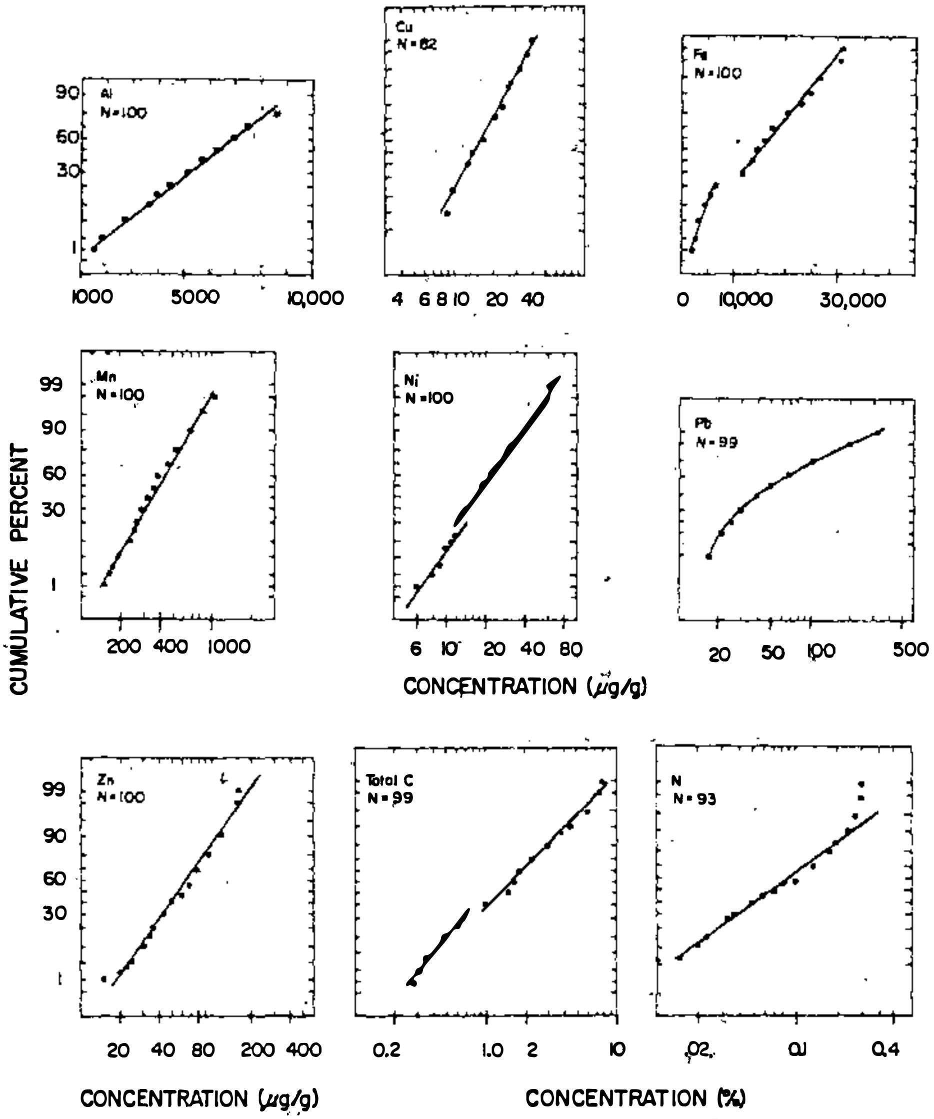


Figure 5. Cumulative frequency distribution plots of bottom sediment nutrient and metal concentrations on a probit scale.

distribution of the sample population.

TABLE 3. STATISTICS FOR THE CONCENTRATIONS OF NUTRIENTS AND METALS AND THEIR LOGARITHMIC TRANSFORMATIONS FOR BOTTOM SEDIMENTS OF THE GENESEE RIVER WATERSHED

Element	Concentration[a]			Log-Transformed Concentration[a]		n
	Mean	SD	CV	Mean	SD	
Al	6,660	2,620	0.39	3.787	0.185	100
Cr	14	9	0.66	1.101	0.173	78
Cu	18	7	0.40	1.231	0.170	82
Fe	15,060	7,312	0.49	4.111	0.266	100
Mn	424	212	0.50	2.585	0.187	100
Pb	40	67	1.69	1.404	0.346	99
Ni	23	13	0.57	1.299	0.210	98
Zn	69	37	0.54	1.780	0.235	99
Total C	2.06	1.68	0.82	0.185	0.344	99
Organic C	1.37	1.28	0.94	-0.0553	0.441	95
Total N	0.105	0.098	0.93	-1.154	0.410	93
P	0.0560	0.014	0.25	-1.264	0.101	99

[a] For metals, µg/g; for nutrients, %; both on a dry-weight basis.

Several graphic and algebraic techniques are available for establishing the statistical distribution of a sample population. For example, if the relative frequency of a population showing a positive asymmetry (i.e. not normally distributed) is plotted against the concentration on a logarithmic scale, the resulting curve often describes a Gaussian distribution about the geometric mean (i.e. the sample population is log-normally distributed).

A convenient method of determining whether a geochemical distribution is normal or log-normal, is to plot the cumulative frequency data on a probability scale. When the concentrations are plotted on an arithmetic scale, a best-fit linear relation indicates a normal distribution. When the concentrations are plotted on a logarithmic scale, it indicates a log-normal distribution. Thus the plots for Al and Fe in Genesee River watershed bottom sediments (Figure 5) show a normal distribution. The plot for sediment Fe suggests two normal populations, corresponding to the two linear segments of the regression.

Plots for Cu, Mn, and Zn, on the other hand, show a simple log-normal distribution. These three metals are often transported as or by hydrous oxides in fluvial sediments. Sediment Ni and total C concentrations are also log-normal, but each plot has two linear segments, suggesting that each element may be distributed among two log-normal populations. Sediment N concentrations are also log-normal, but the linear portion of the curve covers a much narrower range of frequencies (30% to 80%) than is found for the other sediment constitutents examined. This may indicate additional variance arising from nonconservative biological processes (nitrification and denitrification), which in large measure influence sediment N concentrations.

Bottom sediment Pb concentrations show the most pronounced positive asymmetry of any sediment component examined in this study (Figures 4 and 5), indicating that Pb is neither normally nor log-normally distributed. From the frequency distribution plots (Figure 4) we can determine the statistical distribution of sediment concentrations and, with this information the basin mean concentrations and SD. For the normally distributed components (Al, Cr, Fe, and P) these are calculated in the usual way. For the log-normally distributed components they are calculated from the logarithmic transformation of the sediment concentrations. The mean and values for -1 SD and +1 SD are given in Table 4. For log-normal populations the levels ±1 SD are shown as antilogs to facilitate comparison with the normally distributed populations.

Comparisons of statistics in Tables 3 and 4 illustrates the change in the mean and the range (± 1 SD) when a log-normal analysis is applied. Copper, Mn, Ni, and Zn are log-normally distributed, and use of the appropriate statistical analysis gives a slightly lower basin mean and ± 1 SD range than do calculations intended for a normally distributed population. As shown by Koch and Link (30), the small CV associated with these parameters (Table 3) is consistent with the close agreement between the normal and log-normal statistical analyses.

Sediment nutrient concentrations, organic C and N, and sediment total C, on the other hand, show a much greater change in the mean and ± 1 SD range after a logarithmic transformation of the data. Although neither normally nor log-normally distributed, Pb also exhibits a marked change in mean and ± 1 SD range in a log-normal analysis.

For bottom sediments collected in the Genesee River watershed, and possibly in other basins tributary to the North American Great Lakes, either a normal or log-normal statistical analysis is appropriate for estimating the basin mean concentration and range of several sediment heavy metal components. In the case of Pb, total and organic C and N a log-normal statistical analysis is preferred. This may also be required for toxic substances, such as high-molecular-weight chlorinated hydrocarbons, which

TABLE 4. ESTIMATES OF MEAN CONCENTRATIONS OF NUTRIENTS AND METALS AND THE RANGE OF CONCENTRATIONS ENCOMPASSING ± 1 SD FOR BOTTOM SEDIMENT SAMPLES COLLECTED IN THE GENESEE RIVER WATERSHED

Element	Statistical Distribution	Concentration[a]				n
		Arithmetic Mean	Geometric Mean	Mean -1 SD	Mean +1 SD	
Al	Normal	6,660	*	4,040	9,280	100
Cr	Normal	14	*	5	23	78
Cu	Log-normal	*	17	12	25	82
Fe	Normal	15,060	*	7,750	22,400	100
Mn	Log-normal	*	385	250	590	100
Pb	Log-normal	*	25	12	56	99
Ni	Log-normal	*	20	12	32	98
Zn	Log-normal	*	60	35	102	99
Total C	Log-normal	*	1.530	0.692	3.380	99
Organic C	Log-normal	*	0.880	0.319	2.431	95
Total N	Log-normal	*	0.070	0.027	0.180	93
P	Normal	0.0560	*	0.0420	0.0700	99

[a] For metals, µg/g; for nutrients, %; both on a dry-weight basis.

*Statistic not determined.

are often associated with sediment organic materials. In the case of organic C, for example, the arithmetic mean is 40% greater than the geometric mean. Sediment Pb concentrations show an even more striking difference between the arithmetic and geometric means.

It is interesting to compare the estimates of the mean basin sediment concentrations shown in Table 4 with the bottom sediment analyses for samples collected at the Wellsville station on March 13, 1976 (Appendix A 1) Sample 53, which probably reflects freshly deposited uncontaminated sediment from the southernmost area of the basin, has concentrations of heavy metals (Cu, Ni, and Zn) and major nutrients 1 SD <u>below</u> the basin means. Sample 52, which appears to be contaminated by waste effluents, has concentrations of heavy metals (Cu, Mn, Ni, Pb, and Zn) and major nutrients 1 SD <u>above</u> the basin means.

While the basin means and ± 1 SD ranges for groups of components can be used to identify background and contaminated sediments, the occurrence of a single component concentration beyond this range is not statistically unlikely. As seen in the Wellsville samples, background and contaminated sediments typically have concentrations of several heavy metals and nutrients above + 1 SD. The likelihood of this occurring on a random basis is small.

Taken together, the sediment concentrations and their statistical distribution do not provide evidence of major pollution of this watershed by heavy metals.

The relationships among sediment constituents at each station are illustrated in Figure 6 with sediment elemental concentrations plotted as deviations from basin means in terms of each element's standard deviation (data from Tables 3 and 4). Arithmetic data were used to plot normally distributed components; log-transformed data were employed for log-normally distributed components. In the uncontaminated sample from the Wellsville station (#53) concentrations are at or below basin means. In particular, the nutrients (organic C, N, and P) are 1 SD below the basin mean. The same pattern (each metal at the basin mean and each nutrient approximately 1 SD below it) is apparent for other sampling points on the Genesee River. However, the contaminated sediment at Wellsville (#52) shows an entirely different pattern, with nutrient and heavy metal concentraions well above the basin means.

Interpretation --

Variations in nutrient and metal concentrations of fluvial sediment are due to basin geology, surface erosion, riverbank erosion, industrial or other cultural contamination, the presence of minerals rich in trace elements (e.g. chromite), sediment ion-exchange capacity, sediment organic content, and the presence of metallic oxides.

The mean sediment metal concentrations of the Genesee watershed are compared in Table 5 with an average shale composition (31) and with a typical lacustrine sediment containing carbonates (32). Differences between the shale and lake sediment are due to a dilution effect from carbonate

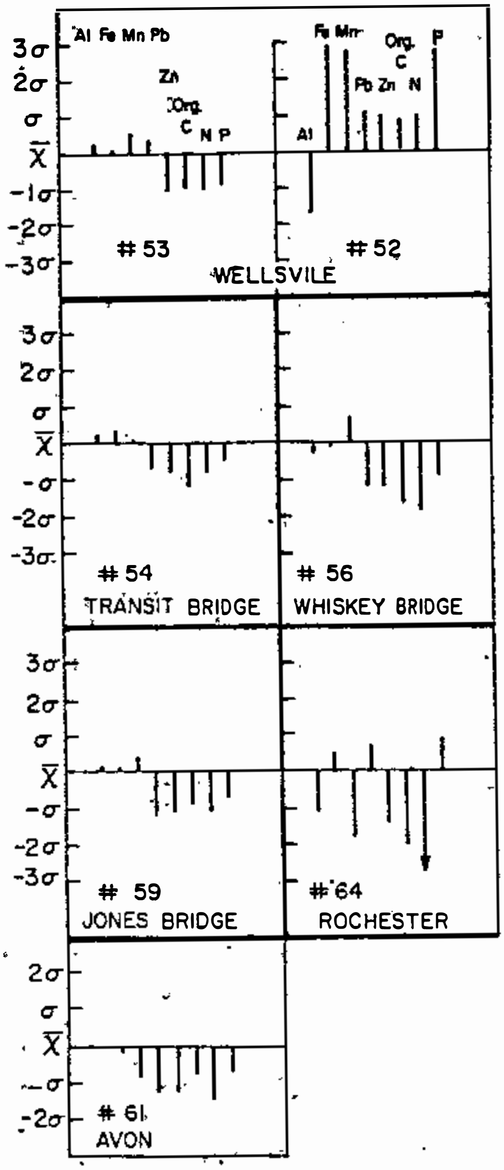


Figure 6. Bottom sediment elemental concentration plotted as deviations from basin means in terms of each elements standard deviation.

minerals which have a lower heavy metal content than shale. This dilution is greatest for iron and somewhat less for nickel, chromium zinc, and manganese (Förstner, 1977). Approximately this sequence is seen in the Genesee watershed sediments. In the Genesee Basin sediment metal concentration may be diluted by non-reactive rock components such as silica.

TABLE 5. MEAN METAL CONCENTRATIONS (μg/g) IN GENESEE RIVER WATERSHED SEDIMENT, AVERAGE SHALE COMPOSITION, AND TYPICAL LAKE SEDIMENTS RICH IN Ca-Mg CARBONATES

Metal	Genesee River watershed sediment	Shale[a]	Lake Sediment rich in Ca-Mg carbonates[b]
Iron	15,060	46,700	16,900
Manganese	424	850	475
Zinc	69	95	63
Chromium	14	90	42
Nickel	23	68	46
Copper	18	45	34
Lead	40	20	21

[a] 31

[b] 32

Elemental Ratios for Sediment

The atomic ratios of major and minor nutrients (C, N, P) in natural waters and sediments indicate the source and nature of nutrient inputs and the suitability of a sediment for biological transformation as a source of nutrients for primary productivity (33).

