

## DISTRIBUTION OF SOME TRACE METALS AND THEIR FLUXES IN THE GENESEE RIVER, NY

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Total and particulate metal concentrations, measured during intensive synoptic studies of the Genesee River, NY, correlated with suspended-sediment concentration and river discharge. Dissolved metal concentrations, on the other hand, showed little systematic variation over the length of the river. Metal and sediment fluxes for two elevated-discharge periods peaked at a midbasin sampling site. For most metals at most sampling sites particulate materials comprised over one-half of the total material. Comparison of particulate material metal concentrations, normalized to the measured suspended-sediment concentration, with basinwide average values shows that sites having low suspended-sediment concentrations had high particulate material metal contents relative to the basin averages, while sites with high suspended-sediment concentration had low metal contents. These results are consistent with a metal transport mechanism in the Genesee River involving (1) a nearly constant dissolved component, (2) a fine acid-soluble component, and (3) a coarse component that is effectively a neutral diluent in the sediment. Chemical factors, such as sediment organic content, also appear to affect metal transport in the Genesee River.

### Introduction

Although fluvial transport is a major mechanism for removing metals and nutrients from the continental land masses to lakes and oceans, relatively little information is available on how trace-metal concentrations vary with fluvial characteristics such as discharge and suspended-sediment concentration (Meybeck, 1977; Boyle *et al.*, 1976; Sholkovitz and Prince, 1980).

Intensive studies have characterized trace-metal concentrations and distributions in saline waters (Boyle *et al.*, 1976; Sclater *et al.*, 1976; Alberts *et al.*, 1976; Eaton, 1976; Bowers *et al.*, 1976; Bruland *et al.*, 1978; Mukherji and Kester, 1979). Results of these and other recent oceanic trace-metal research have emphasized the importance of solid-solution interactions in regulating the concentration of dissolved metal ions. Many of these investigators have attempted to define the dominant mechanism regulating metal ion concentration. For example, concentrations of dissolved aluminum (Hydes, 1979) and copper (Boyle *et al.*, 1977) ions ap-

pear to be controlled by particulate reactions in seawater.

Knowledge of river metal content and transport mechanisms is needed to characterize metal cycling and bioavailability in receiving waters, such as the North American Great Lakes. Transport mechanisms, which identify the physical state of metals moving with river flow, can be characterized through a variety of procedures (Gibbs, 1973). A convenient technique employs filtration to determine the total metal concentration and that portion of riverborne metal carried by particulate material (Brewer and Spencer, 1974). While numerous investigations have attempted to develop laboratory or theoretical descriptions of trace-metal behavior in freshwater (Stiff, 1971a, 1971b; Chau and Lum-Shue-Chan, 1974; Gardiner and Stiff, 1975; Benes *et al.*, 1979; McGrady and Chapman, 1979), these approaches have been criticized on several grounds (Brezonik *et al.*, 1976).

In this paper we report water-column metal concentrations and fluxes and particulate metal concentrations measured in synoptic surveys conducted in December 1975 and March 1976 in a watershed located in central New York State. These periods were chosen, in part, because they had elevated river discharge, and also

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because they immediately preceded and followed the snow-melt runoff event of the 1975-1976 water year. A network of basinwide sampling sites was monitored during each synoptic survey. Results presented here will focus on synoptic samples obtained along a 130-mi reach of the Genesee River during the basinwide surveys. The advantages of synoptic sampling, discussed elsewhere (Rickert and Hines, 1978), include acquisition of representative materials from widely separated areas of the basin under similar climatic and hydrological conditions. A complete description of procedures employed in the Genesee River Pilot Watershed Study and results of the investigation are available (Hetling *et al.*, 1978). All sampling sites (Fig. 1) were at United States Geological Survey gaging stations and were away from known point sources of pollution.

A goal of this investigation was to determine what, if any, relationship exists between the distribution and flux of trace metals in the Genesee River and the two

most widely monitored stream parameters, discharge and suspended-sediment concentration. The bulk of trace metals are transported in a river system during peak discharge periods; the mechanisms for this transport may involve a number of processes. For example, organic carbon content of suspended sediment can be important, because organic coatings on the fine sediment can serve as binding sites for metal ions. Another factor leading to variations in metal distribution could be the amounts of fine and coarse sediment entrained at the sampling point. A description of metal transport in terms of discharge and suspended sediment would yield both practical and mechanistic information.

