

NBP-91-66

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Narragansett Bay Estuary Program

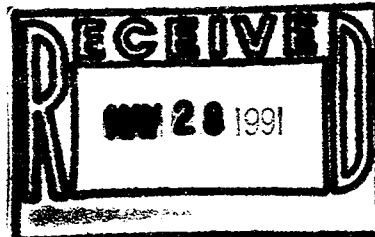
RECENT METAL INPUTS TO NARRAGANSETT BAY

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Final Report
Submitted to the
Narragansett Bay Project

May 1991



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FOREWORD

The United States Congress created the National Estuary Program in 1984, citing its concern for the "health and ecological integrity" of the nation's estuaries and estuarine resources. Narragansett Bay was selected for inclusion in the National Estuary Program in 1984, and the Narragansett Bay Project (NBP) was established in 1985. Narragansett Bay was designated an "estuary of national significance" in 1988. Under the joint sponsorship of the U.S. Environmental Protection Agency and the Rhode Island Department of Environmental Management, the NBP's mandate is to direct a program of research and planning focussed on managing Narragansett Bay and its resources for future generations.

The NBP will develop a draft Comprehensive Conservation and Management Plan (CCMP) by December, 1991, which will recommend actions to improve and protect the Bay and its natural resources.

The NBP has established the following seven priority issues for Narragansett Bay:

- management of fisheries
- nutrients and potential for eutrophication
- impacts of toxic contaminants
- health and abundance of living resources
- health risk to consumers of contaminated seafood
- land-based impacts on water quality
- recreational uses

The NBP is taking an ecosystem/watershed approach to address these problems and has funded research that will help to improve our understanding of various aspects of these priority problems. The Project is also working to expand and coordinate existing programs among federal, state and local agencies, as well as with academic researchers, in order to apply research findings to the practical needs of managing the Bay and improving the environmental quality of its watershed.

This report represents the technical results of an investigation performed for the Narragansett Bay Project. The information in this document has been funded wholly or in part by the United States Environmental Protection Agency through Cooperative Agreement #CX812680 to the Rhode Island Department of Environmental Management. It has been subject to the Agency's and the Narragansett Bay Project's peer and administrative review and has been accepted for publication as a technical report by the Management Committee of the Narragansett Bay Project. The results and conclusions contained herein are those of the author(s), and do not necessarily represent the views or recommendations of the NBP.

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ABSTRACT

In spite of the fact that no systematic attempt has yet been made to measure the total annual input of any metal to Narragansett Bay, sufficient information exists to develop a rough preliminary inventory of the inputs of many metals.

With the exception of Pb, direct deposition from the atmosphere (wet and dry) onto the surface of the bay probably accounts for less than 2% of the annual input of the metals examined in this report (Cd, Cr, Cu, Ni, Pb, Zn, Ag). In the case of lead, direct atmospheric deposition may provide about 25% of the total input. The atmosphere may be an important pathway by which some metals enter the bay, however, because non-point sources appear to contribute to the metals load carried by rivers in amounts equal to or greater than those provided by point sources. This is particularly true for Cd. Unfortunately, I have not been able to find any reports of measurements of the deposition of this metal in the Narragansett Bay watershed.

Rivers and streams and the upstream sources that contribute to their metal loads appear to add over 60% of the total Cd entering the bay proper and about one-third of the Cr, Cu, Ni, and Pb. These sources amount to less than 10% of the annual Ag input. Rivers and upstream sources provide over twice as much Zn as direct discharges to the bay.

The only known significant anthropogenic discharges of metals directly to the tidal waters of the bay come from publicly owned sewage treatment plants (POTWs). For Narragansett Bay proper, these sources contribute 13% of the Cd, 32% of the Cr, 41% of the Cu, 36% of the Ni, 16% of the Pb, and 89% of the Ag entering the system each year. It is possible that electric power generating plants may release significant amounts of some metals, but this potential source requires further study. Preliminary work suggested that cooling water may provide almost as much Ni to Mt. Hope Bay as does the Taunton River.

Metals also enter the bay in offshore water as part of the tidal and gravitational circulation. This source is poorly quantified, but, with the exception of Ag, it may provide about 25% of the total input of Cd, Cr, Cu, Ni, and Pb. The offshore water could supply only a few percent of the Ag input and there are no data with which to estimate the input of Zn from this source.

In order to develop a more accurate and complete assessment of the inputs of metals to the bay it will be important to:

1. obtain measurements of the deposition of metals from the atmosphere in a variety of urban and rural areas of the watershed over an annual cycle. The measurements should include Cu and Cd as well as those metals presently studied by the atmospheric chemistry group at URI;

2. obtain more frequent measurements of metal concentrations and flows in the smaller urban rivers such as the Moshassuck and Woonasquatucket. The data base for Cr is particularly weak in these systems, and they may be important sources of this metal;
3. Obtain measurements of metal concentrations in the free-flowing portion of the Taunton River. The flux of all metals from the Tuanton River is virtually unknown. Moreover, there has been no assessment of Mt. Hope Bay as a settling basin that may remove metals from the river and from the Fall River POTW before they enter Narragansett Bay proper;
4. obtain better and more frequent data from POTWs. Many plants do not measure metals or only report that concentrations in effluents are "less than" a permitted value. Flow data should be reported along with concentration data. The practice of including only the highest monthly value in RIPDES files leads to overestimates of metal inputs to the bay;
5. obtain better data on metal concentrations over an annual cycle in offshore waters that enter the bay.

RECENT METAL INPUTS TO NARAGANSETT BAY

Introduction

It is useful to begin this inventory of metal inputs to Narragansett Bay with a few comments about our perception of the amount of fresh water that enters the bay. This is true not just because much of the metal flux to the bay comes in rivers and streams, but also because the difficulty of developing a complete accounting of fresh water input emphasizes the even more serious limits to our knowledge of the inputs of anthropogenic pollutants such as metals.

The earliest estimate I have found of the total fresh water flow into Narragansett Bay was provided by Wehe (1953), who calculated that the flow averaged $76 \text{ m}^3 \text{ s}^{-1}$ for the 22 years from 1930 through 1951. He arrived at this value by applying the ratio of gauged flow to gauged watershed area of the Blackstone River to his estimate of the entire drainage area of the bay. Such an indirect approach was necessary because the fresh water flow from about 58% of the drainage area had never been measured. The ratio of gauged to ungauged flow has varied somewhat in subsequent years as gauges have been added, deleted, or moved, and the ratio is also sensitive to the choice of boundaries for the drainage basin. According to Pilson (1985), the largest drainage area reported in recent publications (4836 km^2) is 18% greater than the smallest.

Unfortunately, Wehe's calculations were contained in an obscure unpublished report, while the measured flows appeared annually in official reports from the U.S. Geological Survey. In spite of the fact that there was a general awareness among those concerned with Narragansett Bay that a portion of the watershed was not gauged, the measured flow began to appear more frequently in the literature, often with little or no qualification about how small a fraction of the total it might represent. A general perception began to form that the input of fresh water to the bay was less than $50 \text{ m}^3 \text{ s}^{-1}$ (Hess and White 1974, Kremer and Nixon 1978, Olsen et al. 1980).

In 1985, as part of his efforts to determine the flushing rate of Narragansett Bay, Pilson expanded and refined Wehe's approach of 30 years earlier and concluded that the more recent "long-term" total input of fresh water to the bay was on the order of $105 \text{ m}^3 \text{ s}^{-1}$, with less than 50% of the drainage area measured. This revision then prompted an even more extensive analysis by the U.S.G.S. (Ries 1989) that agreed with Pilson's (1985) long-term average input and assigned an uncertainty of $\pm 10\%$ to the long-term annual input estimate, and $\pm 20\%$ to the calculated inflow for any particular month. The U.S.G.S. reported that 63% of the watershed was monitored by continuously recording stream gauges.

Assuming that the long-term average input of fresh water is now approximately correct, our working estimates have gone from about 75 to less than 50 to about 100 $\text{m}^3 \text{s}^{-1}$ in the past 30 years. And a "correct" value has been available only in the last five years. Since large proportions of many of the metals that enter the bay are carried by surface water, the errors in our knowledge of fresh water flow set a minimum uncertainty on our estimates of metal fluxes. In addition are errors associated with the calculation of long-term fluxes from a relatively small number of measurements of metal concentrations in the fresh water, the lack of any sampling in many fresh water sources, and errors involved with the chemical analyses of the metals themselves. Moreover, in contrast to the water budget, anthropogenic discharges from sewage treatment plants, industries, and storm water runoff are important terms in the total input inventory for many metals.

Metal Inputs

In principle, developing an inventory of the inputs of various metals to Narragansett Bay is a straightforward exercise in accounting. In practice, however, it involves an often frustrating accumulation of uncertainty. The problem is particularly difficult with Narragansett Bay because there has never been a systematic attempt to measure the inputs of any metal. In fact, with the notable exception of the discharge from the Fields Point Sewage Treatment Plant as it has recently been operated by the Narragansett Bay Commission, none of the major inputs of metals to the bay has been the subject of a regular and effective monitoring program.

Because of these constraints, it must be admitted at the outset that the inventory developed in the following sections will be very approximate and incomplete. However, I think it is useful to present the results in spite of their imperfections. Many of the major sources of a number of important metals are "reasonably" well described, and the extent of uncertainty in various estimates may stimulate a program of more thorough measurements.

Since the fluxes of metals carried by rivers and deposited from the atmosphere vary with rainfall and river flow, I have made estimates of the inputs in the driest (92 cm y^{-1}), wettest (171 cm y^{-1}), and average (115 cm y^{-1}) precipitation years for the period 1964-1987 (Pilson 1989). Other inputs from publicly owned sewage treatment works (POTWs), combined sewer outfalls (CSOs), and urban runoff must also vary in wet and dry years, but data were not available to quantify the relationships.

Deposition from the Atmosphere

The only direct measurements of the deposition of metals from the atmosphere near Narragansett Bay were made in downtown Providence during a one week period in March

of 1982 (Latimer 1984). Unfortunately, it was a dry week with only 4 mm of precipitation that fell largely as snow flurries. However, an extensive series of measurements of the concentrations of many metals in precipitation and in the atmosphere near the ground has been collected on a regular basis by Professor Kenneth Rahn of the Center for Atmospheric Chemistry Studies at the University of Rhode Island (Rahn 1990). He has used the data resulting from measurements made on 198 occasions between February, 1985 and September, 1987 to calculate the estimated wet and dry deposition of numerous metals per unit area during a year with 1.2 m of precipitation (K. Rahn, personal communication 1989). In keeping with the framework adopted for this report, I have pro-rated his calculated fluxes to dry, wet, and average precipitation years and multiplied the results by the area of Narragansett Bay to estimate the total input of each metal directly from the atmosphere to the surface of the bay (Table 1).

Unfortunately, deposition rates calculated from measurements of metal concentrations in the air are sensitive to the choice of an appropriate "wash-out" factor for each metal, and these are known only approximately, perhaps within a factor of about 2 (see Nixon 1990, Table 23). I have assumed that the "wash-out" factors remain constant regardless of rainfall, but this may not be correct. There is also some error introduced by extrapolating fluxes calculated from metal concentrations measured in air collected adjacent to the lower West Passage of Narragansett Bay, at the Graduate School of Oceanography, to more urban areas of the bay. The deposition measurements made under essentially dry conditions in Providence were much larger than the dry deposition fluxes calculated from lower bay concentration data (Table 2), and the results of air quality monitoring by the R. I. Department of Health (1986) suggest that concentrations of total particulates and particulate lead may be 2.9 and 8 times larger, respectively, in Providence than at rural sites (Table 3).

There is a great variability in the deposition rates reported for various metals at different coastal sites around the world (Hoffman and Quinn 1984, Nixon and Lee 1986, Windom 1986), and it is difficult to use comparative data to estimate the degree by which the calculations provided in Table 1 may underestimate the total input of any one metal from the atmosphere to Narragansett Bay. For example, the measured deposition of Zn at five coastal sites summarized by Windom (1986) ranged from 3.4 (South Atlantic Bight) to 81 (New York Bight) $\text{mg m}^{-2} \text{y}^{-1}$ compared to the 11 $\text{mg m}^{-2} \text{y}^{-1}$ calculated for Narragansett Bay during a year with average precipitation. Extensive measurements of metal deposition at the mouth of Delaware Bay during 1982 and 1983 showed a Zn flux of 7.5 $\text{mg m}^{-2} \text{y}^{-1}$ (adjusted to 115 cm y^{-1} precipitation), but much lower fluxes of Cu, Pb, Fe, and Mn than calculated for lower Narragansett Bay (Church et al. 1984).

Table 1

Estimated deposition of various metals from the atmosphere directly onto the surface of Narragansett Bay (328 km²)^a. The estimates were calculated by Prof. Kenneth Rahn (U.R.I. Center for Atmospheric Chemistry Studies) using his measurements of metal concentrations in precipitation and on particles in air sampled at the Graduate School of Oceanography on 198 occasions during 1985-1987. The estimates are for total wet and dry deposition. Units are metric tons.

	Average Year ^b		Dry Year ^b	Wet Year ^b
	<u>mg m⁻² y⁻¹</u>	<u>tons y⁻¹</u>	<u>tons y⁻¹</u>	<u>tons y⁻¹</u>
As	<0.13	<0.04	<0.03	<0.06
Cr	0.36	0.12	0.10	0.18
Ni	1.6	0.52	0.42	0.77
Cu*	2.8	0.92	0.74	1.4
Mn	3.9	1.3	1.0	1.9
Zn	10.9	3.6	2.9	5.4
Pb	17.6	5.8	4.6	8.6
Fe	148	49	39	73
Al	466	153	122	228

^aBay surface area from Pilson (1985) does not include the Sakonnet River. Ratios of dry/wet deposition for the average year were: As = 0.044, Cr = 0.096, Ni = 0.73, Mn = 0.89, Zn = 0.44, Pb = 0.035, Fe = 1.41, Al = 3.3

*Cu taken as 30% of Zn.

^bAverage year precipitation = 115 cm; dry year = 92 cm; wet year = 171 cm based on data compiled by Pilson (1989) for 1964-1987.

Table 2

Comparison of the measured deposition of various metals from the atmosphere in downtown Providence¹ during one dry week in 1982 (Latimer 1984) with the average dry deposition calculated from metal concentration measurements made adjacent to the lower West Passage of Narragansett Bay between 1985 and 1987 (K. Rahn, URI Center for Atmospheric Studies).

	$\mu\text{g m}^{-2} \text{d}^{-1}$	
	<u>Providence</u>	<u>Lower West Passage</u>
Cd	4.3	--
Cu	59	2.9
Pb	269	1.7
Zn	381	9.5
Mn	61	4.3
Fe	453	248

¹Near Rt. 195 and the Narragansett Electric power generation facility.

Table 3

Concentrations of total particulates and particulate lead in the air at various locations in Rhode Island during 1986. Units are $\mu\text{g m}^{-3}$. Data from R. I. Dept. of Health (1986).

	<u>Total Particulates</u> ¹	<u>Particulate Lead</u> ²
Providence		
mean for 6 stations (range)	46(43-53)	
mean for 3 stations (range)		0.13 (0.1-0.16)
Pawtucket	42	
East Providence (2 stations)	35-38	
Cranston	38	0.09
Newport	31	
West Greenwich (rural)	18	0.02

¹Annual geometric mean.

²Annual arithmetic mean.

The one short-term set of deposition measurements obtained by Latimer (1984) in downtown Providence produced metal fluxes that were lower than those calculated from metal concentration data collected in the city in 1958 (see Nixon 1990, Table 23), but that is hardly surprising considering the reductions in metal emissions that have taken place. The reliability of the earlier metal concentration measurements is also a potential problem.

	<u>Calculated Deposition for 1958 (Nixon 1990)</u>	<u>Measured Deposition in 1982 (Latimer 1984)</u>
	$\text{ug m}^{-2} \text{d}^{-1}$	
Cu	57-115	59
Pb	274-548	269
Zn	1000-2000	381

Unfortunately, there are no earlier estimates of atmospheric deposition in the lower bay to compare with Rahn's calculations. If the calculated deposition in Providence in 1958 applied to the bay as a whole, the flux of metals to the bay would have been very much higher than at present (Table 4).

Inputs from Rivers

Of the 14 river and stream systems identified by the U.S.G.S. as contributing significant amounts of fresh water to Narragansett Bay, the three largest—the Taunton, Blackstone, and Pawtuxet Rivers— drain 75% of the land area of the watershed (Ries 1989). The Taunton River supplies 34% of the long-term average fresh water flow, the Blackstone 28%, and the Pawtuxet 13%. The concentrations of metals in the free-flowing portion of the Taunton River appear to have been measured on only two occasions, both of which occurred in 1986 as part of the SINBADD program (Pilson and Hunt 1989). Total metal concentrations in the Blackstone and Pawtuxet Rivers have been measured twice each year since 1978, usually in March and September, by the U.S.G.S., and both rivers have received additional short-term study by various groups from the University of Rhode Island (Table 5). While the URI studies have differed in their purposes, with some collecting samples in transects along the rivers, in dry or wet weather, during individual storm events, at fixed time intervals, etc., they have all collected samples just above the point where the rivers first meet salt water (Fig. 1). The U.S.G.S. samples are collected about 13 km and 5 km above these points in the Blackstone and Pawtuxet Rivers, respectively. Some of the URI studies have also included measurements of metals in the Woonasquatucket and Moshassuck, two smaller urban rivers that pass through Providence (Fig. 1), and provide about 3.2% and 1.3%, respectively, of the long-term fresh water flow (Ries 1989). The more recent SPRAY sampling (Table 5) and a storm sampling program by R. Wright and

Table 4

Comparison of the calculated deposition of various metals from the atmosphere to the surface of Narragansett Bay (328 km²) based on concentrations of metals in the air in Providence during 1958 and in precipitation and on particles in the air at the Graduate School of Oceanography, on the lower bay, during 1985-1987. The concentration data for both periods have been applied to an annual precipitation of 115 cm, the average for 1964-1987 (Pilson 1989).

	Deposition, metric tons y ⁻¹	
	<u>1958^a</u>	<u>1985-1987^b</u>
Cr	2.3-4.6	0.1
Cu	5.8-11	0.9
Ni	6.7-13	0.5
Pb	29-58	6
Zn	105-210	4

^aModified from Nixon (1990), Table 23.

^bFrom Table 1.

Table 5

Summary of data sources for estimating the flux of various metals into Narragansett Bay in surface fresh water flow.

<u>Study</u>	<u>River</u>	<u>Sampling</u>	<u>Form</u>	<u>Metals</u>
U.S.G.S. Annual Reports	Blackstone at Manville, RI Pawtuxet at Cranston, RI	Twice each year, 1978-1989	Total	As, Cd, Cu, Pb, Mn, Ni, Zn, Cr ^a
Hunt (1982)	Blackstone and Pawtuxet "above the influence of salt water"	Biweekly, Jan.-Sept., 1980	Total	Fe, Mn, Cu, Pb, Cd
Quinn et al. (1985)	Pawtuxet at Broad St. Bridge, Warwick-Cranston, RI	3 low-flow dates in 1983	Dissolved ^b and Particulate	Cd, Cr, Cu, Pb, Ni, Ag, Zn
Quinn et al. (1987)	Blackstone at Main St. Bridge Pawtuxet, RI	3 low-flow dates in 1985	Dissolved ^c and Particulate	Cd, Cr, Cu, Pb, Ni, Ag, Cr
SINBADD Pilson and Hunt (1989)	Tauton at Berkley Bridge Blackstone at Main St. Bridge	2 dates in 1986 4 dates in 1985 and 1986	Dissolved ^c and Particulate	Cd, Cr, Cu, Pb, Ni, Ag
	Pawtuxet at Broad St. Bridge Moshassuck—250 m below Smith St. Bridge Woonasquatucket at Stillman St. Bridge	" " "	" " "	" " "
SPRAY Doering et al. (1988)	Blackstone, Pawtuxet, Moshassuck, Woonasquatucket —as for SINBADD. Ten Mile above Omega Pond	18 dates in 1986 and 1987	Dissolved ^b and Particulate	Cd, Cu, Ni, Pb
Wright (Personal communication)	Blackstone, Pawtuxet, Moshassuck, Woonasquatucket —as for SINBADD. Ten Mile above Omega Pond	Numerous samples during 3 storms in 1988 and 1989	Dissolved and Particulate	Cd, Cu, Pb

^aCr measurements begin in 1987.^bPassing a 0.4 µm filter.^cPassing a 0.45 µm filter.

