Pergamon

Geochimica et Cosmochimica Acta, Vol. 63, No. 19/20, pp. 3321–3336, 1999

0016-7037/99 $20.00 + .00

PII S0016-7037(99)00254-9

Temporal variability of trace metals in New Jersey Pinelands streams: Relationships to discharge and pH

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(*Received October* 15, 1998; *accepted in revised form April* 29, 1999)

Abstract—Dissolved and particulate trace metal (Al, Cd, Cu, Pb, and Zn) concentrations were determined over a 21 month time period at four streamwater sites in the Pinelands (New Jersey, USA), a coastal plain region characterized by low-pH waters and highly weathered soils. Al and Zn were also determined at two sites over a 5 day period following a major precipitation event. In the Batsto River (pH 4.4–6.3), a representative Pinelands stream draining a largely forested watershed moderately impacted by agriculture, discharge-weighted mean concentrations of dissolved metals were (in nM): Al = 4610; Cd = 0.39; Cu = 4.6; Pb = 1.0; and Zn = 149. Dissolved Cd, Cu, and Zn in the undeveloped Bass River (pH 4.1–4.8) are in a similar range, but Pb concentration is 2–3 times greater. Dissolved metals show highly significant positive correlations to discharge, and weaker inverse relationships to pH over both the long- and short-term time series. Overall, seasonal and short-term variability in dissolved metal concentrations is most consistent with control by hydrologic flow path changes during high discharge, when shallow groundwaters mobilize anthropogenic metals stored in near-surface soil horizons and bypass potential metal removal processes in bordering wetlands. The data also suggest that in-stream metal removal driven by summertime biological productivity may further reduce low-discharge metal concentrations, as a secondary effect. For these metals, the particulate fraction is generally minor, and variations in solution/particle partitioning are unimportant to spatial/temporal variations dissolved concentrations, except for Pb. Estimates of atmospheric input can account for riverine fluxes of these metals, and suggest that Zn retention is minimal in this system, while Pb, Cu and Cd are more strongly retained. The positive relationship between discharge and metals concentration, and the unusually high concentrations in Pinelands streams compared to other world rivers, suggest that riverine effects on metals distributions in the estuary and nearby coastal ocean will be measurable and strongly seasonal.

1. INTRODUCTION

An understanding of the processes controlling trace metal cycling in natural waters is critical to assessing and anticipating anthropogenic impacts on the hydrosphere (Stumm and Morgan, 1996). Processes governing trace metal concentrations in rivers and streams remain relatively poorly understood, despite the importance of metals to aquatic ecosystems and drinking water quality. With a few exceptions (Rozan and Benoit, 1999; Shiller, 1985; 1997; Hurley et al., 1996; Van der Weijden and Middelburg, 1989), attempts to quantify the variability of riverine metal concentrations in relation to watershed lithology, hydrology, pollution sources, and in-stream geochemical processes have been limited by the lack of accurate data sets for many metals in freshwaters. Despite extensive trace metal monitoring in U.S. streams, clean sampling and analytical techniques pioneered by the oceanographic community (Bruland, 1983) have only more recently been adopted by aquatic chemists, hydrologists, and government agencies responsible for monitoring freshwater quality (Benoit, 1994; Nelson and Campbell, 1991; Windom et al., 1991; Shiller, 1997; Shafer et al., 1997). Recent studies using ultraclean methods have reported metal concentrations that are substantially lower than previously accepted values, indicating that much existing data may be seriously in error because of contamination during sampling and handling (Benoit, 1994; Coale and Flegal, 1989; Nelson and Campbell, 1991; Shiller and Boyle, 1987; Windom et al., 1991). In addition, many data sets do not distinguish between dissolved and particulate metals, limiting understanding of transport phenomena as a function of physico-chemical state. Both accurate data and quantification of dissolved/particulate partitioning are required to construct meaningful predictive models of metals behavior in rivers (Yeats and Bewers, 1982). A third important limitation associated with existing high-quality data sets is temporal resolution; only a handful of studies have produced time-series data from which mechanisms governing variability in riverine metals can be inferred and from which accurate long-term mean fluxes can be estimated (Benoit, 1995; Pettine et al., 1994; Shiller and Boyle, 1987; Van der Weijden and Middelburg, 1989).

Detailed quantification of solution/particle partitioning and temporal variability of riverine metals has several important justifications: (1) Evaluation of contaminant transport and bioavailability requires accurate metal concentration and speciation data (Scheuhammer, 1991; Weiner and Stokes, 1990); (2) Annual flux estimates incorporating accurate discharge/concentration relationships are critical to the formulation of watershed geochemical budgets; (3) Variability in riverine flux of metals to coastal marine ecosystems may play a key role in governing metal distributions and metal/biota interactions on continental shelves; and (4) Finally, temporal correlations of metal con-

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centrations with fundamental variables including suspended mass, pH, and discharge may be used to infer potential mechanisms controlling trace metal fluxes.

At least three broad mechanisms control temporal variability of dissolved metals in rivers. First, changes in hydrologic flow paths at high discharge, in which metal-rich, low-pH soil waters are flushed into streams, have been widely invoked to explain short-term increases in streamwater Al in small watersheds (Cook et al., 1994; Driscoll et al., 1987; Johnson et al., 1981; Turner, 1991). However, control of Cd, Zn, Cu, and Pb by this mechanism has received little attention, in part because of a lack of accurate data for these metals. A second control on riverine metals is variable partitioning between suspended or bed-load particles and dissolved phases (Honeyman and Santschi, 1988; Morel and Gschwend, 1987; Shiller, 1985). Partitioning is influenced by temporal variations in the concentration and characteristics of dissolved organic ligands and suspended particulate and colloidal matter, as well as by changes in pH. A third process influencing metal concentrations in many anthropogenically impacted rivers is discharge-driven dilution of point-source contaminants (Van der Weijden and Middelburg, 1989; Yang and Sañudo-Wilhelmy, 1999).

Considerable progress has been made in clarifying the role of sorption processes and particulate/dissolved partitioning as metal controls, both in controlled laboratory experiments using a variety of synthetic and natural solids, and in natural systems (Stumm, 1992; Honeyman and Santschi, 1988; Benoit, 1995). Understanding of these processes in river water is critical if the geochemical controls occur in the streams themselves. However, if the reactions which mobilize metals occur in the surrounding watershed, in-stream reactions may be less important to metal composition of the streams. In this case, research efforts should be aimed at exploring interactions between changes in stream hydrology and physically distinct reaction zones for metals within the aquifer. Published evaluations of temporal relationships between discharge, with associated changes in watershed hydrology, and the concentrations and partitioning of streamwater metals remain rare (Nelson and Campbell, 1991; Shiller, 1997; Shafer et al., 1997).

