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Abstract

Trace metal concentrations were determined in the six river systems entering the Great Bay Estuary, New Hampshire through a 15 month period. With the possible exception of copper there was no relationship between river flow and metal concentration. Budgetary calculations indicate that copper input is dominated by sewage input into the estuary while the major copper "sink" is the estuarine sediments. The chromium budget suggests that former industrial effluent has dominated the Cr input into the Great Bay System.

Introduction

In order to establish mass geochemical budgets of estuarine systems, as well as to assess the role of terrestrial (natural as well as anthropogenic) input into such systems, the chemical monitoring of rivers must be undertaken. In addition, because of the role of varying riverine flow on chemical distributions in rivers, seasonal, if not more frequent, monitoring should be accomplished. This is particularly true if adequate input data and hence budgetary considerations are to be established for any given river-estuary system.

The work reported here was undertaken to establish the seasonal input of the trace metals iron, manganese, copper and chromium from the six rivers entering the Great Bay Estuary, New Hampshire. This was done to ascertain the role of changing river flow on river geochemistry as well as to provide better constraints on the quantitative input of riverine trace metals into the estuarine system.

Methods

Samples were collected above the dams over a period of 15 months before salt water intrusion of all the rivers under investigation (Figure 1). An acid rinsed linear polyethylene (LPE) jug on a nylon line was used. Samples were immediately decanted into precleaned (Patterson and Settle, 1976) 120 ml LPE bottles. These bottles were then placed in an ice filled cooler and returned to our laboratory. The samples were then acidified to pH \sim 1 with our own ultrapure nitric acid. In addition, an aliquot of