In the sediments of the Genesee River and two of its major tributaries, Oatka and Canasarega Creeks, the atomic ratios for organic carbon, total phosphorus and for minor nutrients (total extractable iron, manganese and zinc) were determined for two moderate flow periods. The sampling periods precede and follow the snowmelt runoff during 1976. The atomic ratios for organic carbon, nitrogen and phosphorus are 54:5:1 and 54:3:1 for bottom sediments (15 Dec. 75, 15 Mar. 76, averages of 6 and 19 replicate analyses respectively) 79:9:1 and 53:5:1 for suspended sediment for the same dates (N=5 and N=10 respectively). For iron, manganese and zinc the ratios are 278:9:1 and 511:9:1 for bottom sediment (15 Dec. 75, N=10; and 15 Mar 76, N=28 respectively) 333:8:1 and 388:9:1 for suspended sediments (same dates, N=4 or N=13 respectively).

The ratios are in agreement for the two sampling periods. This suggests that the ratios which were here determined for the river and largest streams in the basin, reflect long term trends in basin development and utilization. The Genesee River and Oatka Creek sediments contain an excess of phosphorus compared to a balanced nutrient input (33). However, apparent excess phosphorus may not be available for biological uptake because of its chemical form.

Organic Carbon to Nitrogen Ratio in Sediments

Wetzel (34) has suggested, for dissolved constituents in lakes, that a high ratio of organic carbon and total nitrogen indicates allochthonous input of low nitrogen carbonaceous material into a watershed.

Genesee River sediments collected on March 15, 1976 showed a C/N ratio related to the organic carbon content by the expression

$$C/N = aC + b \qquad (1)$$

where C/N is the organic carbon to nitrogen atomic ratio, C the sediment organic carbon content in mg/g and a and b are constants. The expression is based on seven samples from five sampling sites on a 100 mile section of the river between Wellsville and Avon, N.Y. An eighth sample collected at Wellsville, N.Y. at the same time did not follow this relationahip and may have been contaminated by a nearby sewage treatment plant outfall. In the equation a = 1.51 with a standard error of 4.68 and the correlation coefficient for the least squares line was r = 0.59.

Equation one indicates that the relation between C:N ratio and organic carbon content of dissolved constituents in lakes may also apply to river and stream sediments. Scatter associated with the data may be due to inputs of high nitrogen organic material from municipal and agricultural wastes and to nitrogen losses from sediments by denitrification (35, 36). For comparison we analyzed sediment-like substances with high and low nitrogen contents, commercial peat (low nitrogen) and Milorganite, a high organic nitrogen fertilizer manufactured from Milwaukee sewage sludge, with waste pickling liquid added to precipitate phosphates. The peat had C = 216.98 mg C/gm and C/N = 108 while the Milorganite had C = 375.91 mg C/gm and C/N = 6.2. While these limiting cases do not follow the relationship obtained for the Genesee River sediments, they do illustrate the range of C/N values which might be encountered in areas of point or non-point source pollution. The carbon-nitrogen ratios for these limiting cases are also well outside the range cited by Wetzel (1975): allochthonous organic matter C:N = 50:1; autochthonous organic matter C:N = 12.1.

Organic Carbon to Phosphorus Ratio in Sediments

The sediments from the Genesee River which showed a linear relationship between C/N ratio and the organic carbon content of the sediment also show a linear relationship between sediment organic carbon content and the carbon to phosphorus atomic ratio.

$$C/P = aC + b \qquad (2)$$

where C/P is the carbon to phosphorus atomic ratio, C is the organic carbon content of the sediment in mg/g and a and b are constants. The values for the constants obtained by a least squares best fit procedure for the seven data points were: a = 4.72 with a standard error of 0.39; b = 2.0 with a standard error of 1.72 and the correlation coefficient, r = 0.98. As for the C:N ratio, an eighth sediment sample appeared to be contaminated by sewage and did not follow equation 2.

LOCAL VARIATIONS IN SEDIMENT AND WATER COLUMN CONCENTRATIONS

The major sources of fluvial sediment in North American streams and rivers are: agricultural runoff, stream bank erosion and urban runoff. The annual suspended load of the Maumee River, Ohio, U.S.A. has been reported to be largely surficial in origin. Stall (37) reported that most fluvial sediment in the U.S.A. originated from agricultural land.

Superimposed upon the sediment constitutents derived from erosion are nutrients and metals from point source input.

To identify point source inputs to river sediments it is useful to have an estimate of sediment homogeniety at each sampling site. For this purpose, replicate samples were collected at each site. Replicate samples collected at different locations at each site were generally in good agreement for all parameters. Agreement between replicates was excellent at Transit Bridge, at Whiskey Bridge, and at Jones Bridge. Replicate results for metal concentrations were in satisfactory agreement at Rochester and, to a greater extent, at Avon. Nutrient concentrations at each of these two sites fluctuated, however, suggesting that wastewater inputs to the lower reach of the river do not distribute uniformly within the sediments.

A pronounced example of the input of wastewater effluents on fluvial sediment composition is seen at Wellsville, where sediments show large fluctuations in all metals and nutrients (Figure 6). Evidently two types of sediments are present in the channel but are not mixing to form a uniform material having some intermediate or average composition. One sediment type (samples 49, 51, 53) is characteristic of uncontaminated basin mineral sediments, while the other appear to be relatively contaminated by organic material from domestic wastewater discharges.

Sediment sample 53 was collected 200 m upstream of the Wellsville Bridge sampling site on a shoal recently formed in the main channel of the river. The composition of this sample reflects uncontaminated river sediments deposited during the spring runoff. Samples 50 and 52, obtained at the bridge in the eastern half of the channel, have the high organic carbon concentrations characteristic of sediments contaminated by sewage effluents. The remaining samples, collected in the western section of the channel (in the vicinity of the bridge) or upstream show little evidence of contamination.

The uncontaminated sediments are characterized by high concentrations of extractable Al and low concentrations of heavy metals and nutrients, while the contaminated ones are low in Al and high in Fe, heavy metals, and nutrients.

In general, as shown for total analysis (Appendix A 1) there is little evidence of pronounced contamination of river-bed materials.

As shown in the total analysis, specific sampling sites such as Wellsville, N.Y. appear to have some contaminated sediments in the channel. Two samples collected at Wellsville on 13 March 1976 (Appendix A 3) which show elevated total nutrient and metal concentrations are the only samples showing significant amounts of hydroxylamine hydrochloride extractable lead and copper. The accumulation of these extractable metals in the sediments may arise in an area of active precipitation of manganese from the water column. This may occur near a sewage outfall. Elevated sediment manganese values indicate that sediment oxidation-reduction potentials were not sufficiently lowered by the presence of organic matter to solubilize the precipitated hydrous manganese oxides in the sediments.

Extraction of amorphous iron oxides by ammonium oxalate-oxalic acid reagent also shows two samples collected at Wellsville on March 13 have elevated levels of Cu and Zn. Indeed the extractable concentration of Cu and Zn from the iron oxides is nearly equal to that obtained by hydroxylamine. This result suggests that both iron and manganese hydrous oxides are involved in heavy metal accumulation by sediments. With the exception of sediment samples apparently contaminated by wastewater discharges at Wellsville, New York, transported sediments do not exhibit elevated levels of total or extractable metals. The phosphorus fractional analysis in large measure supports this conclusion (Appendix 1 B). The apparently contaminated sediments at Wellsville have the highest concentrations of NaOH extractable phosphorus and elevated phosphorus extracted from hydrous oxides. Thus sediment hydrous oxides are apparently involved in immobilization of sewage phosphorus inputs.

A comparison of sediment extractable major metals (aluminum, iron, and manganese) and extractable phosphorus shows that each of the metal oxides may be involved in phosphorus fixation. The exact chemical composition of the phosphorus-hydrous oxide compound formed under these circumstances is unknown.

Analyses of resuspended sediment samples do not exhibit the local variations seen in bottom sediment analyses. These samples uniformly exhibit higher levels of metals and nutrients than seen in bottom sediment samples. This is consistent with the higher specific surface exhibited by these samples. Resuspended sediment elemental concentrations show less variation over the length of the river than the bottom sediment samples. This observation is true at the Wellsville station as well, where as noted in the previous section, bottom sediment composition showed dramatic flucatuations.

Total phosphorus content of resuspended bottom sediment is 2 to 3 times greater than that of bottom materials at the same station. Metal contents are also higher by a similar factor.

Local variations are also seen in some water column concentrations, for example, elevated metal concentrations at Mount Morris, the mid-basin station (Appendix 2,C and D). High particulate metal level reflects the high suspended solids concentration at this site. In addition the data show a decrease in the downstream particulate metal concentrations suggesting that the elevated metal levels seen at Mount Morris do not lead to increased loadings to Lake Ontario.

Particulate iron concentrations are significantly higher than the measured total water column iron concentration for samples collected at the same station at the same time (Appendix 2,C and D). This difference arises because of a better release of particulate iron through a hot, concentrated acid digestion, rather than a mild pH adjustment. The improved analysis of particulate metals brought about by digestion may also hold true for water column phosphorus which may be associated with iron during transport.

For all metals, the total water concentration was calculated as the sum of the dissolved and particulate concentrations. Cadmium concentrations were also examined in this study and the dissolved, particulate and total concentrations were at or less than the analytical detection limit. Results of the calculation of percent metal carried by the particulate phase in the Genesee River are in Table 6 .
Fluctuations in the percent metal carried by the particulate phase reflect variations in the water column particulate concentration. Indeed, the highest percent metal carried by suspended sediment and the highest total water column metal concentrations do not occur at the river mouth (where flow is the highest) but at a station 60 miles downstream from Lake Ontario (Mt. Morris). This station is located below a large impoundment and increased suspended sediment loads may result from river bed erosion. The next sampling station, 30 miles closer to Lake Ontario (Avon), has the same flow as the Jones Br. station on the sampling date; however, the water column total concentrations and thus the total loads for both zinc and manganese decrease substantially between the two stations.

The data shown in Table 6 indicate that, for the period examined here, the predominant mode of metal transport in the Genesee River is via the particulate phase. It appears that the particulate load carried by a river, and its associated metal content, are influenced by factors other than flow. In the Genesee Basin for example, sediment downstream from the mouth of the river temporarily increases water column total concentrations and loads. However, the results indicate that this increases suspended sediment load is not stable in the river, settling out of the water column well before Rochester. Mid-basin elevated total metal concentrations thus do not contribute directly or indirectly to Lake Ontario loading.

TABLE 6. PERCENTAGE OF TOTAL METAL CONCENTRATION TRANSPORTED BY PARTICULATE MATERIAL IN GENESEE RIVER WATER AT SIX SAMPLING STATIONS, DECEMBER 14, 1975

Station	Al	Cu	Fe	Mn	Pb	Zn
Wellsville	--	93	77	40	---	30
Transit Br.	79	66	98	58	94	60
Portageville	96	80	97	73	82	61
Mount Morris	96	84	99	79	82	66
Avon	--	69	75	44	78	53
Rochester	100	40	95	52	77	40

BOTTOM SEDIMENT ANALYTICAL RESULTS COMPARED WITH OTHER PUBLISHED DATA FOR THE GENESEE RIVER

Total Analysis

Total sediment content for a number of elements has been determined for samples obtained from 25 stations throughout the watershed over the seasons of the year. The ranges were: aluminum, 2,8000 - 11,000 µg/g; chromium, 10 - 79 µg/g; copper, 11-41 µg/g; iron, 2,350-26,000 µg/g; manganese, 180-1,035 µg/g; nickel, 10-87 µg/g; lead, 10-320 µg/g; zinc, 35-210 µg/g; total carbon, 0.31-8.26%; organic carbon, 0.09-5.69%, total nitrogen, 0.011-0.63% and total phosphorus, 0.033-0.096%. Total sediment concentration ranges can be compared with data obtained by the U.S.E.P.A. for analysis of sediments collected in Lake Ontario at the mouth of the Genesee River (12 sampling stations) from June 1972 to May 1973 (38). The ranges for selected results from this investigation were: copper, 6-50 µg/g; manganese, 25-800 µg/g; nickel, 10-450 µg/g; lead, 5-80 µg/g; zinc, 25-350; organic carbon, 0.10-3%, total nitrogen, 0.025-0.26%; total phosphorus, 0.01-0.1%. The agreement between the watershed and lake sediments is generally satisfactory. Lower values in lake sediments for manganese may result from solubilization under reducing conditions. High values for zinc and nickel in the lake sediments reflect point source inputs adjacent to the lake. Larger ranges for lead, organic carbon and total nitrogen in the watershed sediments probably reflect local point and non-point input sources of these elements. Total phosphorus analytical ranges are quite similar for the fluvial and lacustrine sediments. Total sediment phosphorus content from a sample collected in the Genesee River on October 9, 1973 (8) of 825 µg P/g is consistent with phosphorus result range found in this study.

Fractional Analyses

The sediment contents extracted by selective reagents have been determined for bottom sediment samples from 25 stations within the watershed Ranges for phosphorus fractional analysis were: sodium hydroxide extractable phosphorus, 11-410 µg P/g; hydrochloric acid (following sodium hydroxide) extractable phosphorus, 187-731 µg P/g; hydroxylamine extractable phosphorus, 6-313 µg P/g; and ammonium oxalate (following hydroxylamine) extractable phosphorus, 71-405 µg P/g. Values reported for extractable phosphorus from sediments collected in the Genesee River on October 9, 1973 (8) are in agreement with the results of this study (sodium hydroxide extractable phosphorus 100 µg P/g and hydrochloric acid extractable (following sodium hydroxide and citrate-dithionite-bicarbonate extraction) phosphorus 328 µg P/g).

Fractional analysis of sediments from the Rochester Basin of Lake Ontario show significantly higher minimum extractable phosphorus fractions than bottom sediments from the Genesee River Watershed. The minimum NaOH extractable phosphorus content from sediments collected in the watershed was 11 µg P/g (N=30) while the minimum value for sediments collected in the Rochester Basin of Lake Ontario was 129 µg P/g (N=9). This difference between lake and river sediments reflects the general increase found in total phosphorus content of lake sediments with increasing water depth (39) and results from transport and deposition of fine-textured materials in low-energy areas of lakes. Suspended sediment in the Genesee River Watershed has a higher phosphorus content than bottom sediments indicating that phosphorus accumulates in the smaller size fraction components of basin sediments. Recent research has indicated the importance of phosphorus transport by suspended sediment (40, 41).

Bottom sediment iron and manganese fractional extraction analysis ranges were: hydroxylamine extractable iron, 33-150 µg/g; hydroxylamine extractable manganese, 41-385 µg/g; ammonium oxalate (following hydroxylamine) extractable iron, 800-5, 700 µg/g and ammonium oxalate (following hydroxylamine) extractable manganese 15-133 µg/g. These results can be compared with the range of values for 10 lake sediment samples from the central and western U.S.A. (extractable iron, 3,700-11,800 µg/g; extractable manganese, 120-660 µg/g (42). For these lake sediments both oxides of iron and manganese were dissolved with a strong reducing agent, sodium dithionite, and the ranges were slightly higher than the results for the Genesee River Watershed sediments. Higher lake sediment extractable metal values than those for Genesee River Watershed sediments are due to differences in sample types and analytical procedure. A comparison of manganese extraction from stream sediments using two different methods, a dithionite procedure and a hydroxylamine procedure, showed that the dithionite extracts 10% to 20% more of the total manganese present in a sediment (43).