In this paper, we describe a 21 month time-series (2/94–9/95) of trace metal concentrations (dissolved and particulate Al, Cd, Cu, Pb, and Zn) at several streamwater sites in the Mullica River drainage basin in the Pinelands region of southern New Jersey, USA. In a companion paper, we examined the role of the colloidal fraction of these metals in a subset of these samples (Ross and Sherrell, 1999). The Pinelands region is a useful area in which to investigate the role of discharge and hydrologic regime in controlling temporal variability of Cd, Cu, Pb, and Zn in a low-pH system. Since there is only one well-characterized point source of anthropogenic pollution to this system (see Site Description, below), metal variability is likely to be influenced by hydrologic and/or biogeochemical processes, rather than temporal changes in point-source inputs. The Pinelands in general are relatively free of industrial and municipal inputs. Previous studies in this region have demonstrated significant temporal variability of streamwater Al, Fe, Mn, H^+, and SO_4^{2-}, with positive correlations to discharge (Johnsson and Barringer, 1993; Means et al., 1981; Turner et al., 1985a). Although other metals have not been studied extensively, Zn concentrations in the Mullica are high in comparison to most world rivers, (Means et al., 1981; Shiller, 1985; Yan, 1989), suggesting the potential for high mobility of metals within the watershed.

To understand the Pinelands time series results, we examine the relative roles of discharge variations and attendant changes in hydrologic flow path, spatial-temporal pH variations, and sorption/desorption processes involving suspended particles in generating temporal variations in dissolved metal concentrations at several sites in the Pinelands.

2. METHODS

2.1. Site Description

The Pinelands covers an area of approximately 3000 km^2 in the coastal plain of southeastern New Jersey. The area is underlain by unconsolidated quartzose gravels, sands, silts, glauconitic sands, and clays of Cretaceous and Tertiary age that vary from 300 to 1300 m in thickness, increasing toward the southeast (Rhodehamel, 1979a). The uppermost major layer, the Cohansey Formation, was deposited approximately 18 million years ago. It ranges from 8 to 61 m in depth and is predominantly a yellow limonitic (mostly goethitic) quartz sand containing minor amounts of pebbly sand, fine to coarse sand, silty and clayey sand, and interbedded clay (Rhodehamel, 1979a). The northwestern part of the Cohansey Formation, which includes the area where this project was conducted, consists of 76% sand, 13% silt, and 11% clay (Means et al., 1981; Rhodehamel, 1979a).

The topography of the region is relatively flat, and the Pinelands are poorly drained overall; approximately 25% of the surface area is wetlands (Morgan et al., 1988). The area's principal river, the Mullica, drops only 1.5 m in 25 km (Means et al., 1981). Chemistry of surface waters is unusual and reflects the highly weathered, largely unreactive nature of the underlying geology. Surface waters are acidic (pH 3.5–6.0), a result of small concentrations exchangeable bases in the soil and contributions from organic acids. Total dissolved solids are 20–30 ppm, compared to 110 ppm in world average rivers (Berner and Berner, 1987; Crerar et al., 1981). Surface waters are tea-colored, more strongly in summer and almost colorless in winter. Average DOC values (2.5 mg/L) are similar to those of other temperate-zone rivers (Berner and Berner, 1987; Means et al., 1981). Several researchers have concluded that the major ion (Mg^{2+}, Ca^{2+}, K^+, Na^+, SO_4^{2-}) chemistry of surface waters is largely determined by atmospheric inputs, not weathering (Means et al., 1981; Morgan, 1990; Morgan and Good, 1988). These major ions show no significant net export from the Pinelands, especially in watersheds unaffected by agriculture (Means et al., 1981; Morgan, 1990; Morgan and Good, 1988).

The major anion balancing H^+ in surface waters is SO_4^{2-}, indicating that acid rain is likely affecting the region (Morgan, 1991). However, the fact that acid-tolerant aquatic organisms have been noted since at least 1906, well before the accepted onset of acidic precipitation in this region (1950–60), indicates that the low pH of surface waters is not solely a recent anthropogenic effect (Likens et al., 1996; Morgan, 1984). The occurrence of less acidic water (pH > 5.0) are attributed to the influence of agricultural and residential development (Morgan and Philipp, 1986; Zampella, 1992). The Pinelands overall are relatively unimpacted by human development; streams show agricultural and residential impacts only in the southern and western edges of the region.

2.2. Sampling Locations

Stream and river water samples were taken from five sites in the drainage basin of the Mullica River (Fig. 1). The Batsto River site is located at the USGS gauging station 1.6 km from the confluence with the main stem of the Mullica. The Batsto is comparable in discharge to the upper Mullica and thus is a major tributary, with a drainage area of 176 km^2. Its drainage basin is impacted by agriculture on the western side. There is a dam 90 m upstream of the sampling site that impounds a lake of 220,000 m^3 (Batsto Lake). The Bass River site (East Branch) is at the USGS gauging station 8.5 km from the confluence with the main stem of the Mullica. The East Branch of the Bass is a small stream

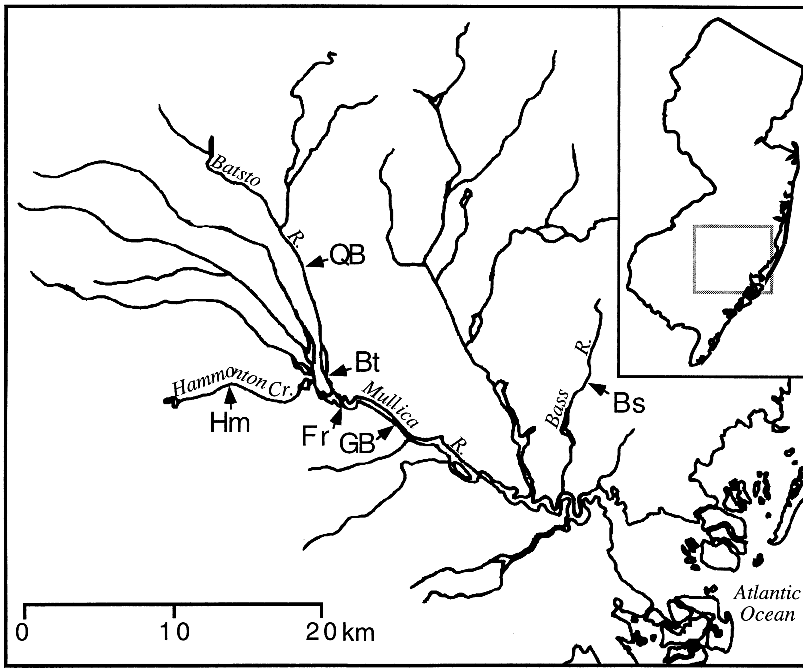

Fig. 1. Map of study area in New Jersey Pinelands. Arrows indicate sampling points at Hammonton Creek (Hm), Batsto River (Bt), Quaker Bridge (QB), Forks (Fr) and Green Bank (GB) on the main trunk of the Mullica River, and Bass River (Bs).