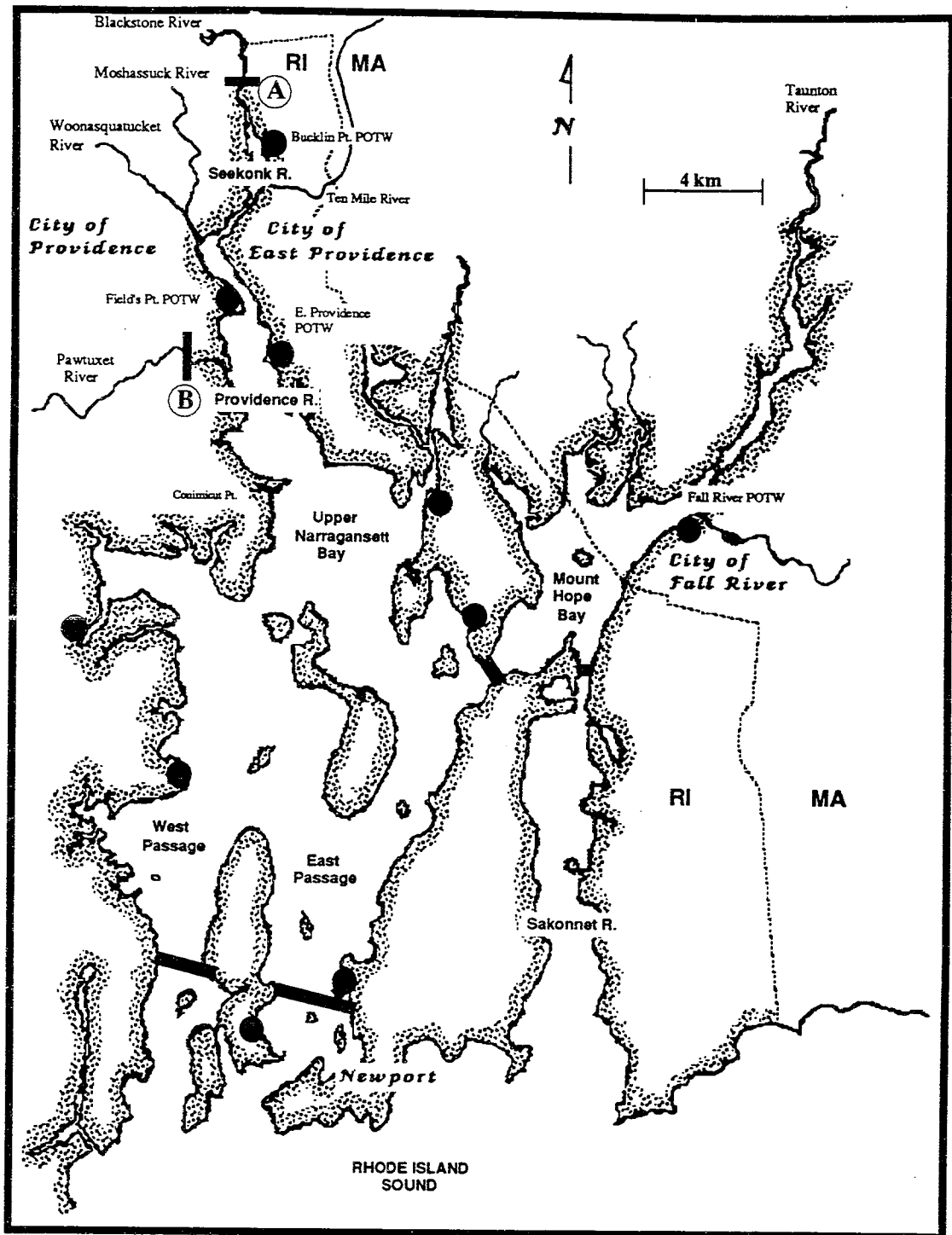


Fig. 1 Narragansett Bay, Mt. Hope Bay, and the Sakonnet River. The major sources of fresh water are also shown, along with stations at the mouth of the Blackstone River (A) and the Pawtuxet River (B) where measurements of the concentrations of metals were made by all of the sampling programs discussed in this report except the U.S.G.S. Details are given in Table 5. Locations of publicly owned sewage treatment plants that discharge directly into Narragansett Bay are shown with dark circles.

colleagues at U.R.I. also collected water from the Ten Mile River (Fig. 1) and this tributary was also analyzed for metals on some occasions in 1984 by the Rumford River Laboratories (1985) under contract to the Massachusetts Department of Environmental Quality. The Ten Mile River samples were all collected above Omega Pond, however, and the amount of each metal removed in the pond is not known. Because of this uncertainty, and the fact that only 3.4% of the average fresh water input is involved, I have not attempted to analyze the metal flux and river flow relationship of this system. Overall, there appear to be sufficient data available to provide a reasonably credible estimate of the input of at least some metals from the Blackstone, Pawtuxet, Woonasquatucket and Moshassuck Rivers. These systems provide a total of about 45% of the fresh water inflow to Narragansett Bay (Ries 1989). The calculation of input from the largest river, the Taunton, rests on only two sets of measurements and can only be described as a "best guess." Moreover, it is not known how much of each metal that is delivered to Mt. Hope Bay by the Taunton River actually enters Narragansett Bay proper. A large fraction of at least some metals must be retained in the sediments of Mt. Hope Bay, and a small portion must pass into the Sakonnet River (Fig. 1). As far as I am aware, no metal analyses have been reported for the rivers and streams that contribute the remaining 20% or so of the fresh water input to the bay.

Of the various sampling programs summarized in Table 5, only the one carried out by Hunt (1982) was designed to provide an estimate of metal fluxes from the rivers over time periods longer than a day or over the course of an individual storm. Hunt approached the problem of determining an annual flux by measuring the concentrations of metals in the Blackstone and Pawtuxet Rivers every other week during the eight months between 25 January, 1980 and 26 September, 1980. He then multiplied the measured concentrations by the average river flow on the day of sampling as reported by the U.S.G.S. to produce an estimate of the daily metal flux on each day of sampling. These fluxes were then averaged and multiplied by 365 to give an estimate of the annual input from each river (Table 6).

Since these unpublished values are the only long-term river flux estimates that have been available for the past decade and they have contributed significantly to several metal budgets that have been prepared for Narragansett Bay (e.g., Hoffman and Quinn 1984, Santschi et al. 1984, Nixon et al. 1986), they deserve some further comment. The U.S.G.S. river flow data used by Hunt came from gauges upstream of the points where the metal samples were collected and where the rivers actually first enter salt water. As a result, some adjustment may be necessary to account for runoff that entered the rivers below the gauges. Correction factors based on the ratio of total watershed area to gauged area of 1.17 and 1.15 have been reported for the Blackstone and the Pawtuxet, respectively, by Pilson

Table 6

Estimates of the fluxes of metals into the Seekonk and Providence Rivers from the Blackstone and Pawtuxet Rivers, respectively, during 1980 as reported by Hunt (1982) and after adjustment for ungauged river flow using factors provided by Pilson and Hunt (1989). Units are metric tons.

	<u>Blackstone River</u>	<u>Pawtuxet River</u>
Fe adjusted	592 (691)	207 (238)
Mn adjusted	88 (103)	44 (51)
Cu adjusted	12 (14)	4 (4.6)
Pb adjusted	7.2 (8.4)	1.2 (1.4)
Cd adjusted	1.7 (2.0)	0.25 (0.29)

and Hunt (1989) and I have applied them to Hunt's original estimates in Table 6. It is also worth noting that river flows during the eight month period studied by Hunt were low. For example, for the Blackstone River the mean February-September flows in 1980 were only 78% of the mean for comparable months during 1963-1984 (Pilson 1989). Precipitation averaged over the Narragansett Bay drainage basin amounted to only 96 cm in 1980 compared to the long-term mean of 120 cm (Pilson 1989). Since regression analyses described in the next paragraph show that the flux of most metals in the rivers appears to be determined largely by flow, it seems reasonable to assume that the daily average fluxes calculated from 1980 river flow data would lead to a significant underestimate of metal inputs during average flow conditions.

Aside from these considerations, the averaging of daily flux estimates is only one of a number of approaches for dealing with the common problem of estimating the long-term (monthly, annual) flux of materials carried by rivers (Dolan et al. 1981, Bierman et al. 1988). Because the sampling programs applied to the rivers entering Narragansett Bay have provided estimates of metal fluxes under a wide range of flow conditions, but at irregular and relatively infrequent intervals, I have used a standard regression technique to relate the daily flux of each metal to the average flow of the river on the day of sampling. The U.S.G.S. flow data were increased by the factors provided by Pilson and Hunt (1989) to compensate for ungauged flow and linear regressions performed on the logarithmic transforms of flux and flow data. It was then possible to use the regressions or "rating curves" with daily river flow measurements during dry (1980), wet (1972), and "average" (1973) years to calculate the daily metal fluxes that might result. The calculated fluxes were corrected for the bias introduced by the logarithmic transformations (Ferguson 1986) and summed to provide estimates of the monthly and annual inputs of the various metals. The regression format also made it possible to account for differences in river flow when comparing the results of the different sampling programs (Figs. 2 and 3).

It is evident from the analyses that the fluxes of all of the metals examined, with the notable exception of nickel in the Pawtuxet River and in the small urban rivers, were governed largely by variation in river flow (Figs. 2 and 3; Table 7). In general, the correlations were stronger for dissolved and total metals than for the particulate portion, and in virtually every case the flux of metals was more strongly correlated with flow in the Blackstone River than in the Pawtuxet River or the two smaller systems (Table 7). In both the Blackstone and the Pawtuxet, total metal fluxes computed from the concentration measurements reported by the U.S.G.S. tended to be greater than those obtained from the more recent SINBADD and SPRAY programs (Figs. 2 and 3). The discrepancy is particularly clear for lead, and it may be that the U.S.G.S. data set is elevated because it

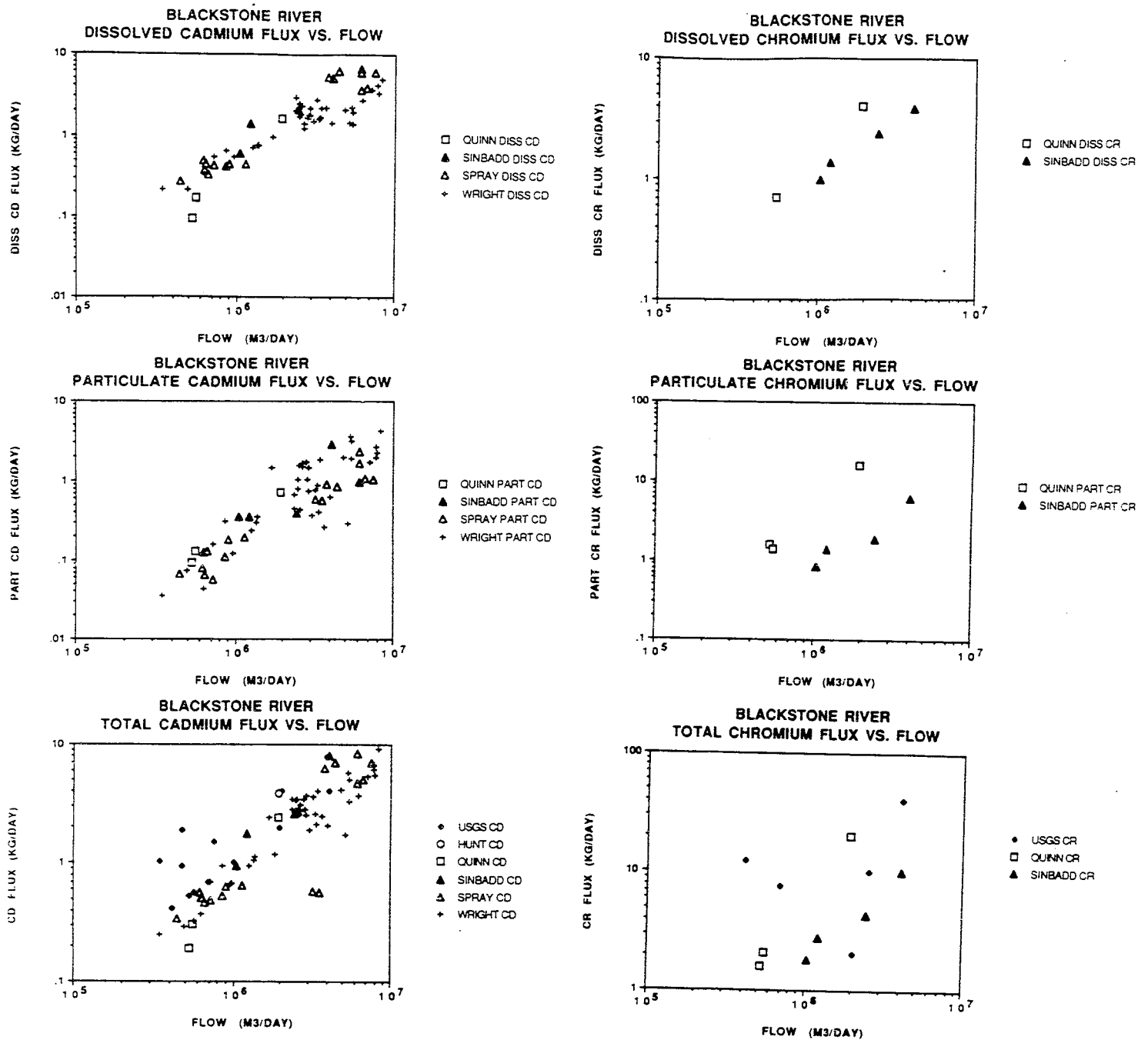


Fig. 2 Daily fluxes of dissolved ($< 0.4 \mu\text{m}$), particulate, and total metals at the mouth of the Blackstone River as a function of water flow on the day of sampling. Plots for Cu, Pb, Ni and Zn are shown on the following two pages. Data from Quinn et al (1987), Pilson and Hunt (1989) for SINBADD, Doering et al. (1988) for SPRAY, R. Wright (personal communication), Hunt (1982) and annual water quality reports of the U. S. Geological Survey. Regressions for the SINBADD-SPRAY and Wright data are given in Tables 7 and 15, respectively. Sampling programs are described in Table 5.

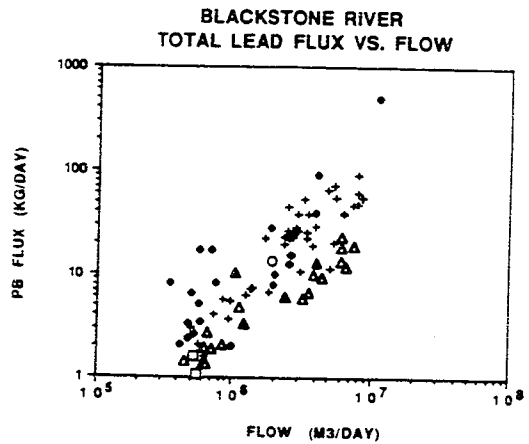
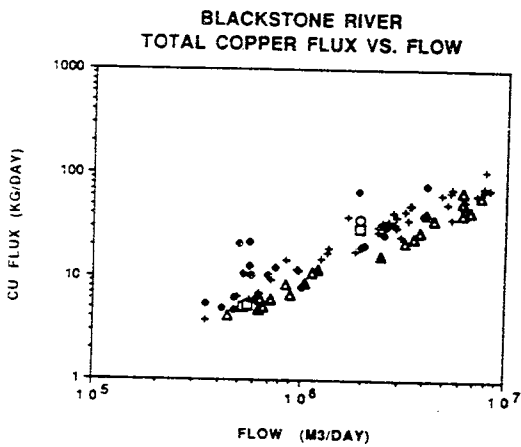
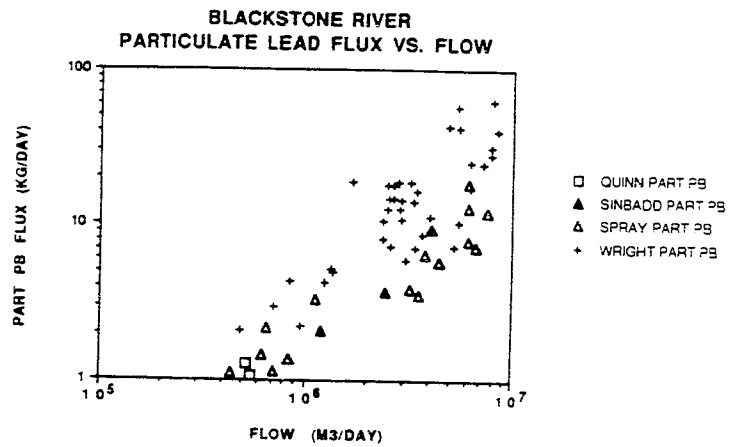
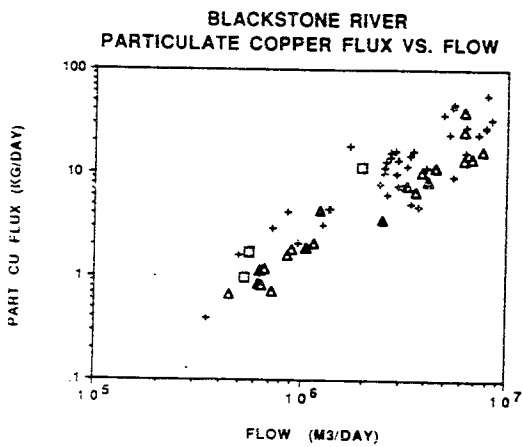
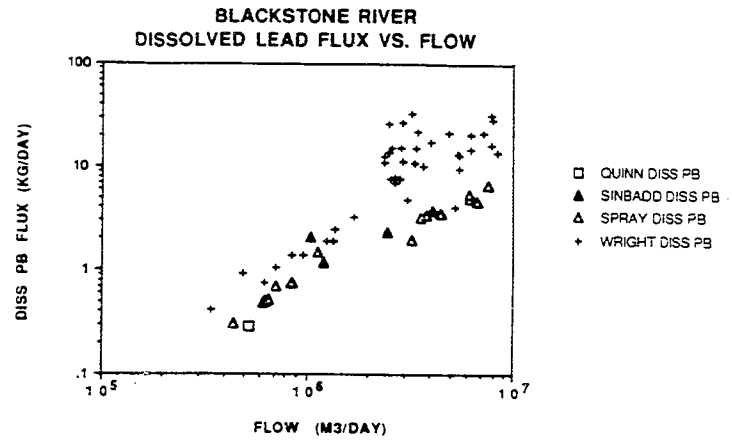
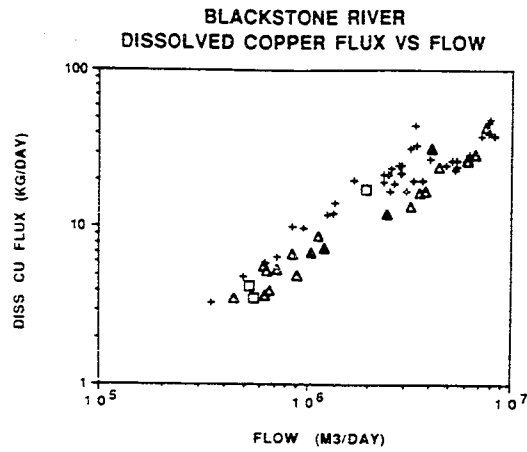


Fig. 2 (continued)

Daily fluxes of dissolved ($< 0.4 \mu\text{m}$), particulate, and total metals at the mouth of the Blackstone River as a function of water flow on the day of sampling.

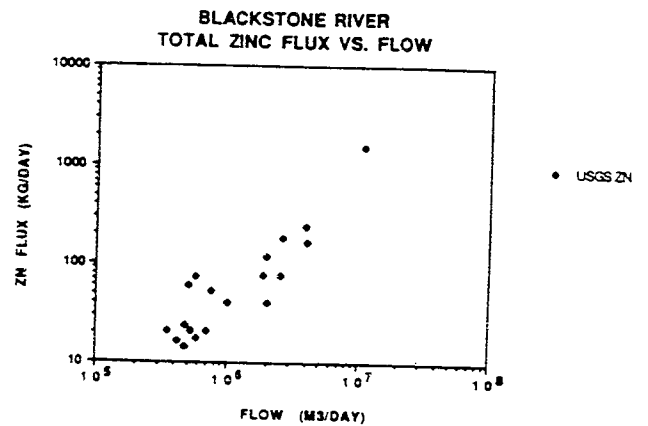
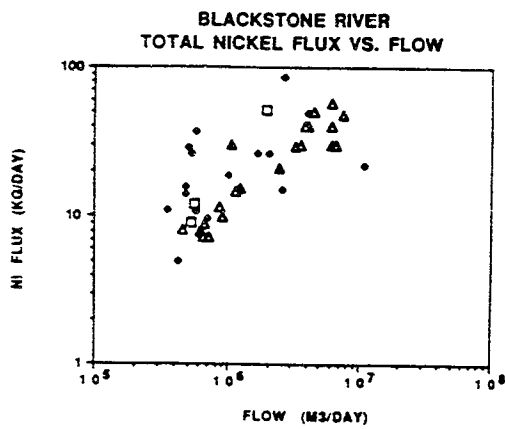
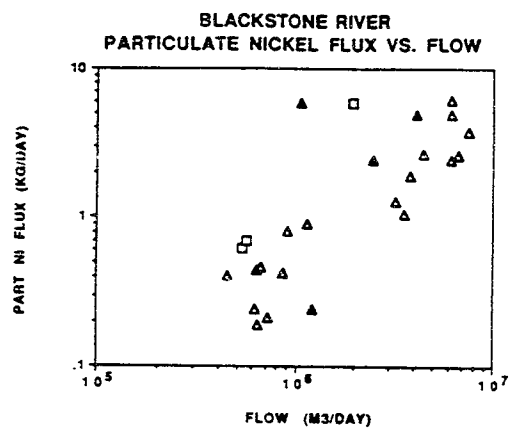
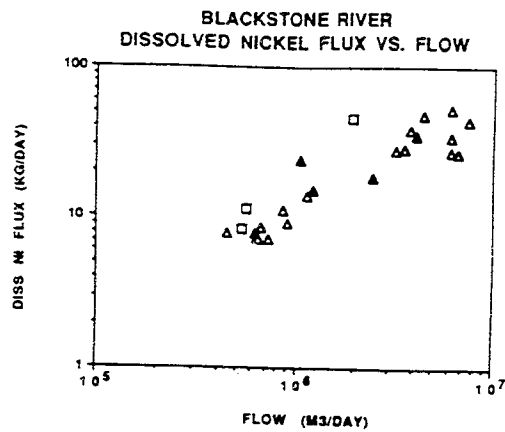


Fig. 2 (continued)

Daily fluxes of dissolved ($< 0.4 \mu\text{m}$), particulate, and total metals at the mouth of the Blackstone River as a function of water flow on the day of sampling.