PHOSPHORUS IN THE GENESEE WATERSHED

Understanding the fate of phosphorus in a watershed is critical to the development of strategies to cope effectively with eutophication (44). Sediment-bound phosphorus is contributed by sewage, eroded soil, plant material, and urban runoff. These solids are transported as suspended sediment and as bedload. Transport of phosphorus associated with larger particle size sediment occurs only during periods of high river discharge. Soluble phosphorus entering a watershed in runoff or wastewater, on the other hand, is apparently sorbed on suspended particles and/or reacts with other water column constitutents to form insoluble substances which are transported by water and eventually deposited in fine grained sediment. In lakes, soluble phosphorus is typically converted to biomass, recycled through the water column, and eventually deposited in bottom sediments. Establishment of realistic and successful strategies for controlling phosphorus inputs to the North American Great Lakes requires that periods of intense hydrological activity in a basin be carefully studied and characterized.

Chemical reactions influencing phosphate distribution in the Genesee River were identified using three separate techniques: (1) as discussed in previous sections sediment samples collected during synoptic surveys were analyzed using a variety of selective phoshorus extraction procedures to differentiate the physical and chemical state of sediment phosphorus; (2) water column chemical concentrations from samples obtained concurrently with the sediment samples were used to calculate equilibria for the determination of ion activity products of several mineral phases which may remove phosphorus from the water column; and (3) a crystallization procedure with seeding was used to monitor the distribution of inorganic phosphate between solution and solid phases during calcite precipitation in simulated natural water.

Phosphorus Distribution

The major sediment phosphorus fraction is that extracted by hydrochloric acid. This extraction, which is preceded by a sodium hydroxide extraction, yields occluded phosphorus incorporated in hydrous metal oxides, carbonate and phosphate minerals. Phosphorus extracted from sediments by NaOH has been related to surface-exchangeable or bioavailable phosphorus (19) (Table 7).

Ammonium oxalate-oxalic acid solution extracts somewhat less phosphorus than hydrochloric acid, while sodium hydroxide as well as hydroxylamine reagents extract much less. Hydrous oxides of iron and aluminum are extracted by the oxalate reagent. An extraction procedure which specifically removes hydrous manganese oxides (hydroxylamine hydrochloride plus nitric acid) preceded the oxalate extraction. Total extractable sediment phosphorus includes the organic sediment phosphorus in addition to the inorganic portions determined by the selective extraction analyses.

The absolute amounts and classes are related to the sediment particle size and surface area (M. Reddy, unpublished data). The variation in total extractable sediment phosphorus concentration among the three sediment types is shown in Table 7 is clear. A statistical analysis of these data shows that both the suspended sediment and particulate total phosphorus concentrations are greater than the bottom sediment value at the 99% confidence level. Phosphorus content increases in the sequence; bottom sediment, suspended sediment, and particulate material in correlation with the increase in the surface area of the sediment (M. [illegible]y, unpublished results). High surface

TABLE 7. STATISTICS FOR PHOSPHORUS ANALYSES FOR SEVERAL SEDIMENT TYPES COLLECTED IN THE GENESEE RIVER WATERSHED, NEW YORK, (μg/g)

Sample	$\bar{x}$	Range	σ	CV	N
Bottom Sediment					
Total Analysis	560	330 - 980	140	0.25	99
NaOH Extractable	58	5 - 410	62	1.07	98
HCl Extractable	398	177 - 731	99	0.25	98
NH_2OH Extractable	74	6 - 313	63	0.86	98
$(NH_4)_2C_2O_4$ Extractable	184	49 - 453	93	0.50	83
Suspended Sediment					
Total Analysis	770	390 - 2020	360	0.46	46
NaOH Extractable	163	19 - 1000	232	1.43	17
HCl Extractable	528	258 - 664	109	0.21	17
NH_2OH Extractable	70	3 - 385	102	1.46	17
$(NH_4)_2C_2O_4$ Extractable	474	119 - 1110	222	0.47	17
Particulate Analysis					
Total Analysis	910	400 - 3000	640	0.70	61

area sediment components may adsorb phosphorus-containing substances from the water column, increasing their phosphorus content; other possible explanations include dilution of bottom sediment by inert material such as sand.

Phosphorus Transport

Sediments are recognized as a major transport medium for phosphorus to the North American Great Lakes. Phosphorus transport in watersheds such as the Genesee occurs in large part during rainfall and snowmelt discharge events. The transport of elements from a watershed can be expresses as unit load. This quantity is defined as the amount of material carried by a river at a given point divided by the area drained by the river above that point. For the synoptic studies described here the unit loads are expressed as grams of phosphorus per second per acre (Figure 7). The major component of the phosphorus load transported by the Genesee River during the two sampling periods discussed here (December 14, 1975 and March 13, 1976) is that associated with the suspended sediment. Dissolved phosphorus in the water column during these periods was typically less than half of the total water column concentration.

Unit loads varied widely (Figure 7). A flood control impoundment, located just upstream of the Mount Morris sampling station markedly influences the Genesee River discharge and suspended sediment concentrations at the downstream stations. Three sampling stations upstream of the Mount Morris impoundment (Wellsville, Transit Br., and Portageville) show a smooth and systematic increase in the phosphorus unit load going downstream. In contrast, unit loads at the mid-basin sites show much larger absolute values and fluctuations than the other stations. These stations exhibit large variations in discharge and therefore in suspended sediment concentrations.

Equilibrium Calculation of Mineral Saturation in the Genesee River

The importance of heterogeneous equilibria in regulating dissolved inorganic phosphorus concentrations in the Genesee River was examined by calculating the ion activity products of several mineral phases using the WATEQF (45) chemical model and/or mass action and mass balance equations with a small laboratory computer. During high discharge periods in December and March there is extensive undersaturation in the water column with respect to calcium carbonate and phosphate phases, while during August 1976, a relatively lower flow period, the first four downstream sampling stations in the Genesee showed saturation or supersaturation with respect to calcite (Figure 8). Thus during the summer it appears that in the lower reach of the Genesee River, sediment surface calcium carbonate is stable.

Saturation levels for the stable calcium phosphate mineral, hydroxyapatite are 10^{10} below the equilibrium values for the Genesee River stations during the high flow sampling periods of December and March. Fertilizer applied to calcareous soils produces minerals such as hydroxyapatite (46). When such soils are eroded, and subsequently carried to the Genesee River, this mineral phase will be in a markedly subsaturated solution and will tend

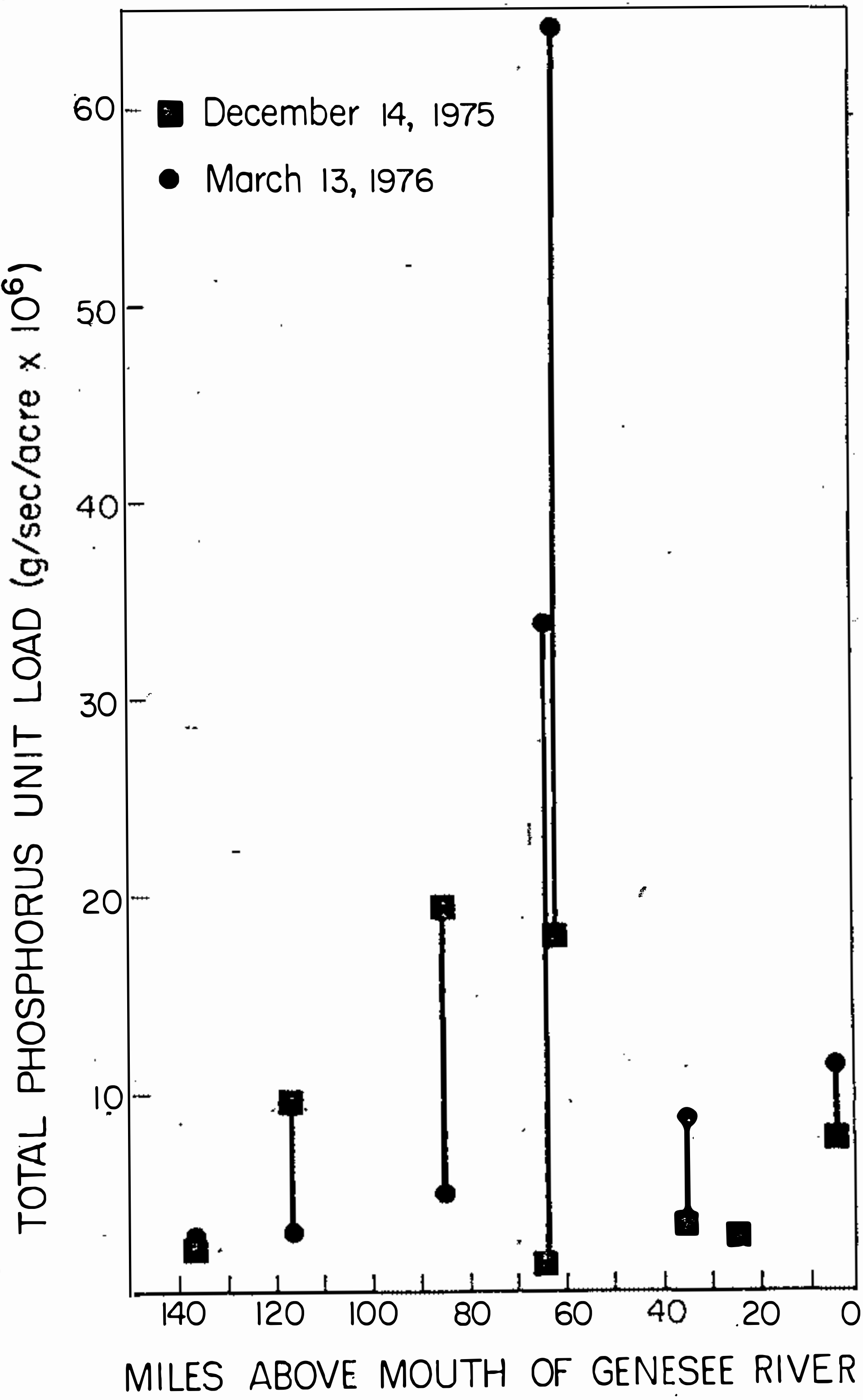


Figure 7. Total phosphorus instantaneous unit load, percent load as dissolved phosphorus, and discharge for six stations on the Genesee River.

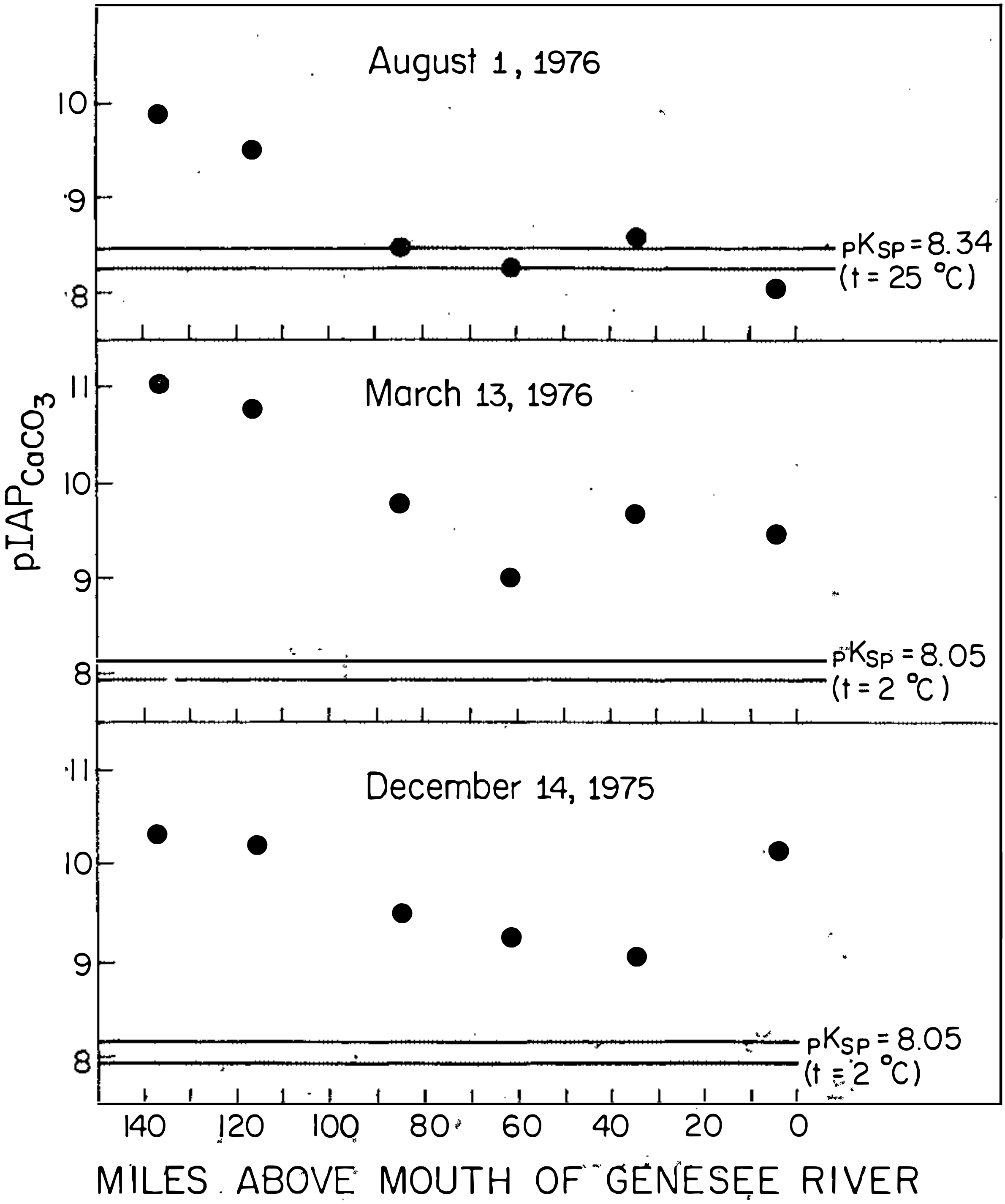


Figure 8. Ion activity product of calcite plotted as a function of sampling point distance from Lake Ontario.

to dissolve releasing inorganic phosphate ion to the water column. Release of phosphorus from agriculturally derived soils and sediments during high discharge periods may be counteracted by runoff dilution. Data reported by the U.S.G.S. for the St. Lawrence and Lake Ontario basins, for the period considered here shows phosphorus concentration in rainwater to be 0.010 mg P/l (47). This concentration is much less than the soil water phosphorus concentration. Base flow Genesee River dissolved inorganic phosphorus concentrations are 0.004 mg P/l, while peak flow values are approximately 0.011 mg P/l. Since recent evidence (48) indicates that less than 25% of rain water phosphorus is dissolved inorganic phosphorus, these results support the suggestion that some form of solid dissolution is involved in the regulation of the water column phosphorus concentration. During summer low flow periods calcium carbonate in sediments may serve as a sink for dissolved phosphorus.