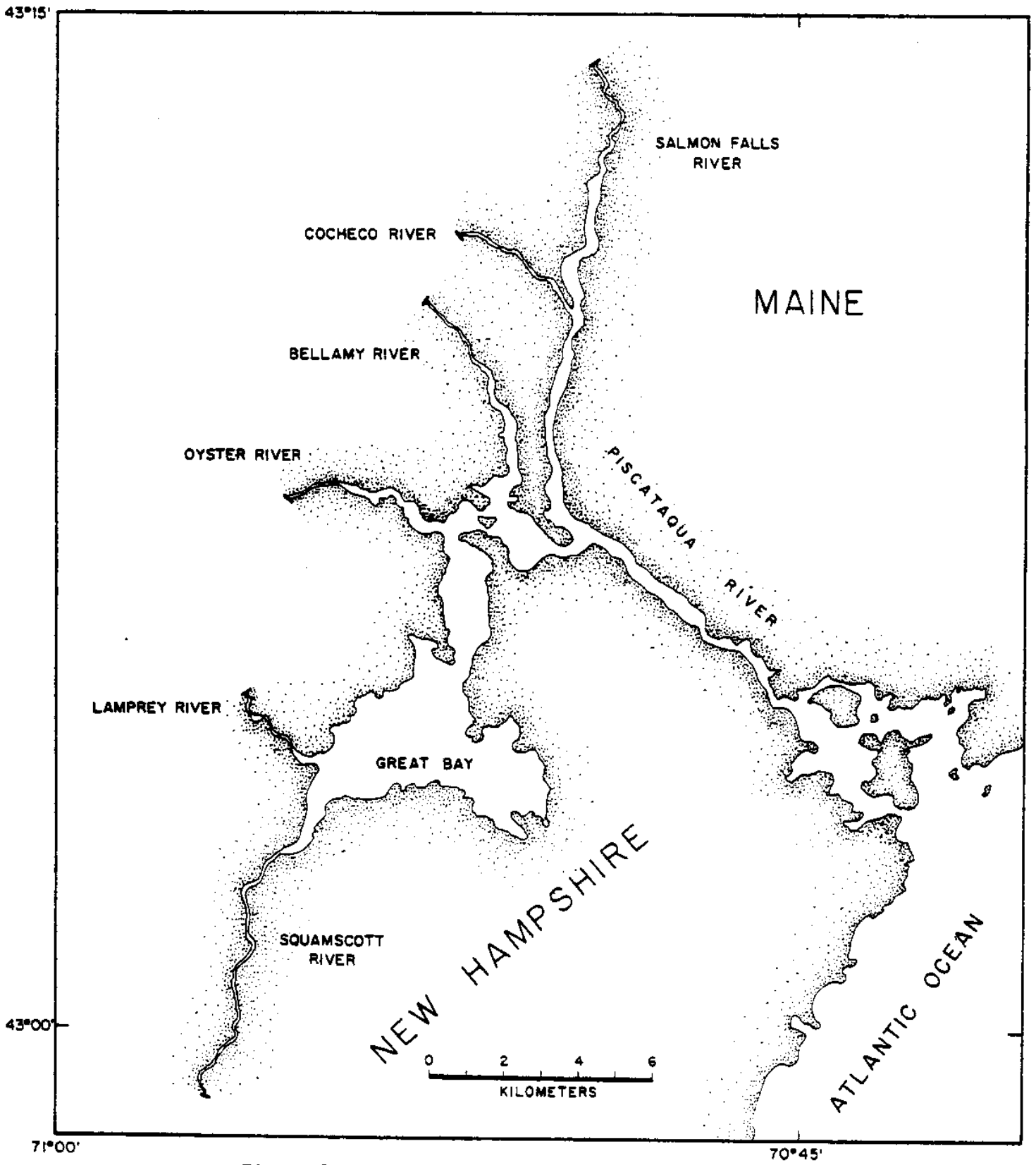


Figure 1. Great Bay Estuary, New Hampshire

sample was filtered through an acid-rinsed polycarbonate filtering unit containing a 0.4 μ Nuclepore^{T.M.} filter. These samples are termed "dissolved." The unfiltered values presented here represent the dissolved metal fraction as well as that metal that is leached from the particulate matter at pH \sim 1. This fraction should include the dissolved metal as well as that metal present as colloidal material, and that associated with oxide coatings and labile organic material. We choose to refer to this metal fraction as "environmentally available" metal.

Iron (Fe) and manganese (Mn) were analyzed colorimetrically using the methods of Stookey (1970) and Goto et al (1962) respectively. Copper (Cu) and chromium (Cr) were analyzed via direct injection flameless atomic absorption spectrophotometry. The precision of the measurements reported as coefficients of variation are: Fe \pm 0.6% @ 500 μgkg^{-1} , Mn \pm 1% @ 119 μgkg^{-1} , Cu \pm 5% @ 5.0 μgkg^{-1} , and Cr \pm 4% @ 7.0 μgkg^{-1} . National Bureau of Standards Reference Material 1643 (trace elements in fresh water) was also analyzed for Fe, Cu and Cr. This reference is certified at: Fe 75 \pm 1 μgkg^{-1} , Cu 16 \pm μgkg^{-1} and Cr 15 \pm μgkg^{-1} . We found the following: Fe 60 \pm 10 μgkg^{-1} , Cu 13.4 \pm 0.5 μgkg^{-1} and Cr 12.2 \pm 0.4 μgkg^{-1} .

Results and Discussion

The range and means of the environmentally available Fe, Mn Cu and Cr for each of the six rivers under investigation are shown in Table 1a. "Dissolved" Fe and Mn data for the four major rivers entering the Bay are shown in Table 1b. These rivers account for approximately 85% of the

Table 1a. Range and mean environmentally available trace metal data for rivers entering Great Bay Estuary (values in $\mu\text{g kg}^{-1}$). Values in parenthesis are average values.