draining 21 km^2, is almost completely unimpacted by direct discharge, but borders a major highway (Garden State Parkway). The Hammonton Creek site is 6 km upstream from the confluence with the Mullica and drains an area of 24 km^2. It is impacted by agricultural runoff and also by a sewage treatment plant 3 km upstream from the site. The fourth and fifth sites, Forks and Green Bank, were chosen to represent the freshwater endmember of the Mullica estuary. For the first year of the time series a site at Green Bank, 5 km downstream from the confluence of the Batsto, was used. After it became clear that this site was influenced occasionally by salt water intrusion during low discharge and high tide, the Forks site, $<$1 km downstream from the Batsto confluence and never saline, was subsequently adopted from 12/94 on. Data from these two sites are not differentiated in our interpretation (hereafter designated F/GB). The final site, Quaker Bridge, is located on the Batsto River 8 km upstream from the main Batsto River site, and is hydrologically separated from it by Batsto Lake. The Batsto River drains largely undeveloped forest land, with some agricultural influence (cranberry and blueberry production).

To examine chemical variability on short and long time scales, two time series data sets were collected, one over a period of 21 months, and the other over a period of five days during and following a rain storm. Samples from the long-term time series were collected monthly to bimonthly at the Batsto, Bass, Hammonton, and Forks/Green Bank sites. Sampling was begun 1/31/94 at Hammonton and Forks/Green Bank, 2/21/94 at Batsto, and 7/22/94 at Bass. Final samples were collected 9/13/95 at all sites. Winter and early spring of 1994 were relatively wet, winter and spring of 1995 were dryer than average, and summer 1995 was extremely dry, culminating in a drought of 41 days that ended on 9/17/95 with 3.6 cm of rain. The five-day time-series was initiated at this event, and continued over 9/17 to 9/21 to study chemical response to significant water input when the river discharge was at low base flow. Representative post-storm hydrographs from the Batsto gauging station showed that five to six days were necessary for discharge to return to pre-storm levels. Four or five sets of samples were collected daily at Batsto, between approximately 7:00 a.m. and 7:00 p.m., and one set of samples daily from the Quaker Bridge site.

2.3. Sampling Methods and Filtration

Trace metal-clean procedures were employed to avoid contamination during sampling and subsequent treatment of samples. All bottles, filters, and filtration equipment were leached in 1 N HCl and rinsed in doubly deionized, distilled water (ddH_2O). Laboratory filtration and other treatment of samples were restricted to a Class 100 clean bench. Plastic gloves were worn during sampling and whenever samples were handled.

Duplicate water samples (250 mL) were collected from shore into HDPE bottles held on the end of a non-metallic pole (duplicates sampled only on the first and last samplings of the day during the 5 day intensive time series). Samples were vacuum-filtered at 20 cm Hg through 0.45 μm pore size, 47 mm diameter polysulfone filters (Gelman Supor®). From 1/94–10/94 samples were transported at 4°C in the dark to Rutgers University where filtrations were carried out within 12 hr of collection. From 11/94–9/95 filtrations were done immediately ($\leq$1hr) in the field, in a metal-clean Plexiglas glove box. Procedural blanks of ddH_2O were filtered as per samples. Filtered samples were preserved by acidifying to pH $\approx$ 1.5 with double-subboiling distilled HNO_3 (Savillex® Teflon PFA still). Filters were desiccated and stored for later digestion (Batsto samples only). Suspended particulate mass (SPM) was measured gravimetrically on the dried, pre-weighed filters. Streamwater pH was measured on site within 5 min of sampling using a field pH meter and a glass electrode, standardized immediately before each reading.

2.4. Analyses

Preconcentration was necessary to overcome detection limits for analysis of Cu, Pb, and Cd. Prior to analysis, a 12 mL aliquot of each $<$0.45 μm and CFF permeate fraction was preconcentrated evaporatively by a factor of 20–30 (factor determined gravimetrically to $\pm$1% for each sample) for analysis of Cu, Pb, and Cd; all other metals were analyzed directly. This was carried out in Teflon vials within glass evaporation chambers flushed by filtered air and heated by overhead IR lamps. For quality control, evaporation blanks of 0.2% double-subboiling distilled HNO_3, aliquots of procedural blanks, duplicate aliquots of selected samples, and aliquots of the standard reference river water SLRS-3 (see below) were also evaporatively preconcentrated.

All metals were analyzed by graphite furnace atomic absorption spectroscopy on a Hitachi® Z-9000 multi-element instrument, which allows elements with similar atomizing temperatures to be run simultaneously by means of up to four independent optical pathways through the graphite tube. In this study, Al and Mn were analyzed simultaneously, as were Cd and Pb; Cu and Zn and Fe were analyzed individually (Mn and Fe data presented elsewhere; Ross and Sherrell, 1999). The method of standard additions was used for all samples. To determine analytical precision, selected samples were analyzed in duplicate, both within the same run and on separate days. These analytical duplicates generally agreed to within ±5% for all elements, and often agreed to 2–3%. Accuracy was determined by analysis of SLRS-3 standard river water (National Research Council of Canada) and "Trace Metals in Drinking Water" standard (High-Purity Standards); measured values matched certified values within the 2-sigma uncertainty. Taking preconcentration into account for Cd, Cu and Pb (below), detection limits for aqueous fractions were Al, 35 nM; Cd, 0.005 nM; Cu, 0.3 nM; Pb, 0.02 nM; and Zn, 1 nM.