Dissolved metals other than calcium have a minor effect on the distribution of phosphorus between the water column and sediment in this fluvial system. The two principal metals of interest, iron and aluminum, are present in Genesee River water almost entirely in the particulate phase (49). Dissolved concentrations are below the detection limit (less than 50 ug/l). Iron and aluminum minimum detectable concentrations were used to estimate thesaturation levels of the corresponding phosphate minerals. Both iron and aluminum phosphate minerals are substantially below saturation levels. The solid surfaces exhibited by iron and aluminum hydrous oxides (as particulate material in the water column) undoubtedly serve as sites for phosphorus adsorption and incorporation in the fluvial system. Data presented for the oxalate extraction procedure in Table 7 demonstrate the importance of phosphorus binding by hydrous metal oxides.

Nriagu (50) has proposed that basic metal phosphates are important sinks for heavy metals in the environment. In most natural waters of New York State dissolved basic metals including Pb, Cu, and Zn are at low concentrations (below 10 ug/l), and therefore these metals would not be expected to be a major factor governing phosphorus distribution.

Phosphate Distribution During Calcite Crystallization

The crystallization rate data illustrated in Figure 9 follow a rate equation

$$dN / dt = -ksN^2 \qquad (1)$$

where N is calcium carbonate (in mol/l) at time t to be precipitated from solution before equilibrium is attained; k is the crystal growth rate constant; and s is the seed crystal concentration, which is proportional to the surface area available for growth. Examination of calcite growth rate data is facilitated by presentation in the integrated form of Equation 1

$$N^{-1} - N_o^{-1} = k \cdot s \cdot t \qquad (2)$$

where N_o is calcium carbonate to be precipitated from the supersaturated solution at zero time. The linear plot of $N^{-1} - N_o^{-1}$ as a function of time (Figure 10) confirms the validity of Eq. 2 for the interpretation of the

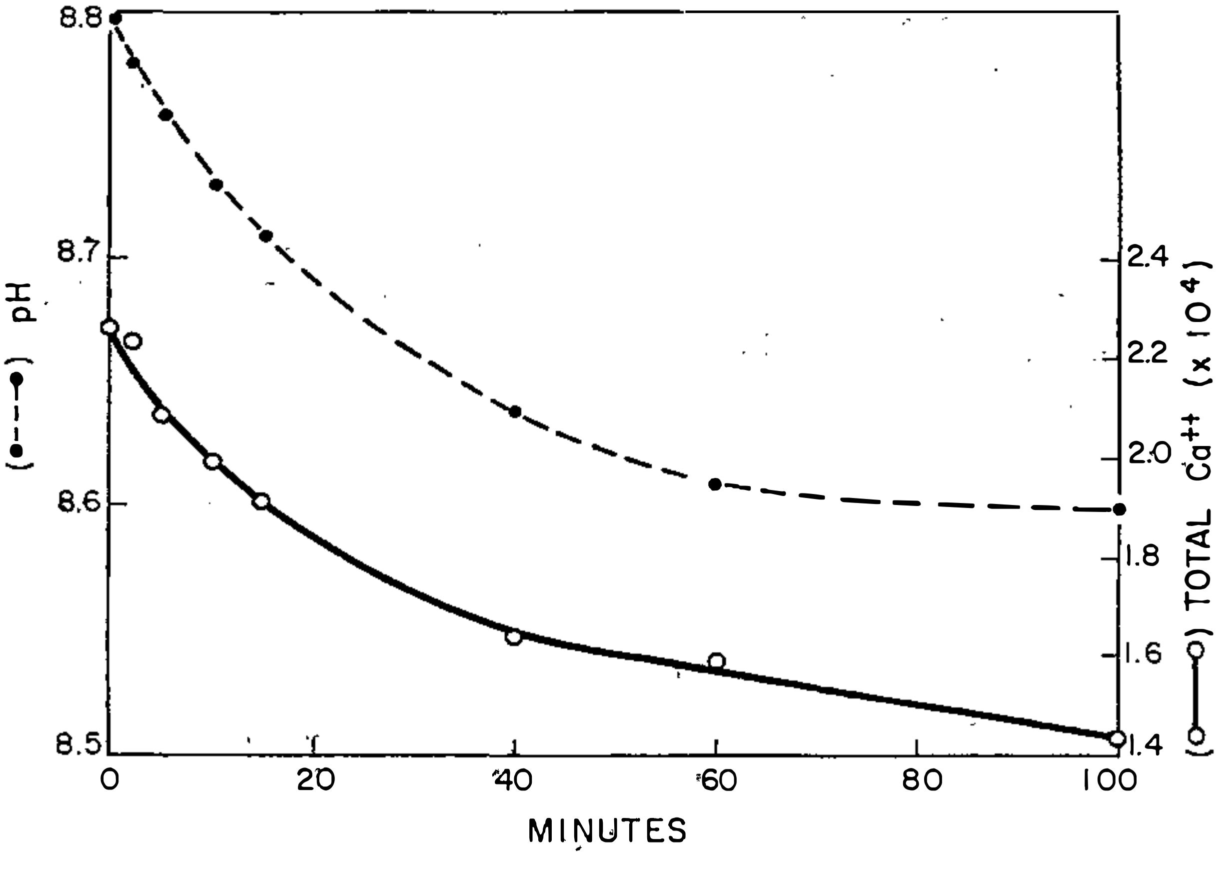


Figure 9. Plots of solution total calcium concentration and pH as a function of time for a typical calcite seeded crystallization experiment in simulated natural water.

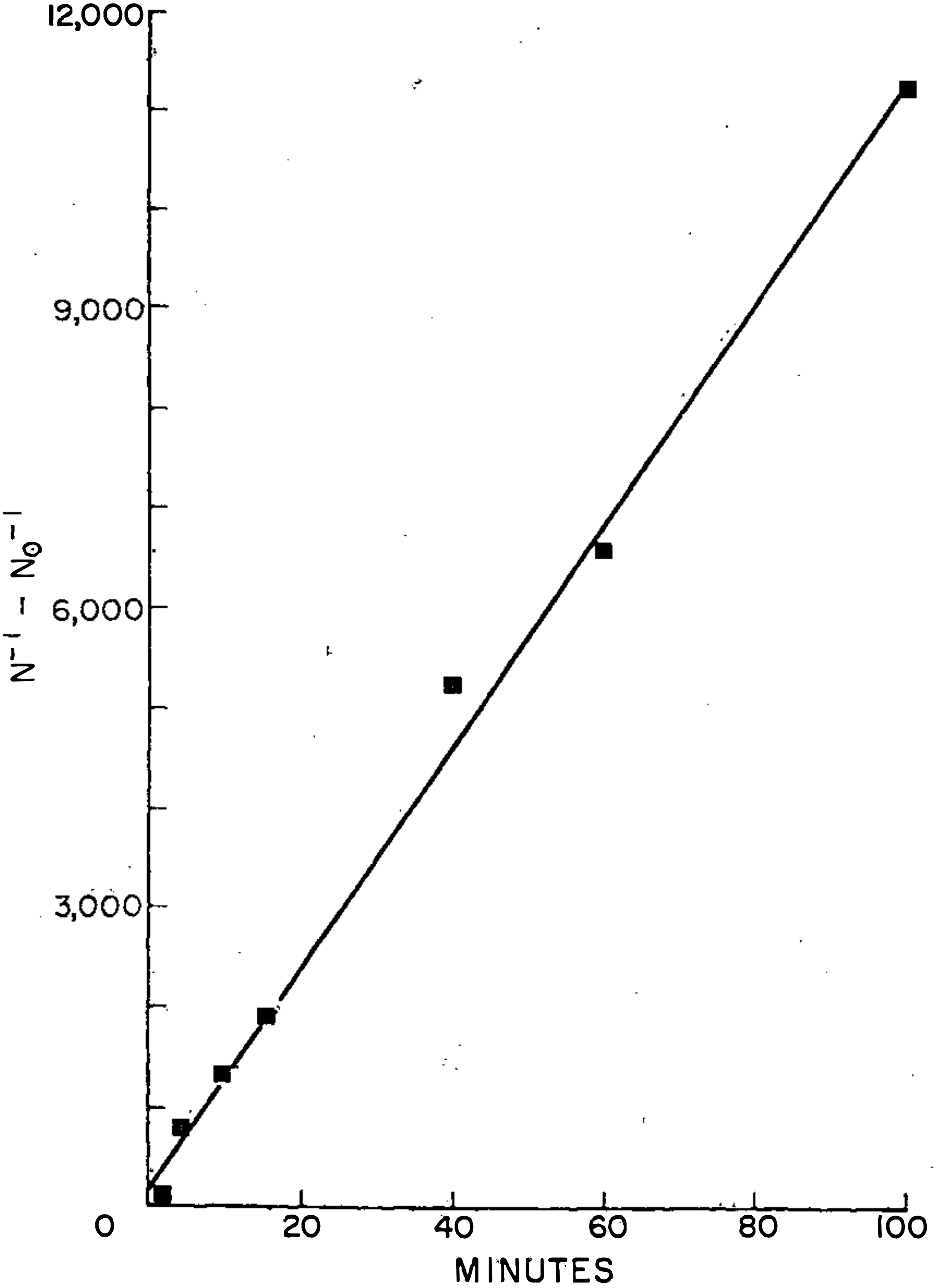


Figure 10. Calcite crystallization rate function $N^{-1}-N_0^{-1}$ versus time for data shown in Figure 9.

experimental results. The inhibition of crystallization by phosphate is marked (Figure 11) and appears to be due to simple adsorption of the ions at growth sites on the crystal surface. This is demonstrated by plotting the rate constants, in the presence and absence of phosphate, in a form corresponding to a simple Langmuir-type adsorption (51)

$$k_o / (k_o - k) = 1 + k_2 / k_1 \cdot \text{phosphate} \qquad (3)$$

where k_o is the crystal growth rate constant in the absence of phosphate ion and k_1 and k_2 are the adsorption and desorption rate constants for these ions, respectively. In Figure 12, $k_o / (k_o - k)$ is plotted against the reciprocal of the phosphate concentration. The linear relation with an intercept of unity indicates that the Langmuir isotherm satisfactorily describes the marked inhibitory effect of phosphate in terms of a monomolecular blocking layer of these ions at the growth sites on the crystal surface. There is not evidence for the formation of a second phase on the surface of the calcite seed even though these solutions are supersaturated with respect to the thermodynamically stable calcium phosphate phase, hydroxyapatite. This can be clearly seen in Figure 13 which shows solution phosphate concentration during a series of calcite crystallization experiments. In experiments with low phosphate concentrations (less than 10^{-5} m), extended reaction times (1 day) yielded significant reductions in solution phase phosphate concentration (10 to 20% removal). These long-term phosphate changes showed little systematic behavior and may be related to the surface nucleation of solid calcium phosphate.

Conclusions Relative to Phosphate Distribution in Alkaline Natural Waters

Selective extractions, chemical equilibrium calculations, and crystallization measurements presented here suggest that the hydrous iron oxides, even in the carbonate-dominated Genesee River, play a major part in inorganic phosphorus transport by sediments in the fluvial system. Saturation levels of inorganic phosphate and calcium carbonate minerals in the Genesee River indicate that phosphate mineral dissolution, and not precipitation, may be the predominant heterogeneous reaction during periods of high discharge. Elevated discharge and sediment transport occur primarily in March through May. Phosphate mineral dissolution occurring during fluvial transport then has an immediate impact on Lake Ontario. Dissolution of phosphorus-containing minerals transforms sediment phosphorus from a biologically unavailable form to a form that is readily incorporated by microorganisms in the lake. Evidence of the relationship between lake water phosphorus contents and algal productivity is the correlation of spring phosphorus values with summer chlorophyll concentrations (52).

In the lower reaches of the Genesee River, the results of the extractions suggest that substances other than hydrous oxides are phosphorus sinks. This is evident where the amount of sediment phosphorus extracted by hydrochloric acid steadily increases downriver, while the oxalate-extractable phosphorus remains relatively constant. Schwertmann (6) emphasized that the results of such procedures are best considered as a measure of an element's reactivity in a sediment under carefully controlled

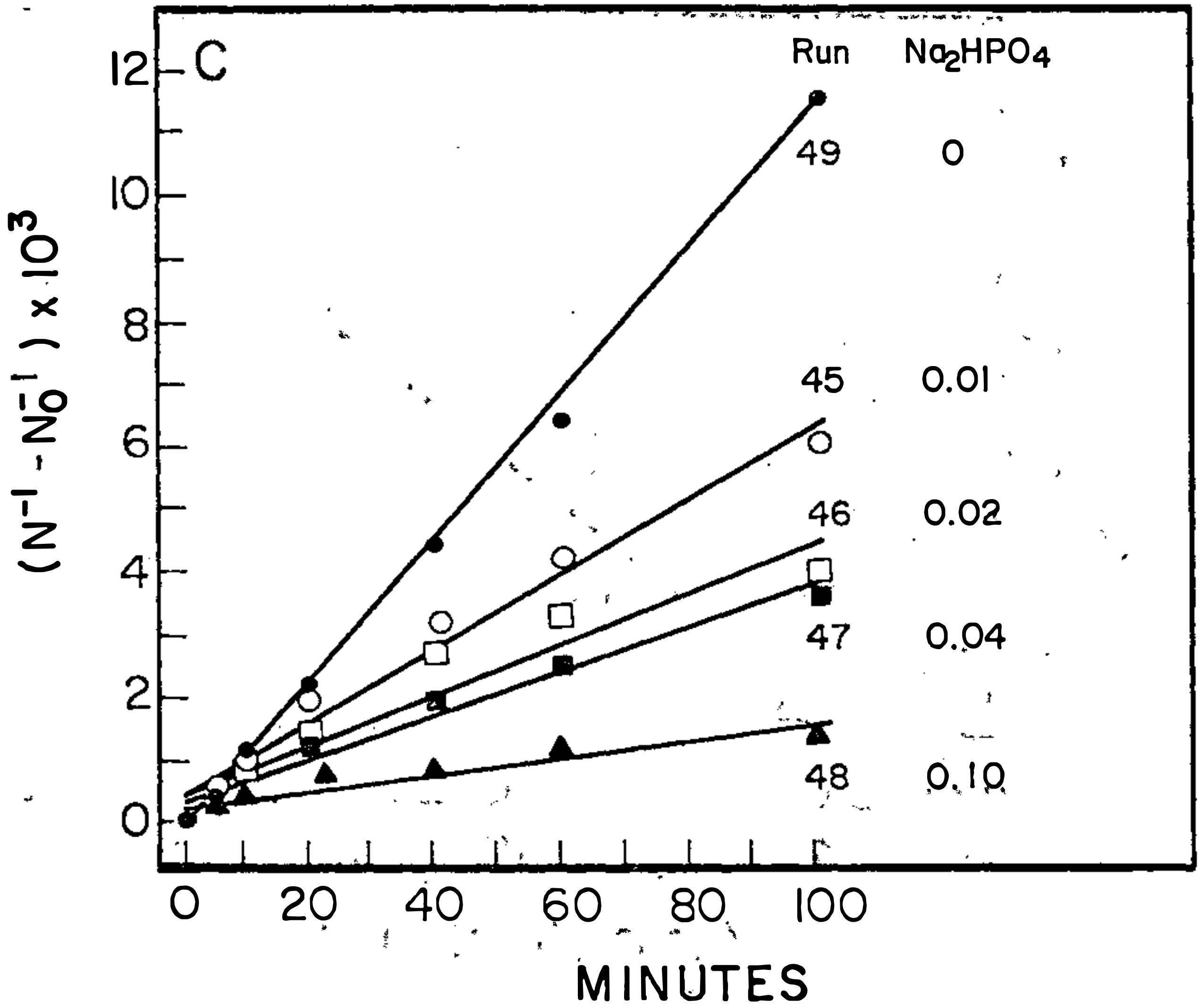


Figure 11. Calcite crystal growth in the presence and absence of phosphate ion, as expressed by the rate function $N^{-1}-N_0^{-1}$ versus time. The symbols and the numbers beside the curves indicate phosphate concentration multiplied by 10^4. Adapted, by permission, from the J. Crystal Growth 41 (1977) p. 294.