| River | Fe | Mn | Cu | Cr |
|--------------|---------------|-------------|---------------|---------------|
| Lamprey | 168- 708(351) | 51-267(135) | 0.1- 9.2(3.1) | 0.4- 7.6(2.5) |
| Salmon Falls | 173- 546(331) | 57-209(122) | 0.9-17.3(4.8) | 5.0-13.7(9.4) |
| Oyster | 234- 817(448) | 67-350(188) | 0.4- 6.2(3.3) | 0.6- 1.4(0.9) |
| Cochecho | 247-1172(615) | 58-245(134) | 0.9- 9.8(6.6) | 1.0- 3.1(2.2) |
| Bellamy | 268-1218(786) | 72-282(180) | 0.6- 8.3(4.0) | 0.4- 1.4(0.9) |
| Exeter | 212-1035(498) | 70-473(239) | 0.4-20.7(5.4) | 0.4- 2.2(1.1) |

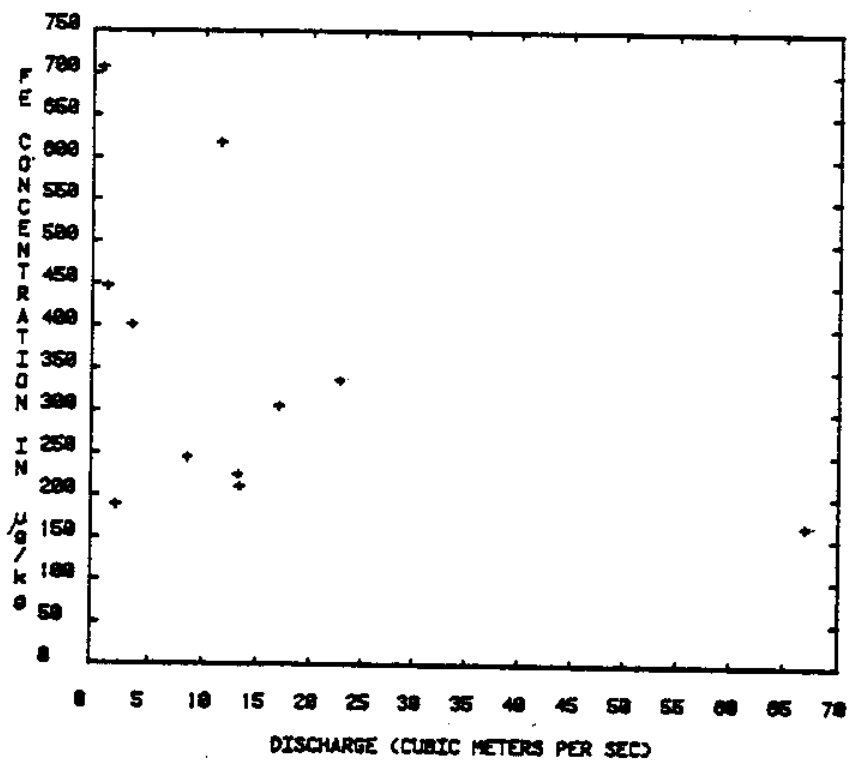
Table 1b. Range and mean of "dissolved" (i.e. passing 0.4μ membrane filter) Fe and Mn for the Lamprey, Salmon Falls, Cochecho and Exeter Rivers.

| River | Fe | Mn |
|--------------|---------------|--------------|
| Lamprey | 89-596 (227) | 38-151 (99) |
| Salmon Falls | 106-320 (184) | 32-140 (90) |
| Cochecho | 106-494 (279) | 26-137 (89) |
| Exeter | 123-688 (332) | 42-342 (170) |