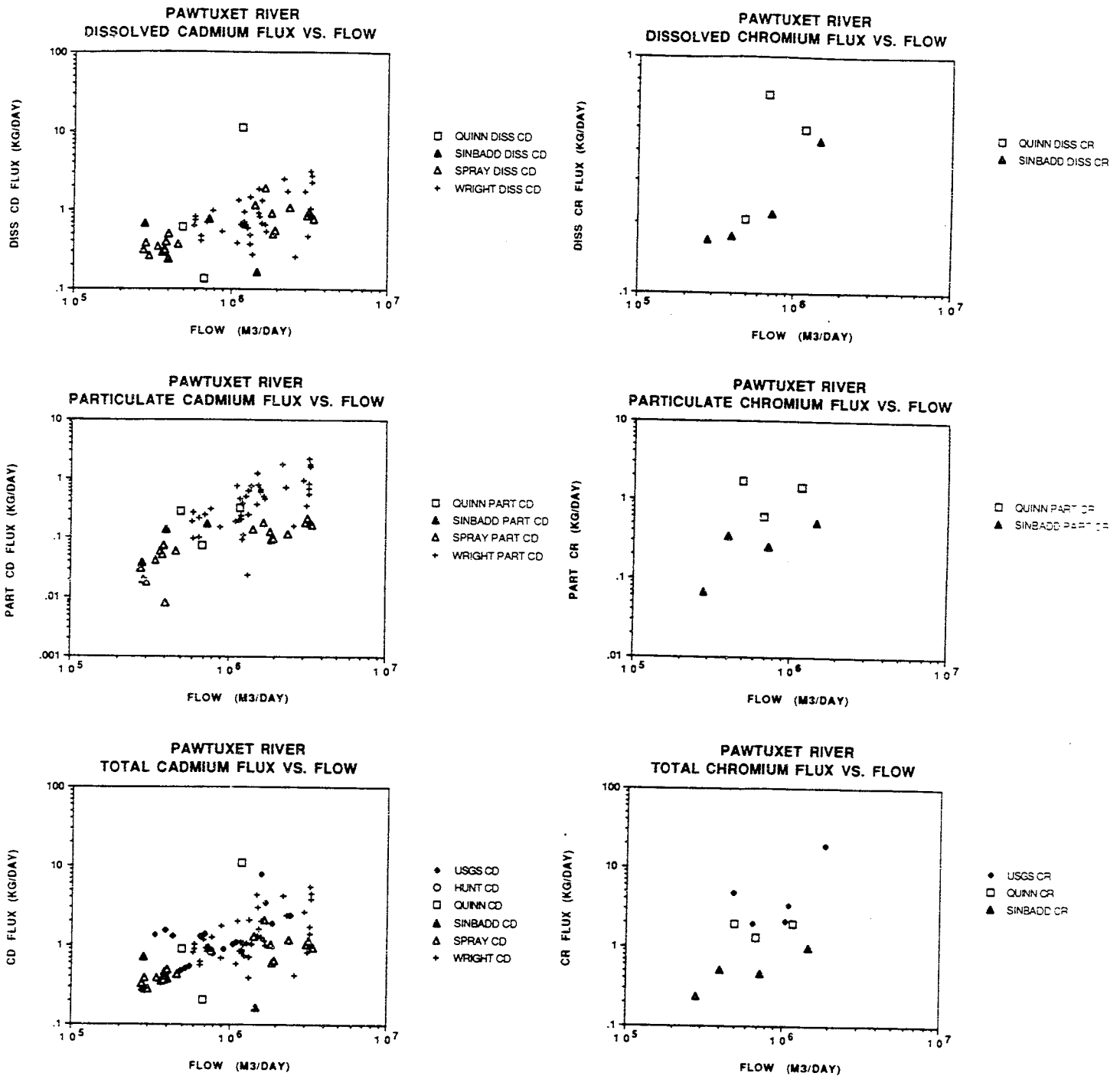


Fig. 3 Daily fluxes of dissolved ($< 0.4 \mu\text{m}$), particulate, and total metals at the mouth of the Pawtuxet River as a function of water flow on the day of sampling. Plots for Cu, Pb, Ni and Zn are shown on the following two pages. Data from Quinn et al (1987), Pilson and Hunt (1989) for SINBADD, Doering et al. (1988) for SPRAY, R. Wright (personal communication), Hunt (1982) and annual water quality reports of the U. S. Geological Survey. Regressions for the SINBADD-SPRAY and Wright data are given in Tables 7 and 15, respectively. Sampling programs are described in Table 5.

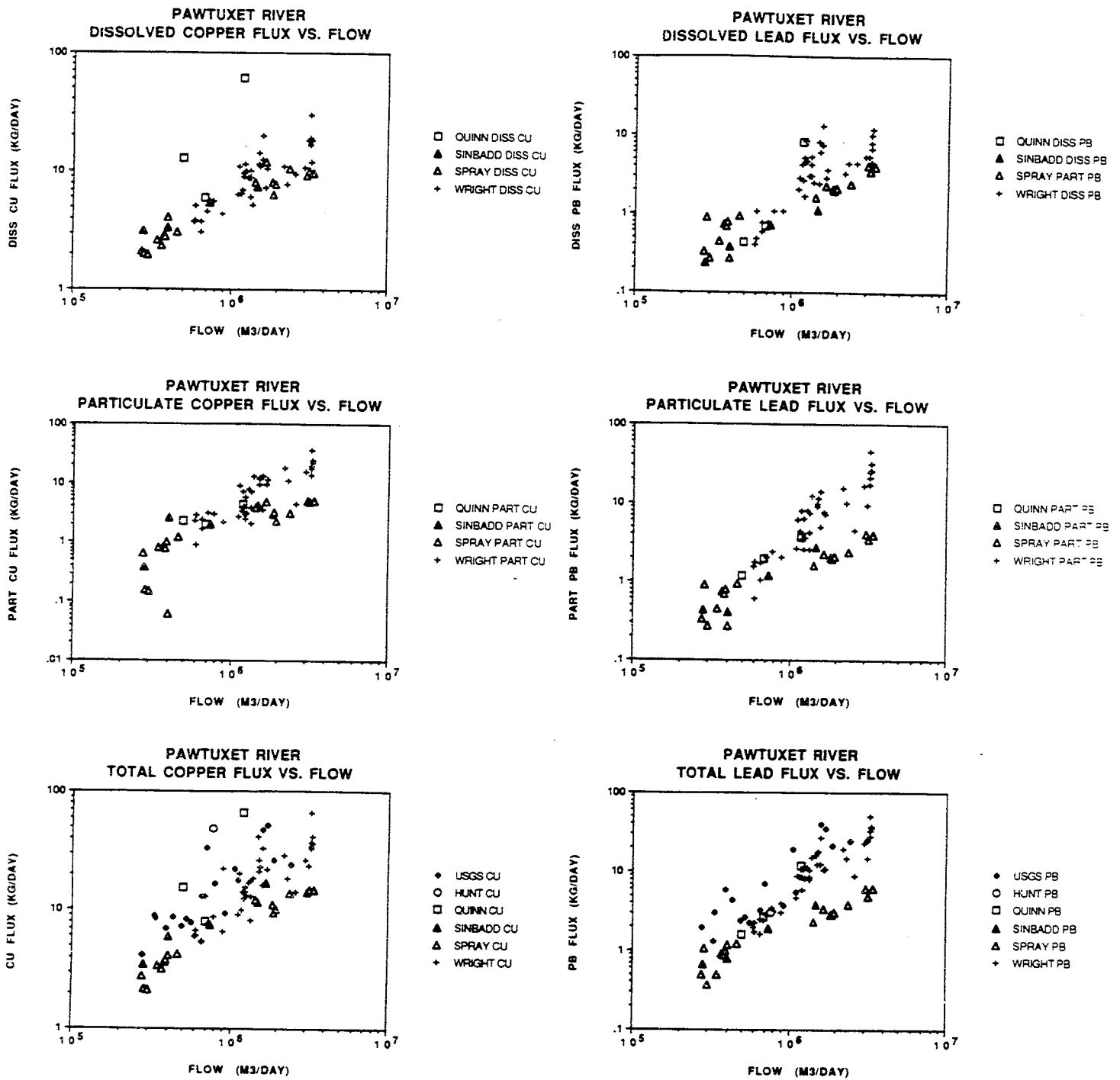


Fig. 3 (continued)

Daily fluxes of dissolved ($< 0.4 \mu\text{m}$), particulate, and total metals at the mouth of the Pawtuxet River as a function of water flow on the day of sampling.

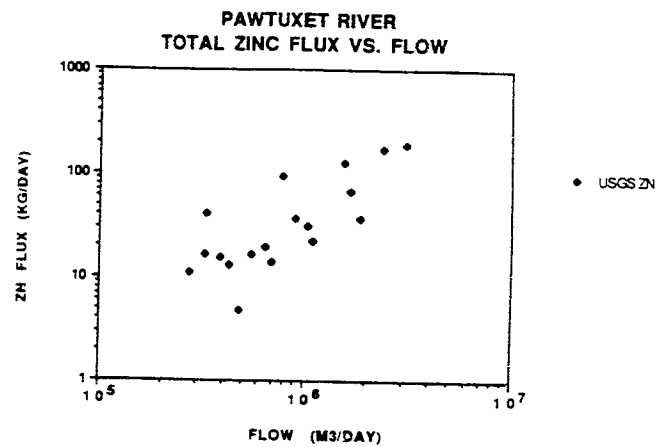
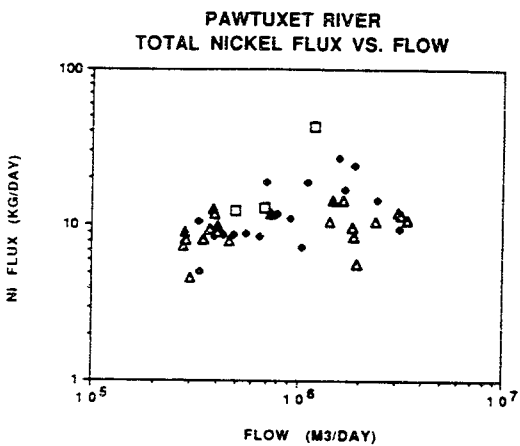
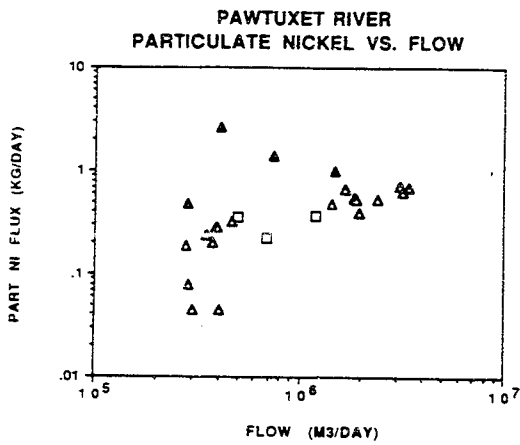
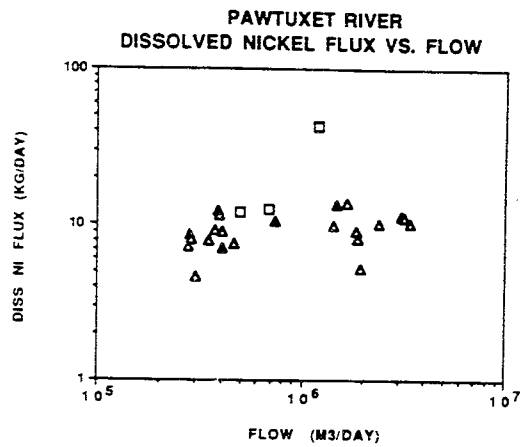


Fig. 3 (continued)

Daily fluxes of dissolved ($< 0.4 \mu\text{m}$), particulate, and total metals at the mouth of the Pawtuxet River as a function of water flow on the day of sampling.

Table 7

Slope, intercept, and r^2 values for regression equations relating log metal flux (kg d^{-1}) to log river flow ($\text{m}^3 \text{d}^{-1}$, corrected for ungauged watershed area) used to estimate monthly and annual metal inputs to Narragansett Bay from rivers (see Figs. 2-5). Data for dissolved ($< 0.4 \mu\text{m}$) (d), particulate (p), and total metals (t) from SINBADD and SPRAY sampling programs; others from U.S.G.S. (see Table 5).

Metal	Slope	Blackstone		Slope	Pawtuxet	
		Intercept	r^2		Intercept	r^2
Cd (d)	1.20	-7.40	0.94	0.40	-2.67	0.37
Cd (p)	1.17	-7.77	0.87	0.71	-5.33	0.56
Cd (t)	1.09	-6.64	0.75	0.42	-2.71	0.40
Cr (d)**	0.96	-5.74	0.98	0.59	-4.05	0.89
Cr (p)**	1.30	-7.87	0.90	0.97	-6.21	0.64
Cr (t)**	1.15	-6.60	0.95	0.72	-4.48	0.82
Cu (d)	0.82	-4.07	0.96	0.64	-3.12	0.90
Cu (p)	1.26	-7.30	0.94	1.10	-6.36	0.64
Cu (t)	0.94	-4.69	0.97	0.72	-3.44	0.90
Pb (d)	1.00	-6.04	0.98	1.00	-6.25	0.78
Pb (p)	0.90	-5.15	0.88	0.88	-5.14	0.86
Pb (t)	0.93	-5.15	0.93	0.88	-4.98	0.91
Ni (d)	0.67	-2.98	0.86	0.10	0.38	0.11
Ni (p)	0.97	-6.03	0.65	0.56	-3.75	0.27
Ni (t)	0.70	-3.07	0.85	0.11	0.35	0.13
Zn (t)	1.08	-4.79	0.80	1.08	-4.90	0.61
As (t)	0.69	-3.90	0.79	0.96	-5.66	0.70
Mn (t)	0.99	-3.92	0.92	0.60	-1.39	0.74
Ag (d)*	1.03	-7.46	1.00	0.72	-5.51	0.73
Ag (p)	1.27	-8.94	0.95	1.09	-7.59	0.57
Ag (t)	1.16	-7.96	0.98	0.94	-6.47	0.65
		Woonasquatucket			Moshassuck	
Cd (d)	0.43	-3.81	0.32	0.40	-2.67	0.37
Cd (p)	0.62	-5.46	0.35	0.71	-5.33	0.56
Cd (t)	0.45	-3.82	0.34	0.42	-2.71	0.40
Cr (d)**	0.79	-4.31	0.69	0.59	-4.05	0.89
Cr (p)**	0.61	2.08	1.00	0.97	-6.21	0.64
Cr (t)**	0.49	-2.68	0.51	0.72	-4.48	0.82
Cu (d)	0.92	-5.10	0.73	0.64	-3.12	0.90
Cu (p)	0.46	-3.02	0.24	1.10	-6.36	0.64
Cu (t)	0.76	-4.05	0.61	0.72	-3.44	0.90

Table 7 (continued)

<u>Metal</u>	<u>Slope</u>	<u>Intercept</u>	<u>r²</u>	<u>Slope</u>	<u>Intercept</u>	<u>r²</u>
	<u>Woonasquatucket</u>			<u>Moshassuck</u>		
Pb (d)	1.01	-6.01	0.53	1.00	-6.25	0.78
Pb (p)	0.39	-2.38	0.26	0.88	-5.14	0.86
Pb (t)	0.56	-3.11	0.28	0.88	-4.98	0.91
Ni (d)	0.46	-2.45	0.39	0.10	0.38	0.11
Ni (p)	0.67	-4.77	0.33	0.56	-3.75	0.27
Ni (t)	0.46	-2.45	0.39	0.11	0.35	0.13
Ag (d)	1.48	-9.98	0.98	0.72	-5.51	0.73
Ag (p)	0.45	-4.85	0.27	1.09	-7.59	0.57
Ag (t)	1.61	-10.60	0.93	0.94	-6.47	0.65
	<u>Taunton***</u>					
Cd (d)	1.32	-8.90	--			
Cd (p)	1.73	-11.79	--			
Cd (t)	1.44	-9.48	--			
Cr (d)	0.61	-3.84	--			
Cr (p)	0.07	-0.64	--			
Cr (t)	0.34	-1.93	--			
Cu (d)	0.80	-4.28	--			
Cu (p)	1.34	-8.51	--			
Cu (t)	0.85	-4.54	--			
Pb (d)	1.12	-6.76	--			
Pb (p)	--	--	--			
Pb (t)	2.02	-12.0	--			
Ni (d)	0.71	-3.91	--			
Ni (p)	--	--	--			
Ni (t)	0.54	-2.84	--			
Ag (d)	--	--	--			
Ag (p)	--	--	--			
Ag (t)	--	--	--			

*Dissolved Ag values were often set at the lowest detectable concentration of 0.05 $\mu\text{g kg}^{-1}$. See text.

**While regressions for other metals entering the Seekonk and Providence Rivers were based on about 20 measurements, only three measurements of Cr were available from SINBADD on the Woonasquatucket River and four for the other rivers. The SPRAY program did not include Cr.

***Taunton "regressions" based on two measurements only.

contains older measurements. Presumably, both rivers are now carrying lower concentrations of metals, especially lead, than they did in the late 1970s and early 1980s when the U.S.G.S. began sampling (Table 5). Unfortunately, at twice each year, their sampling is not frequent enough to be appropriate for a trend analysis. It is also possible that the concentrations of metals are higher at the U.S.G.S. sampling sites than at the mouths of the rivers or that the analytical procedures used by the U.S.G.S. produce higher values than those used by the metals laboratory at the Marine Ecosystems Research Laboratory (MERL) at URI, the analytical facility for the SINBADD and SPRAY studies. There is a notorious variability in the analysis of metals among different laboratories, and there has never been an intercalibration among the four different laboratories producing the data shown in Figs. 2 and 3.

Because their samples were collected upstream of the SINBADD and SPRAY samples and during a period of over 10 years, I have only used the U.S.G.S. regressions to calculate annual loadings of As, Mn, and Zn, metals that were not included in the SINBADD and SPRAY programs. Because the fluxes of other metals reported by the U.S.G.S. appear high relative to those measured by SINBADD-SPRAY (Figs. 2 and 3), the annual fluxes of As, Mn, and Zn are reported here as being "less than" the values computed from the regressions based on the U.S.G.S. data (Tables 8 and 9). Annual fluxes of other pollutant metals have been calculated from regressions based on a combined data set from the SINBADD and SPRAY sampling programs (Tables 8, 9, 10). These data are generally consistent, the samples were collected recently (1985-1987) at points where the rivers enter tidal salt water, samples were collected in all seasons under a wide range of flow conditions, and the sampling and analyses were carried out by the same laboratory (URI-MERL). Coefficients of variation (%) for mean bias-corrected residuals of the daily metal fluxes calculated from the SINBADD-SPRAY regressions were as follows for an "average flow" year:

	<u>Blackstone</u>	<u>Pawtuxet</u>
Cd	63	46
Cr	11	11
Cu	25	22
Ni	31	22
Pb	37	17

Since particulate and dissolved ($< 0.4\mu\text{m}$) metals were analyzed separately, it was also possible to estimate the contribution made by each fraction to the annual flux under different flow conditions (Tables 11 and 12). The slopes of the flux vs. flow

Table 8

Estimates of the annual flux of various metals into the Seekonk River from the Blackstone River during years with low, high, and average rainfall. Data from SINBADD and SPRAY sampling programs unless noted. Flow data used in regressions were corrected for ungauged watershed areas according to Pilson and Hunt (1989). Units are metric tons.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average Year</u>
As (USGS)	<0.9	<1.6	<1.3
Fe (Hunt) ¹	690	--	--
Mn (Hunt) ¹	103	--	--
Mn (USGS)	<64	<151	<109
Cd	0.6	1.5	1.0
Cr (SINBADD)	1.2	3.3	2.3
Cu	4.9	11.0	8.2
Ni	6.4	11.5	9.4
Pb	1.6	3.5	2.6
Zn (USGS)	<30	<76	<53
Ag*	<0.07	<0.18	<0.12

¹C. Hunt (1982), concentrations measured in 1980. Flow used by Hunt has been corrected here to include ungauged portions of the watershed as reported by Pilson and Hunt (1989).

*Dissolved Ag concentrations in the Blackstone were frequently below the detection level of $0.05 \mu\text{g kg}^{-1}$. When this was the case, a value of 0.05 was added to the particulate concentration used in the total metal flux vs. flow regression. Therefore, the actual total Ag flux was less than computed from the regression.