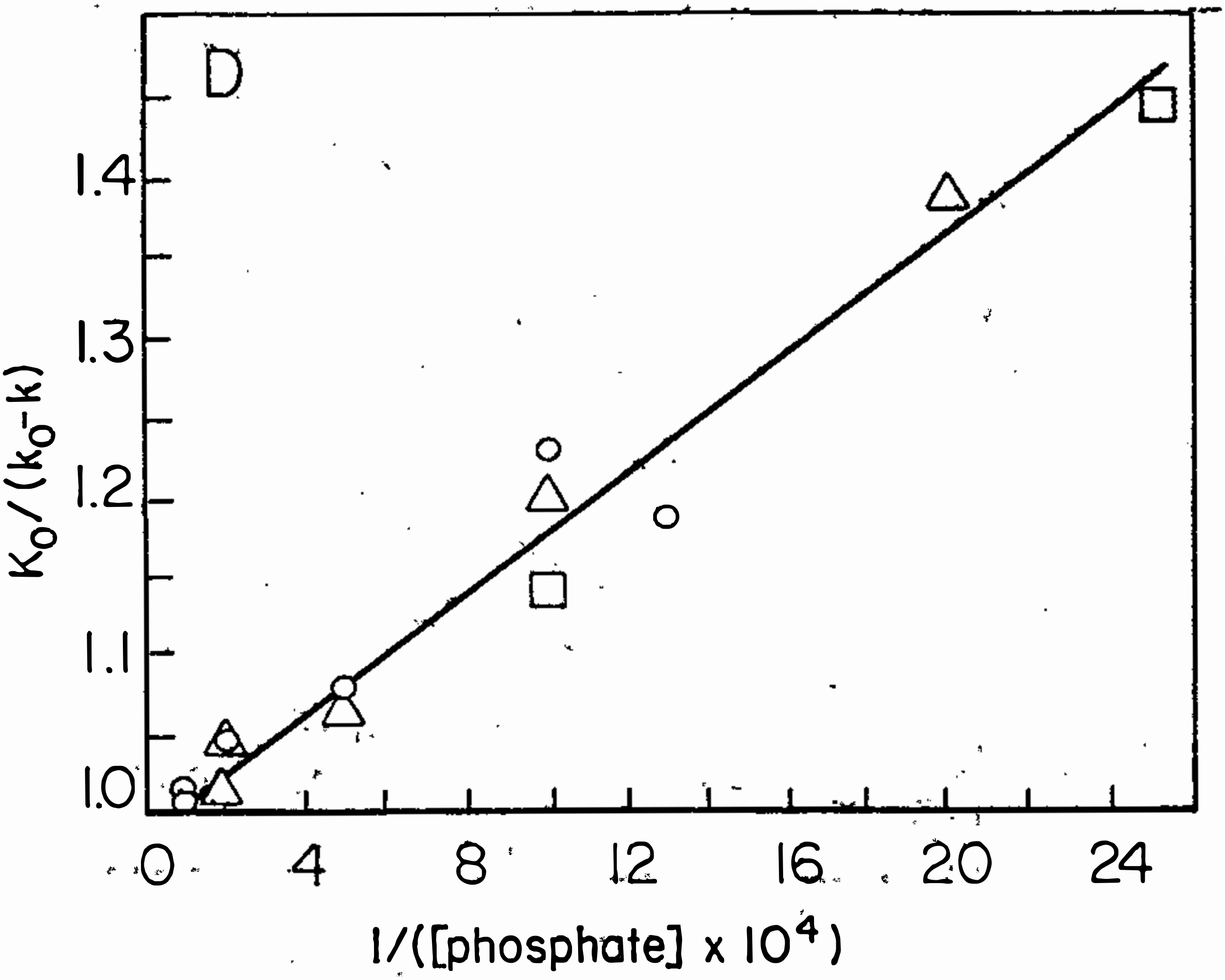


Figure 12: Langmuir isotherm plot of $k_0/(k_0 - k)$ against the reciprocal of the phosphate concentration, where k_0 is the calcite growth rate constant in the absence of phosphate and k is the rate constant in the presence of phosphate: (○) $k_0 = 0.824$; (□) $k_0 = 1.205$; (▲) $k_0 = 0.790$. Adapted, by permission, from the J. Crystal Growth 41 (1977) p. 294.

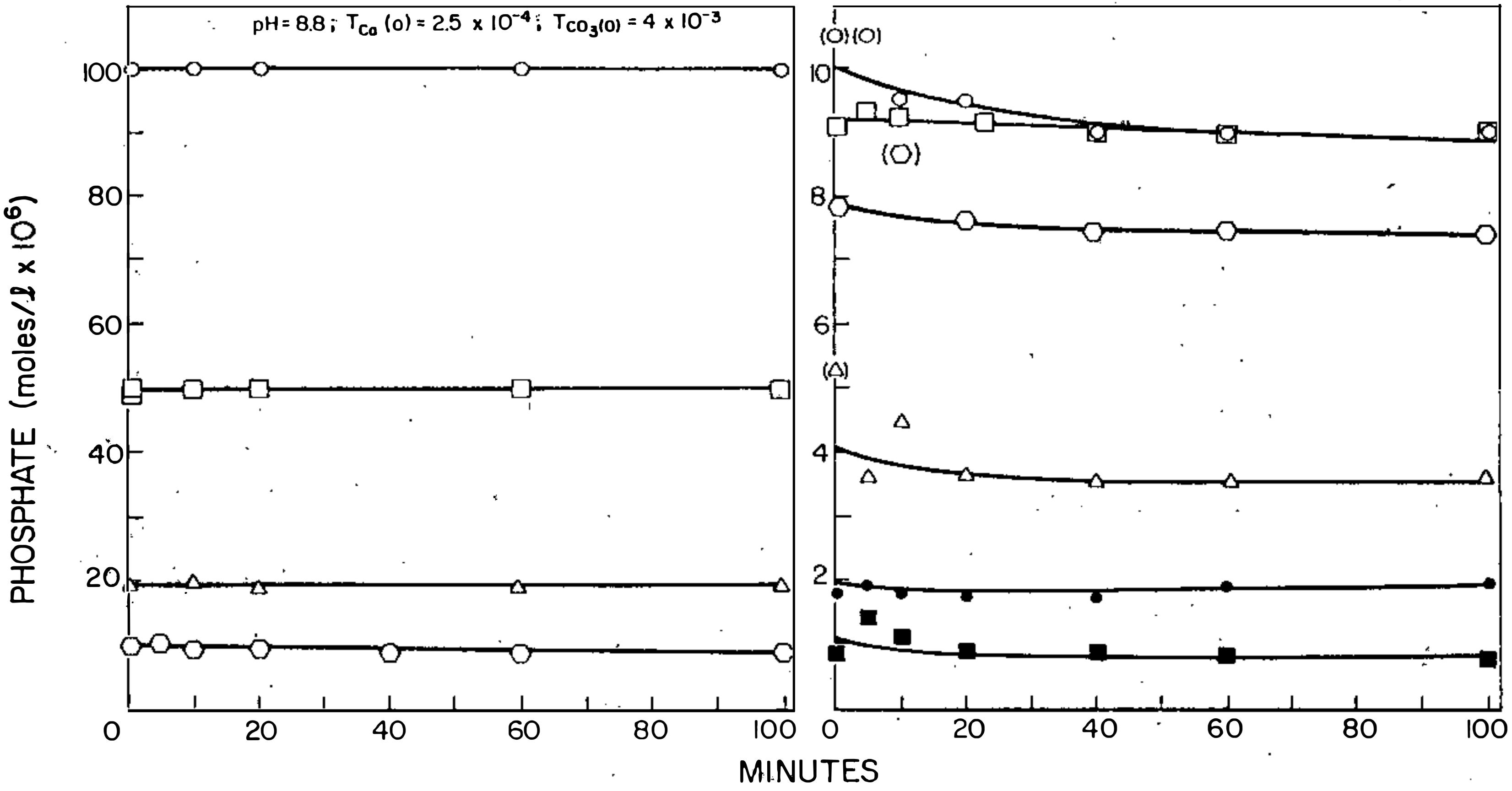


Figure 13. Phosphate concentration versus time for several calcite seeded growth experiments in the presence of phosphate ion.

conditions. Laboratory experiments (Figure 13) show that phosphorus uptake by calcium carbonate, under simulated natural conditions, proceeds slowly. The large hydrochloric acid-extractable component observed at Rochester may arise from slow uptake and subsequent mineralization of dissolved inorganic phosphorus by carbonate minerals.

From the selective extraction analysis of sediment, chemical equilibrium calculations, and seeded crystallization measurements, several conclusions can be reached concerning the behavior of phosphate in alkaline surface waters.

(1) Inorganic phosphorus in bottom sediment appears to reside primarily in association with surface hydrous oxide coatings of sediments. Hydrous metal oxides, in particular those of iron, transported as suspended sediment may scavenge phosphate from the water column in a fluvial system.

(2) Inorganic phosphorus incorporated with easily reducible hydrous manganese oxides is typically less than that found for the hydrous oxides of iron and aluminum.

(3) A fraction of the sediment-bound phosphorus exists in a form which is not extracted with the hydrous metal oxides, but is removed by treatment with dilute hydrochloric acid. This suggests the occurrence of phosphorus in carbonate minerals and/or the occurrence of phosphate minerals.

(4) Phosphorus transport in the Genesee River, expressed as instantaneous unit load of total water column phosphorus, shows moderate agreement for the stations reported here, with the exception of two mid-basin sites. These locations exhibit discharge dependent bottom sediment remobilization which leads to inappropriately high unit loading.

(5) During high discharge, many areas of the Genesee basin are subsaturated with respect to calcite, while during summer baseflow periods calcite saturation or supersaturation is widespread. Under these conditions calcite could mediate phosphorus mineral formation.

(6) A detailed examination of phosphate distribution between solution and solid phase during calcite crystallization in a simulated natural water shows that phosphorus adsorbs as a monolayer, causing slight changes in the solution phosphorus concentration. It appears that under the conditions examined in this study, calcite-mediated phosphorus mineralization has a role in the movement of phosphorus from the water column to sediments, although the extent and rates of the process in natural systems remain to be determined.

Differences in river basin morphology, soil characteristics, precipitation, and land-use in a watershed influence phosphorus transport in a fluvial system. However, the dominance of iron oxides as an inorganic phosphate sink, and the discharge-dependent behavior of calcium carbonate-phosphate minerals would be expected to exist in other calcareous agricultural regions of New York State as well. Mountainous terrain and areas of sand and muck soil would probably not exhibit the same behavior. It would seem that the results of this study could also apply to other agricultural watersheds adjacent to the North American Great Lakes.

SECTION 5

CONCLUSIONS

Metal and nutrient concentrations in the Genesee were typical for a non-polluted environment except for a moderate enrichment of phosphorus and a slight enrichment of lead. The phosphorus enrichment in the sediment arises both from agricultural activities and agricultural and municipal wastes. Lead enrichment, in the predominantly non-urban setting, may be due to a diffuse atmospheric input.

GENESEE RIVER WATERSHED SEDIMENT COMPOSITION

Sediment Phosphorus

Enrichment of Genesee River watershed sediments with phosphorus is attributable to man's activities in the basin. The major components of the culturally derived phosphorus enriched sediment are: eroded fertilized agricultural soils and, agricultural and domestic wastes. Wastes contain both soluble and particulate phosphorus. Dissolved phosphorus in a stream or river may adsorb reversibly to suspended sediment. Adsorbed sediment phosphorus is highly bioavailable, but if it is not utilized it will eventually transform to a non-reactive, non-bioavailable phosphorus containing mineral. A large percentage of the annual phosphorus load delivered to Lake Ontario by the Genesee River is transported as eroded soil and river bank material. Phosphorus is also apparently sorbed, either directly or through biological processes, to suspended particles which are transported by water and deposited eventually in areas of active sedimentation. Chemical equilibrium calculations performed in this laboratory indicate that a significant driving force exists for the formation of an epitaxial calcium phosphate mineral (hydroxyapatite) on carbonate minerals transported in the Genesee River watershed sediments during summer months.

Sediment Phosphorus - Organic Carbon Relationship

Sediments with high organic carbon content in the Genesee River probably arise principally from inputs of low phosphorus allochthonous carbonaceous material to the river. Excellent agreement between the data points and the best fit line for the C/P vs C relation may result from the conservative nature of phosphorus in natural waters and sediments (41).

Sediment Lead and Other Metals

The elevated lead concentrations in the Genesee Watershed sediments may be due to atmospheric inputs of lead transported from the highly industrialized midwestern United States. Point-source inputs of lead in the predominantly forested and agricultural basin are probably negligible. Durum and co-workers (54) have shown that in high-alkalinity surface waters, lead solubility will be low, and most of the rainfall and dustfall lead will be transferred to river sediments, where it will tend to accumulate. Water in the Genesee River watershed typically has moderate to high alkalinity.

Until more results from concurrent studies in the Great Lakes Basin become available, the magnitude of cultural metal input into the Genesee watershed sediments can be evaluated by comparing them with sediments in four tributaries of Chesapeake Bay: the Elizabeth, Delaware, Potomac, and James rivers (55). The Elizabeth River supports a highly industrialized port facility. The others are less intensively developed: The Delaware is an industrial tidal system, the Potomac an estuary with mainly municipal inputs, and the James a relatively light municipal and industrial input system.