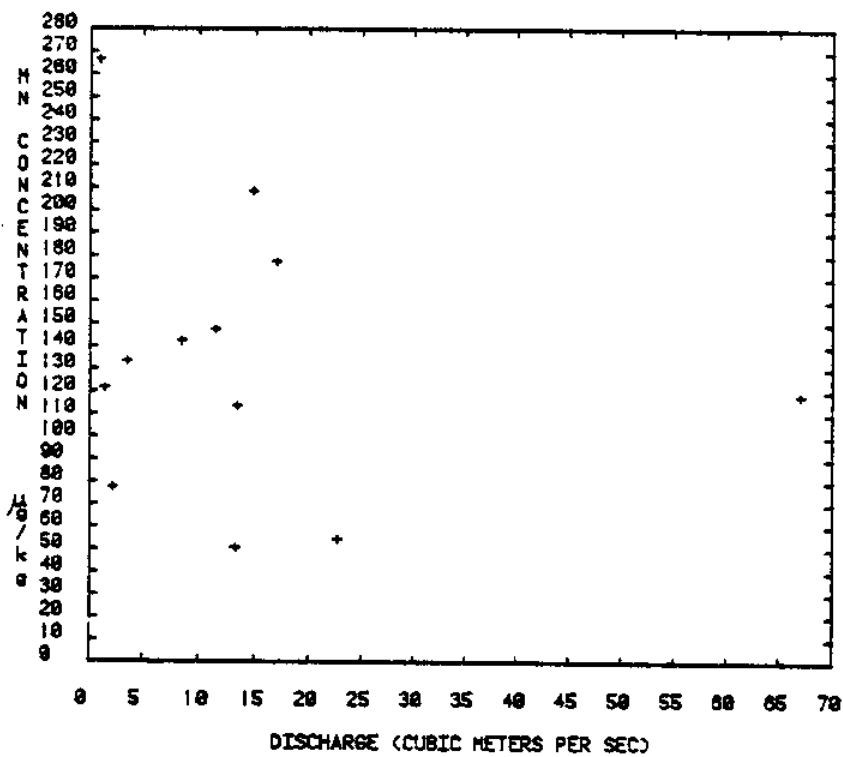
fresh water input into the estuary. The rivers with the largest discharge (i.e. Lamprey and Salmon Falls) have the lowest mean Fe values and low mean Mn values. Yet there appears to be no relationship between discharge rate and the concentration of these two metals for either river (Figures 2 and 3). (River discharge values were calculated using the U.S. Geological Survey's Water Years 1979-1980 flow data of the day plus the day prior to when the rivers were sampled.) Mayer (1982) has found a similar lack of relationship between dissolved Fe and flow in the Saco River, Maine.

This lack of relationship between discharge volume and elemental concentration has been observed for major cations and anions in northern New England streams (Likens et al., 1977) and has been attributed to the chemical equilibria between the aqueous phase and the solid phases in the soils. Therefore streamwater chemistry may be essentially established in the soil zone (Likens et al., 1977). This is possibly the case for Fe and Mn as well. The mean atomic ratios (Fe:Mn) of the Lamprey, Salmon Falls, Oyster and Exeter Rivers lie between 2-3 to 1, while the ratios of the other two rivers fall between 4-5 to 1. The Fe/Mn ratio in northern New Hampshire 'A' horizon soil is ~100 to 1 (R. Harter, personal communication).

An examination of the literature indicates that dissolved and total Mn concentrations in river water can vary widely. The values obtained by us for the rivers entering Great Bay are on the higher side of those values observed in New England and eastern Canadian rivers (Tables 1,2). Although the "average" dissolved riverine