Table 9

Estimates of the annual flux of various metals into the Providence River from the Pawtuxet River during years with low, high, and average rainfall. Data from SINBADD and SPRAY sampling programs unless noted. Flow data used in regressions were corrected for ungauged watershed areas according to Pilson and Hunt (1989). Units are metric tons.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average Year</u>
As (USGS)	<0.4	<0.8	<0.7
Fe (Hunt) ¹	238	--	--
Mn (Hunt) ¹	51	--	--
Mn (USGS)	<49	<74	<72
Cd	0.22	0.32	0.29
Cr (SINBADD)	0.20	0.37	0.32
Cu	2.0	3.8	3.3
Ni	3.5	3.9	3.8
Pb	0.52	1.1	0.95
Zn (USGS)	<11	<27	<21
Ag*	<0.05	<0.11	<0.09

¹C. Hunt (unpublished), concentrations measured in 1980. Flow used by Hunt has been corrected here to include ungauged portions of the watershed as reported by Pilson and Hunt (1989).

*While dissolved Ag concentrations in the Pawtuxet were not below detection levels ($0.05 \mu\text{g kg}^{-1}$) as frequently as in the Blackstone, the regression for this river also contained enough detection level readings that the computed fluxes are overestimates.

Table 10

Estimates of the annual flux of various metals into the Providence River from the Woonasquatucket and Moshassuck Rivers during years with low, high, and average rainfall. Data from SINBADD and SPRAY sampling programs. Units are metric tons.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average Year</u>
	<u>Woonasquatucket River</u>		
Cd	0.01	0.02	0.02
Cr (SINBADD)*	18	29	25
Cu	0.28	0.54	0.44
Ni	0.34	0.52	0.46
Pb	0.22	0.37	0.32
Ag	0.01	0.04	0.03
	<u>Moshassuck River</u>		
Cd	0.21	0.30	0.28
Cr (SINBADD)*	0.18	0.34	0.29
Cu	1.8	3.5	3.0
Ni	3.5	3.8	3.8
Pb	0.46	1.0	0.84
Ag	0.04	0.10	0.08

*Regressions derived from only three and four measurements of concentration (See Table 7).

Table 11

Estimated fraction (%) of the total flux of various metals from the Blackstone River that is in dissolved form during years with low and high rainfall and during months with the lowest and highest river flow in a year with average rainfall.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average February</u>	<u>Average October</u>
Cd	81	81	82	78
Cr	49	42	42	58
Cu	73	65	65	81
Ni	95	94	93	97
Pb	31	33	33	29

Ag has not been partitioned because the dissolved fraction was usually below the detection level of $0.05 \mu\text{g kg}^{-1}$.

Table 12

Estimated fraction (%) of the total flux of various metals from the Pawtuxet River that is in dissolved form during years with low and high rainfall and during months with the lowest and highest river flow in a year with average rainfall.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average February</u>	<u>Average October</u>
Cd	89	87	85	92
Cr	46	41	40	45
Cu	77	72	70	81
Ni	87	90	92	85
Pb	29	34	36	28

Ag has not been partitioned because the dissolved fraction was often below the detection level of $0.05 \mu\text{g kg}^{-1}$.

regressions for dissolved and particulate metals are sufficiently similar that there appears to be only a modest increase in the relative transport of particulate metals in high flow years or during wet compared to dry months. The Blackstone and Pawtuxet Rivers contribute most of their Ni, Cd, and Cu in dissolved form; most of their Pb is delivered in association with particles; and Cr is distributed about equally between particulate and dissolved fractions (Tables 11 and 12).

Since the flux of metals is determined so strongly by the discharge of the rivers, there is a marked seasonality in the calculated input of metals from this source (Figs. 4 and 5). The effective metal loading on Narragansett Bay may be less variable, however, because the residence time of water in the bay is shorter when fresh water inflow is high. Using Pilson's (1985) relationship between total freshwater input and flushing rate, the monthly average residence time of water during the "average" flow year for this report (1973) varied from 17 days in December to 36 days in October. If the average flushing rate (days) for each month is multiplied by the computed combined metal inputs from the Blackstone and Pawtuxet Rivers (kg d^{-1}), it is possible to gain some appreciation for the interaction of input and flushing rate on the relative loading of metals from the rivers (Fig. 6). For example, while the computed input of Cu from the two rivers varied by a factor of 4.8 between the months with lowest and highest river flow, the flushing-corrected loading rate only varied by a factor of 2.3. The importance of this interaction in setting ambient concentrations of metals in the bay will vary depending on the conservative or non-conservative behavior of individual metals and the influence of temperature and other factors on that behavior (Santschi et al. 1980, Bender et al. 1989).

The weaker relationships between metal fluxes and river flows in the two small urban rivers (Table 7) are not surprising, and it is tempting to dismiss the uncertainty involved because the combined flow of the Woonasquatucket and Moshassuck is only about 16% of the Blackstone (Ries 1989). Unfortunately, however, the regressions suggest that their combined metal inputs may amount to 30-45% of the flux from the Blackstone and exceed that of the Pawtuxet (Table 13). It seems clear that it will require a more intensive sampling than provided by the SINBADD or SPRAY programs to adequately characterize the metal inputs from these sources. The problem may be particularly important for chromium, since the very limited sampling for this metal during the SINBADD program showed a potential for very high fluxes from the Woonasquatucket (Table 10). However, as emphasized in the tables summarizing metal inputs from the rivers, chromium has only been measured a few times in any of the rivers, and data from the U.S.G.S. and from Quinn et al. (1985, 1987) show generally higher concentrations in the Blackstone and Pawtuxet Rivers than reported

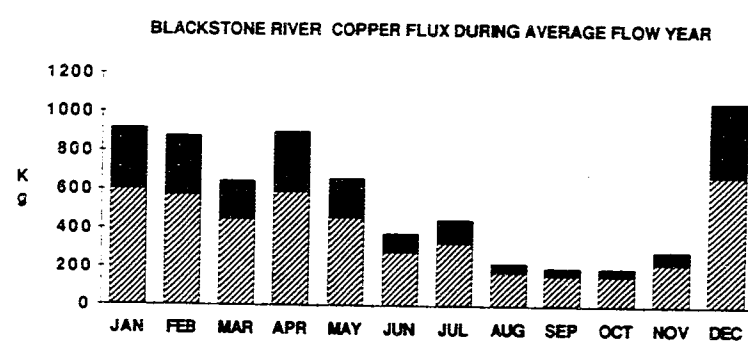
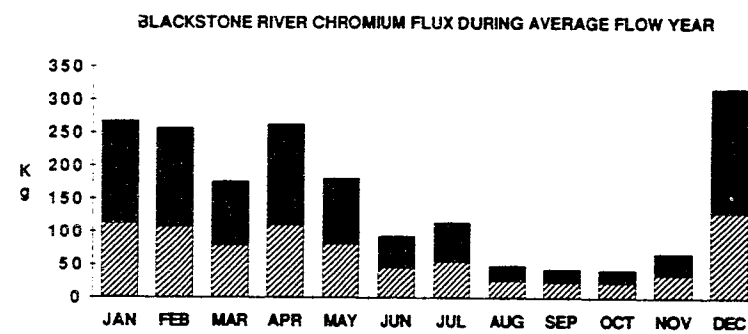
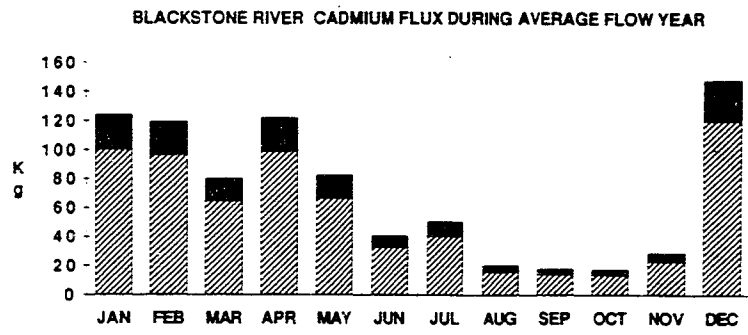


Fig. 4 Monthly fluxes of dissolved ($<0.4 \mu\text{m}$), particulate, and total metals from the Blackstone River into the Seekonk River (Fig. 1) computed from regression equations summarized in Table 7 using daily river flow rates reported by the U. S. Geological Survey for 1973, a year that represented approximately average flow conditions. Reported flows were increased to account for ungauged watershed area (Pilson and Hunt 1989). Fluxes were corrected for bias introduced by the logarithmic transformation of the regressions (Ferguson 1986). The particulate fraction is shown in black except for Zn, for which only total metal data were available. Fluxes of Pb, Ni, and Zn are shown on the following page.

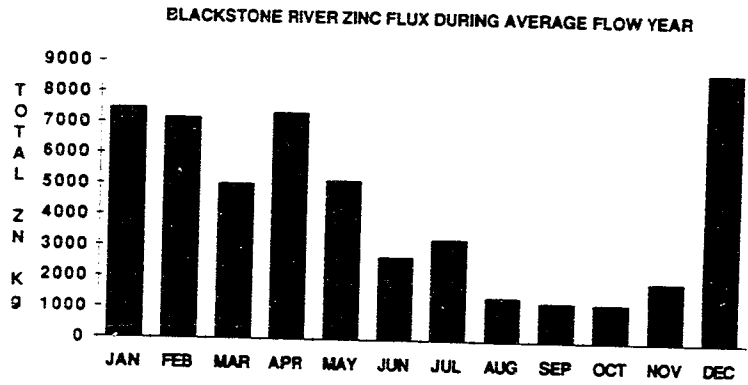
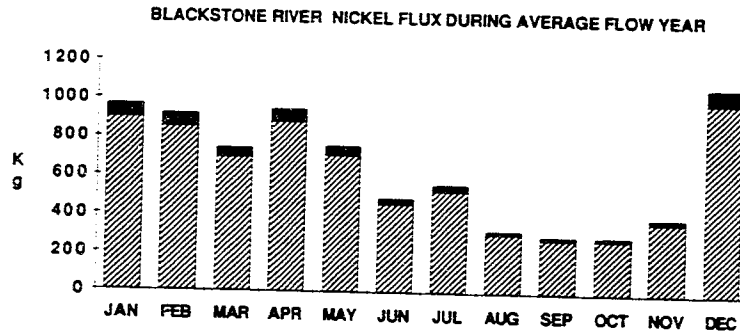
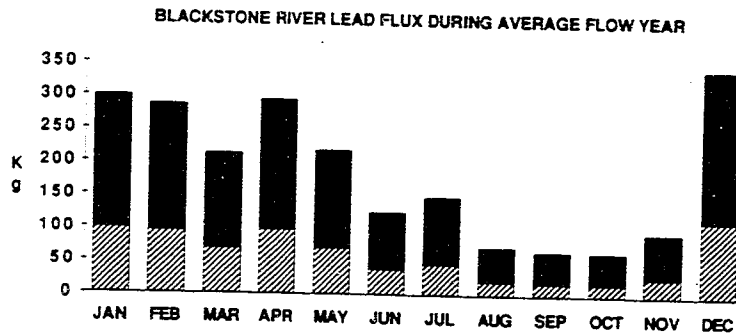


Fig. 4 (continued)

Monthly fluxes of dissolved (<math><0.4 \mu\text{m}</math>), particulate, and total metals from the Blackstone River into the Seekonk River.

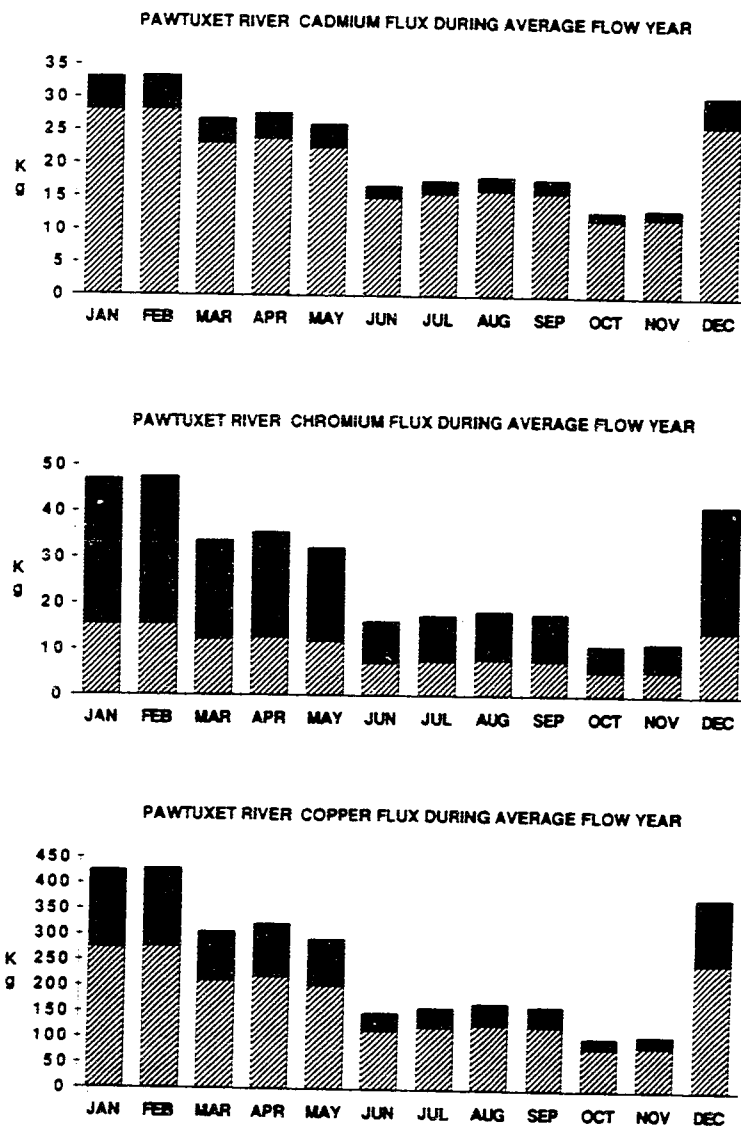


Fig. 5 Monthly fluxes of dissolved ($<0.4 \mu\text{m}$), particulate, and total metals from the Pawtuxet River into the Providence River (Fig. 1) computed from regression equations summarized in Table 7 using daily river flow rates reported by the U. S. Geological Survey for 1973, a year that represented approximately average flow conditions. Reported flows were increased to account for ungauged watershed area (Pilson and Hunt 1989). Fluxes were corrected for bias introduced by the logarithmic transformation of the regressions (Ferguson 1986). The particulate fraction is shown in black except for Zn, for which only total metal data were available. Fluxes of Pb, Ni, and Zn are shown on the following page.

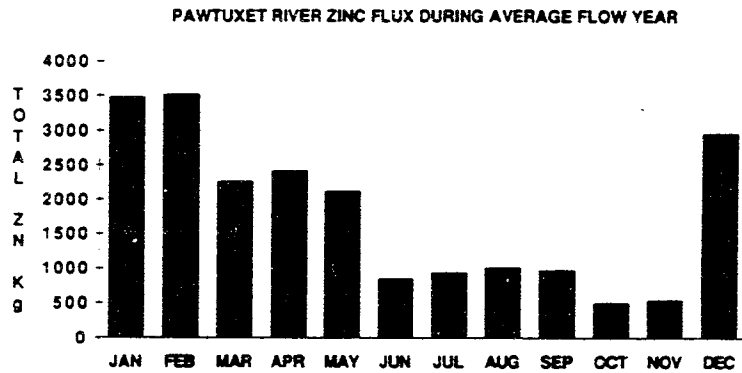
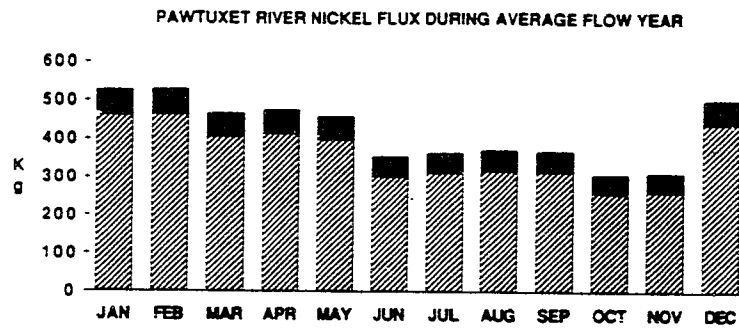
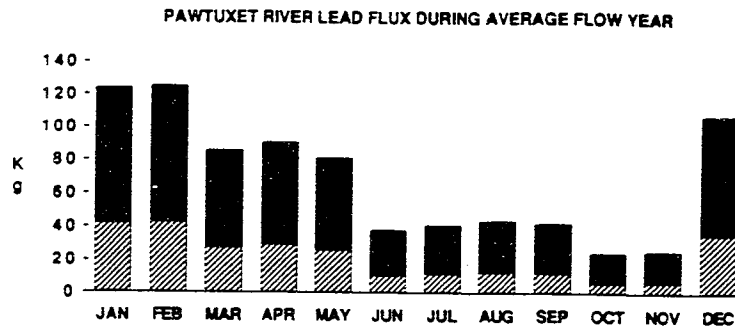


Fig. 5 (continued)

Monthly fluxes of dissolved (<0.4 μm), particulate, and total metals from the Pawtuxet River into the Providence River.

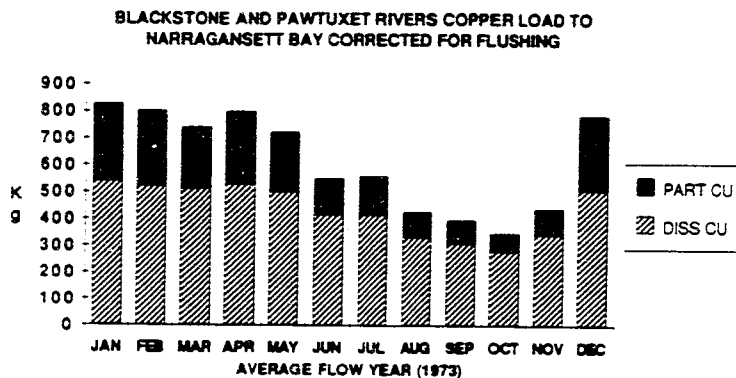
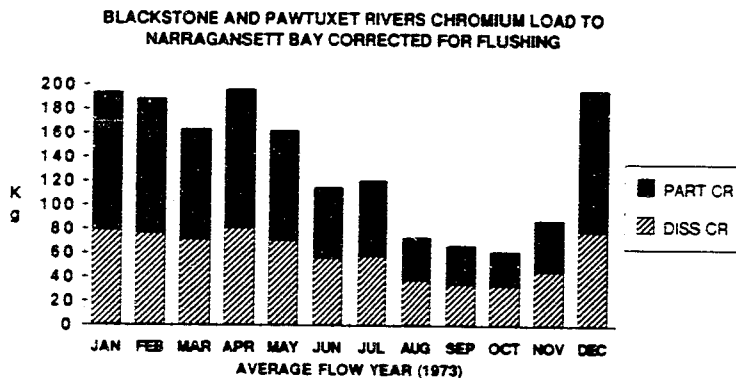
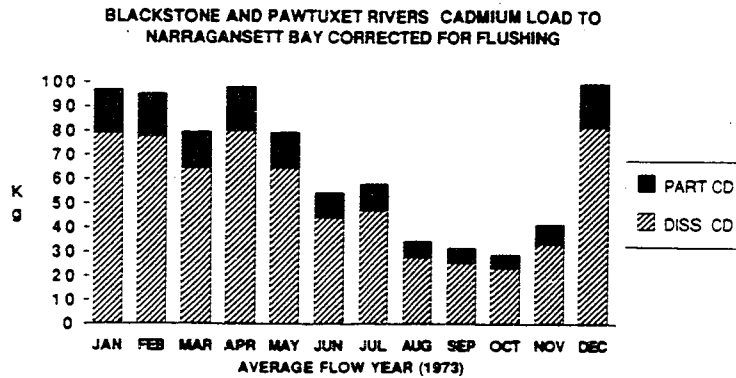
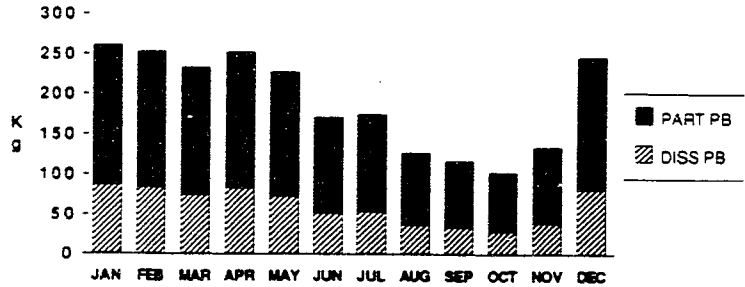
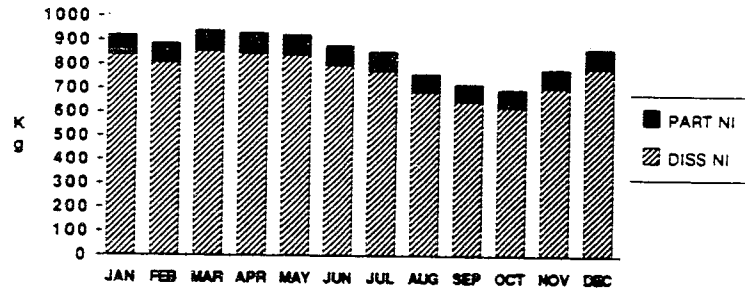


Fig. 6 Relative monthly loading rates of the dissolved ($<0.4 \mu\text{m}$), particulate, and total fractions of various metals discharged to Narragansett Bay by the Blackstone and Pawtuxet Rivers in a year with approximately average river flow rates. Daily metal fluxes (kg d^{-1}) were computed using regressions summarized in Table 7 and multiplied by flushing times (days) computed from the regression relating this parameter to fresh water flow developed by Pilson (1985). Plots for Pb, Ni and Zn (total metal only) are given on the following page.