Mean sediment concentrations of three metals for the Genesee River watershed are lower by at least a factor of 2 than the Chesapeake Bay tributary sediments (Table 8). This and the comparably lower ranges suggest that predominantly agricultural and forested watersheds, such as that of the Genesee River, yield smaller concentrations of sediment metals than the more industrialized basins of the eastern seacoast. Sediment lead concentration, an exception to this general trend, may reflect a loading in the Genesee watershed not present in the James and Potomac rivers. This interpretation is consistent with the observation by Durum and Hem (56) that lead was found most often in waters of the northeastern and southeastern United States. In addition, Lazarus and co-workers (57) reported that the highest rates of lead fallout occurred in the same area. Lower zinc concentrations in Genesee sediments may reflect fewer commercial sources of this metal in the Genesee watershed than in basins adjacent to Chesapeake Bay.

TABLE 8. METAL CONCENTRATIONS IN SEDIMENTS FROM THE GENESEE RIVER WATERSHED AND FOUR TRIBUTARIES TO CHESAPEAKE BAY

			Chesapeake Bay tributary[a]							
Metal	Genesee River		Elizabeth River		Delaware River		Potomac River		James River	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Copper	18	8-41	65	2-393	73	4-201	*	10-60	*	*
Lead	40	6-550	91	3-382	145	26-850	*	20-100	27	4-55
Zinc	69	15-210	379	38-2,380	137	523-1,364	*	125-1,000	131	10-708
Chromium	14	10-79	44	9-110	58	8-172	*	20-80	*	*

[a] Reference 57

*Data not available

REFERENCES

1. Golterman, H. L., ed. Interactions Between Sediments and Fresh Water. Dr. W. Junk, B. V. Publishers. The Hauge, The Netherlands, 1977. 473 pp.

2. Division of Pure Waters. October 1975. PCB Monitoring in the Upper Hudson River Basin. NYS Department of Environmental Conservation, Albany New York, 110 pp.

3. Division of Pure Waters and Division of Fish and Wildlife. October 1976 Hudson River PCB Monitoring: Data Summary - Past, Present, Proposed. NYS Department of Environmental Conservation, Albany, New York. 106 pp.

4. Kemp, A. L. W. and R. L. Thomas. Air, Water and Soil Pollution, 5:469, 1976.

5. Gibbs, R. J. Science, 180:71, 1973.

6. Schwertmann, V. Can. J. Soil. Sci., 53:244, 1973.

7. Reddy, M. M., In: Interactions Between Sediments and Fresh Water, Golterman, ed., Dr. W. Junk B. V., The Hague, The Netherlands 1977. pp. 244-251.

8. R. T. Bannerman, D. E. Armstrong, R. F. Harris, and G. C. Holdren. Phosphorus Uptake and Release by Lake Ontario Sediments. EPA-660/3-75-006 U. S. Environmental Protection Agency, Corvallis, OR 97330.

9. P. E. Moffa, C. B. Murphy, and D. A. MacArthur. Water Pollution Investigation: Genesee River and Rochester Area. EPA-905/9-74-016, U.S. Environmental Protection Agency, Chicago, Ill., 60604.

10. W. G. Heines, D. A. Rickert, and S. W. McKenzie. J. Water Poll. Cont. Fed. 49:2031, 1977.

11. C. J. Velz. Applied Stream Sanitation, John Wiley and Sons, Inc., New York, NY 1970.

12. F. W. Kittrell. A Practical Guide to Water-Quality Studies of Streams, U.S. Federal Water Pollution Control Adm. Pub. CWR-5, 1969.

13. Krishnamurty, K. V. and M. M. Reddy. The Chemical Analysis of Water and Sediments in the Genesee River Watershed Study. On file in the library of International Joint Commission, Regional Office, Windsor, Ontario, Canada, 1975.

14. Krishnamurty, K. V., E. Shpirt, and M. M. Reddy. Atomic Absorption Newslett. 15:68, 1976.

15. Fuhs, G. W., Inter. J. Environ. Anal. Chem., 1:123, 1971.

16. Williams, J. D. H., J. K., Syers, R. F. Harris and D. E. Armstrong. Soil Sci. Soc. Am. Proc., 35:250, 1971.

17. Williams, J. D. H., J. K. Syers, D. E. Armstrong, and R. F. Harris. Soil Sci. Soc. Am. Proc., 35:556, 1971.

18. M. M. Reddy and E. Shpirt, Phosphorus bioavailability in river sediments, in preparation for publication.

19. Sagher, A, Microbial Availability of Phosphorus in Lake Sediments, M. S. Thesis, Depart. Soil Science, University of Wisconsin, Madison 1974.

20. Chao, T. T. Soil Sci. Am. Proc., 36:764, 1972.

21. Krishnamurty, K. V. and M. M. Reddy. Anal. Chem., 49:222, 1977.

22. Reddy, M. M. Chemistry of Wastewater Technology, Rubin, A. ed. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan 1978 pp 31-58.

23. Diehl, H. Calcein, Calmogite and o,o' dehydroxyazobenzene titrimentric, colorimetric and fluorometric reagents for calcium and mangnesium. G. F. Smith Chemical Co. Columbus, Ohio, 1964.

24. Nancollas, G. H. Interactions in Electrolyte Solutions. Elsevier Publishing Co., Amsterdam, 1966.

25. Davis, C. W. Ion Association. Butterworths, Washington, D. C., 1963.

26. L. H. Ahrens. Distribution of the Elements in Our Planet. McGraw-Hill, New York, NY 1965.

27. H. E. Hawkes and J. S. Webb. Geochemistry in Mineral Exploration. New York, NY, 1962.

28. F. R. Siegel. Applied Geochemistry. John Wiley and Sons, New York, NY, 1974.

29. A. T. Miesch. Methods of Computation for Estimating Geochemical Abundance. U. S. Geological Survey, Professional Paper 574-B.

30. G. S. Koch, Jr. and R. F. Link. Economic Geology, 66:293, 1971.

31. Turekian, K. K. and K. H. Wedepohl. Bull. Geol. Soc. Amer., 72:175, 1961.

32. Förstner, U. In: Interactions between Sediments and Fresh Water, H. L. Golterman, ed., Dr. W. Junk B. V., The Hague, The Netherlands, 1977. pp. 94-103.

33. Fuhs, G. W., S. D. Demmerle, E. Canelli and M. Chen. In: Nutrients and eutrophication: the limiting nutrient controversy, G. E. Likens, Special Symposium, Amer. Soc. Limnol. Oceanogr., 1:113, 1972.

34. Wetzel, R. G. Limnology. W. B. Saunders Co, Philadelphia, PA, 1975, p. 208-212.

35. Keeney, D. R. J. Environ. Qual. 2:15, 1973.

36. Isirimah, N. O., D. R. Keeney and E. H. Dettmann. J. Environ. Qual., 5:182, 1976.

37. Stall, J. B. J. Environ, Quality, 1: 353, 1972.

38. Carlson, G. A. unpublished data supplied by USEPA.

39. Delfino, J. J., G. C. Bortleson and G. F. Lee. Environ. Sci. Technol., 3:1189, 1969.

40. Gill, A. E., J. J. R. McHenry and J. C. Ritchie. J. Environ. Qual., 5:310, 1976.

41. Johnson, A. H., D. R. Bouldin, E. A. Goyette and A. M. Hedges. J. Environ. Qual., 5:148, 1976.

42. Jenne, E. A., J. W. Ball and C. Simpson. J. Environ. Quality, 3:281, 1974.

43. Chao, T. T. and B. J. Anderson. Chemical Geology, 14:159, 1974.

44. Stumm, W. Water Research, 7:131, 1973.

45. Plummer, L. N., Jones, B. F. and Truesdell, A. H. WATEQF A Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. U. S. Geol. Survey Water Resour. Invest. 76-13.

46. Mattingly, G. E. G., Soil Sci., 119:369, 1975.

47. Water Resources Data for New York Water Year 1976. Vol. 1. U. S. Geol. Survey Water Data Report NY761.

48. Nicholls, K. H. and Cox, C. M. Water Resour. Research, 14:589, 1978.

49. Reddy, M. M., Particulate Metal Transport in the Genesee River, New York, presented at the American Chemical Society National Meeting, Los Angeles, Calif. March 1978.

50. Nriagu, J. The Geochemical Consequences of Phosphate Interaction with Heavy Metals, presented at the Geological Society of America Meeting, Salt Lake City, Utah. October, 1975.

51. Reddy, M. M. and G. H. Nancollas, Desalination, 12:61, 1973.

52. Lorenzen, M., In: Water Pollution Microbiology, Vol. 2, Mitchell, R., ed. John Wiley and Sons, Inc., New York, 1978. pp. 31-50.

53. Johnson, A. H., D. R. Bouldin, E. A. Goyette and A. M. Hedges. J. Envir. Qual., 5:386, 1976.

54. Durum, W. H., J. D. Hem, and S. G. Heidel. Reconnaissance of Selected Minor Elements in Surface Waters of the United States, U. S. Geological Survey Circular, 643, 1971.

55. Johnson, P. G., and O. Villa, Jr. Distribution of Metals in Elizabeth River Sediments. EPA Report EPA 903/9-76-023, U. S. Environmental Protection Agency, NTIS.

56. Durum, W. H., and J. D. Hem. In: Geochemical Environment in Relation to Health and Disease, H. C. Hopps and H. L. Cannon, eds. Annals of the New York Academy of Sciences, 199:26-36, 1972.

57. Lazarus, A. E., E. Lorange, and J. P. Lodge, Jr. Environ. Sci. Technol., 4:55, 1970.

APPENDIXES

1. Analytical Results for Sediment Samples from the Genesee River.
2. Analytical Results for Water Column Samples from the Genesee River.
3. Illustrations of Sediment Sampling Procedures and Equipment.
4. Illustrations of Selected Sediment Sampling Sites in the Genesee River Watershed.

Appendix 1. Analytical Results for Sediment Samples from the Genesee River

A. Concentrations of Metals (µg/g) and Nutrients (%) in Bottom Sediment from the Genesee River, 13 March 1976. Replicate Samples.

B. Concentrations of Extractable Phosphorus (%) in Bottom Sediment from the Genesee River, 13 March 1976. Replicate Samples.

C. Concentrations of Extractable Metals (µg/g) in Bottom Sediment from the Genesee River, 13 March 1976.

D. Concentrations of Metals (µg/g) and Nutrients (%) in Fine Material Washed from Bottom Sediment in the Genesee River, 13 March and 14 July 1976.

Appendix 1 A. CONCENTRATIONS OF METALS (μg/g) AND NUTRIENTS (%) IN BOTTOM SEDIMENTS FROM THE GENESEE RIVER, 13 MARCH 1976. REPLICATE SAMPLES

Station	Metals								Nutrients			
	Al	Cu	Cr	Fe	Mn	Ni	Pb	Zn	Total C	Organic C	Total N	P
Wellsville	8,250	10	10	17,000	530	16	20	41	0.49	0.49	0.035	0.043
Wellsville	1,550	27	20	30,500	1,300	30	60	94	1.62	1.48	0.132	0.082
Wellsville	7,250	9	10	16,000	430	14	25	34	0.39	0.31	0.017	0.045
Wellsville	1,800	28	20	36,500	1,300	32	60	100	2.33	2.20	0.170	0.095
Wellsville	7,100	8	10	15,000	470	13	20	33	0.41	0.29	0.028	0.044
Transit Br.	7,250	12	10	17,000	385	13	15	40	0.44	0.35	0.033	0.049
Transit Br.	6,200	10	10	14,000	310	10	15	30	0.49	0.28	0.022	0.046
Portageville	5,750	10	10	14,000	280	10	10	32	0.43	0.15	0.012	0.044
Portageville	5,950	10	10	14,000	290	14	10	29	0.46	0.16	0.014	0.035
Portageville	6,550	12	10	15,000	380	15	10	33	0.67	0.34	0.028	0.045
Mount Morris	7,000	14	10	15,500	325	17	10	34	0.60	0.34	0.024	0.046
Mount Morris	7,775	16	10	17,000	430	19	10	41	0.64	0.44	0.037	0.050
Avon	6,700	11	[1]LT 10	14,000	275	13	10	31	0.63	0.42	0.019	0.048
Avon	7,200	17	10	17,000	380	17	[2]ND	ND	1.32	0.81	0.054	0.051
Avon	7,150	14	10	16,500	375	17	20	40	0.84	0.54	0.297	0.054
Rochester	4,000	9	LT 10	11,500	175	9	45	28	0.35	0.11	<0.01	0.069
Rochester	3,900	8	LT 10	11,500	150	10	30	23	0.35	0.14	<0.01	0.049

[1] LT = less than

[2] ND = not determined

Appendix 1-B. CONCENTRATIONS OF EXTRACTABLE PHOSPHORUS (%) IN BOTTOM SEDIMENT FROM THE GENESEE RIVER, 13 MARCH 1976. REPLICATE SAMPLES

Station	Extraction Reagent				Total Available
	NaOH	HCl	NH_2OH	$(NH_4)_2C_2O_4$	
Wellsville	0.009	0.019	0.0067	0.0217	0.0427
Wellsville	0.019	0.036	0.0134	0.0414	0.0816
Wellsville	0.008	0.028	0.0048	0.0173	0.0450
Wellsville	0.028	0.032	0.0122	0.0453	0.0952
Wellsville	0.006	0.024	0.0055	0.0154	0.0442
Transit Br.	0.005	0.028	0.0098	0.0164	0.0491
Transit Br.	0.004	0.032	0.0072	0.0122	0.0460
Portageville	0.003	0.031	0.0147	0.0096	0.0444
Portageville	0.003	0.027	0.0066	0.0094	0.0354
Portageville	0.003	0.032	0.0098	0.0126	0.0453
Mount Morris	0.002	0.034	0.0149	0.0139	0.0463
Mount Morris	0.004	0.034	0.0176	0.0139	0.0496
Avon	0.003	0.033	0.0151	0.0107	0.0479
Avon	0.006	0.036	0.0061	0.0193	0.0507
Avon	0.004	0.037	0.0145	0.0149	0.0539
Rochester	0.004	0.047	0.0037	0.0113	0.0690
Rochester	0.003	0.045	0.0050	0.0099	0.0493

Appendix 1 C. CONCENTRATIONS OF EXTRACTABLE METALS (μg/g) IN BOTTOM SEDIMENT FROM THE GENESEE RIVER, 13 March 1976. REPLICATE SAMPLES