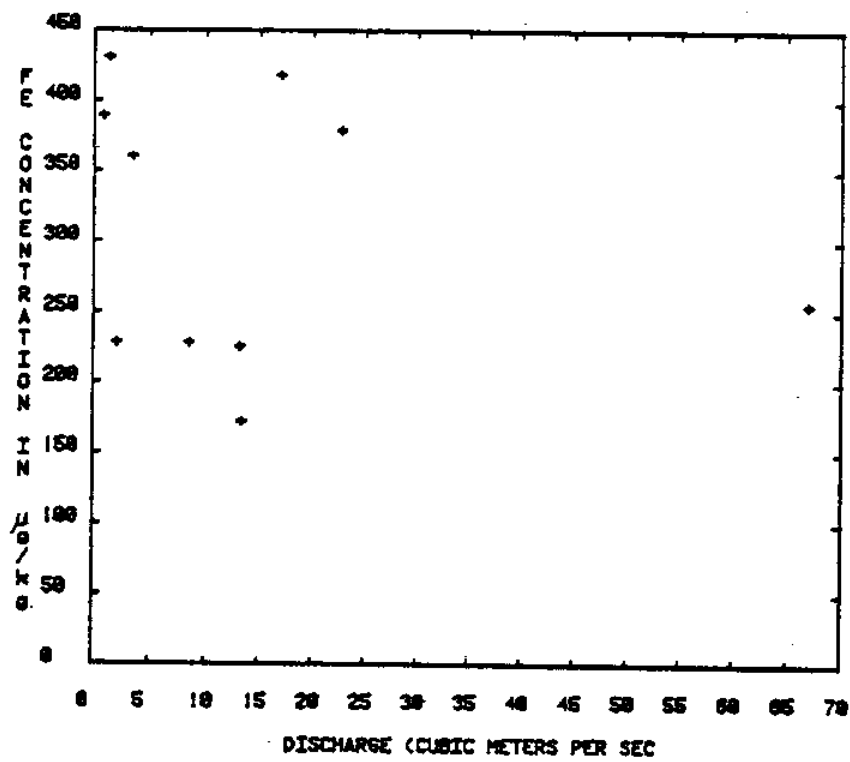


IRON CONCENTRATION VS. DISCHARGE FOR LAMPREY RIVER

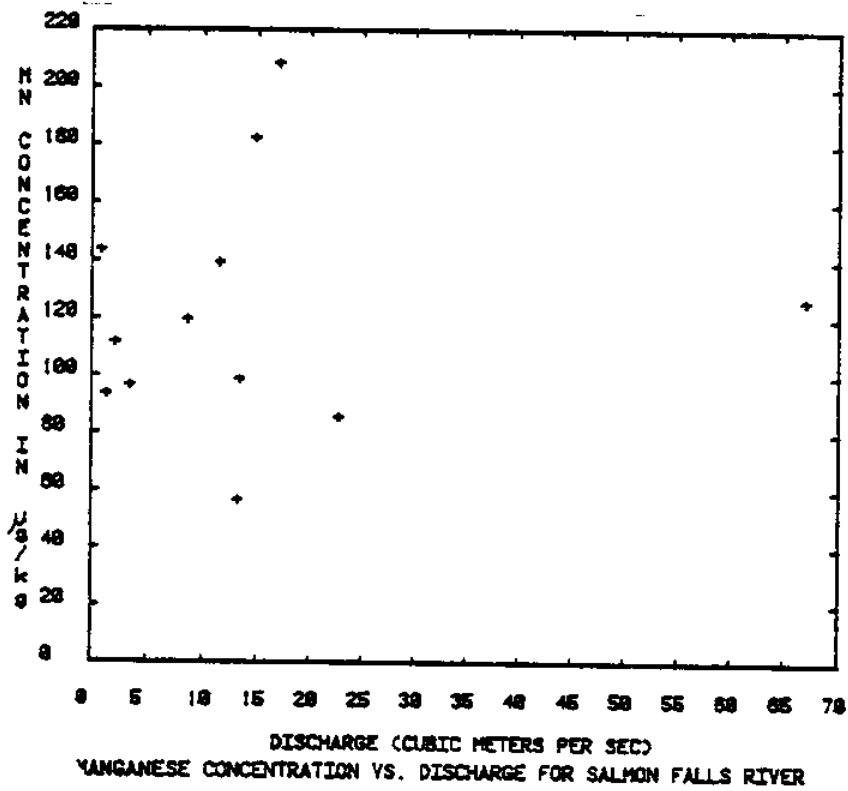


MANGANESE CONCENTRATION VS. DISCHARGE FOR LAMPREY RIVER

Figure 2. Lamprey River discharge vs Mn and Fe concentrations in μgkg^{-1} .



IRON CONCENTRATION VS. DISCHARGE FOR SALMON FALLS RIVER



MANGANESE CONCENTRATION VS. DISCHARGE FOR SALMON FALLS RIVER

Figure 3. Salmon Falls Discharge vs Mn and Fe concentrations in μgkg^{-1} .