Particulate metals were analyzed only for Batsto samples collected from 8/94 on. Filters were cut in quarters using a template and stainless steel scalpel, and two opposite quarters (exact fraction determined gravimetrically) were placed in Teflon bombs and digested on a hot plate in a mixture of 400 μL double-subboiling distilled HNO_3, 400 μL ddH_2O, and 100 μL concentrated HF (Ultrex, J. R. Baker ®) for 6 hours. This mixture was optimized to effect a total digestion of particulate material while leaving the filter material relatively intact, and is a modification to a digestion method used previously for oceanic particulate matter (Sherrell 1991; Sherrell and Boyle 1992). After digestion, the solution was diluted with ddH_2O. To test the reproducibility of the procedure, duplicate digestions were done for selected samples. In addition, for selected dates, filters of duplicate samples were also digested. Analyses for duplicate samples agreed to within ±8% for Al, ±10% for Cu, ±8% for Pb, and ±15% for Zn. Particulate Cd was below the detection limit for this method (0.02 nM in streamwater) for all samples analyzed. Unused and procedural blank filters were also digested. Blanks were below detection limits for all metals except Zn, for which a ≈50% blank correction was needed for the lowest sample. Blanks for most other Zn determinations and for all other metals were <10% of sample concentration.

3. RESULTS AND DISCUSSION

3.1. Temporal Variability of Dissolved Metal Concentrations Relative to Discharge and pH

The variability of streamwater metals and relationship to discharge and pH for the Pinelands as a whole can be estimated by an analysis of these relationships in the main stem of the major river (Mullica at Forks/Green Bank) and in a major tributary (Batsto). Average daily discharge, pH, and suspended particulate matter (SPM) data for the long-term time series at the Batsto and Forks/Green Bank sites are shown in Figs. 2a and 3a. Discharge maxima at both sites occurred in winter/spring 1994, midsummer 1994, and winter 1994–95. Discharge maxima generally occur in winter and spring in this system, largely because evapotranspiration is at a minimum at this time of year (Rhodehamel, 1979b). In late summer 1995, discharge fell to a minimum during the 41 day drought. Minima in pH occurred in winter-spring 1994 and winter 1994–95 at both sites; there was also a sharp minimum at Batsto on 7/22/94. SPM was measured from 11/8/94 on and shows covariation with pH.

Long-term time series of dissolved Al, Cd, Cu, Pb, and Zn for Batsto and Forks/Green Bank are shown in Figs. 2b and 3b, respectively. All dissolved metals at Batsto vary in a similar fashion. They are highest in winter–spring 1994 and during winter 1994–1995, and are lower during late spring and summer of each year. A sharp maximum for all metals occurred on July 22, 1994, coincident with the discharge peak and pH minimum. Metal concentrations vary widely through the year—the range of variability observed is largest for dissolved Al (factor of 17) and smallest for Cd (factor of 7). Similar behavior is seen at Forks/Green Bank, where Al, Cd, Pb, and Zn also co-vary. However, Cu shows a distinct seasonal pattern not seen at Batsto; it reaches maxima in summers of 1994 and 1995 and is relatively invariant at other times.

The close positive relationship of dissolved Al, Cd, Cu (Batsto only), Pb, and Zn to discharge at these two sites is striking (Fig. 2a, b, 3a, b). Metal maxima occur at high discharge periods during the winter of 1994–95, midsummer 1994, and especially in winter/early spring 1994, while minima occur at times of low discharge. The absolute minimum for all metals is seen on 9/13/95, after several weeks of drought. It is apparent from these data that dissolved metal concentrations respond to the hydrologic conditions of the system. Correlation coefficients (R) of dissolved metal concentrations to discharge (Table 1) are highly significant ($p < 0.01$) for all metals except Cu at Forks/Green Bank. The linear regressions improve somewhat if discharge is averaged over the three-day period prior to and including the sampling date, suggesting that metal concentrations may be phase-lagged and less spiky than discharge variations. The temporal relationships between discharge and metals on the scale of hours/days are discussed below in the context of our short-term variability measurements.

Time series patterns of Al, Cd, Pb, and Zn are similar at both sites, although concentrations at Forks/GreenBank are generally somewhat higher (Table 2). The differences between the two sites on 7/22/94 (F/GB higher Cu, all other metals lower) probably reflect distinct short-term responses to the high-discharge event which peaked on 7/21/94; water seen at Batsto may not have propagated to the downstream site or, alternatively, water from the other tributary (upper Mullica, not sampled) may have followed a different time course. In addition, the F/GB site is influenced by input from Hammonton Creek, which has mean Cu concentrations an order of magnitude above those at Batsto and F/GB. On the whole, however, the similar temporal behavior of metals at the two sites indicates that processes controlling dissolved metal fluxes at Batsto likely act throughout the western end of the Mullica watershed, and that these processes control riverine fluxes of dissolved metals to the estuary.

At Batsto and Forks/Green Bank, pH varies inversely to discharge and metal concentration (Table 1; Figs. 2a and 3a). Correlations of pH to discharge are weaker than those of metals to discharge, but are still significant at the $p < 0.01$ level at Forks/Green Bank (Table 1). While pH control in the Pinelands has been a subject of some controversy (Morgan, 1984, 1991), important influences include hydrologic and biogeochemical processes, as well as a possible direct effect of acid precipitation. A potentially important hydrologic control is variable mixing ratio of two or more distinct source waters to the stream, including wetland surface waters and deeper groundwater. Wetland surface waters have higher pH than the deeper groundwater (Lord et al., 1990), so variations in their contribution to streamwater during high-discharge events could result in changes in stream pH. The sharp pH minimum at Batsto on