Station	Hydroxylamine Extraction						Oxalate Extraction					
	Al	Cu	Cr	Fe	Mn	Pb	Al	Cu	Cr	Fe	Mn	Pb
Wellsville	350	[1]LT 1	LT 1	318	153	LT 10	760	4	LT 1	1850	125	LT 10
Wellsville	820	3	LT 1	1225	310	16	1200	15	LT 1	3075	188	8
Wellsville	135	1	LT 1	218	775	LT 10	630	9	LT 1	2100	83	LT 10
Wellsville	1020	LT 1	LT 1	1550	248	20	1900	11	LT 1	3050	193	14
Wellsville	455	LT 1	LT 1	203	725	LT 10	495	2	LT 1	1275	85	LT 10
Transit Br.	335	LT 1	LT 1	215	208	LT 10	570	4	LT 1	3000	68	LT 10
Transit Br.	205	LT 1	LT 1	223	183	LT 10	435	3	LT 1	2075	53	LT 10
Portageville	145	LT 1	LT 1	210	158	LT 10	390	3	LT 1	1950	40	LT 10
Portageville	210	LT 1	LT 1	195	163	LT 10	375	3	LT 1	1575	40	LT 10
Portageville	200	LT 1	LT 1	223	213	LT 10	510	4	LT 1	1675	63	LT 10
Mount Morris	335	LT 1	LT 1	298	148	LT 10	555	5	LT 1	2150	65	LT 10
Mount Morris	490	LT 1	LT 1	415	240	LT 10	570	6	LT 1	2375	73	LT 10
Avon	225	LT 1	LT 1	318	120	LT 10	390	4	LT 1	1600	50	LT 10
Avon	220	LT 1	LT 1	305	180	[2]ND	765	9	3	2125	65	58
Avon	285	LT 1	LT 1	370	143	LT 10	570	6	LT 1	1675	80	LT 10
Rochester	110	LT 1	LT 1	268	58	17	615	3	3	4600	48	LT 10
Rochester	LT 50	LT 1	LT 1	213	53	8	555	4	2	3675	40	LT 10

[1] LT = less than
[2] ND = not determined

APPENDIX 1 D. CONCENTRATIONS OF METALS (μg/g) AND NUTRIENTS (%) IN FINE MATERIAL WASHED FROM BOTTOM SEDIMENT IN THE GENESEE RIVER, 13 MARCH AND 14 JULY 1976

Station	Metals								Nutrients			
	Al	Cu	Cr	Fe	Mn	Ni	Pb	Zn	Total C	Organic C	Total N	P
March 13, 1976												
Wellsville	[1]ND	ND	ND	ND	ND	ND	ND	ND	2.548	2.150	0.386	ND
Transit Br.	27,000	33	30	46,000	1,100	50	40	130	1.337	1.054	0.181	0.0895
Portageville	26,000	26	30	45,000	1,050	48	45	130	1.740	1.383	0.201	0.0704
July, 1976												
Wellsville	26,500	100	30	58,000	1,800	44	110	225	ND	ND	ND	0.1420
Wellsville	25,000	110	30	44,000	1,800	42	170	270	3.47	3.21	0.37	0.1030
Transit Br.	23,500	77	30	51,500	1,550	40	80	210	1.50	1.14	0.17	0.0726
Portageville	25,000	100	35	48,500	1,350	49	45	185	2.20	1.60	0.26	0.0645
Mount Morris	ND	ND	ND	ND	ND	ND	ND	ND	2.54	1.26	0.20	ND
Avon	24,000	70	30	45,000	720	46	90	190	1.87	1.37	0.23	0.0705
Rochester	23,000	130	30	38,000	1,100	50	340	44	3.43	1.82	0.21	0.0882

[1] Nd = not determined

Appendix 2. Analytical Results for Water Column Samples from the Genesee River.

A. Total Metal Concentrations (mg/l) in the Genesee River, 14 December 1975. Samples Preconcentrated by Evaporation.

B. Dissolved Heavy Metal Concentrations (µg/l) in the Genesee River, 14 December 1975 and 13 March 1976 (Duplicate Analyses) Determined by Differential Pulse Anodic Stripping Voltammetry.

C. Total and Dissolved Concentrations of Iron and Manganese (mg/l) in the Genesee River, 13 March 1976. Duplicate Analyses.

D. Particulate Metal Concentrations (mg/l) in the Genesee River, 13 March 1976. Duplicate Analyses.

APPENDIX 2 A. TOTAL METAL CONCENTRATIONS (mg/l) IN THE GENESEE RIVER, 14 DECEMBER 1975. SAMPLES PRECONCENTRATED BY EVAPORATION

Station	Cr	Cu	Fe	Pb	Mn	Zn	Al	Ni
Wellsville	[1]LT 0.01	LT 0.005	0.36	0.01	0.098	0.001	0.17	LT 0.005
Transit Br.	LT 0.01	0.005	3.3	0.01	0.08	0.011	1.4	0.005
Portageville	LT 0.01	0.007	3.2	0.01	0.07	0.02	2.3	0.01
Mount Morris	LT 0.01	0.009	6.1	0.02	0.17	0.27	2.7	0.013
Avon	LT 0.01	0.006	3.3	0.02	0.07	0.015	1.5	0.01
Rochester	LT 0.01	0.006	1.9	0.02	0.06	0.015	0.8	0.01

---

[1] LT = less than

APPENDIX 2 B. DISSOLVED HEAVY METAL CONCENTRATIONS (μg/l) IN THE GENESEE RIVER, 14 DECEMBER 1975 AND 13 MARCH 1976 (DUPLICATE ANALYSES) DETERMINED BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

Station	Pb	Cd	Cu	Zn
December 14, 1975				
Wellsville	0.78	0.49	1,0	10.5
Transit Br.	0.35	[1]LT 0.1	1.8	8.5
Portageville	1.1	0.26	1.4	10.8
Mount Morris	1.05	0.3	1.4	11.9
Avon	1.38	0.37	1.5	9.7
Rochester	1.5	0.36	6.1	16.4
March 13, 1976				
Wellsville	0. 0.3	LT 0.1	[2]ND	ND
Wellsville	10.2	ND	ND	ND
Transit Br.	0.3	ND	ND	ND
Transit Br.	LT 0.1	ND	ND	ND
Portageville	1.5	LT 0.1	ND	ND
Portageville	0.3	0.2	ND	ND
Mount Morris	LT 0.1	LT 0.1	ND	ND
Mount Morris	LT 0.1	LT 0.1	ND	ND
Avon	14.8	0.3	ND	ND
Avon	1.3	0.3	ND	ND
Rochester	LT 0.1	LT 0.1	ND	ND
Rochester	0.7	LT 0.1	ND	ND

[1] LT = less than

[2] ND = not determined

APPENDIX 2 C. TOTAL AND DISSOLVED CONCENTRATIONS (mg/1) OF IRON AND MANGANESE IN THE GENESEE RIVER 13 MARCH 1976. DUPLICATE ANALYSES.

Station	Total		Dissolved	
	Fe	Mn	Fe	Mn
Wellsville	0.14	0.03	0.09	0.03
Wellsville	0.14	0.04	0.08	0.04
Transit Br.	0.23	0.04	0.05	0.02
Transit Br.	0.24	0.04	0.05	0.02
Portageville	0.29	0.03	0.05	0.02
Portageville	0.37	0.04	0.05	0.02
Mount Morris	1.50	0.17	0.06	[2]LT 0.02
Mount Morris	0.76	0.14	0.05	LT 0.02
Avon	1.00	0.10	0.12	0.02
Avon	0.71	0.09	0.08	LT 0.02
Rochester	0.70	0.08	0.06	LT 0.02
Rochester	[1]ND	ND	0.10	LT 0.02

[1]ND = not determined

[2]LT = less than

APPENDIX 2 D. PARTICULATE METAL CONCENTRATIONS (mg/l) IN THE GENESEE RIVER 13 MARCH 1976. DUPLICATE ANALYSES

STATION	Al	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Wellsville	0.13	0.001	LT 0.003	0.17	0.005	[1]LT 0.001	LT 0.003	0.002
Wellsville	0.11	0.001	LT 0.003	0.15	0.004	LT 0.001	LT 0.003	0.003
Transit Br.	0.58	0.001	LT 0.003	1.10	0.20	0.001	0.003	0.007
Transit Br.	0.70	0.001	LT 0.003	1.23	0.21	0.001	0.003	0.006
Portageville	0.73	0.002	0.003	1.65	0.025	0.003	0.005	0.007
Portageville	1.03	0.002	0.003	1.68	0.028	0.003	0.003	0.009
Mount Morris	5.75	0.007	0.008	11.00	0.185	0.013	0.010	0.033
Mount Morris	5.75	0.008	0.010	11.50	0.195	0.013	0.010	0.035
Avon	3.00	0.003	0.005	4.50	0.075	0.007	0.003	0.018
Avon	3.00	0.005	0.005	5.50	0.073	0.007	0.008	0.023
Rochester	2.25	0.004	0.008	4.50	0.070	0.006	0.005	0.018
Rochester	2.75	0.005	0.005	4.53	0.068	0.007	0.007	0.017

[1] LT = less than

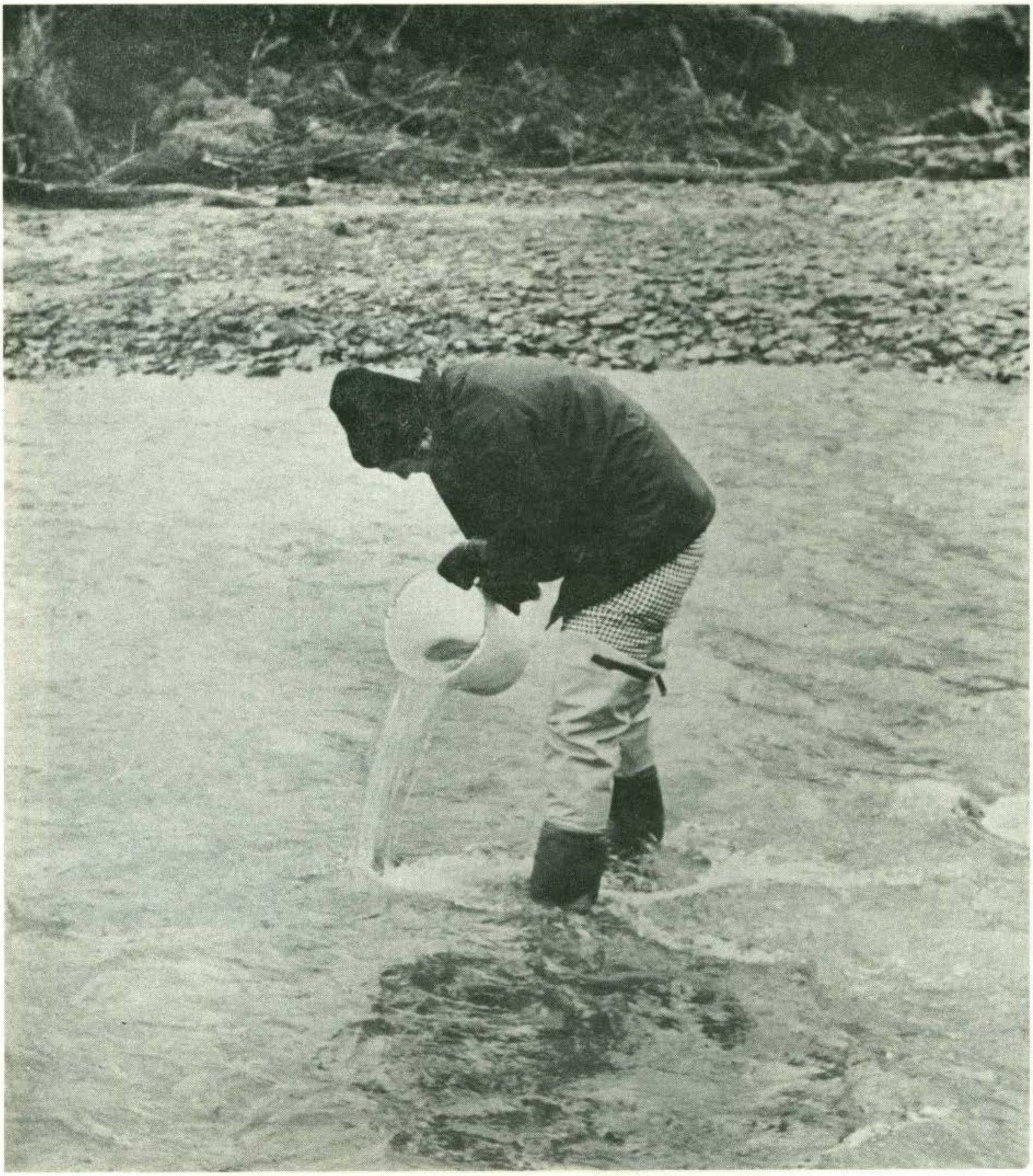
Appendix 3. Illustrations of Sediment Sampling Procedures and Equipment

A. A mid-stream collection site.

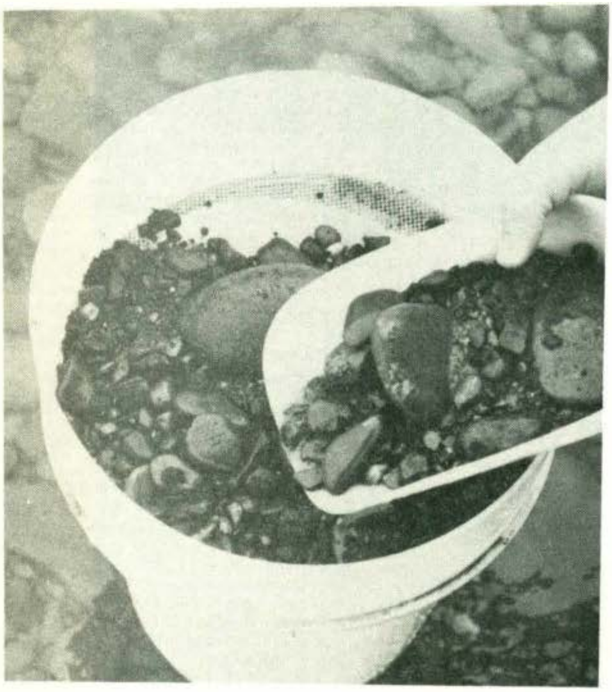
B. Field wet-sieving of three different bottom sediment samples.