BLACKSTONE AND PAWTUXET RIVERS LEAD LOAD TO NARRAGANSETT BAY CORRECTED FOR FLUSHING



BLACKSTONE AND PAWTUXET RIVERS NICKEL LOAD TO NARRAGANSETT BAY CORRECTED FOR FLUSHING



BLACKSTONE AND PAWTUXET RIVERS ZINC LOAD TO NARRAGANSETT BAY CORRECTED FOR FLUSHING

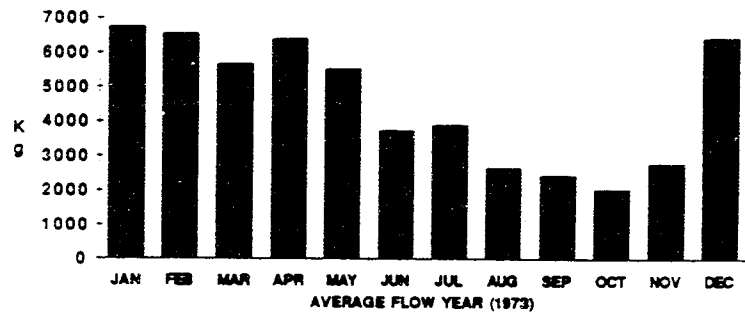


Fig. 6 (continued)

Relative monthly loading rates of the dissolved (<math><0.4 \mu\text{m}</math>), particulate, and total fractions of various metals discharged to Narragansett Bay by the Blackstone and Pawtuxet Rivers in a year with approximately average river flow rates.

Table 13

Estimated flux of various metals into Narragansett Bay proper (i.e., excluding Mt. Hope Bay) from rivers and streams during a year with average flow. Many of the values are quite uncertain, and the reader is advised to review the preceding text and footnotes carefully. Units are metric tons.

	<u>Blackstone</u>	<u>Pawtuxet</u>	<u>Woonasquatucket Plus Moshassuck</u>	<u>Others^a</u>	<u>Total</u>
As ^b	<1.3	<0.7	<0.52 ^c	1.0	<3.5
Fe ^d	>690	>238	>113 ^e	528	>1569
Mn ^d	>103	>51	>17 ^e	79	>250
Cd	1.0	0.29	0.30	0.77	2.4
Cr ^f	2.3	0.32	>0.29 ^g	1.8	>4.7 ^h
Cu	8.2	3.3	3.4	6.3	21
Ni	9.4	3.8	4.3	7.2	25
Pb	2.6	0.95	1.2	2.0	6.8
Zn ^b	<53	<21	<21 ^c	41	<136
Ag	<0.12	<0.09	<0.11	0.09	<0.41

^aMetal concentrations in other fresh water inflows have not been measured. The estimates provided here are 76.6% of the calculated loading from the Blackstone River. The average long-term input of fresh water from these sources is equal to the same percentage of the average annual long-term discharge of the Blackstone (Ries 1989). The actual inputs probably fall somewhere between zero and the values given here.

^bThese metals were only measured by the USGS upstream of the final dams over which the rivers enter salt water. As discussed in text, the metal concentrations found by the USGS were always higher than measured by other investigators sampling at the dams.

^cThe measured flux of pollutant metals in these two rivers is equal to approximately 40% of the flux from the Blackstone River. Since As and Zn have not been measured in the Woonasquatucket and Moshassuck Rivers, the estimated flux given here is 40% of the flux of these metals from the Blackstone River.

^dAs discussed in text, these metals were only measured by Hunt (1982) during a dry year. Fluxes during the "average flow" year would, presumably, have been greater. The flow of water from the Blackstone during an average year is 1.7 times the dry year flow.

^eThese metals have not been measured in the Woonasquatucket or Moshassuck Rivers. The values here are 16.4% of the reported flux from the Blackstone River. The combined long-term average annual flow of these two rivers is equal to the same percentage of the long-term Blackstone River flow (Ries 1989).

^fAs emphasized earlier, the data base for Cr consists of only 3-4 measurements.

^gIf the very high calculated flux from the Woonasquatucket is accepted (Table 10), the total would be 25 tons.

^hIf note f (above) is followed, the overall total would exceed 30 tons.

by SINBADD (Pilson and Hunt 1989) (Figs. 3 and 4). For all these reasons, my estimates of chromium input from the rivers are particularly uncertain.

As noted earlier, there are other small rivers and streams that enter Narragansett Bay proper and contribute about 20% of the total fresh water flow. With the exception of the Ten Mile River, these systems are ungauged and appear never to have been monitored for metals. Like the Ten Mile, many of them do not have a clear fall line separating free flowing fresh water from salt, and some flow into ponds that may act as settling basins retaining some of the metals carried by the streams. Some of these systems drain largely undeveloped land and probably have low concentrations of pollutant metals, while others flow through urban areas and probably carry a heavy burden of pollutants. In the absence of data, I have set metal fluxes from these combined sources as being equal to 76.6% of the calculated input from the Blackstone River (Table 13). Their combined long-term average flow amounts to this fraction of the Blackstone flow, and the Blackstone provides the best combination of a large drainage area with a wide mix of land uses and a "reasonably" well-characterized flux of most of the pollutant metals. It is evident that these unmeasured sources could contribute significantly to the total flux of metals into Narragansett Bay from surface fresh water flow (Table 13). If the Woonasquatucket and Moshassuck Rivers are combined with the "unmeasured sources", it appears that 40-50% of the estimated flux of metals into Narragansett Bay proper from rivers and streams may come from sources that are either unmeasured or very uncertain.

The situation in Mt. Hope Bay is much more difficult, since the "rating curve" for the Taunton River is based on only two sets of measurements and fewer metals were sampled (Table 5). The very preliminary estimates from these data suggest that the inputs of cadmium, chromium, copper, and nickel from the Taunton are only 5-20% of those from the fresh water sources entering Narragansett Bay proper, while lead may be about the same (Table 14). Characterizations of inputs from the Taunton River should be a high priority for any future monitoring program.

The Influence of Storms

Neither the SINBADD nor the SPRAY programs were intended to sample the rivers during or immediately following rain storms. By sampling at all seasons, however, they were able to capture a very wide range in flow conditions. For example, in the Blackstone River, metal concentrations were measured when flow rates ranged from less than $5 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ to over $7 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ and in the Pawtuxet River, from less than $3 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ to over $3 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. These flow conditions span most of the range found by R. Wright and colleagues in their study of the effect of storms on metals in the rivers (Figs. 2 and 3).

Table 14

Estimates of the annual flux of various metals into Mt. Hope Bay from the Taunton River during years with low, high, and average flow. Flux and flow regressions were based on only two sampling measurements from the SINBADD sampling program. Flow data used in regressions were corrected for ungauged watershed areas according to Pilson and Hunt (1989). Units are metric tons.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average Year</u>
Cd	0.08	0.41	0.33
Cr	0.50	0.73	0.71
Cu	1.7	4.5	4.0
Ni	0.09	1.7	1.6
Pb	1.0	10.5	7.1

While the "instantaneous" flux of metals in the rivers during and after individual storms is obviously influenced by factors in addition to flow, the combined data from the three storms studied by Wright and colleagues show a strong relationship between the flux of metals and the discharge of water in the Blackstone and, to a lesser degree, in the Pawtuxet Rivers (Fig. 7, Table 15). The flux of cadmium in the Pawtuxet was a notable exception. This metal was not a function of flow during storms and was only weakly correlated with flow in the SINBADD and SPRAY data (Table 7). Cadmium also presented problems in the Pawtuxet for Latimer et al. (1988) in their attempt to develop mass balances for metals in the river during low flow. On average, over 100 times more cadmium was discharged from the Pawtuxet than they could account for in their measured inputs to the river. The puzzling behavior of cadmium in the Pawtuxet River deserves further study.

A comparison of the regressions generated from the storm sampling data and the SINBADD-SPRAY data for the Blackstone River shows similar fluxes of cadmium and copper, but a much higher flux of lead during storms (Fig. 2, Table 16). This is consistent with earlier conclusions based on land use and measurements of metal runoff during storms, that urban runoff was potentially the major source of lead, but only a minor contributor of copper, to Narragansett Bay (Hoffman 1987). It is not clear, however, which regression serves as the better tool for estimating the annual input of lead from the river. In this report, I have relied on the SINBADD-SPRAY data for lead in order to be consistent with most of the other pollutant metals and because they were collected over a longer period of time. The storm-based regressions probably represent an upper bound to the estimate of lead input from rivers.

Some Implications of the Metal Flux-River Flow Relationship

The observation that the amounts of most metals carried by the rivers entering Narragansett Bay increase with increasing river flow (Figs. 2 and 3; Tables 7 and 15) does not necessarily mean that the concentrations of metals do not decrease at higher flow rates. For some metals, such as dissolved Cu and Ni, there is clear evidence of dilution, while for others, such as Pb or particulate Ni, concentrations remain relatively constant across a wide range in flow (Fig. 8). In most of the cases where the concentration declines with flow, however, the decline is small relative to the increase in flow, with the result that the total flux increases. For example, during the SINBADD and SPRAY programs, dissolved Cu concentrations in the Blackstone River varied by a factor of about 2.2, while river flow varied over 17 fold (Fig. 8).

This behavior suggests that the source of most metals entering the rivers must increase with the input of water. While it seems unlikely that industrial discharges of metals, either

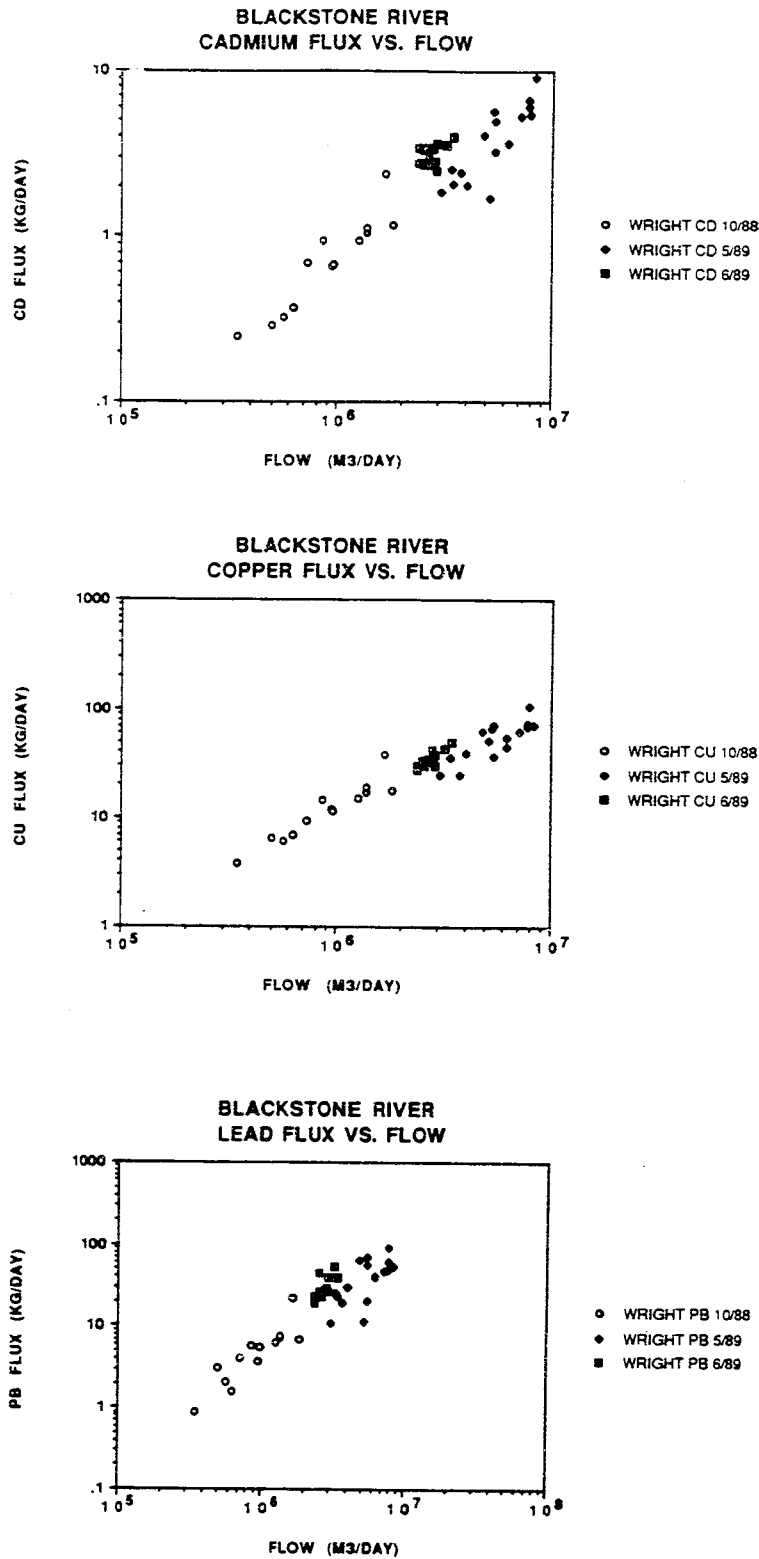


Fig. 7 "Instantaneous" fluxes of total Cd, Cu, and Pb from the Blackstone River as a function of "instantaneous flow" during three rainstorms as determined by R. Wright and colleagues at The University of Rhode Island. Regressions for the pooled data from all three storms are given in Table 15.

Table 15

Slope, intercept, and r^2 values for regressions relating the log of metal flux (kg d^{-1}) to the log of river flow ($\text{m}^3 \text{d}^{-1}$) using data collected during three rainstorms* at the mouths of the Blackstone and Pawtuxet Rivers by R. Wright and colleagues at the University of Rhode Island.

	Blackstone			Pawtuxet		
	<u>Slope</u>	<u>Intercept</u>	r^2	<u>Slope</u>	<u>Intercept</u>	r^2
Cd (d)	0.87	-5.43	0.83	0.49	-3.09	0.18
Cd (p)	1.21	-7.94	0.69	1.09	-7.12	0.37
Cd (t)	1.01	-6.15	0.87	0.61	-3.65	0.25
Cu (d)	0.71	-3.27	0.87	0.84	-4.28	0.69
Cu (p)	1.20	-6.70	0.79	1.33	-7.38	0.64
Cu (t)	0.89	-4.25	0.92	0.99	-4.86	0.69
Pb (d)	1.26	-7.24	0.74	1.29	-7.46	0.60
Pb (p)	1.17	-6.50	0.76	1.65	-9.45	0.79
Pb (t)	1.24	-6.67	0.83	1.56	-8.61	0.84

*Oct. 1988, May 1989, June 1989

Table 16

Comparison of estimates of the annual flux of various metals into the Seekonk River from the Blackstone River using regressions developed from data collected during storms (R. Wright, personal communication) and regressions developed with data collected during a regular monitoring program (SINBADD and SPRAY). Units are metric tons.

	<u>Dry Year</u>	<u>Wet Year</u>	<u>Average Year</u>
Cd (storms)	0.4	1.1	0.8
Cd (SINBADD-SPRAY)	0.6	1.5	1.0
Cu (storms)	6.1	13	9.9
Cu (SINBADD-SPRAY)	4.9	11	8.2
Pb (storms)	3.6	10	6.8
Pb (SINBADD-SPRAY)	1.6	3.5	2.6

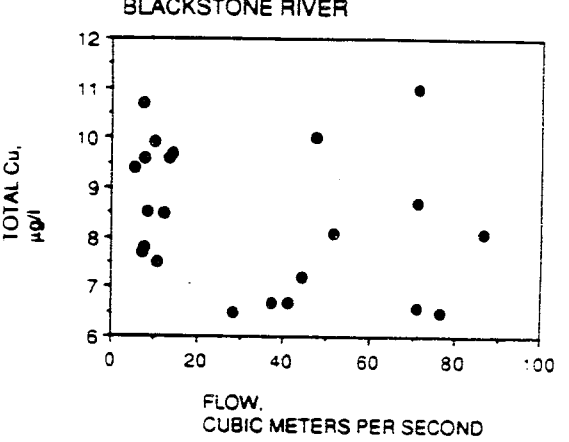
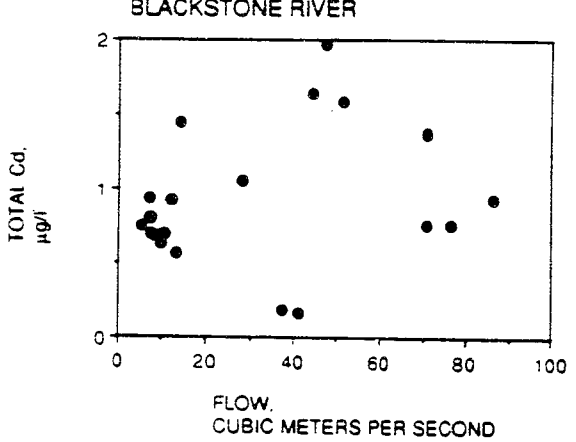
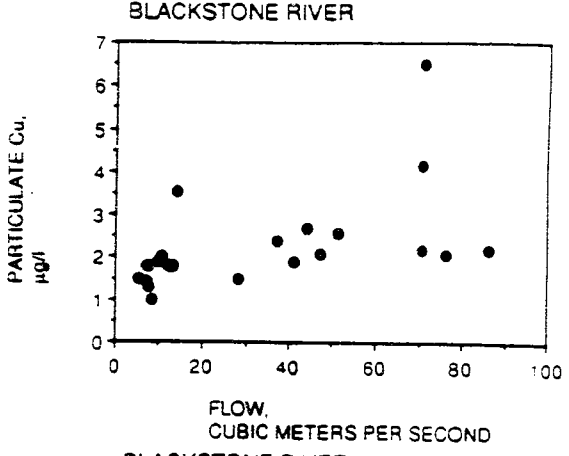
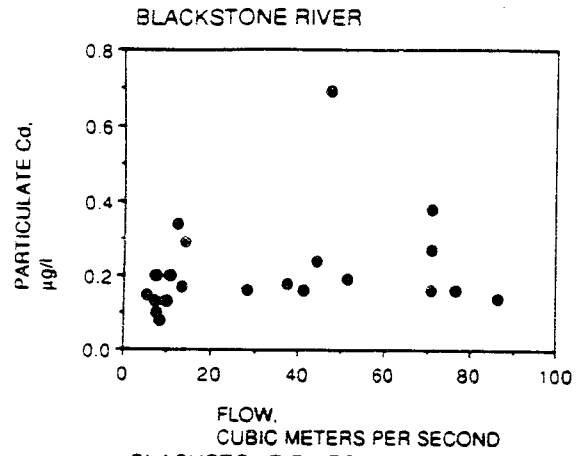
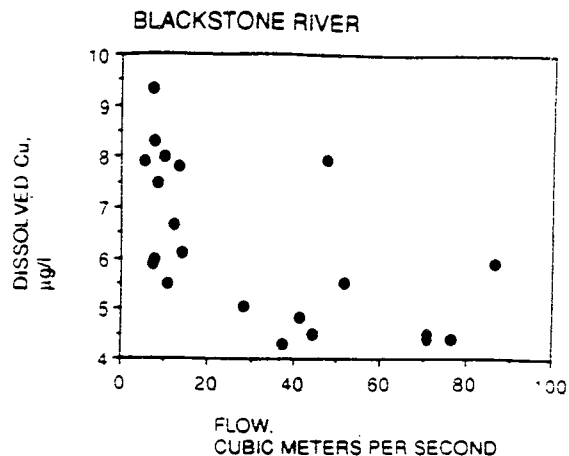
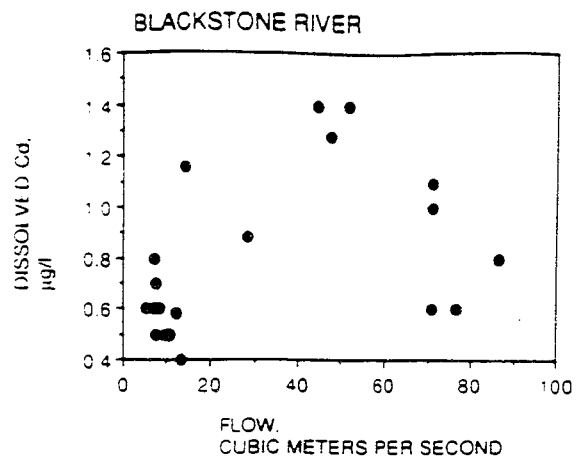


Fig. 8 Concentrations of dissolved ($<0.4 \mu\text{m}$), particulate, and total metals reported by the SINBADD and SPRAY sampling programs (see Table 5) at the mouths of the Blackstone and Pawtuxet Rivers (Fig. 1) at various rates of river flow. Flow data reported by the U. S. Geological Survey have been adjusted to account for ungauged watershed area (Pilson and Hunt 1989). Data for Pb and Ni in the Blackstone are shown on the following page. Pawtuxet River data are on pages 3 and 4 of this figure.