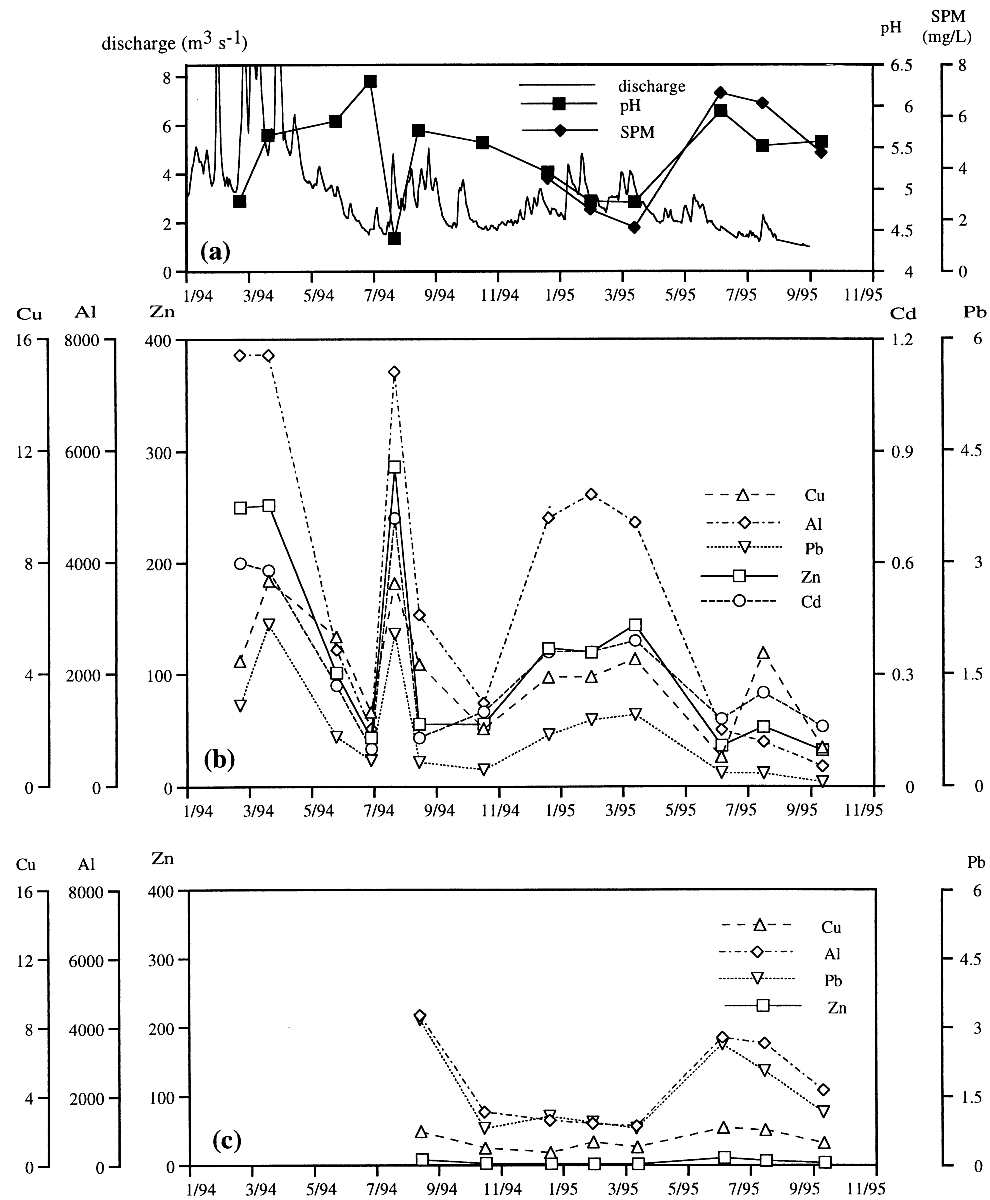

Fig. 2. Time-series data from Batsto River site. (a) Discharge, pH and SPM; (b) dissolved metals; (c) suspended particulate (>0.45 μm) metals. Time scale ticks at first day of month.

7/22/94, which apparently occurred in response to a high-discharge event, is an indication that pH can be driven by strong hydrologic flow variability. Biogeochemical processes that affect pH include sulfate reduction and photosynthesis (Morgan, 1985; Morgan et al., 1988). Both of these processes increase alkalinity in the pH range of Pinelands waters. Surface-water photosynthesis rates are substantially higher in streams whose watersheds receive nutrients from agricultural and residential development (Morgan and Philipp, 1986). Thus, pH is higher overall in these streams and is also more variable seasonally, in concert with seasonal changes in photosynthetic activity (Morgan and Good, 1988; Zampella, 1992). The balance of hydrologic, biogeochemical, and external source (precipitation) effects on surface water pH in the Pinelands appears, therefore, to be variable in space and time.

At issue for the present discussion is whether dissolved metal concentrations are simply a function of discharge-mediated flushing of geochemically distinct portions of the aquifer, or whether pH variations directly control the magnitude of the soluble pool by affecting adsorption/desorption reactions with suspended or bedload particles. In the following sections, we explore this issue by examining dissolved metals variability at sites with large and small temporal variations in pH, but similar discharge variability. The bulk of the evidence suggests that for most of the metals investigated, hydrologic controls on dissolved metal variability appear to dominate over pH-driven

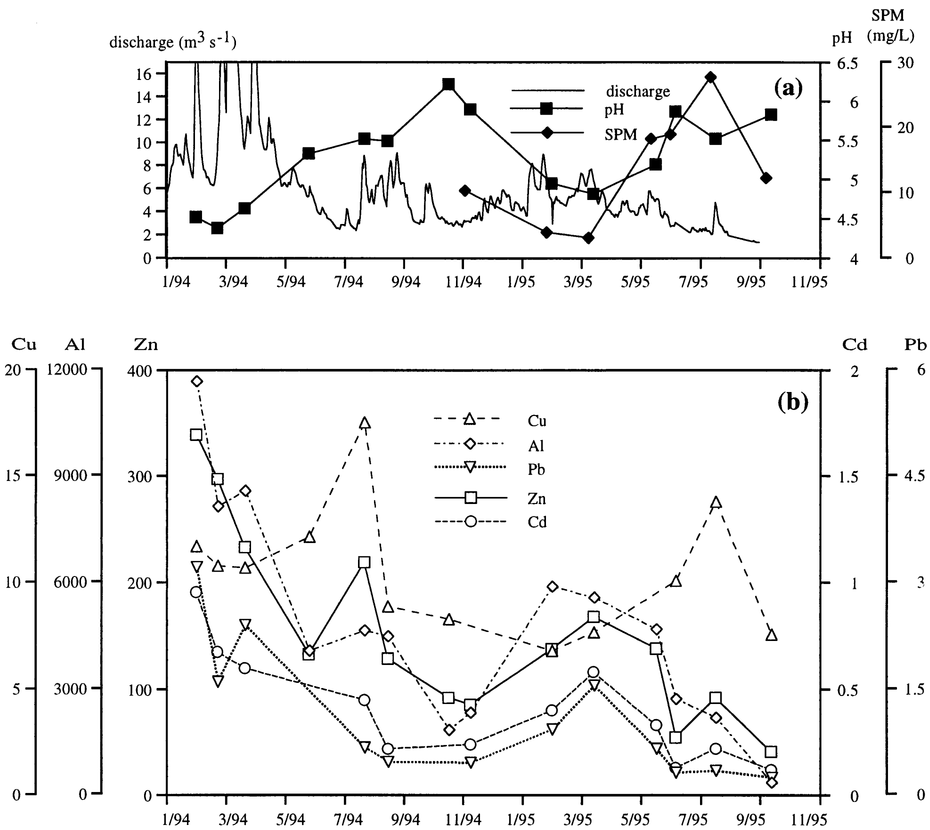

Fig. 3. Time-series data from Forks/Green Bank site. (a) Discharge, pH and SPM; (b) dissolved metals.

changes in streamwater metals partitioning. Biological productivity during summer may mediate streamwater metal removal in some parts of the watershed, but simple variations in dissolved/particulate partitioning appear to be a major control on dissolved concentration variations only for Pb.