C. A kinar-coated Ekman bottom sediment sampler.

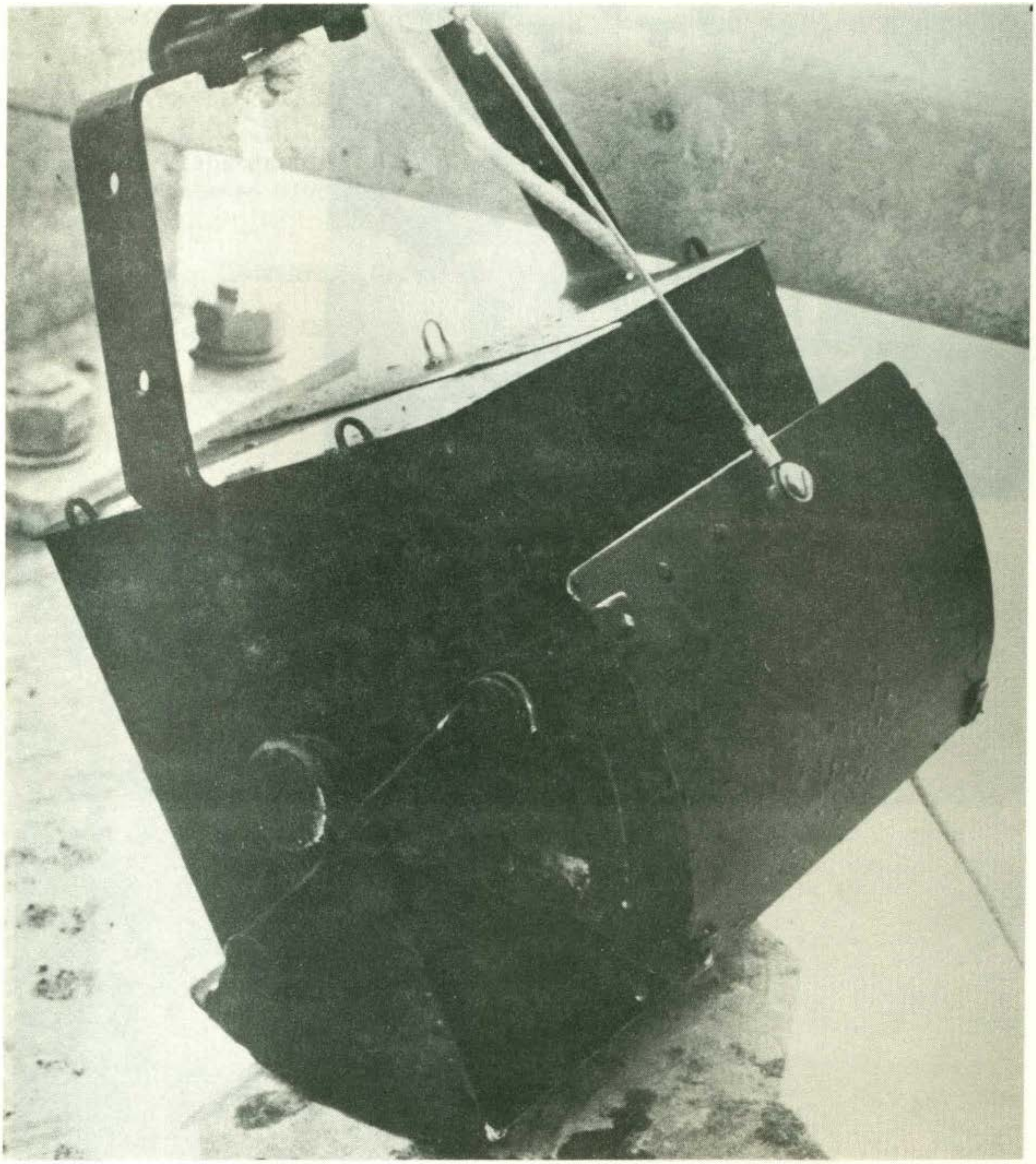
D. Equipment used for pressure filtration of water column samples during collection of particulate material.



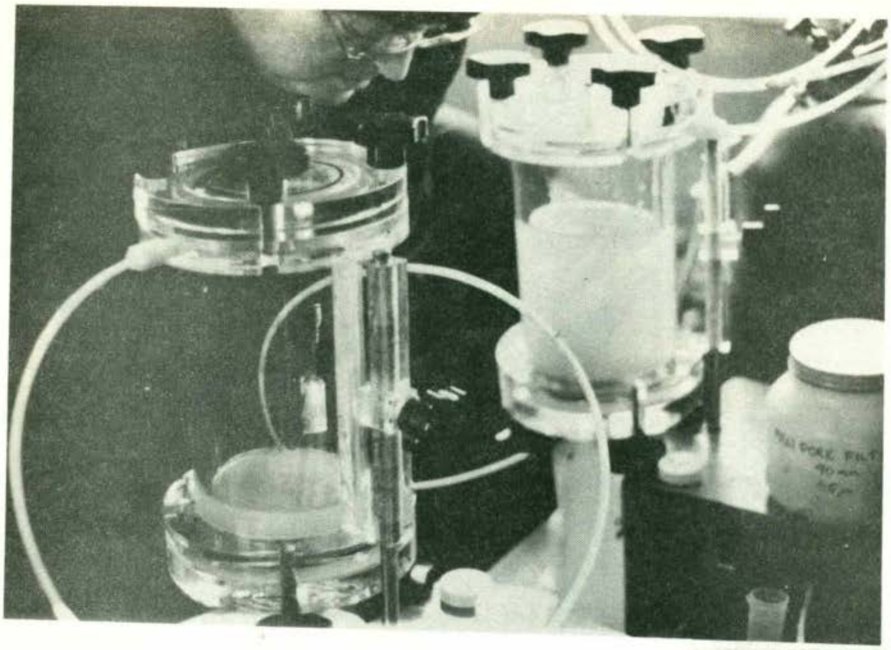
A 3a



A



A 3c

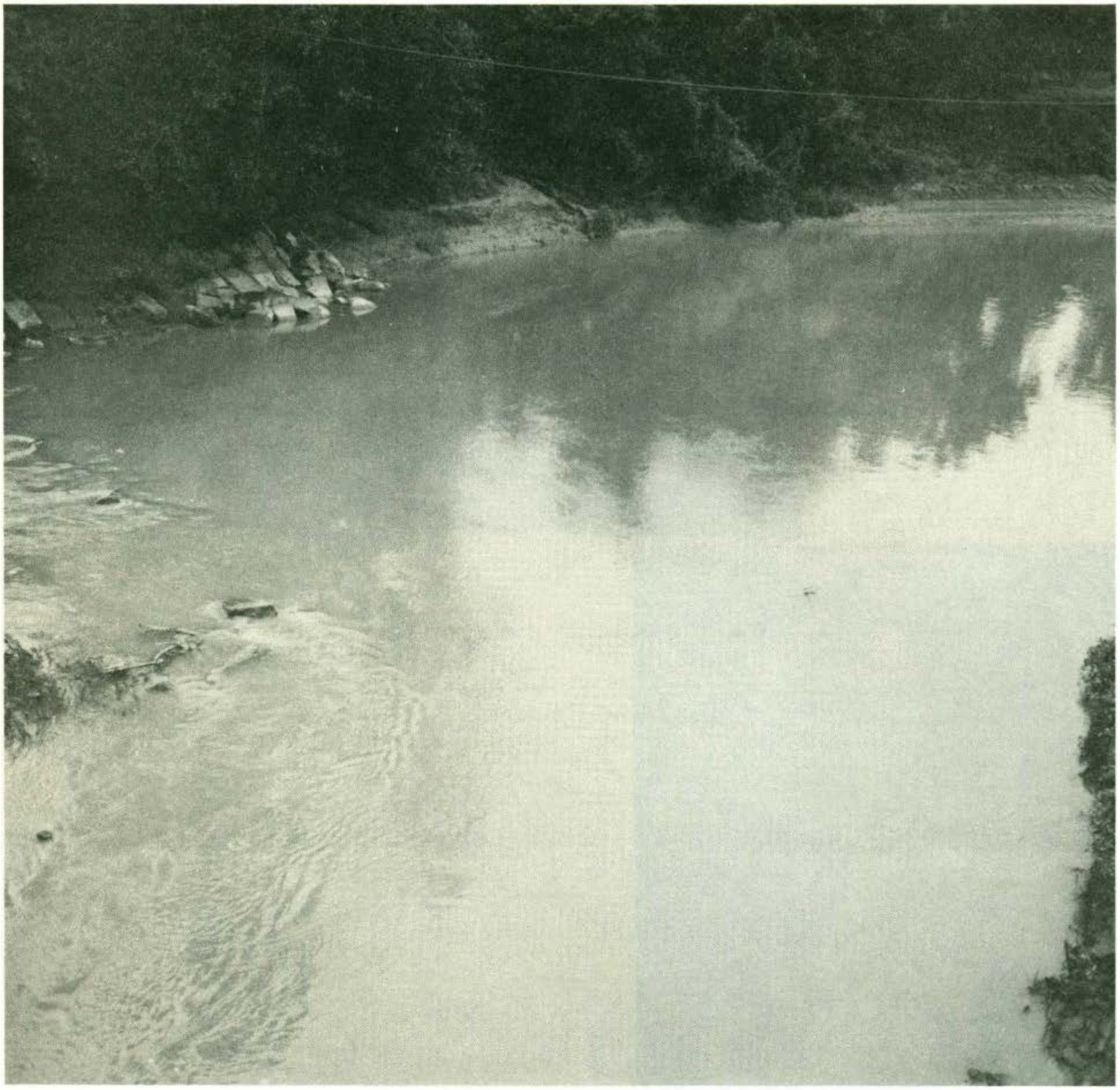

PORE FILT
90 mm

Appendix 4. Illustrations of Selected Sediment Sampling Sites in the Genesee River Watershed.

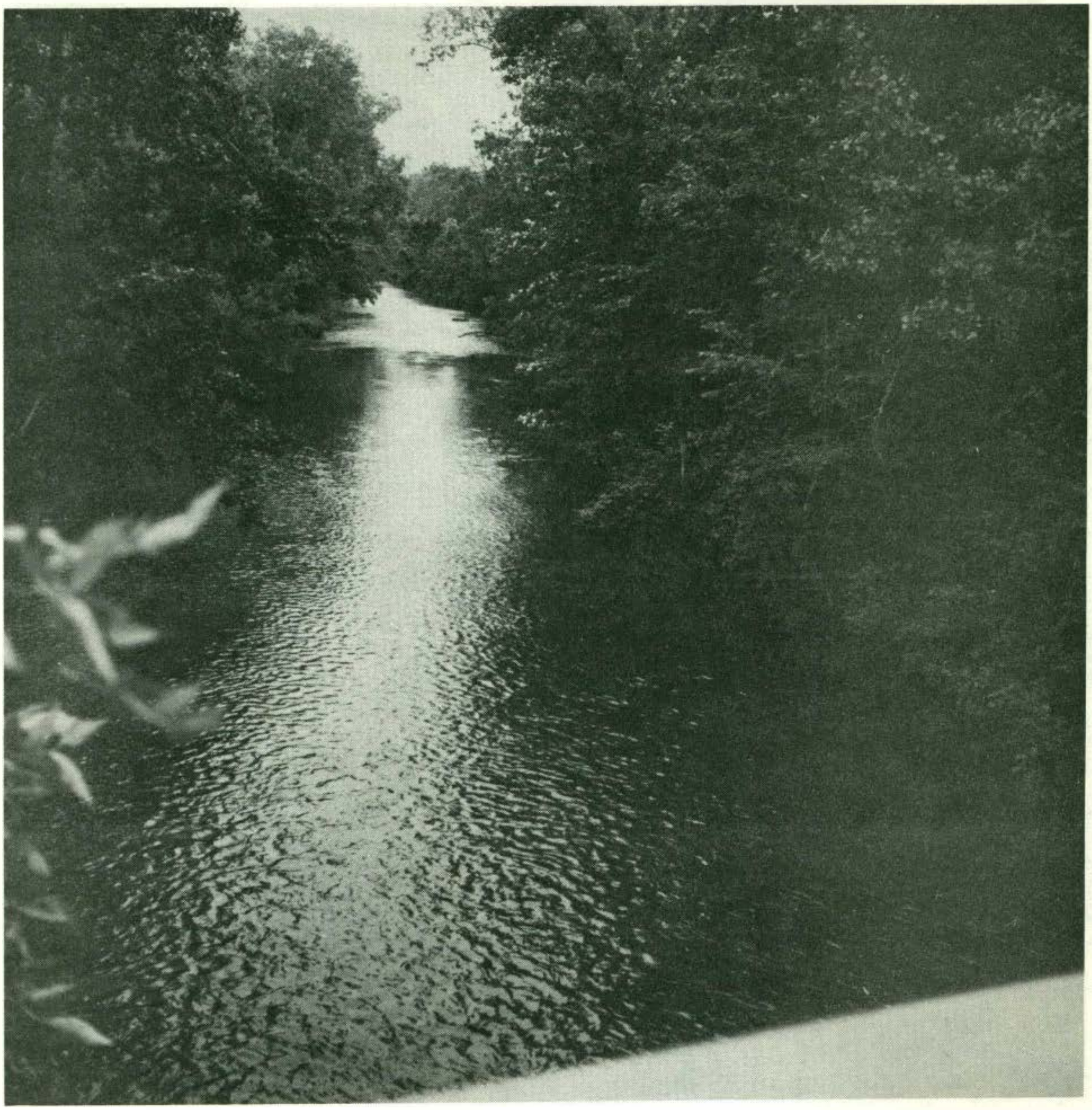
A. Canasaraga Creek at Shakers Crossing.

B. Oatka Creek at Garbutt, NY.

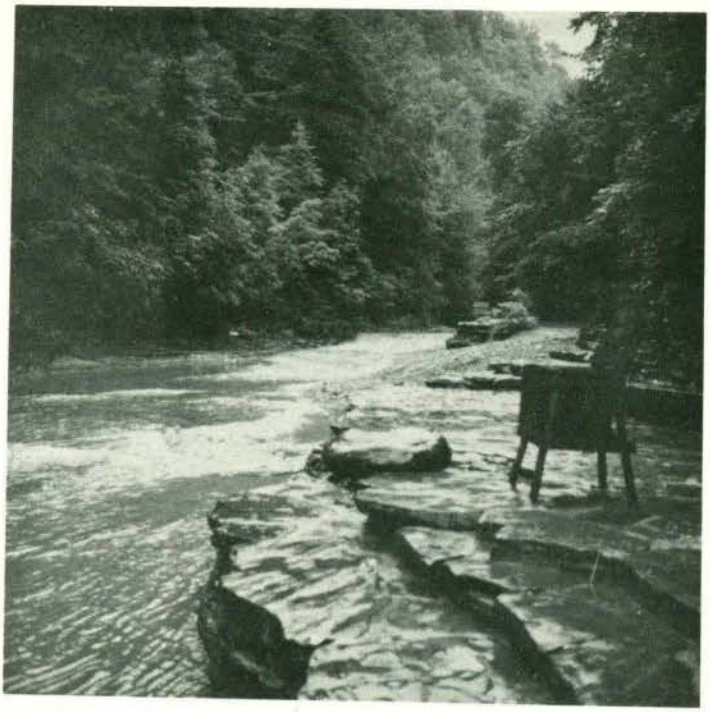
C. Stony Brook Creek at Stony Brook State Park.



A 4a



A 4b



A 4c