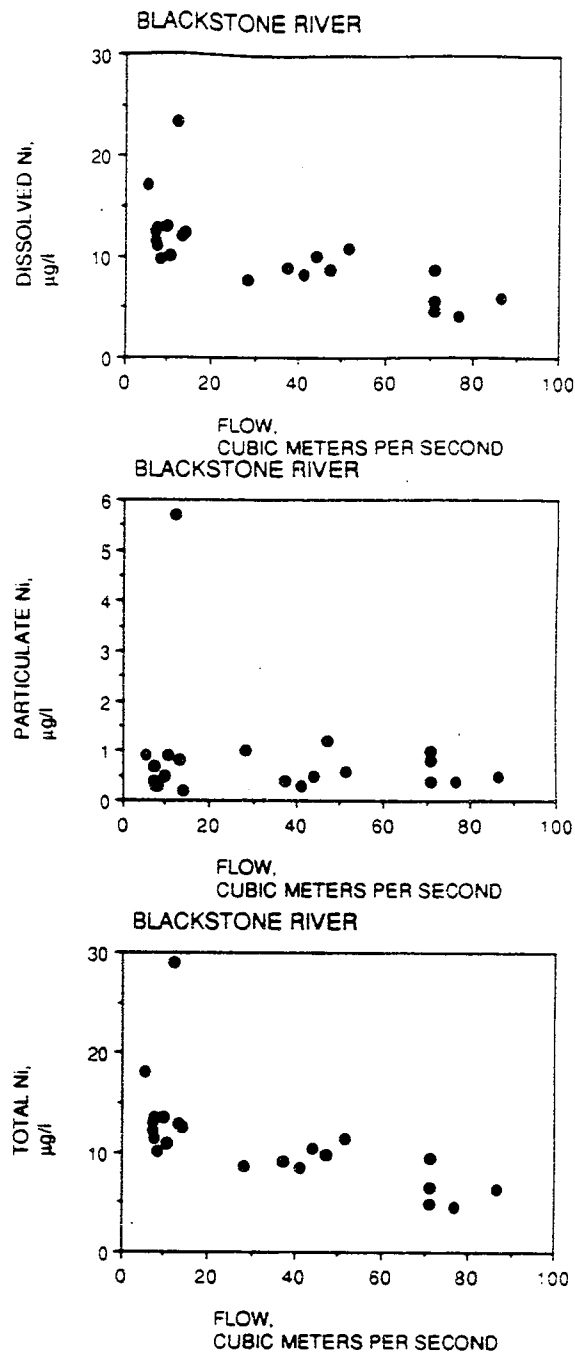
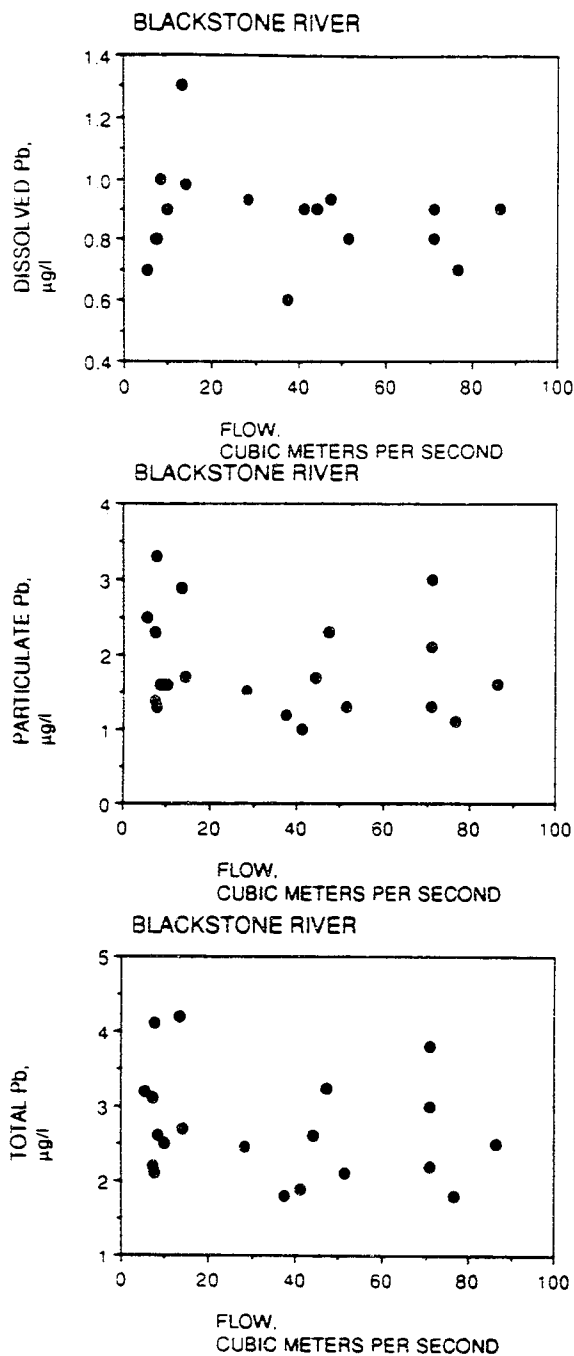


Fig. 8 (continued)

Concentrations of dissolved ($<0.4 \mu\text{m}$), particulate, and total metals reported by the SINBADD and SPRAY sampling programs (see Table 5) at the mouths of the Blackstone and Pawtuxet Rivers.

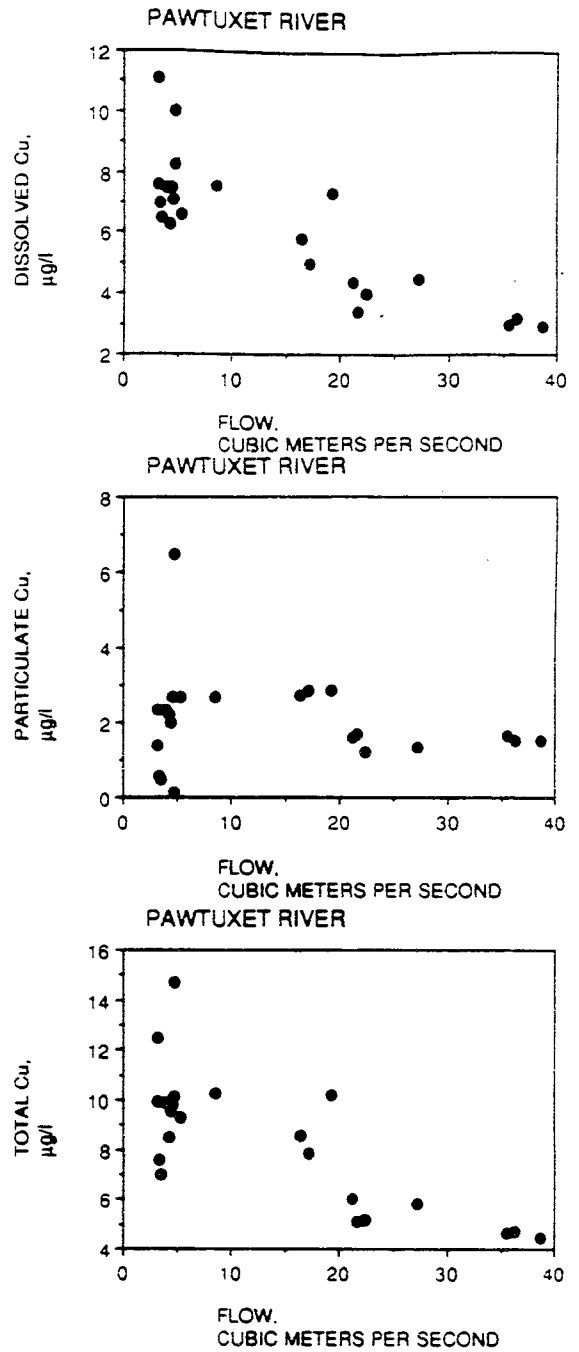
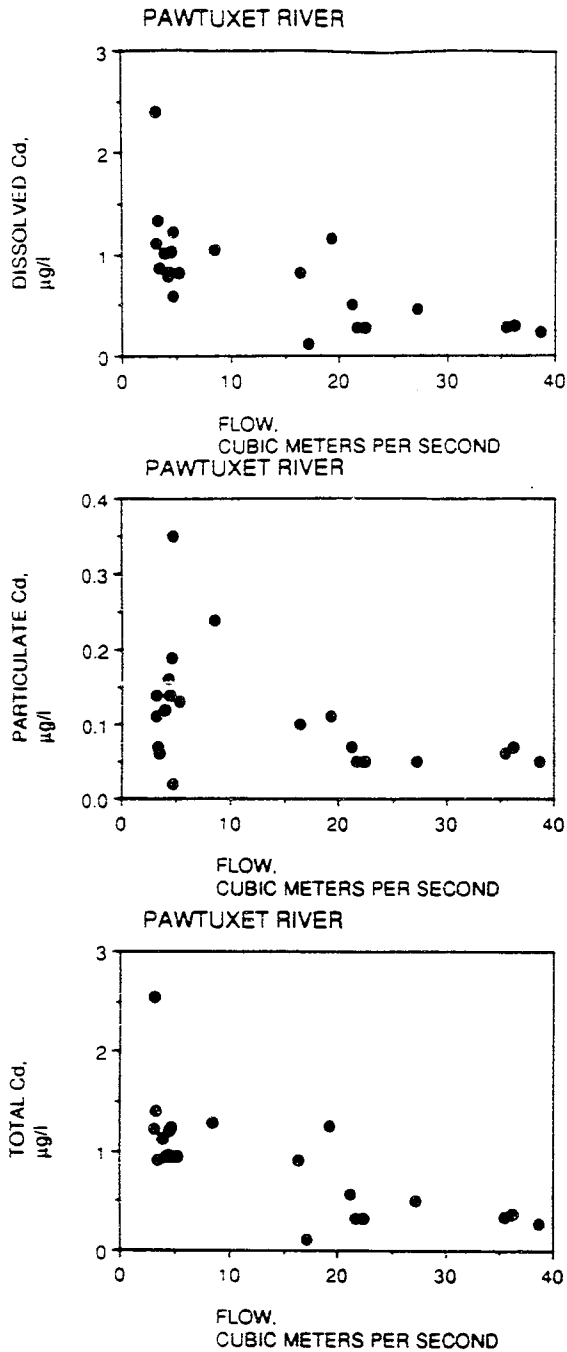


Fig. 8 (continued)

Concentrations of dissolved ($<0.4 \mu\text{m}$), particulate, and total metals reported by the SINBADD and SPRAY sampling programs (see Table 5) at the mouths of the Blackstone and Pawtuxet Rivers.

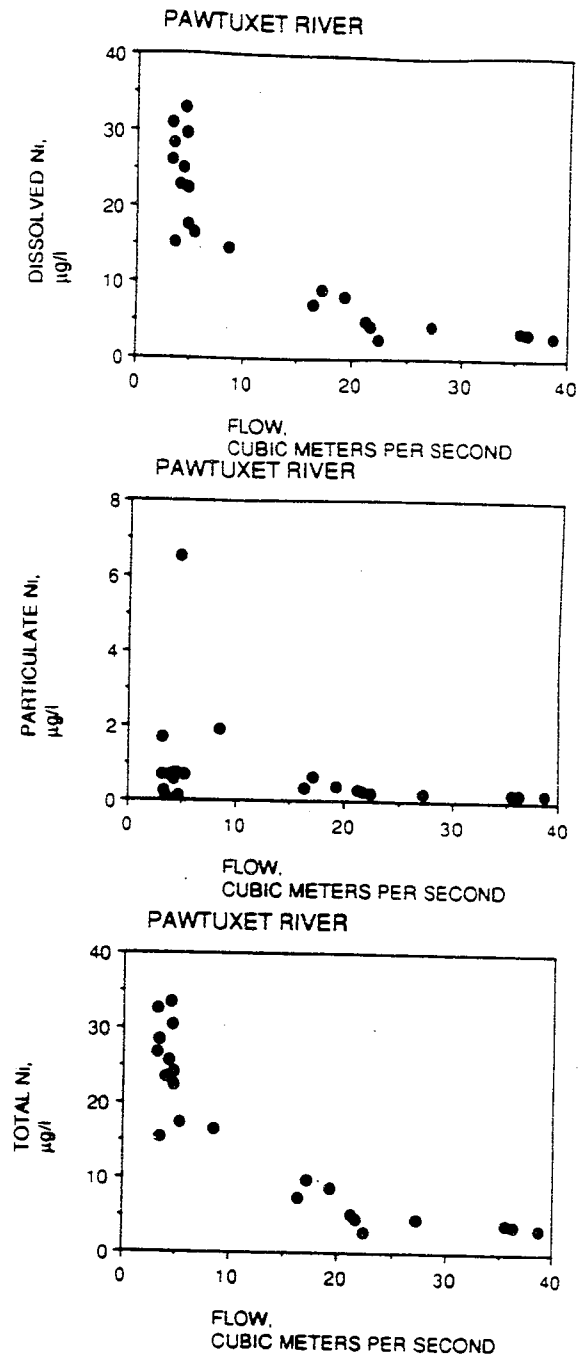
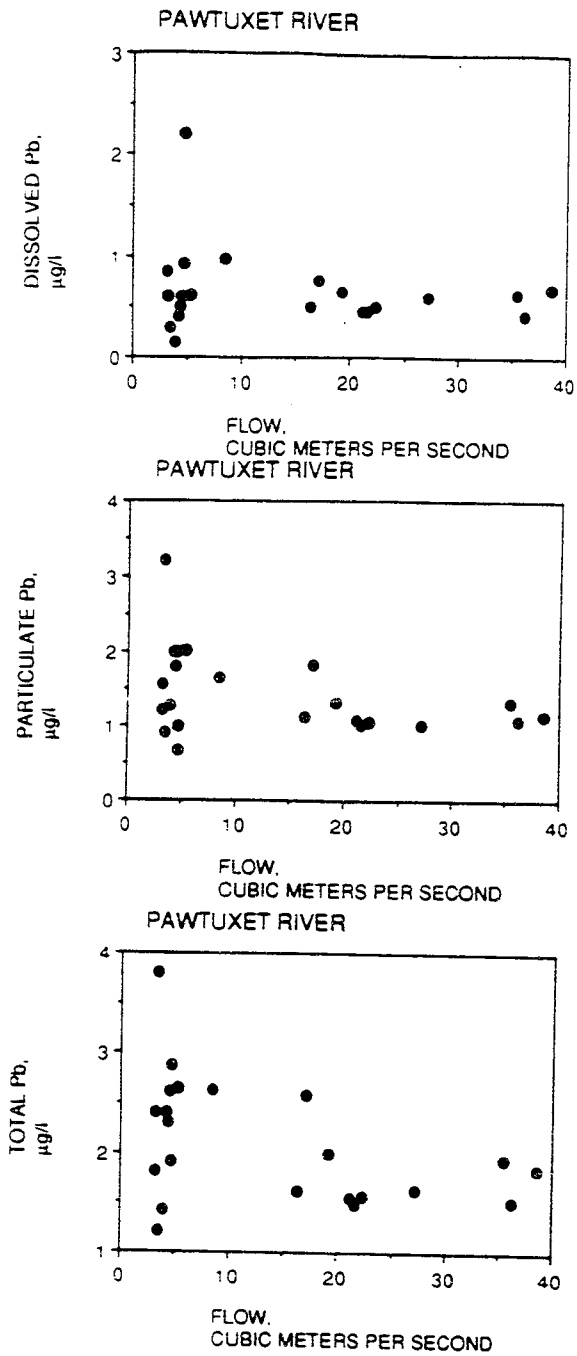


Fig. 8 (continued)

Concentrations of dissolved ($<0.4 \mu\text{m}$), particulate, and total metals reported by the SINBADD and SPRAY sampling programs (see Table 5) at the mouths of the Blackstone and Pawtuxet Rivers.

directly to the rivers or to sewage treatment plants, would necessarily increase with runoff, a recent study by Hoffman et al. (1988) has shown that the release of some pollutants, including Pb, from the Fields Point POTW increased during storms due to hydraulic surges and the loss of sludge. However, while their analysis suggested that the discharge of Pb could increase by at least 50% during an average rainstorm, they found little or no influence of storms on the release of Cd, Cu, or Ni. Moreover, the influence of storms on the release of metals from POTWs should be relatively evenly distributed throughout the year, following the distribution of precipitation (Pilson 1989) and urban runoff, while the source for the rivers must have a strong seasonality that follows total surface runoff and groundwater flow.

The sources of metals carried into the rivers by surface and groundwater flows could include deposition from the atmosphere, disposal of metals on natural or paved surfaces (for example, Zn in crankcase oil leaked onto highways as reported by Hoffman and Quinn 1984), and the leaching of metals contained in landfills.

As a first step in evaluating the potential importance of these sources, I have used the deposition calculations from Table 1, along with measurements of Cd deposition on lower Delaware Bay (Church et al. 1984), to estimate the total flux of metals from the atmosphere to the watershed of the Blackstone River. With the notable (and not surprising) exception of Pb, the flux of metals from the atmosphere is small relative to the mass of metals discharged by the river (Table 17). This is in marked contrast to the Delaware River, where Church et al. (1988) found that inputs of Cd, Cu, Ni, Zn and Fe from the atmosphere to the watershed exceeded the fluxes of these metals in the river by factors of 1.4, 5.9, 7.7, 46, and 206, respectively. Only Mn transport by the Delaware exceeded atmospheric deposition (by a factor of 53).

A major difference between the Delaware and the Blackstone Rivers is that there is very little industrial activity along the Delaware above Trenton, N. J., where the metal fluxes in the river were measured, while the Blackstone receives major sewage and industrial loadings upstream of the sampling station used to measure fluxes (Quinn et al. 1987, Lewis and Brubaker, undated). Assuming that point source discharges from POTWs and industries provide most of the metals carried by the Blackstone during dry weather, low flow conditions, I have extrapolated the calculated transports of metals during October of the "average flow year" (Fig. 4) to a full year for comparison with the annual fluxes calculated from the metal flux vs. river flow regressions. The results suggest that the source or sources of metals supporting the "excess" fluxes during higher flows are larger than those providing the flux of metals under base flow conditions (Table 18). Since the "excess" fluxes (excepting Pb) are also still larger than the estimated fluxes from atmospheric deposition

Table 17

Comparison of the estimated deposition of various metals from the atmosphere to the watershed of the Blackstone River¹ with the flux of metals from the river into Narragansett Bay.

	<u>Estimated Deposition</u> ²	<u>Estimated River Flux</u> ³
	tons y ⁻¹	
As	<0.16	<1.3
Cd	0.26*	1.0
Cr	0.44	2.3
Cu	3.4	8.2
Ni	2.0	9.4
Pb	21	2.6
Zn	13	<53
Mn	4.8	<109
Fe	180	>690

¹1222 km² (Ries 1989).

²See Table 1, average year.

³See Table 8, average year.

*Calculated using deposition measurements from lower Delaware Bay (Church et al. 1984) pro-rated to average year rainfall for Narragansett Bay.

Table 18

Comparison of the estimated deposition of various metals from the atmosphere to the watershed of the Blackstone River¹ with the flux of metals from the river into Narragansett Bay that is in excess of base flow transport² in a year with average precipitation.

	<u>Estimated Deposition</u>	<u>Base Flow Flux</u> metric tons y ⁻¹	<u>Excess Flux</u> ³
As	<0.16	<0.61	<0.69
Cd	0.26*	0.29	0.71
Cr	0.44	0.58	1.7
Cu	3.4	2.8	5.4
Ni	2.0	4.3	5.1
Pb	21	0.9	1.7
Zn	13	<17.6	<35.4
Mn	4.8	<34.4	<68.6

¹1222 km² (Ries 1989).

²October flux, average year (Fig. 4).

³Excess = Annual flux - (October flux x 12), average year.

*Calculated using deposition measurements from lower Delaware Bay (Church et al. 1984) pro-rated to average year rainfall for Narragansett Bay.

(Table 18), it seems probable that other sources are also important in contributing to the metals carried by the Blackstone. As mentioned earlier, highway and parking lot runoff may be major sources of Pb and Zn (Hoffman and Quinn 1984), but used crankcase oil and gasoline do not contain large concentrations of Cd, Cu, or Mn (Latimer 1984).

While the major source of Mn in the Blackstone, as in the Delaware, appears to be natural weathering of the rocks in the watershed (Graham et al. 1976), additional anthropogenic sources contribute significantly to the As, Cd, Cr, Cu, and Ni carried by the Blackstone. These sources could enrich storm water surface runoff through processes not involving atmospheric deposition or automobiles, though it is not clear how this might be achieved. It is also possible that there may be significant flows of metal-enriched groundwater into the Blackstone. Latimer et al. (1988) found very much elevated concentrations of Cd, Cu, and Ni in groundwater samples near a sanitary landfill in Cranston, R.I., and it seems likely that similar sites could be found along the Blackstone. Given the evidence available thus far, it would seem important to make some further assessment of the impact of industrial and urban landfills on the metal budgets of the Blackstone and other rivers entering Narragansett Bay. It is also important to obtain direct measurements of the metal fluxes from the atmosphere at several locations in the bay watershed rather than relying on calculated deposition rates from a site on the lower bay. It is possible that atmospheric deposition may be the largest source of metals entering Narragansett Bay through the Blackstone River.