Table 2. Trace metal data for New England and eastern Canadian rivers (values in ppb)

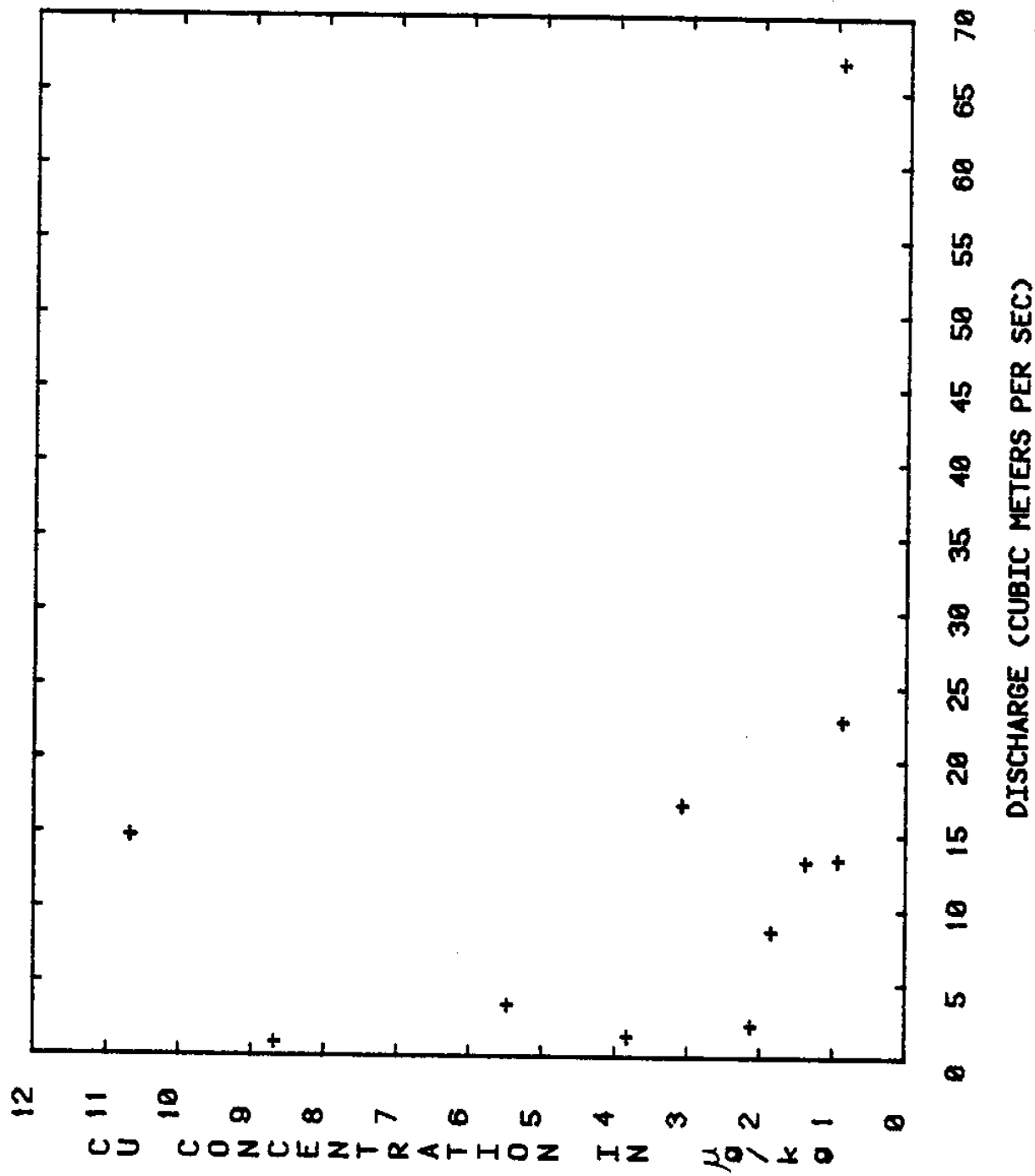
| | Fe | Mn | Cu | Cr |
|---|-----|-------|---------|-----|
| Salmon Falls* | 190 | - | 2.8 | - |
| Saco, Maine* | 140 | - | 1.5 | - |
| Kennebec, Maine ^o | - | - | <10 | 2-3 |
| St. Francois, Quebec Vermont+ | - | - | 7-33 | - |
| Narragansett Bay, R.I. rivers [•] | - | 190 | | |
| St. Lawrence River** | 705 | 23 | 3.7 | - |
| Hudson River++ | 910 | 19-29 | 5.2-5.8 | - |
| Exeter River, N.H. ^{oo} | 900 | 100 | 0.6 | - |
| Squam River, N.H. ^{oo} | 400 | 30 | 0.6 | - |