## Experimental Procedures

### Sample collection and pretreatment

Water and suspended-sediment samples were collected with a 4-l nonmetallic horizontal Van Dorn sampler at a depth of 1 m in the main channel (Fig. 2). Sampling locations were selected by U.S. Geological Survey staff to verify that samples were representative of river conditions at that point and were away from any significant point sources of pollution. Three separate samples were obtained at each sampling location: unfiltered, filtered, and particulates retained during filtration. Unfiltered samples were stored in a pre-washed polyethylene bottle and acidified immediately after collection with 5 ml of reagent-grade concentration nitric acid per liter of sample. A separate water sample was filtered through a prewashed 0.45- $\mu\text{m}$  Millipore filter using compressed argon gas with a Plexiglas filtration system. The filtered sample was placed in a polyethylene bottle and acidified immediately with nitric acid as for the unfiltered samples. Filtered and unfiltered samples were frozen on site and were kept frozen until analysis. Particulate material retained on the filter was dried with a brief flow of argon gas, folded to prevent loss of material, and stored in a plastic Petri dish until analysis.

### Sample analysis

Analytical procedures for filtered and unfiltered samples have been described in detail elsewhere (Krishnamurty and Reddy, 1977). Detection limits, calibration procedures, analytical instrumentation and analytical blank values were similar to those given for published methodologies (APHA, 1976) and are summarized in detail in Krishnamurty and Reddy (1975 and 1977). Filters with particulate material were digested using a technique (Fig. 2) developed for the analysis of river sediments (Krishnamurty *et al.*, 1976).

During the analysis of water samples, quality control check samples and reagent blanks were interspersed with field samples. Blank water samples, prepared at the sampling sites with distilled water and analyzed with each batch of samples, had metal concentrations below

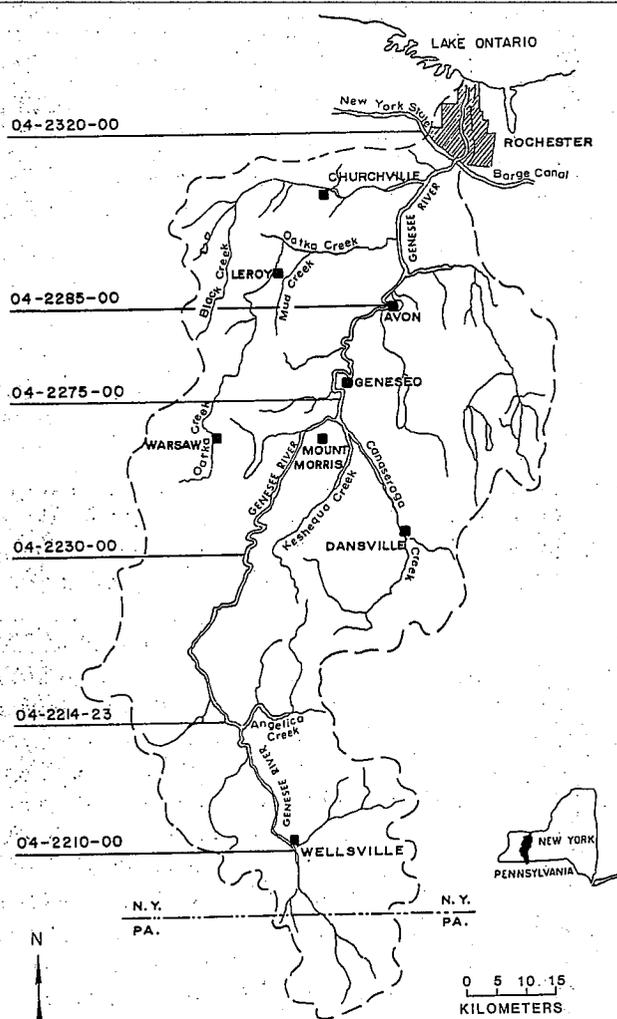


Fig. 1. Genesee River sampling sites. Each site is identified by its United States Geological Survey site number: Rochester, 04-02320-00; Avon, 04-2285-00; Mt. Morris, 04-2275-00; Portageville, 04-2230-00; Transit Bridge, 04-2214-23; Wellsville, 04-2210-00, (from Reddy, 1979 pg. 738, with permission).