3.2. Dissolved Metal Relationships to Discharge for Diffuse vs. Point Source Inputs

3.2.1. Discharge-metal relationships at an unimpacted site

In an attempt to distinguish the effects of anthropogenically driven pH changes on metals from other causes of metal variability, the Bass River, draining an undeveloped watershed, was sampled starting in summer 1994. Bass River pH, SPM, and USGS daily average discharge data are presented in Fig. 4a. Because of the very spikey nature of discharge at this site, and because this time series commenced 7/22/94, after the most extreme high discharges of early 1994, we were able to sample only one high-discharge event (8/15/94, 1.0 $m^3\ sec^{-1}$). Discharge on other sampling dates was relatively invariant (0.19–0.34 $m^3\ sec^{-1}$). The Bass River pH varies from 4.1–4.8, lower and less variable than at Batsto or Forks/Green Bank, and there is no clear winter/spring maximum. Instead, pH is lowest in summer 1994, rises through fall and winter 1994–95, and reaches a maximum on the last two dates of the time series.

Bass River dissolved metals data are presented in Fig. 4b. Metal concentrations do not show the winter 1994–95 maxima seen at the other sites. All metals reach minima on 9/13/95, near the end of the 30-day drought. With the exception of Pb, metal concentrations are roughly in the same range as at Batsto and Forks/Green Bank (Table 2). Discharge-weighted mean Cd and Zn concentrations are 35 and 14% lower, respectively, than at Batsto, Cu is slightly higher, while Pb is 287% higher (Batsto values calculated for 7/22/94-on only). In addition, Cd, Cu and Zn have smaller relative temporal variability than at the other sites, while Pb varies over a larger range.

Dissolved metals vary directly with discharge at the Bass River site. Since most discharge values cluster around a narrow range of values, however, correlations of dissolved metals and pH to discharge are not especially meaningful (e.g., Cd: Fig. 5a). If three-day average discharge is used, as discussed above, correlations to discharge improve and a more even distribution of discharge values is obtained (Fig. 5b). The regressions of metal concentration on 3-day discharge are stronger than on pH for all elements (Table 1). Because metal response to discharge at Bass was in general similar to that seen at the other sites, we conclude that a similar hydrologic mechanism is likely controlling metals in both agriculturally impacted and unimpacted watersheds. Further, because maximum dissolved concentrations for Cd, Cu and Zn are somewhat lower at Bass than at Batsto (Table 2), despite the lower pH range at Bass, differences in metals sources in the western and eastern parts of the watershed appear to be more important than the pH differences in controlling mean dissolved metal concentrations. Finally, it

Table 1. Correlation coefficients (R) of dissolved metals to discharge and pH.

Site	Parameter	Al	Cd	Cu	Pb	Zn	pH
Batsto	discharge	0.91[a]	0.82[a]	0.85[a]	0.84[a]	0.88[a]	−0.53
	3-day discharge	0.94[a]	0.87[a]	0.87[a]	0.92[a]	0.92[a]	−0.57
	pH	−0.70[a]	−0.76[a]	−0.45	−0.55	−0.68[a]	
Forks/Green Bank	discharge	0.91[a]	0.92[a]	0.35	0.89[a]	0.92[a]	−0.72[a]
	3-day discharge	0.95[a]	0.95[a]	0.34	0.93[a]	0.95[a]	−0.80[a]
	pH	−0.89[a]	−0.89[a]	−0.02	−0.85[a]	−0.83[a]	
Bass	discharge	0.76	0.80[a]		0.77	0.21	−0.45
	3-day discharge	0.86[a]	0.84[a]		0.80[a]	0.57	−0.61
	pH	−0.62	−0.56		−0.53	−0.76	
Hammonton	discharge[b]	0.53	0.36	−0.45	0.37	0.14	−0.73[a]
	3-day discharge[b]	0.45	0.37	−0.49	0.26	0.10	−0.65
	pH	−0.84[a]	−0.37	0.34	−0.59	−0.29	
Batsto short term	discharge	−0.39				−0.39	0.35
	3-day discharge	0.75[a]				0.66[a]	−0.59[a]
	pH	−0.74[a]				−0.56[a]	

[a] Correlation significant at $p < 0.01$ level.
[b] Batsto River discharge used because Hammonton Creek has no gauging station.

appears that the lower average pH values at Bass do not result in significantly different average levels of dissolved metals, with the exception of Pb, which has substantially higher concentrations than at other sites (Table 2). Overall, we conclude that temporal variability in metals is a function of discharge, and maximum metal concentrations are more closely related to source proximity than to pH, suggesting control by an exchangeable metal reservoir within the watershed rather than pH-driven desorption from similar in-stream particles (with the exception of Pb, see Section 3.2.3. below).

3.2.2. *Discharge-metal relationships at a heavily impacted site*

A different relationship of metals to discharge is seen at the Hammonton Creek, which is impacted by both urban runoff and sewage treatment plant effluent. Concentrations of dissolved Cu are an order of magnitude higher than at Batsto, and Zn, Cd, and Pb are somewhat higher than at other sites (Table 2). Since Hammonton Creek is not gauged, we correlate Hammonton metals to Batsto River discharge (Table 1). Cu shows a significant inverse correlation to discharge, consistent with variable dilution of a point source, likely the sewage treatment plant upstream from our sampling site (Fig. 6a). Discharge-driven dilution of a point source is common for rivers with industrial and sewer sources, but exactly the opposite of the relationship seen in the other Pinelands streams, exemplified by the Batsto Cu-discharge regression (Fig. 6b). With the exception of Cu, the general lack of correlation between dissolved metals and discharge in the Hammonton (Table 1) suggests that variability in the point source, rather than discharge-related watershed phenomena, controls metal levels in this stream.