Before leaving the subject of rivers, it is worth noting that, within the range of flows covered by the data, there is no evidence of stream bed erosion. While the slopes of the particulate metal flux regressions tend to be steeper than for dissolved metals (Tables 7 and 15), there were no clear "steps" or breaks in the data indicating that threshold current speeds necessary for sediment erosion and resuspension had been attained (Figs. 2, 3, 7). It is certainly possible that river bed and bank erosion occur during extreme flows, but it is difficult to assess the contributions of such events to the inventory of metal inputs without additional study.

Inputs from Direct Industrial Discharges

With the possible exception of three electric power generating facilities, there appear to be no discharges of industrial waste waters directly to Narragansett Bay that are of consequence in the inventory of metal inputs. There are numerous direct discharges to the tributaries that enter the bay, but they contribute Cu, Pb, and Zn loads that are small relative to the metals entering the bay from publicly owned sewage treatment plants (POTWs) and urban runoff (Hoffman and Quinn 1984, Hoffman 1987). Direct industrial discharges may

contribute a significant portion of the Ag (Hoffman and Quinn 1984) as well as Cr, Cu, and Pb carried by the fresh waters entering the bay (Table 19), but these inputs are included in the calculated loadings from the rivers and streams. The great majority of industrial discharges will be included in the next section of this report that covers the assessment of metal releases from publicly owned sewage treatment plants.

As noted by Hoffman (1987), the large flows of cooling water used by electric power generating plants on the Providence River and in Mt. Hope Bay could provide a large input of metals even if there is only a modest increase in metal concentrations as water passes through the plants. In most cases, however, it is impossible to evaluate the addition because the concentrations of metals in the influent water are not measured or reported. For the largest power plant discharging into Mt. Hope Bay, Hoffman and Quinn (1984) appear to have obtained data on the actual increase in some metals (Hoffman 1987), and their work suggests that the plant may add almost as much Ni to Mt. Hope Bay as the input from the Taunton River (Table 20).

Publicly Owned Sewage Treatment Plants

There are 32 sewage treatment facilities that collect and discharge waste waters within the Narragansett Bay drainage basin. Twenty-two of these discharge their effluents into rivers and streams, and their contribution to the total metal input to the bay has already been included in the calculation of metal loadings from rivers. Nine of the remaining plants discharge directly into the tidal waters of Narragansett Bay proper, and one discharges into Mt. Hope Bay (Table 21, Fig. 1).

Since the mid 1970s, treatment plants have been required to report the concentrations of various metals in their effluents, and it is often assumed that these data provide adequate information for calculating their discharges of metals to the bay. Unfortunately, this is not the case.

In a recent discussion of metal inputs from sewage treatment plants, Brubaker and Byrne (1989) correctly concluded that ". . . it is impossible to determine the level of discharge to Narragansett Bay." There are several contributing factors. Since metal loadings arise from the activities of numerous industries and manufacturing plants, there is no simple flux-flow relationship for POTW effluents as found for river inputs, and the concentrations of metals vary from day to day. For example, composite daily samples of the effluent from the Fields Point treatment plant, the largest that discharges to the bay, showed the following concentrations of metals on three consecutive days (SPRAY data, Doering et al. 1988):

Table 19

Comparison of the calculated inputs of various metals to Narragansett Bay (including Mt. Hope Bay) from rivers and streams with the direct discharge of metals reported by industries in the watershed.

	Estimated Input from Rivers and Streams ¹	Direct Industrial Discharges in the watershed ²
	metric tons y ⁻¹	
Cd	2.7	0.09
Cr	>5.4	13
Cu	25	15
Ni	27	0.04
Pb	14	8.0
Zn	<136	7.3

¹Sum of Tables 13 and 14 for "average year".

²Hoffman (1987) for 1983. Data from R. I. and Mass., not including power plants.

Table 20
 Comparison of some estimated inputs of metals to Mt. Hope Bay.
 (49.2 km², Pilson 1985)

	<u>Electric Power Plant Cooling Water¹</u>	<u>Taunton River²</u>	<u>Direct Atmospheric Deposition³</u>
	metric tons y ⁻¹		
Cu	0.17	4.0	0.14
Ni	1.3	1.6	0.08
Zn	0.29	--	0.54

¹Hoffman and Quinn (1984).

²From Table 14, average year.

³From Table 1, average year.

Table 21

Volume of effluent discharged directly into Narragansett Bay by publicly owned sewage treatment plants. Data for R. I. plants from R. I. Department of Environmental Management, RIPDES files.

	1986 Average Daily Flows	
	<u>$10^3 \text{ m}^3 \text{ d}^{-1}$</u>	<u>Percent</u>
Seekonk River		
Blackstone Valley District Commission (Bucklin Point)	78	22
Providence River		
Narragansett Bay Commission (Fields Point)	195	56
East Providence	22	6
West Passage		
East Greenwich	3	<1
Quonset	3	<1
East Passage		
Warren	6	2
Bristol	8	2
Jamestown	2	<1
Newport	32	9
Mt. Hope Bay ¹		
Fall River	<u>73</u>	21
	349	

¹From Hoffman (1987).

		mg m ⁻³			
		<u>Cd</u>	<u>Cu</u>	<u>Ni</u>	<u>Pb</u>
8	March, 1987	2.15	118	249	11.3
9	March	2.59	309	300	19.9
10	March	0.70	281	255	20.2
9	August, 1987	2.33	283	138	41.1
10	August	1.10	167	77	28.8
11	August	1.32	178	357	23.3

In three-day sequential sampling on six occasions throughout an annual cycle at three treatment plants, coefficients of variation for concentrations of Cd, Cu, Pb, and Ni in effluent ranged from 35% to 67% (Table 22). Most smaller treatment plants are sampled for metals only a few times each year, and not all of the pollutant metals of interest are included in the analyses. Moreover, even when an analysis is reported, the results frequently appear as "less than" the allowable discharge concentration or "less than" the lowest detection limit of the analytical facility. While this type of report may be adequate for enforcement monitoring, it is not very useful for calculating mass loadings of metals or other pollutants.

Even for the Narragansett Bay Commission plant at Fields Point, a facility that is monitored frequently (weekly-monthly) with respect to metal discharge by an excellent "in house" analytical laboratory, there are difficulties in assessing the actual flux of metals to the bay. As pointed out by Brubaker and Byrne (1989), the standard data set on metals in sewage treatment plant effluents maintained by the R. I. Department of Environmental Management is the R. I. Pollution Discharge Elimination System (RIPDES) file, a continuation of the older National Pollution Discharge Elimination System (NPDES). For the Fields Point treatment plant and a few others that measure their effluent frequently, the discharge monitoring report (DMR) entered in the RIPDES file for each month contains only the highest concentration observed during that month. Moreover, flow data are not reported for the time during which the DMR concentrations are measured, and fluxes are calculated from the average daily flow for each month (Brubaker and Byrne 1989). Again, this may be appropriate for permit enforcement, but the practice almost certainly leads to a significant overestimate of the metals actually released from the treatment plants.

I have used the SPRAY data collected by Doering et al. (1988) on metal concentrations in composite daily samples of effluent collected on 18 occasions over an annual cycle in 1986-1987 from the three largest treatment plants that discharge directly into Narragansett Bay proper to calculate estimates of the mean concentrations of Cd, Cu, Pb, and Zn in each

Table 22

Concentrations of some metals in effluents from the Narragansett Bay Commission sewage treatment plant at Fields Point, the Blackstone Valley District Commission plant at Bucklin Point, and the East Providence treatment plant. Daily composite samples were analyzed for three consecutive days at six different times during 1986 and 1987 (Doering et al. 1988).

	Total Concentration (# of samples) mean \pm 1 S.D., $\mu\text{g kg}^{-1}$			
	<u>Cd</u>	<u>Cu</u>	<u>Pb</u>	<u>Ni</u>
Fields Point	(18) 1.9 ± 0.7	(18) ^a 327 ± 205 (15) 247 ± 101	(18) 26 ± 9.2	(18) 279 ± 149
c.v., %	37	41-63	35	53
Bucklin Point	(5) 1.6 ± 0.7	(17) 52 ± 22	(17) 21 ± 5.9	(17) 96 ± 49
c.v., %	44	42	28	51
East Providence	(5) 0.7 ± 0.4	(16) 33 ± 21	(17) 10 ± 6.7	(18) 92 ± 40
c.v., %	57	64	67	43
% Dissolved ($< 0.4 \mu\text{m}$)				
Fields Point	67 ± 15	67 ± 10 69 ± 10	25 ± 18	85 ± 7
Bucklin Point	60 ± 37	44 ± 17	43 ± 27	92 ± 4
East Providence	68 ± 18	79 ± 26	74 ± 23	93 ± 5

^aSamples collected on 24, 25, 26 July, 1987 had very high Cu concentrations of 700-770 $\mu\text{g kg}^{-1}$. This sampling was scheduled in an attempt to coincide with anticipated cleaning of electroplating tanks by the jewelry industry. The lower value based on 15 samples excludes these data.

of the effluents (Table 22). Multiplying these means by the average daily flow of effluent from each treatment plant for 1986 (Table 21) provides estimates of metal fluxes that are considerably lower than those calculated from the RIPDES files (Table 23). The discrepancy is large and particularly serious for the Fields Point plant, since it is such a major source of many metals. And the discrepancy, at least for Fields Point, must be due to differences in sampling and reporting rather than to analytical problems, because the Fields Point laboratory analyzed the SPRAY samples from the treatment plant (Doering et al. 1988). Unfortunately, the SPRAY program did not include other metals, such as Ag, Cr, Zn, or Hg, that are reported for these plants in the RIPDES files.

As in the rivers, the SPRAY data show that most of the Ni from treatment plant effluents is in dissolved form (Table 22). Copper was also similar, except at the Bucklin Point plant, where particulate Cu was more abundant than in the other effluents or in the rivers. Cadmium was also somewhat more particle-bound in the sewage effluents, but Pb tended to be a bit more soluble than in the rivers (compare Tables 11 and 12 with Table 22).

The problem of assessing the metal inputs from treatment plants is also compounded by the fact that the discharges from many, perhaps all, of the plants have been changing as a result of improvements in plant operations and/or the implementation of industrial pretreatment programs that have reduced the flows of metals into the plants (Brubaker 1986, Brubaker and Byrne 1989). While pretreatment programs were to be fully implemented by 1984, there have been numerous delays and problems in enforcement (Brubaker and Byrne 1989, Sutinen and Lee 1990). Nevertheless, the Narragansett Bay Commission reports that between 1981 and 1989 the following reductions in metal flows to the Fields Point treatment plant were achieved:

Ag — 81%	Ni — 84%
Cd — 87%	Pb — 81%
Cr — 90%	Zn — 72%
Cu — 95%	Hg — 35%

With the exception of Zn and Hg, the fluxes of metals from the Fields Point facility to the bay, as calculated from RIPDES data, showed equivalent or only somewhat smaller (~10%) declines when comparing the same years. For unknown reasons, the export of Zn from the plant declined only 49% and Hg increased 32% in 1989 compared to 1981.

The decline in metal discharges from Fields Point has not been consistent, though the overall reduction in the discharge of Cu, Ni, Zn and Pb since 1982 has been dramatic (Fig. 9). Chromium and silver discharges remained relatively low, if erratic, after 1982, while Cd appears to have declined sharply only in 1989 (Fig. 9).

Table 23

Comparison of metal inputs from publicly owned sewage treatment plants discharging into the Seekonk and Providence Rivers as reported in RIPDES files for 1986 and 1987 and as calculated using concentration measurements from the 1986-1987 SPRAY program (Doering et al. 1988) and mean flows from RIPDES files for 1986. Numbers of samples are shown in (). Values are metric tons per year \pm 1 S.D.

	<u>Cd</u>	<u>Cu</u>	<u>Ni</u>	<u>Pb</u>
Narragansett Bay Commission,				
Fields Point				
RIPDES 1986 (12)	0.62 \pm 0.60	36.9 \pm 17.0	42.5 \pm 18.0	6.1 \pm 4.8
RIPDES 1987 (12)	0.66 \pm 0.45	33.8 \pm 15.9	37.8 \pm 13.9	5.7 \pm 3.1
SPRAY 1986-1987 (18)	0.14 \pm 0.05	23.3 \pm 14.6 17.6 \pm 7.2*	19.9 \pm 10.6	1.8 \pm 0.6
Blackstone Valley Commission,				
Bucklin Point				
RIPDES 1986 (4)		3.13 \pm 0.84	5.89 \pm 2.39	
RIPDES 1987 (4)		3.55 \pm 3.30	5.87 \pm 3.18	
SPRAY 1986-1987 (16,18)		1.49 \pm 0.63	2.74 \pm 1.40	
East Providence				
RIPDES 1986 (7)	0.01 \pm 0.01	0.21 \pm 0.06	0.41 \pm 0.08	0.08 \pm 0.04
RIPDES 1987 (12)	0.02 \pm 0.02	0.25 \pm 0.15	0.91 \pm 0.32	0.13 \pm 0.09
SPRAY 1986-1987 (5,16,18,17)	0.006 \pm 0.003	0.27 \pm 0.17	0.72 \pm 0.32	0.08 \pm 0.05

*Does not include samples from July 1987. The higher SPRAY value should be compared with the RIPDES data.

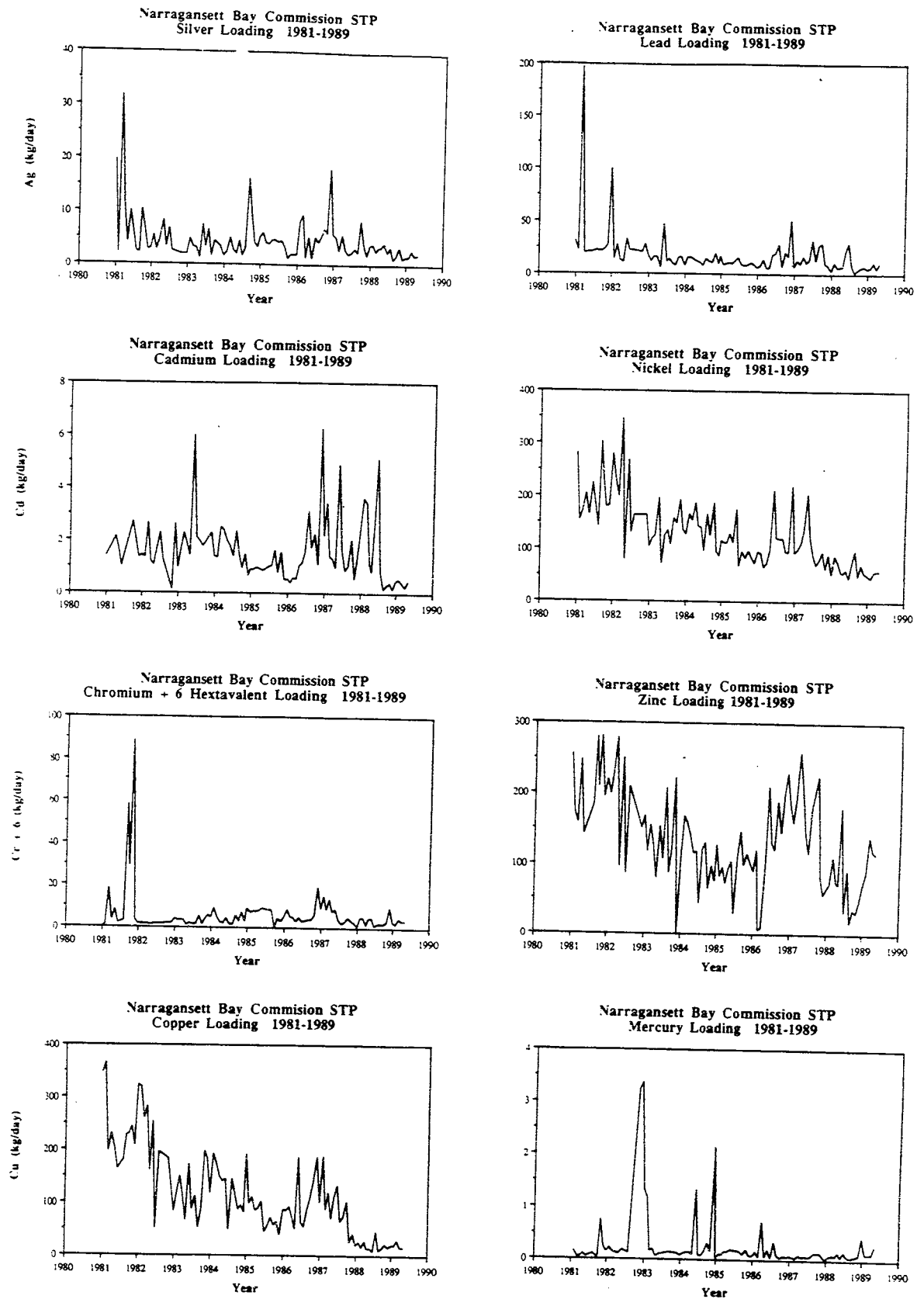


Fig. 9 Discharge of various metals from the Narragansett Bay Commission sewage treatment plant at Fields Point (Fig. 1) between 1981 and 1989 as recorded in RIPDES files.

Some of the earliest metals discharge data for the Fields Point plant were summarized by Olsen and Lee (1979) from R. I. Department of Environmental Management permit and "self-monitoring files", presumably for the period 1976-1978. They show discharges of:

$$\text{Cu} = 88.6 \text{ t y}^{-1}$$

$$\text{Cr} = 13.6 \text{ "}$$

$$\text{Ni} = 80 \text{ "}$$

$$\text{Zn} = 140 \text{ "}$$

If these values are correct, there were already significant declines in the amounts of Cr, and especially Zn, released from Fields Point by 1981, though Cu and Ni showed little change between about 1977 and 1981 (Fig. 9). While the amount of lead in the Fields Point effluent declined by about 80% between 1981 and 1989 (Fig. 9), concentrations of lead in the air in Providence in 1981 had already declined by about 50% from their value in 1978, three years after unleaded gasoline was required for new automobiles (R. I. Department of Health, annual reports). However, since storm water runoff contributed only about 9% to the lead discharged by the plant, at least during 1982 (Hoffman et al. 1988), it does not seem that the removal of lead from gasoline would necessarily have produced a marked drop in lead entering and leaving the treatment plant.

It is also likely that changing economic conditions have played a role in reducing the amounts of metals reaching the treatment plants. With the exception of costume jewelry, the value added by manufacturing in other major metal consuming industries in Rhode Island declined during the late 1970s and early 1980s (Nixon 1990).

Because of the dramatic declines in many of the metals discharged by the treatment plants, their contribution to the total input of metals to the bay will depend on the time when the inventory is taken. I have chosen to use the mean discharges during 1986 and 1987 because data on metal concentrations in the effluents from all of the treatment plants discharging directly to the bay were analyzed on four occasions during 1986 by the SINBADD program (Pilson and Hunt 1989) and the effluents from the three plants discharging directly to the Seekonk and Providence Rivers were also analyzed on 18 days in 1986 and 1987 by the SPRAY program (Doering et al. 1988). As a practical matter, however, I have had to supplement the 1986-1987 data with some earlier measurements in order to assemble even the imperfect inventory summarized in Table 24. In some cases, such as Cd, there were no data reported in the RIPDES file for the Bucklin Point plant in 1986 or 1987, and the flux for 1985 was anomalously high (2.4 t y^{-1}). It seemed more representative to report the mean flux for 1980 through 1984. Similarly, the RIPDES Cr flux from Bucklin Point was very

Table 24

Estimated input of various metals to Narragansett Bay proper and to Mt. Hope Bay from publicly owned sewage treatment plants that discharge directly into tidal waters. Data from RIPDES files for 1986 and 1987 unless noted. Values in () from SPRAY concentration data (see Table 22). Units are metric tons per year.

	Narragansett Bay Proper				
	Narragansett Bay Commission <u>Fields Point</u>	Blackstone Valley District Commission <u>Bucklin Point</u>	East <u>Providence</u>	Others ^{e*}	Total
Ag	1.8	1.4 ^a	<0.2 ^e	<0.6	<4.0
Cd	0.6 (0.14)	0.3 ^a (0.05)	0.02 (0.01)	<0.3	<1.2 (<0.5)
Cr	2.3	1.4 ^a	0.06	<0.7	<4.5
Cu	35 (18-23)	3.3 (1.5)	0.2 (0.3)	<1.1	<39.6 (21-26)
Ni	40 (20)	5.7 (2.7)	0.7 (0.7)	<0.6	<47.0 (<24)
Pb	5.9 (1.8)	4.9 ^b (0.6)	0.1 (0.1)	<0.7	<11.6 (<3.2)
Zn	54	3.9 ^c	0.4	--	>58.3
Hg	0.044	--	--	--	>0.044
Hg	0.006 ^d	0.0006 ^d	0.0003 ^d	--	>0.007

	Mt. Hope Bay	
		<u>Fall River</u>
Ag	<1.0 ^e	
Cd	<0.24 ^e	
Cr	<0.61 ^e	1.2 ^f
Cu	<0.92 ^e	1.8 ^f
Ni	<0.76 ^e	
Pb	<3.2 ^e	
Zn	-	19.1 ^f

^aMean RIPDES file for 1980-1984, N = 12 for 1980-1983, N = 4 for 1984.