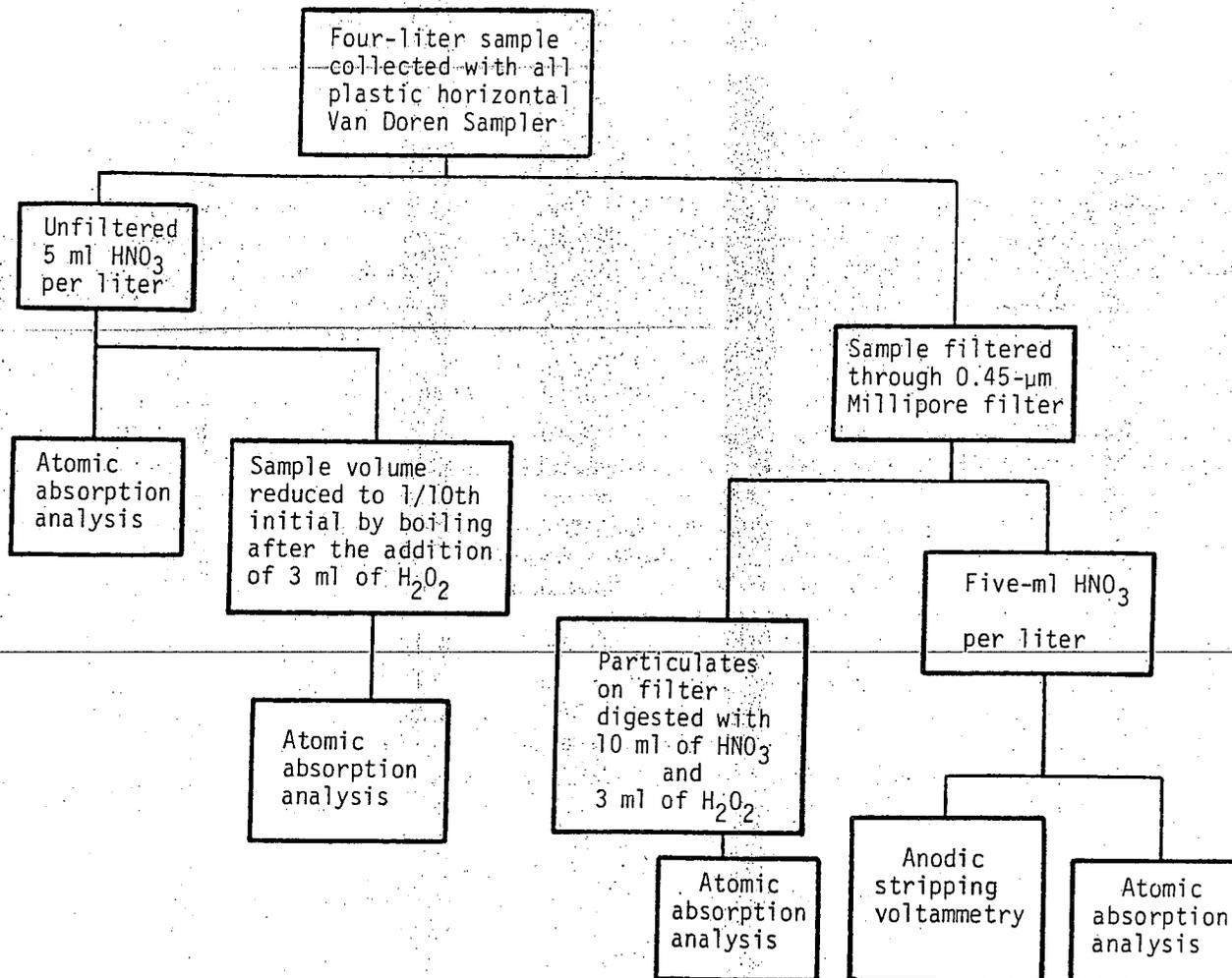


Fig. 2. Water-column sample pretreatment procedures.

the detection limit. Sediment analysis quality control materials were used for particulate material analysis. Homogeneous sediment samples collected from the Genesee Basin were analyzed during each particulate material digestion run; the relative standard deviation of sediment metal analysis was found to be  $\pm 10\%$ . Procedures used in this study were evaluated by participation in an interlaboratory check sample study conducted by the International Joint Commission for the Great Lakes and were found to be acceptable.

Because the analysis procedure used here does not solubilize the silicate rock matrix, it measures only environmentally available metal content, not metals incorporated in unreactive mineral phases.