- * Giesy et al. (1978)
- ^o Friant (1979)
- + Tessier et al. (1980)
- [•] Graham et al. (1976)
- ** Yeats and Bowers (1982)
- ++ Klinkhammer and Bender (1981)
- ^{oo} Piette (1982)

Mn concentration is less than $10 \mu\text{g l}^{-1}$ (Turekian, 1971), it is not uncommon to find that rivers which drain areas with abundant water logged soil, bog and/or lowland of acid soil (Patrick and Turner, 1968; Moore et al., 1979) and rivers which have been affected by human activity probably by lowering the Eh or pH or both (Duinker et al., 1979), have average dissolved Mn values greater than $100 \mu\text{g l}^{-1}$. From 45 to 67% of the environmentally available Fe can be termed "dissolved" (Table 1). The Cocheco River is the only major tributary in which the mean "dissolved" Fe value is less than half of the mean environmentally available Fe. A greater portion of the environmentally available Mn passed the 0.4 filter. The mean "dissolved" Mn was ~70% of the environmentally active metal. Our river water ratios indicate that either Fe has been selectively removed or that Mn has been added compared to the New Hampshire soil values. Because slight changes in pH and Eh effect the redox chemistries of these metals, the riverine ratios may also reflect changes in the redox chemistry as the metals are transported from the soil into the river system. It is conceivable that Fe is lost on transport as FeOOH coatings on larger sediment particles or that Mn is introduced into the river water preferentially (either through the slightly reducing pore waters of the river sediments or through low Eh ground water input).

The Cu and Cr values are well within the range observed for other New England and Canadian rivers (Table 2). Unlike Fe and Mn, the Cu vs. discharge plots suggest lower values at higher discharge (Figure 4).

Copper and chromium budgets for the estuary can be calculated based on all available information, and are shown in Table 3. Iron



COPPER CONCENTRATION VS. DISCHARGE FOR SALMON FALLS RIVER

Figure 4. Salmon Falls River discharge vs Cu concentration in μgkg^{-1} .

Table 3. Cu and Cr budgets, Great Bay Estuary, NH

Cu

| <u>Input</u> in 10^6 g yr ⁻¹ | | <u>Output</u> in 10^6 g yr ⁻¹ | |
|---|------------|--|------------|
| °Municipal sewage | 3.7 | *Sediments | 5.4 |
| +Atmospheric | 0.6 | *Outflow | ~1.1 |
| Riverine | <u>2.2</u> | | |
| | 6.5 | | <u>6.5</u> |

*by difference (input minus sediment output)

Cr

| <u>Input</u> in 10^6 g yr ⁻¹ | | <u>Output</u> in 10^6 g yr ⁻¹ | |
|---|------------|--|-------------|
| °Municipal sewage | 5.7 | *Sediments | 28.5 |
| +Atmospheric | 0.2 | Outflow | ? |
| Riverine | <u>1.0</u> | | |
| | 6.9 | | <u>28.5</u> |

°Volumes of input from Loder and Glibert (1980), concentrations from Morel et al. (1975)