A simple mixing calculation can be used to determine whether metals input from Hammonton Creek into the upper Mullica, then to the main stem of the Mullica (Fig. 1), could account for the observation that Cu concentrations at Forks/Green Bank are more than twice those measured at Batsto (Table 1; Figs. 2 and 3). It was assumed that Cu concentrations of other tributaries feeding the Mullica at Forks/Green Bank are equal to determined values at Batsto and that discharge for the other tributaries is proportional to area of their estimated drain-

Table 2. Summary of mean concentrations and range of metals (nM), pH, and SPM (mg/L).

Site	Bass	Batsto	Forks/Green Bank	Hammonton Cr	Batsto particulate
Al	4162	4605	6141	3921	2367
range	*1689–6520*	*341–7700*	*315–11600*	*669–10800*	*1151–4354*
Cd	0.28	0.39	0.54	0.78	<0.02
range	*0.17–0.36*	*0.10–0.58*	*0.12–0.96*	*0.23–1.27*	
Cu	4.9	4.6	11.1	50.4	1.5
range	*2.9–5.6*	*1.0–7.3*	*7.5–13.8*	*29.5–105.6*	*1.0–2.2*
Pb	3.0	1.0	1.5	2.7	1.6
range	*0.5–5.5*	*0.1–2.2*	*0.2–3.2*	*1.2–5.5*	*0.8–3.2*
Zn	79	149	196	289	4.5
range	*48–113*	*32–286*	*41–339*	*64–420*	*1.6–10.7*
pH	4.49	5.40	5.43	6.30	
range	*4.11–4.75*	*4.40–6.30*	*4.38–5.87*	*4.52–7.11*	
SPM	1.9	4.3	13.4	15.6	
range	*1.2–2.8*	*1.7–6.9*	*3.0–27.6*	*1.8–49.9*	

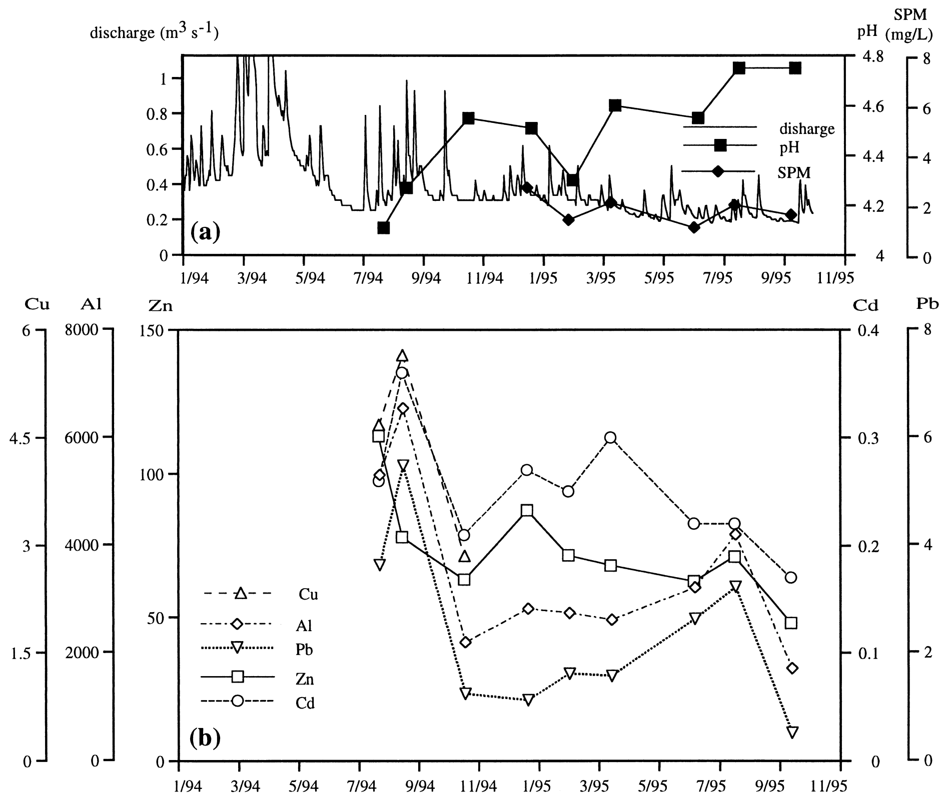

Fig. 4. Time-series data from Bass River site. (a) Discharge, pH and SPM; (b) dissolved metals.

age basins. The contribution of Hammonton Cu to measured Cu concentrations at Forks/Green Bank was calculated as Cu concentration at Hammonton times the ratio of Hammonton discharge to summed discharge for the unmeasured tributaries. This gave a Cu contribution of ≈2.0 nM, enough to account for the difference in concentrations during early 1994 and winter-spring 1995. Summer Cu concentrations at Forks/Green Bank, however, are as much as 9 nM greater than at Batsto. This excess Cu may be derived from upstream sources on unmeasured tributaries or leaching of anti-fouling coatings associated with summertime boat traffic or Cu-Cr-As preserved pilings near Forks/Green Bank.

3.2.3. *Sorption/desorption processes and temporal variations in dissolved Pb*

Particulate metal concentrations, measured at Batsto site only, demonstrate that the $>$0.45 μm fraction exceeds the dissolved concentration only for Pb (Fig. 2c, Table 2). Mean particulate fractions are: Pb 76%; Al 43%; Cu 30%; Zn 5% and Cd $<$ 7%. These fractions are considerably lower than the mean for U.S. East Coast rivers (Windom et al., 1991), reflecting the relatively low SPM and unique chemistry of these waters. While particulate metal fractions of Zn and Cu vary inversely to dissolved metals, as does SPM, the low particulate fractions mean that a positive concentration-discharge relationship holds for total metal as well as dissolved. Thus, the in-stream temporal variations for most of these metals reflect varying input, not simply redistribution between dissolved and suspended particulate fractions.