By convention, chemical constituents of water are reported in the following categories (Brewer and Spencer, 1974; Brown *et al.*, 1970):

(1) *Dissolved material*, the component of the water sample that passes through a 0.45-  $\mu\text{m}$  membrane filter,\*

(2) *Suspended material* (particulate material), the component of the water sample retained by a 0.45-  $\mu\text{m}$  membrane filter, and

(3) *Total (dissolved + suspended) material*, the total amount of material in the water sample, regardless of physical or chemical form.

The specific treatment and analytical procedure chosen for an investigation defines the material analyzed. That is, the analytical result for total manganese concentration in an unfiltered water column sample, for example, may differ significantly from the sum of the dissolved plus particulate analyses for the same sample. To assess the analytical variability associated with different procedures for total analysis (i.e., determination of the total metal concentration), three analytical procedures (Fig. 2) were evaluated in the initial phase of the program: (1) the combined dissolved and particulate analy-

\*The operational definition of dissolved material in terms of 0.45-  $\mu\text{m}$  Millipore filtration will lead to values for some dissolved-metal con-

centrations (i.e., aluminum and iron) substantially above the true values (Wagemann and Brunskill, 1975). Such an effect is believed to be minimal in our study, because high suspended-sediment concentrations of the filtered sample rapidly reduce the filter's effective pore size to 0.1  $\mu\text{m}$ .

ses, (2) direct analysis of an acidified, unfiltered sample, and (3) analysis of a digested, concentrated (10:1) unfiltered sample.

The term "total metal concentration" used here implies that the analytical result is the sum of all metal present in the sample. Although it is generally recognized that complete destruction of the sediment matrix by dissolution in hot concentrated acid is seldom achieved, analyses using this technique are termed by convention "total analyses." Previous work by this laboratory has demonstrated that the strong-acid extraction technique is well suited to environmental analyses (Krishnamurty *et al.*, 1976). In general, total analysis of the undigested, unfiltered samples (procedure 2) yields slightly lower values (poorer recoveries) than the other two methods which employ digestion. Manganese determinations at each sampling site were in good agreement, while zinc analyses showed less consistency (Table 1).

## Results and Discussion

Data presented in this report are synoptic subsets (Fig. 1) obtained during an extensive 2-yr research program involving 28 sampling sites in the Genesee River watershed. A complete report on this project is in preparation for publication.

This study examined trace-metal distributions and fluxes during periods when particulate material transport was anticipated to be most significant. Particulate material erosion is flow-rate dependent and storm or snow-melt runoff events with high discharge are responsible for most of the erosion and transport of particulate material (Likens *et al.*, 1977). Thus erosion and transport of sediments from watersheds is due to a few hydrological events which arise from specific meteorological conditions (Knox, 1977). Characterization of metal transport during periods of significant particulate material movement thus requires intensive synoptic surveys during infrequent periods of peak discharge.

### Total concentrations

A preliminary survey demonstrated that some metal concentrations (arsenic, chromium, copper, lead, mercury, nickel, and zinc) were at or below the detection limits for the routine analytical procedures employed by

this laboratory. For these and other metals the digestion-preconcentration procedure shown on the left-hand side of Fig. 2 was used for analysis. The digestion-preconcentration procedure is appropriate because field blank values are typically below detection limits, and because the samples so prepared yield highly reproducible results which are well above the detection level (Table 1). Total metal concentrations and suspended sediment concentrations exhibited a characteristic longitudinal distribution (Table 2): while consistently low for the southernmost sampling sites, values peaked at the midbasin site.

Total metal concentrations varied over a factor of 10 for elements such as aluminum and iron, which are the major constituents of sediment. Elements with lower abundances in Genesee River sediment, such as copper, lead, and nickel, exhibited smaller ranges in water-column concentration (Table 2). In contrast to the total concentrations, dissolved metal concentrations (Table 1) varied relatively little over the length of the river. Constancy of dissolved metal concentrations suggests either that watershed runoff has a uniform dissolved-metal concentration similar to the river concentration, or that sediments in the river react rapidly to buffer metal concentrations (i.e., the fluvial sediment moderates dissolved metal ion concentration through rapid ion-exchange and/or adsorption reactions). The covariances of several total metal concentrations (aluminum, iron, manganese, and zinc) with suspended sediment were consistent for both sampling dates. For example, the correlation coefficients of aluminum concentration with suspended sediment were 0.74 (significant at the >90% confidence level) for December and 0.92 (significant at the 95% confidence level) for March. Iron also exhibited correlation coefficients significant at the >95% confidence level.