+Galloway and Likens (1979)

*Average sediment values from Armstrong et al. (1976), sedimentation rate from Leavitt, 1980.

and manganese budgets were not attempted due to the fact that undoubtedly the majority of these elements entering the estuary are associated within detrital particles and hence can not be measured by our techniques. The riverine input figures are based solely on average values from the four major tributaries. The atmospheric input values are based on the values determined by Galloway and Likens (1979) for northern New England rural areas and the area of the estuary (i.e. 43 km²). The sewage input value was calculated according to Loder and Glibert (1980) assuming the Cu and Cr values of municipal sewage from Morel et al. (1975). The sewage values are most suspect due to the uncertainty not only in the volume input into the Bay but also to the probable variability in the metal concentration through time. Because of these uncertainties as well as the "single event" sampling of the rivers, these budgets should be taken as rudimentary approximations. Only through more detailed sampling will more adequate budgets be fully developed.

The Cu budget balances quite well considering the inherent difficulties in these sort of calculations. The difference between the input values and the sediment output values are taken to represent the export of metal from the estuary. Because the residence time of the water in Great Bay (Arellano, 1978) is thought to be an order of magnitude larger than the residence time of dissolved copper in the estuary (Lyons and Gaudette, 1978), it appears little (less than 20%) dissolved copper is escaping the estuarine system. Hence, most of the copper entering the estuary is retained. Kim's (1981) calculations of first order removal rates of dissolved copper in the

Merrimack River Estuary, northern Massachusetts also indicate that the residence time of the estuarine water is much larger than that of dissolved copper and that dissolved copper is retained within this estuarine system. Undoubtedly the majority of Cu and Cr leaving these estuarine systems is probably associated with fine-grained oxide and/or organic-rich particles (Lyons and Gaudette, 1979).

The high percentage of the total Cu input into the estuarine system due to sewage is not surprising. High sewage inputs of trace metals have been observed in Narragansett Bay (Goldberg et al., 1977), Long Island Sound (Fitzgerald et al., 1974) and northern Chesapeake Bay (Helz, 1976).

The budgetary calculations for Cr in the Great Bay Estuary reveal a different situation than for Cu. The sedimentary sink alone is ~4 times greater than the calculated input. Chromium was introduced for a number of years into Great Bay and its river systems through tannery operations. Capuzzo and Anderson (1973) have shown that chromium-rich industrial effluent was discharged into the Great Bay system for ~30 years with input rates of dichromate, $\text{Cr}_2\text{O}_7^{2-}$ as large as $2 \times 10^8 \text{ g yr}^{-1}$. Chromium values as high as 0.23% dry wt., have been observed in Great Bay sediments (Armstrong et al., 1976). This source of Cr to the estuary ceased in the late 1960's to early 1970's and hence the average Cr being deposited into the sediments presently is undoubtedly less than that observed by Armstrong et al. (1976). Therefore the calculated output through sedimentation is too high and is an artifact based on past industrial input to the system. The high Cr values found in the Salmon Falls and Lamprey Rivers may

be due to the addition of older riverine sediments enriched in the tannery effluent.

Analysis of the Jeffrey Basin, Gulf of Maine sediments by Lyons and Gaudette (1979) suggest that some of this anthropogenic Cr is escaping northern New England estuaries and is being transported via fine grained particles onto the continental shelf.

Conclusions

The following conclusions can be drawn from this study: 1) with the possible exception of Cr, the riverine concentrations of the trace metals under investigation are within the range of those found in other northern New England river systems 2) Fe and Mn concentrations show no relationship to river discharge 3) Fe:Mn ratios in the river waters bear no relationship to soil ratios suggesting fractionation of these metals has occurred during weathering and transport 4) budgetary calculations indicate that Cu input and output are balanced with the major estuarine "sink" being the sediments and 5) the Cr budget indicates much less input into the system than occurred ~10 years ago when industrial effluent rich in Cr was the major estuarine 'source'.

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