^bRIPDES for 1984, N = 4.

^cBrubaker (1986).

^dPilson and Hunt (1989). Sampling on one day only.

^eMean concentration from four SINBADD samples in 1985 and 1986 (Pilson and Hunt 1989) multiplied by average flow for 1986 (RIPDES files). Metals were often below detection limits resulting in < designation for fluxes.

^fHoffman and Quinn (1984), NPDES data for 1982-1983.

*"Others" includes Warren, Bristol, Newport, E. Greenwich, Jamestown (three samples), Quonset (two samples).

large in 1986 (12 t y^{-1}), and I again calculated a mean for 1980 through 1984. Lead data have not been reported for Bucklin Point since 1984.

The most striking feature of the inventory of direct metal fluxes from treatment plants is the dominance of one source. In 1986-1987, the Narragansett Bay Commission facility at Fields Point accounted for the following proportions of the metals released from treatment plants directly into the bay:

Ag — 45%	Cu — 88%
Cd — 50%	Ni — 85%
Cr — 51%	Pb — 51%
	Zn — 93%

Except for Cd (which declines to 28%), these proportions are roughly the same regardless of whether the RIPDES or SPRAY data are used to calculate the fluxes (Table 24).

Urban Runoff

There is probably no item in the inventory of pollutant inputs to the bay that has aroused more recent concern or been surrounded by more confusion than urban storm water runoff. Much of the concern is due to an intensive study of this source of pollution to Narragansett Bay that was carried out by Hoffman and Quinn (1984) between 1980 and 1984. Their measurements and calculations suggested that urban runoff could provide about 48% of the petroleum hydrocarbons, 44% of the high molecular weight PAHs, 56% of the Zn, and 65% of the Pb entering "waters of the Narragansett Bay basin." I have added emphasis to the term "basin" because their assessment was based on multiplying measured fluxes of each pollutant per unit area from each of four specific land use types by the total amount of each land use type in the watershed of the bay and summing the results. This was a very reasonable and practical approach to the problem, but it is important to remember that the subject of their inventory was the entire drainage basin of the bay, including tributaries, and not just the tidal salt waters of Narragansett Bay itself. For this reason, their assessment of industrial discharges and sewage treatment plants also included outfalls located along the tributaries to the bay as well as those emptying directly into the bay. Rivers were not considered as inputs, but as unquantified transfers **within** the larger system of interest. The Hoffman and Quinn (1984) study did not address the question of how much of the pollutants potentially generated by urban runoff actually reached the various tributaries or how much of the pollutants entering the tributaries from runoff and point source discharges actually reached Narragansett Bay.

The results of some more recent comparisons between metal inputs to the Blackstone and Pawtuxet Rivers and the fluxes of metals from these systems to the Seekonk and Providence River portions of Narragansett Bay have been reported by Quinn et al. (1987) and Latimer et al. (1988), respectively. During three low-flow studies, the masses of Cd, Cr, Cu, Ni, and Ag discharged by the Blackstone River at Pawtucket, R. I. averaged between about 40% (Cr) and 70% (Ni) of the measured inputs (including flow from upstream) between the Rhode Island—Massachusetts state line and the dam at Pawtucket. Virtually all of the Pb was exported. This contrasts markedly with the low-flow mass balance of the Pawtuxet River, where the export of Cd, Cr, Cu, Pb, and Ni averaged three (Ni) to 100 (Cr) times greater than the measured inputs on the three occasions studied by Latimer et al. (1988).

Until more extensive mass balance studies on the watersheds and rivers have been completed during wet weather conditions, it will be difficult to know how large a contribution urban runoff actually makes to the input of metals to the bay. By including the measured fluxes of metals at the mouths of the larger rivers and extrapolating those fluxes on a flow-weighted basis to "all" the fresh water entering the bay, it seems likely that much of the influence of urban runoff has been captured in this inventory. That there is some additional metals input due to runoff is evident from the steeper slopes of the river flux vs. flow regressions for Cu and Pb derived from Wright's storm measurements (Table 15 compared to Table 7), but the storm regressions produce only a modest increase in Cu even if they are applied to an entire year of flow measurements (Table 16). The 2.6 fold higher annual Pb flux computed for the Blackstone River in an average flow year using the Wright storm regression (Table 16) is not surprising considering the large predicted flux of lead in urban runoff, and a similar increase might have been found for Zn if that metal had been measured in the wet weather sampling (Hoffman and Quinn 1984). Since the storm regression would apply for only a fraction of the year, however, the actual increase in Pb and (perhaps) Zn above that predicted using the SINBADD—SPRAY regressions would be considerably less than suggested in Table 16. At this point, I think the most prudent course is to identify urban runoff as an unquantified source that may be found to make a significant additional contribution to the inputs of Pb, Zn, and perhaps some other metals.

The finding that metal fluxes from the rivers increase with flow (Figs. 2 and 3) certainly indicates that non-point sources may be very important in contributing to the total amounts of various metals carried into Narragansett Bay. In fact, as shown for the Blackstone River in Table 18, these sources appear to be larger than the point sources that maintain the base flow concentrations of metals.

Rhode Island Sound

Narragansett Bay is characterized by strong gradients in the concentrations of most of the metals that have been examined, from high values in the water, sediments, and organisms of the Providence River and upper bay to low values near the mouth (Bender et al. 1989). Because of these gradients and the large fluxes of metals that enter the upper bay, we do not normally think of the relatively unpolluted waters offshore as a potential additional source. Nevertheless, the waters of Rhode Island Sound contain dissolved and particulate metals that are carried into the bay twice each day with the flooding tide. The behavior and fate of these metals once they enter the bay are not known, but even if most or all of them are exported during the ebb tide, the Sound contributes to the total inventory of metal inputs.

No attempt has ever been made to obtain a direct measure of the flux of metals into (or out of) any of the passages of Narragansett Bay, and it would probably not be practical to do so. A very rough approximation of the flux due to tidal pumping can be obtained by multiplying the mean tidal volume that enters the bay by the metal concentrations in the bottom waters of Rhode Island Sound. As part of their hypsographic analysis of the bay, Chinman and Nixon (1985) computed the volume at mean high and mean low tide. The difference between the two is equal to $390 \times 10^6 \text{ m}^3$ or, at two tides per day, a flow of $284.7 \times 10^9 \text{ m}^3 \text{ y}^{-1}$. This is about 90 times the annual input of fresh water (Pilson 1985). The tidal prism of the Sakonnet River (Fig. 1) accounts for 14% of the total, leaving $244.8 \times 10^9 \text{ m}^3 \text{ y}^{-1}$ of tidal flow in the East and West Passages of Narragansett Bay proper, assuming that little of the tide enters Mt. Hope Bay through the Sakonnet passage.

Unfortunately, there are few measurements of metals in Rhode Island Sound. The SINBADD program (Pilson and Hunt 1989) did collect offshore samples in October and November of 1985 and April and May of 1986, but total metals from these stations were only analyzed for the first two cruises. Chromium was only measured on the first cruise and only the dissolved fraction was reported. Based on the data that are available from the bottom waters at SINBADD stations 21 and 22, I have assumed offshore total metal concentrations of:

Ag	=	3 $\mu\text{g m}^{-3}$
Cd	=	20 "
Cr	=	110 "
Cu	=	350 "
Ni	=	415 "
Pb	=	130 "

When combined with the tidal flow volume, these concentrations produce fluxes into the bay of:

Ag	=	0.73	metric tons	y ⁻¹
Cd	=	4.9	"	"
Cr	=	27	"	"
Cu	=	86	"	"
Ni	=	100	"	"
Pb	=	32	"	"

These values are larger than all of the other metal inputs combined, and virtually all of the reviewers of an earlier draft of this report objected to them on the grounds that much, most, or all of the metals entering the bay from offshore with the tide are exported again on the ebb. Some reviewers thought metals entering from offshore would not react or accumulate in the bay, and therefore should not be included in the inventory of inputs, though they did not subject metals from anthropogenic activities or land drainage to this same standard. Regardless of their fate or effect, however, it is inescapable that large amounts of metals enter the bay with the tidal prism and, in the strictest sense, they are part of a complete accounting of metal inputs.

It is also appropriate (perhaps more appropriate) to take a more conservative approach to evaluating the offshore source by estimating the mass of each metal associated with the volume of offshore bottom water actually involved in circulation exchanges in the bay. This approach was used earlier to calculate the input of nutrients from offshore (Nixon and Pilson 1984), and recent calculations of the flushing rate of the bay as a function of fresh water input make it easy to arrive at a first-order estimate.

For the period between April 1972 and August 1973, Officer and Kester (1991) report an average flushing rate of $1512 \text{ m}^3 \text{ s}^{-1}$. Subtracting the mean river flow during the same period of $150 \text{ m}^3 \text{ s}^{-1}$ gives an average sea water exchange of $1362 \text{ m}^3 \text{ s}^{-1}$. Multiplying this flow by the bottom water metal concentrations used previously gives a flux into the bay of:

Ag	=	0.13	metric tons	y ⁻¹
Cd	=	0.86	"	"
Cr	=	4.7	"	"
Cu	=	15	"	"
Ni	=	18	"	"
Pb	=	5.6	"	"

These much lower estimates of the potential input from offshore are, with the exception of Cd, still large and comparable to the loadings from rivers. However, it also remains true that we know little about the fate or effects of these metals, and they may, for the most part, return to the sea.

Summary of Metal Inputs

Having emphasized the uncertainty in each of the terms of this inventory, I am a bit uncomfortable with the notion of an overall summary, a final accounting that adds up the result. Impatient readers may turn to such a table without "wasting time" on the details, and the numbers in summary tables begin to assume a look of certainty that belies their often ambiguous origins. Equivocating academics are not much help, however, to those who must get on with the job of issuing permits and planning for the future. How much copper comes into Narragansett Bay? There is an "answer" in Table 25. For Mt. Hope Bay, the "answer" is in Table 26. But, at best, the answers are only first approximations with an undefined uncertainty around them.

On the other hand, some findings seem reasonably clear. For example, the input of all the metals examined is larger in wet years than in dry, and the fluxes of most metals from sewage treatment plants have declined markedly in recent years. With the exception of lead, direct deposition from the atmosphere onto the surface of the bay does not contribute much to the metal inputs (Table 27), though the atmosphere may be an important source for many metals carried into the bay by rivers. Most of the cadmium entering the bay from land comes from sources upstream along the tributaries, rather than from effluents discharged directly into the bay, while almost all of the silver comes from the Bucklin Point and Fields Point sewage treatment plants (Tables 25 and 27). For lead and zinc, the two metals thought to be carried in large quantity by urban runoff, land drainage appears to provide more of the total input than direct sewage discharge, while direct and upstream sources were about equally important in supplying chromium, copper, and nickel. Marked reductions in the discharge of these metals, as well as zinc, from the Fields Point treatment plant during the past two years have almost certainly now made rivers and upstream sources the major input of all the metals considered here, except perhaps silver. Because of the large contribution that runoff and (perhaps) unidentified runoff-related point sources make to the metals carried by the rivers (Table 18), reductions in the discharge of metals by upstream POTWs may achieve only a modest reduction in the metal loading to the bay.

Because Providence and the Blackstone River Valley have had a long and continuing history of intensive industrialization (see Nixon, 1990), it is often assumed that this area is particularly polluted by metals and that the inputs of metals to Narragansett Bay are notably

Table 25

Summary of the estimated annual inputs of various metals to Narragansett Bay proper during approximately 1985-1987.
Units are metric tons per year.

	<u>Fe</u>	<u>Mn</u>	<u>As</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>Hg</u>	<u>Ag</u>
Atmospheric Deposition ^a	41	1.1	<0.04	0.05 ^b	0.10	0.78	0.45	4.9	3.0	?	
Rivers ^c											
Blackstone	>690	>103	<1.3	1.0	2.3	8.2	9.4	2.6	<53		<0.12
Woonasquatucket plus											
Moshassuck	>113	>17	<0.52	0.30	>0.30 ^d	3.4	4.3	1.2	<21		<0.11
Pawtuxet	>238	>51	<0.7	0.29	0.32	3.3	3.8	0.9	<21		>0.09
Others	528	79	1	0.77	1.8	6.3	7.2	2.0	41		0.09
Total Rivers	>1569	>250	<3.5	2.36	>4.7	21.2	24.7	6.7	<136	?	<0.41
Direct Industriale	0	0	0	0	0	0	0	0	0	0	0
Sewage Treatment Plants ^f											
Bucklin Point				0.05	1.4	1.5	2.7	0.6	3.9	0.0006	1.4
Fields Point				0.14	2.3	23	20	1.8	54	0.044	1.8
East Providence				0.01	0.06	0.3	0.7	0.1	0.4	0.0003	<0.2
Others				<0.3	<0.7	<1.1	<0.6	<0.7	?	?	<0.6
Total Sewage	?	?	?	<0.5	<4.5	<26	<24	<3.2	>58.3	>0.044	<4.0
Urban Runoffs								?	?		
Total Atmospheric, Land, and Anthropogenic	>1610	>251	<3.5	<2.9	>9.3	<48	<49	>14.8	>197	?	<4.4
Rhode Island Sound ^h	?	?	?	0.86	4.7	15	18	5.6	?	?	0.13

^aFrom Table 1, adjusted to 279 km². ^bDeposition rate at Lewes, DE (Church et al. 1984) adjusted to average year rainfall for Narragansett Bay.

^cFrom Table 13.

^dThis may be a substantial underestimate. The Woonasquatucket may carry a large burden of Cr (Table 10).

^eIncluded in rivers and publicly owned sewage treatment plants. Power plant cooling waters not included. ^fFrom Table 24.

^gMost runoff included in river inputs. Storms may add significant amounts of Pb and Zn. See text. ^hSee text.

Table 26

Summary of the estimated annual inputs of various metals to Mt. Hope Bay during 1985-1987.
Units are metric tons per year.

	Fe	Mn	As	Cd	Cr	Cu	Ni	Pb	Zn	Hg	Ag
Atmospheric Deposition ^a	7.3	0.19	<0.006	0.007 ^b	0.02	0.14	0.08	0.86	0.53	?	?
Taunton River ^c	?	?	0.33	0.71	4.0	4.0	1.6	7.1	?	?	?
Direct Industrial ^d						0.17	1.3		0.29		
Fall River Sewage ^e			?	<0.24	<0.61	<0.92	<0.76	<3.2	?	?	<1.0
Urban Runoff ^f							?	?	?		
Total Atmospheric, Land, and Anthropogenic	>7.3	>0.19	>0.006	<0.60	<1.3	<5.2	<3.7	>11	>0.8	?	?

^aFrom Table 1, adjusted to 49 km².

^bDeposition rate at Lewes, DE (Church et al. 1984) adjusted to average year rainfall for Narragansett Bay.

^cFrom Table 14. Very rough preliminary estimates only.

^dIncrease in power plant cooling water (Table 20).

^eFrom Table 24.

^fSee text.

Table 27

Relative contribution (%) of various sources to the input of metals to Narragansett Bay proper during 1985-1987. Values in () include the estimated input from Rhode Island Sound. Data from Table 25.

	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>Ag</u>
Atmospheric Depositon	1.7 (1.3)	1.1 (0.7)	1.6 (1.2)	0.9 (0.7)	33 (24)	1.5	?
Rivers and Upstream Sources	81 (63)	51 (34)	44 (34)	50 (37)	45 (33)	69	9 (9)
Direct Sewage Discharge	17 (13)	48 (32)	54 (41)	49 (36)	22 (16)	30	91 (89)
Offshore	(23)	(34)	(24)	(27)	(27)	?	(3)

large, even when compared to other urban coastal waters. It is difficult to know if this is true because few detailed inventories have been prepared for bays and estuaries. The small sample of comparative input data that I have been able to find does not isolate Narragansett Bay, at least at the levels of metal input characteristic of the mid 1980s (Table 28). In the recent past, however, the situation must have been quite different. During the 1950s, the deposition of lead and zinc from the atmosphere onto the bay may have exceeded or roughly equaled the total present input from the atmosphere, rivers, and sewage (Tables 4 and 25). The discharge of copper to the bay from the Fields Point treatment plant was probably about 15 times larger in 1950 than it is today (Table 29).

Remarkable reductions in the inputs of metals to Narragansett Bay have been achieved over the past 40 years, and especially over the past 8-10 years. The evidence for these reductions is in the sediments (see Nixon 1990) and in the monitoring reports of the Department of Environmental Management. The reductions have come about as a result of air and water pollution control legislation as well as changes in the economy of the bay watershed (see Nixon 1990 for an assessment up to about 1975). Among the most important factors have been the shift from wood and coal to oil and natural gas as fuels of choice (See Nixon 1990, Figs. 19, 21 and 23), the development and installation of devices to reduce stack emissions to the atmosphere during the 1950s and 1960s (See Nixon 1990, Figs. 23 and 24), the removal of lead from gasoline in 1974, the termination of sewage sludge dumping in the bay in 1950 (See Nixon 1990, Fig. 14), the initiation of industrial and municipal discharge permits under the NPDES section of the 1972 Clean Water Act, the construction and upgrading of sewage treatment plants during the 1950s, 1960s, and 1970s, the implementation during the early 1980s of the National Pretreatment Program, and, finally, the loss of primary metals manufacturing industry since the late 1960s (See Nixon 1990, Fig. 10).

It is also true, of course, that legislation has no effect if it is not enforced and that sewage treatment plants only function as well as they are staffed and maintained. The growing strength and scientific sophistication of Save the Bay and other environmental groups, and the professionalism of the Department of Environmental Management and the Narragansett Bay Commission have all contributed to bringing Narragansett Bay back to the point where the direct anthropogenic discharge of most metals to the bay is now less than the input from the coastal ocean (Table 25). For metals such as copper, chromium, and lead, the current inputs are almost certainly lower than they have been for over a century.

Table 28

Comparison of estimated volume specific inputs ($\text{mg m}^{-3} \text{y}^{-1}$) of various metals to different estuarine and coastal marine systems.

	<u>Fe</u>	<u>Mn</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Pb</u>	<u>Ni</u>	<u>Zn</u>
Narragansett Bay ¹	>740	>117	<1.4	>4.3	~21	<6.7	<23	~92
Mt. Hope Bay ¹			<3	<6.5	<25	<55	<12	
Chesapeake Bay ²	2748		3.6	13	11	9.1		38
Delaware Bay ³	2755	510	0.6		7.5		9	37
Hudson Estuary ⁴			16	210	352	290	175	972
San Francisco Bay ⁵				~10	~14	~13	~9.3	~31
Baltic Sea ⁶	17		0.02		0.14	0.27	0.13	1.2

¹This report, volumes from Chinman and Nixon (1985), inputs from atmospheric deposition, rivers, and POTWs.

²Bieri et al. (1982) data for 1980 from atmospheric deposition, rivers, and POTWs. Volume from Cronin (1971).

³Church (1986) data for 1981-1982. Inputs do not appear to include direct industrial discharges or POTWs. Volume from NOAA (1985).

⁴Muller et al. (1982) data for 1975-1980 for Hudson-Raritan system, including atmospheric deposition, rivers, POTWs, urban runoff, and landfill leachate.

⁵Aquatic Habitat Institute (unpublished) preliminary assessment for inputs from atmospheric deposition, rivers, industry, and POTWs. There are also large potential inputs from urban and non-urban runoff not included in the values reported here. Volume from NOAA (1985).

⁶Brügmann (1986) data for 1980-1983. Inputs from atmospheric deposition, rivers, POTWs, industry, and sediments.

Table 29

Comparison of the estimated historical and recent inputs of various metals to Narragansett Bay from the sewage treatment plant at Fields Point.
Values are metric tons per year.

	Year				
	<u>1900^a</u>	<u>1925^a</u>	<u>1950^a</u>	<u>1986^b</u>	<u>1988^b</u>
Cd	<1.3	<1.4	1.9	0.6 (0.14)	0.6
Cr	13	17	22	2.3	1.2
Cu	54	76	104	35 (18-23)	6.8
Pb	15	16	22	5.9 (1.8)	3.3
Ni	<31	<51	71	40 (20)	23
Zn	90	125	171	54	25

^aFrom Nixon (1990), Table 20.

^bFrom Table 24. Values in () are from SPRAY concentration measurements; others are from RIPDES files.

ACKNOWLEDGMENTS

This review was made possible by support from the Narragansett Bay Project (a joint effort of the R. I. Department of Environmental Management and the U. S. Environmental Protection Agency) and the R. I. Sea Grant College Program (NOAA). Steve Granger and Andrew Milliken assisted greatly with data analysis and the production of graphics. Carlton Hunt, Jim Quinn, Ken Rahn, Jon Sutinen, and Ray Wright made unpublished data available to me, and I thank them. I also acknowledge, with much appreciation, the stimulating conversations concerning metal inputs to the bay that I have had with Suzanne Bricker, Caroline Karp, John King, Virginia Lee, Michael Pilson, Jim Quinn, and Ken Rahn. A number of others have also helped during various phases of this project, including Charles Roman and Jenny Martin of the Narragansett Bay Project, Connie Carey and Chris Deacutis at the R. I. Department of Environmental Management, Peter Doering at the Marine Ecosystems Research Laboratory, and Alan Desbonnet at the Coastal Resources Center. Dolores Smith produced the final manuscript and assisted with editing.

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