### Metal fluxes

Metal flux, the product of total concentration and discharge, varies directly with discharge. The flux of metal and suspended sediment (Table 3) increased steadily northward with river flow, reflecting both increasing metal concentration and river discharge (Table 2). Maximum fluxes occurred for most metals and suspended sediment at the midbasin site (Mt. Morris), which generally exhibited the highest suspended sedi-

Table 1. Dissolved, particulate, and total manganese and zinc concentrations ( $\text{mg l}^{-1}$ ) in Genesee River samples (December, 14, 1975).

Station	Dissolved		Particulate		Dissolved + Particulate		Total	
	Mn	Zn	Mn	Zn	Mn	Zn	Mn	Zn
Wellsville	0.02	0.011	0.014	0.005	0.034	0.016	0.05	0.007
Transit Bridge	0.03	0.008	0.056	0.012	0.086	0.020	0.08	0.011
Portageville	0.03	0.011	0.088	0.017	0.118	0.028	0.07	0.020
Mt. Morris	0.03	0.012	0.085	0.023	0.115	0.035	0.17	0.027
Avon	0.04	0.010	0.020	0.011	0.060	0.021	0.07	0.015
Rochester	0.03	0.016	0.033	0.012	0.063	0.028	0.06	0.015

Table 2. Metal and suspended-sediment concentrations ( $\text{mg l}^{-1}$ ) and discharge ( $\text{m}^3/\text{s}$ ).

Date	Station	Discharge	Suspended Sediment	Aluminum	Copper	Iron	Lead	Manganese	Nickel	Zinc
December 14, 1975	Wellsville	20.4	16	0.17	0.005	0.36	0.01	0.05	0.005	0.007
	Transit Bridge	43.3	100	1.4	0.005	3.3	0.01	0.08	0.005	0.011
	Portageville	94.6	212	2.3	0.007	3.2	0.01	0.07	0.01	0.020
	Mt. Morris	89.9	1340	2.7	0.009	6.1	0.02	0.17	0.012	0.027
	Avon	90.5	155	1.5	0.006	3.3	0.02	0.07	0.01	0.015
	Rochester	132.0	45	0.8	0.006	1.9	0.02	0.06	0.01	0.015
March 13, 1976	Wellsville	15.2	2	0.07	0.005	0.23	0.01	0.045	0.005	0.006
	Transit Bridge	15.6	174	0.75	0.005	1.4	0.01	0.053	0.005	0.016
	Portageville	58.8	47	0.93	0.005	1.8	0.015	0.054	0.005	0.013
	Mt. Morris	255.0	465	6.3	0.011	13.5	0.02	0.24	0.016	0.047
	Avon	245.9	265	5.2	0.009	10.5	0.015	0.18	0.018	0.035
	Rochester	296.7	387	4.5	0.009	10.0	0.02	0.175	0.019	0.035

ment concentrations in the river. Fluxes declined at the two sampling sites north of Mt. Morris, with the largest decrease associated with suspended sediment. Maximum flux for lead and nickel occurred on both dates at the river mouth (Table 3) due probably to inputs of these metals from the urban Rochester area and high discharge at this site.

The peak lead flux observed at the mouth of the Genesee River is due in part to increased discharge at the river mouth, and is compatible with the well-documented civilizational impact on environmental lead concentrations. For example, Peirson *et al.* (1973) and Lantzy and Mackenzie (1979) have demonstrated that anthropogenic emissions of lead have the most significant effect on the observed lead levels in comparison with all other elements.

Results presented in Table 3 show that metal fluxes were not conservative during the December sampling period. Sediment fluxes were smaller at the river mouth than at midbasin sampling sites, suggesting a net accumulation of sediment in the midbasin channel. On an annual basis, however, published data (U.S. Geological Survey, 1977) shows that the midbasin channel was a net

sediment source. Significantly greater amounts of sediment were transported from this reach than were received. The importance of changes in sediment storage characteristics, and their relationship to pollutant movement through a watershed has been discussed by Trimble (1981). Sediment and several metal (aluminum, iron, and manganese) fluxes decreased sharply downstream from Mt. Morris, but heavy metals, such as copper, lead, nickel, and zinc, did not decrease concomitantly. This suggests that a major portion of these metals are transported by an organic or small particle size mineral phase which does not settle in the midbasin region. Sources of these metals from the adjacent urban area may also counterbalance removal of metals by the decreasing sediment flux. In contrast, samples from March demonstrated little decrease in sediment or metal flux below Mt. Morris.

#### Particulate concentrations

As for total metal (Table 2), particulate metal concentrations exhibited a characteristic distribution with river reach (Table 4). Minimum values were found at the southernmost site, concentrations along the river re-

Table 3. Flux of metals and suspended sediment at six Genesee River sites.

Date	Station	Suspended Sediment ( $\text{g sec}^{-1}$ ) $\cdot 10^{-3}$	Flux (g sec <sup>-1</sup> )							
			Aluminum	Copper	Iron	Lead	Manganese	Nickel	Zinc	
December 14, 1975	Wellsville	0.326	3.47	<0.1	7.3	0.2	2.0	<0.1	0.14	
	Transit Bridge	4.330	60.7	0.22	143	0.43	3.5	0.22	0.48	
	Portageville	20.00	218	0.66	303	0.94	6.62	0.95	1.89	
	Mt. Morris	120	243	0.81	548	1.80	15.3	1.17	2.43	
	Avon	14	135.7	0.54	298.6	1.81	6.33	0.90	1.36	
	Rochester	5.9	105.6	0.79	250.7	2.64	7.92	1.32	1.98	
March 13, 1976	Wellsville	0.03	1.07	<0.1	3.5	0.15	0.69	<0.1	0.09	
	Transit Bridge	2.71	11.68	<0.1	21.8	<0.2	0.83	0.1	0.25	
	Portageville	27.3	54.7	<0.3	105.8	0.88	3.17	<0.3	0.76	
	Mt. Morris	118.6	1606	2.8	3443	5.1	61.2	4.08	12.0	
	Avon	65.2	1278	2.2	2582	3.69	44.3	4.42	8.60	
	Rochester	114.8	1335	2.67	2967	5.93	51.9	5.64	10.4	

Table 4. Particulate metal concentrations ( $\text{mg l}^{-1}$ ) at six Genesee River sites.

Date	Station	Aluminum	Copper	Iron	Lead	Manganese	Nickel	Zinc
December 14, 1975	Wellsville	0.25	0.001	0.40	<0.003	0.014	<0.001	0.005
	Transit Bridge	1.50	0.0035	2.85	0.003	0.056	0.004	0.012
	Portageville	2.35	0.0055	4.45	0.005	0.0875	0.006	0.0175
	Mt. Morris	2.45	0.0075	4.82	0.005	0.085	0.0065	0.023
	Avon	1.22	0.0035	1.27	0.005	0.020	0.004	0.0115
	Rochester	0.85	0.0045	1.70	0.005	0.0335	0.0035	0.012
March 13, 1976	Wellsville	0.12	0.001	0.16	<0.003	0.0045	<0.001	0.0025
	Transit Bridge	0.64	0.001	1.16	0.003	0.0205	0.001	0.0065
	Portageville	0.88	0.002	1.66	0.004	0.0265	0.003	0.008
	Mt. Morris	5.75	0.0075	11.25	0.010	0.190	0.013	0.034
	Avon	3.00	0.004	5.00	0.005	0.074	0.007	0.020
	Rochester	2.50	0.0045	4.51	0.005	0.069	0.0065	0.0175

flecting variations in suspended-sediment concentration. A covariance analysis of samples collected during March 1976 demonstrated that variation in suspended-sediment flux accounted for over 90% of the variation in particulate material fluxes of aluminum, iron, lead, and manganese. The relationship between sediment and metal transport in a river system may thus be useful in extrapolating from available suspended sediment data to obtain estimates of metal flux. However, use of sediment flux as an accurate estimator of metal movement in a basin requires characterization of suspended sediment composition changes during transport.

The patterns of particulate composition variation along the Genesee River can be shown by conversion of the results of Table 4 to a dry-weight basis by dividing each value by the corresponding suspended-sediment concentration (Table 5). These normalized concentrations are in general similar to bottom-sediment average concentrations for the Genesee watershed (Reddy, 1978). However, they illustrate a specific trend with river reach and suspended-sediment concentration. At sites with low suspended-sediment concentrations, such as Wellsville (Table 5), the metal concentrations are greater than the basinwide average values. At midbasin, where suspended-sediment concentrations are high

(Table 5), the metal concentrations are significantly below the basin average value.

Particulate composition changes may be related to the dynamics of sediment transport. Total metal concentrations can be considered to arise from three components: a nearly constant dissolved component, a fine component extractable in a strong acid-oxidizing solution and a coarse component that is effectively a neutral diluent to the suspended sediment. If this description is correct, sites with low flow and low suspended-sediment concentrations should also have low total metal concentrations. The suspended sediment would show metal contents well above basin average values, because of the preponderance of fine sediment. On the other hand, sites with high flow and suspended-sediment values should have high total metal concentrations. Under these conditions, suspended sediment metal content would be well below the basin averages for suspended sediment and would approach that for average bottom sediment, because of the large amount of entrained coarse sediment.

Particulate metal concentrations can be interpreted in terms of the influence of basin processes on fluvial metal transport by calculating the ratio of metal to aluminum concentration (Table 6). This procedure nor-

Table 5. Particulate metal concentrations, on a dry weight basis ( $\mu\text{g/g}$ ).

Date	Station	Aluminum	Copper	Iron	Lead	Manganese	Nickel	Zinc
December 14, 1975	Wellsville	15600	63	25000	—	875	—	312
	Transit Bridge	15000	35	28500	30	560	40	120
	Portageville	11080	26	20990	24	412	28	82
	Mt. Morris	1830	6	3600	4	63	5	17
	Avon	7870	23	8190	32	129	26	74
	Rochester	18890	10	37780	111	744	78	267
March 13, 1976	Wellsville	60000	500	80000	—	2250	—	1250
	Transit Bridge	3680	6	6670	17	118	6	37
	Portageville	18720	42	35320	85	563	64	170
	Mt. Morris	12370	16	24190	22	408	28	73
	Avon	11320	15	18870	19	279	26	76
	Rochester	6460	12	11650	13	178	17	45

Table 6. Particulate metal concentrations ratioed to particulate aluminum concentrations.

Date	Station	Copper $\times 10^{+3}$	Iron	Lead $\times 10^{+3}$	Manganese $\times 10^{+3}$	Nickel $\times 10^{+3}$	Zinc $\times 10^{+3}$
December 14, 1975	Wellsville	4.0	1.6	—	56	—	20
	Transit Bridge	2.3	1.9	2.0	37	2.7	8
	Portageville	2.3	1.9	2.1	37	3.5	7
	Mt. Morris	3.0	2.0	1.9	34	2.6	9
	Avon	2.9	1.0	4.0	16	3.3	9
	Rochester	5.0	2.0	6.0	39	4.1	14
March 13, 1976	Wellsville	8.	1.3	—	37	—	20
	Transit Bridge	1.5	1.8	4.7	32	1.5	10
	Portageville	2.2	1.9	4.5	30	3.4	9
	Mt. Morris	1.3	1.9	1.7	33	2.3	6
	Avon	1.3	1.7	1.7	25	2.3	7
	Rochester	1.8	1.8	2.0	28	2.6	7

malizes each metal concentration to a term which is related to the extractable inorganic portion of the sediment (i.e., the fine component of the three-component sediment model). These ratios (Table 6) exhibit significantly less variation than either particulate metal concentrations expressed on a wet (Table 4) or dry (Table 5) basis. Particulate iron concentrations (Tables 4 and 5), for example, range over two decades, while the normalized concentration has a range of less than a factor of 2.

Since sediment concentration normalization reduces the influence of particle size distribution, surface area, and mineralogy on the metal content, variability in the normalized concentration may arise from specific basin processes causing metal enrichment. A constant value for each normalized metal concentration is consistent with the hypothesis that the metals are being transported by the fine sediment component in a constant amount and with uniform reactivity. Particulate iron, a sediment constituent which is at high concentrations, and thus relatively insensitive to watershed perturbations, exhibits little fluctuations in the normalized concentration values. Trace metal concentrations (i.e., Cu, Ni, Pb, and Zn) show trends over the length of the river and are not correlated with iron- or manganese-normalized concentrations. Peak values for the normalized trace metal concentrations (and thus elevated sediment trace metal up take and/or supply) occurred at each end of the basin (i.e., Wellsville and Rochester) in December. Elevated Cu/Al and Zn/Al ratios at Wellsville may arise from an elevated organic/inorganic ratio in the particulate material at this site relative to sites downstream. Elevated ratios at Rochester are consistent with additional trace metal inputs to the watershed from the large urban area. During the maximum discharge period (March) normalized particulate metal concentrations exhibited little fluctuation along the length of the river. This observation is consistent with the proposed sediment remobilization associated with peak discharge.

Although a simple physical description of the influence of discharge and suspended-sediment concentra-

tion on metal concentration may yield a qualitatively accurate description of the trace-metal distribution mechanism in a river, other chemical factors, such as the presence of organic material, may also be important. For example, sites with low suspended-sediment concentrations may have large amounts of low-density, organic-carbon-rich material in the water column. This organic-carbon enrichment could lead to an enrichment in particulate material metals above the basinwide bottom-sediment average. Sites with high suspended sediment may have a large amount of low specific-surface area, coarse sediment having a comparatively low organic-carbon content. Such material would be depleted in metals relative to basinwide average values.

This hypothesis is consistent with the results in Tables 2 and 4 and with other information available for the Genesee River (M. M. Reddy, unpublished results). For example, particulate material collected at Wellsville on December 14, 1975, contained 4% organic carbon, while material collected at Mt. Morris on the same date had less than one-tenth of that content.

The pattern of longitudinal variation of total and particulate metal concentrations, suspended-sediment concentrations, and discharge in the Genesee River suggests that suspended sediment contributes significantly to the total metal concentration in river water during peak-flow periods. Dissolved metal concentrations, on the other hand, fluctuate only slightly over the length of the river, despite large changes in suspended-sediment concentration and discharge. Additional laboratory and field investigations must be conducted to characterize the mechanism that apparently regulates dissolved-metal levels in the Genesee.

The Genesee River is a major tributary to Lake Ontario, a North American Great Lake undergoing cultural stress; therefore, trace metals transported from the river may have a significant environmental impact. While little information is available concerning the trace metal budget for Lake Ontario, data for hydrological and sediment budget have been published. In addition, limited data for some total trace-metal concentrations at the

lake's inlet and outlet with discharges, allow calculation of flux values.

On an annual basis Allen (1977) reports that for 1966-1967 the Genesee River contributed slightly more than 1% to the hydrological budget and 5% to the sediment budget of Lake Ontario. The Niagara River serves as the principle hydrological and sediment source to the lake (mean residence time of 8 yr). For the 1966-1967 period the Genesee River ranked as the fourth largest source of nutrient and sediment loading to Lake Ontario. In addition to tributary inputs Allen estimates that atmospheric inputs of nutrients and heavy metal may be important to the chemical budget of Lake Ontario.

Instantaneous trace-metal fluxes to Lake Ontario at Rochester during March 1976 (Table 3) can be compared with lake inlet fluxes (Niagara River at Fort Niagara, NY, May 20, 1976) and outlet fluxes (St. Lawrence River at Cornwall, Ontario, near Massena, NY, April 26, 1976). The inlet fluxes for lead and zinc were 186.9 and 77.9 g/sec, respectively. Outlet fluxes were 36.3 and 181.2 g/sec for lead and zinc, respectively. The flux values for the Genesee River at Rochester are smaller than the corresponding values at the inlet and outlet, but are significant in comparison to them. Since the sampling protocol focused on peak discharge periods in the Genesee River watershed, this comparison is an upper value. For smaller discharge periods during the year the Genesee River trace metal flux would be smaller relative to the lake input and output fluxes.

Sediments being desposited along the southern shore of Lake Ontario are derived from the Niagara and Genesee Rivers. Since this area is also one of significant accumulation of toxic substances, characterization of material transported by the Genesee River is of considerable interest in determining the ultimate fate of the toxic materials in the lake ecosystem. The relationship between sediment composition and toxic substance mobility is an area of ongoing investigation.

Sediment sources in the northeastern United States are well known. Sheet erosion of agricultural lands and subsequent transport of eroded soils is a major source of sediments in the region which includes the Genesee Basin. Stream bank erosion may also be a significant sediment source.

Chemical and biological trace metal cycling mechanisms in streams and rivers are poorly understood. Processes described in a general way by Leland *et al.* (1973) for sediments in Lake Michigan apply to trace metal-sediment interactions in the Genesee River watershed. Kubota *et al.* (1974), examining trace metal removal from an area adjacent to the Genesee basin, concluded that stream water trace-metal concentrations were consistent with normal geochemical processes and soil weathering. Atmospheric input of trace metals are largely unknown for the Genesee watershed, although

such input, in the case of lead for example, could be an important component to the overall basin budget.

A detailed ecosystem model is not available for the Genesee watershed. Its relatively large size makes the ecosystem approach difficult to implement. Moreover, long-term influences of precipitation chemistry, biological activity, and seasonal variation in water quality on the distributions and fluxes of trace metals limit the extent to which the data can be modeled. As pointed out by Likens *et al.* (1977), for example, lack of information about ecosystem growth processes can obscure the influence of rock weathering reactions on water quality, an important component of watershed chemical modeling.

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