The same conclusion does not apply for dissolved Pb, however, because suspended Pb fractions are large enough to drive the inverse relationship between dissolved Pb and SPM through adsorption/desorption reactions. For example, while dissolved Pb concentrations are significantly higher at Bass than at the more impacted sites (Table 2; Fig. 4), low SPM at Bass suggests that total Pb is similar among all sites. Plotting all the dissolved Pb data against SPM and pH demonstrates that the Bass data follow relationships to these variables which are broadly consistent with those described by data from the other sites (Fig. 7a, b). Therefore, dissolved Pb in Pinelands streams may be controlled essentially by pH and suspended particle abundance. Seasonal variability in particle composition has a further effect on temporal variations in dissolved Pb within each system. At Batsto, for example, Pb distribution coefficient (K_d) is 10-fold higher in summer than in winter (Ross and Sherrell, 1999). Metal sorption/desorption behavior in these streams may be somewhat atypical because refractory clays account for a very small fraction of SPM; particles are composed largely of Fe oxyhydroxides (Fe/Al is 10–30 times average crustal ratio; Ross and Sherrell, 1999) and organic matter. Similarly consistent relationships to SPM and pH are not observed for other metals, consistent with their smaller particulate fractions. For example, Zn vs. pH (Fig. 7c) shows that Bass data plot in a distinct sector from the other sites.

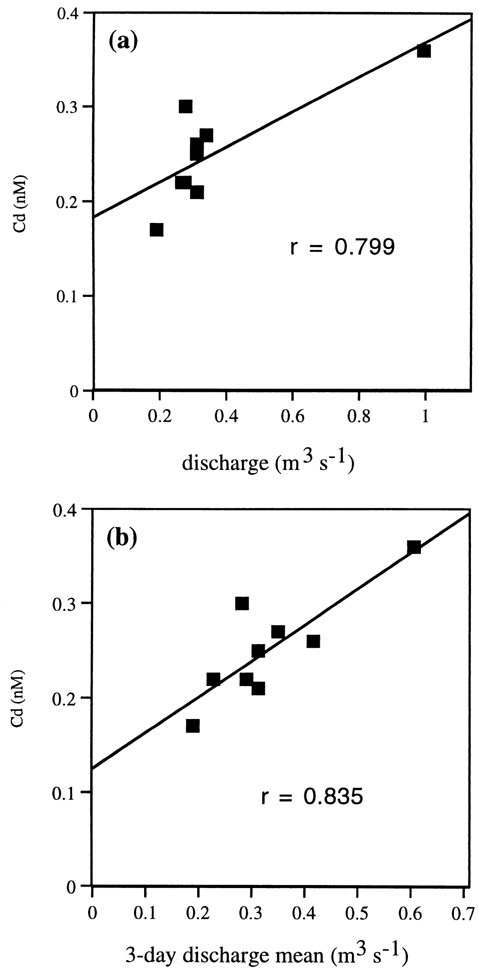

Fig. 5. Dissoved Cd relationship to (a) daily discharge and (b) average discharge over 3 days up to and including sampling date at Bass River.

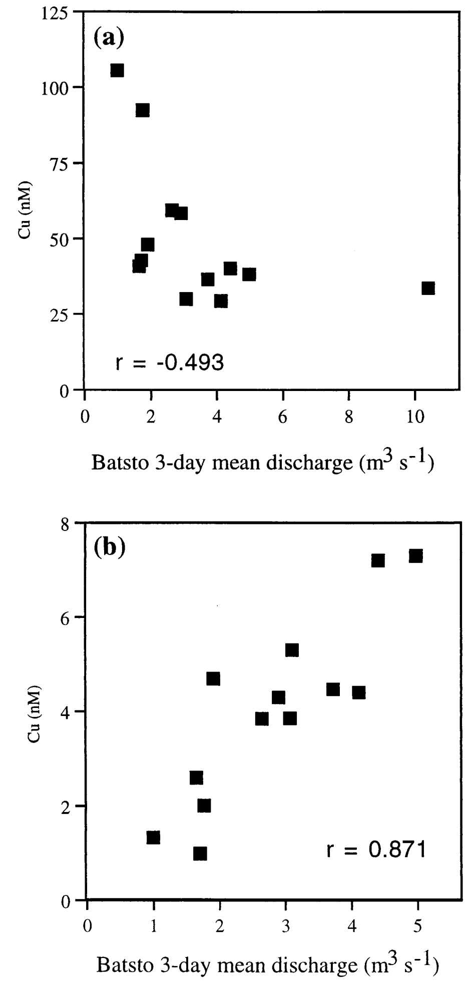

Fig. 6. Dissolved Cu relationship to 3 day averaged discharge at (a) Hammonton Creek and (b) Batsto River. Batsto discharge used for both because Hammonton Creek is not guaged.

3.3. Effects of In-Stream Processes Revealed by Short-Term Variability

3.3.1. Event-scale variability relative to seasonal variability

Dissolved metal concentrations at Batsto (Fig. 2b) appear to vary sharply in response to an individual discharge event (7/22/94), the most striking feature of the record. Given the sampling frequency for the long-term record, it is not clear whether the relatively smooth seasonal patterns in metal concentration reflect chemical variability, which is generally damped relative to discharge, or whether most sampling times were temporally displaced from discharge peaks by a sufficient interval to miss transient concentration spikes. In other words, since short-term relationships between discharge and metals concentrations cannot be determined from this record, the broad seasonal trends we observe could, in principle, result from aliasing. To address this uncertainty, and characterize the response of streamwater-chemical composition to event-driven discharge variation, we investigated the magnitude and timing of dissolved metal concentrations associated with a single discharge event. The Batsto and Quaker Bridge sites were sampled intensively for 5 days during and after the 3.6 cm rainstorm which occurred over seven hours early on 9/17/95. This was the first substantial rainfall in 41 days. Data from this short-term time series, including 15 min average discharge, pH, SPM, and dissolved Al and Zn are shown in Figs. 8a, b. Discharge rose only about 0.3 m^3 sec^{-1}, a relatively small response, likely because much of the post-drought precipitation went to aquifer recharge rather than stream flow. The return to pre-event discharge was almost complete by the end of the experiment. One limitation to the generality of conclusions from this study is that the range of discharge represented by this event was less than 10% of the total discharge variation seen over the course of the long-term time series.

At the start of the short-term experiment, dissolved Zn and Al concentrations were similar to values measured four days earlier (9/13/95), the last date of the long-term time series, and were the lowest of the 21 month long-term time series. Al and Zn increased roughly in parallel over the 5 day experiment (Fig. 8b). By the last sampling, dissolved Al had increased approximately 50% and Zn had doubled. In contrast to the increasing then decreasing trend in discharge, Al and Zn concentrations

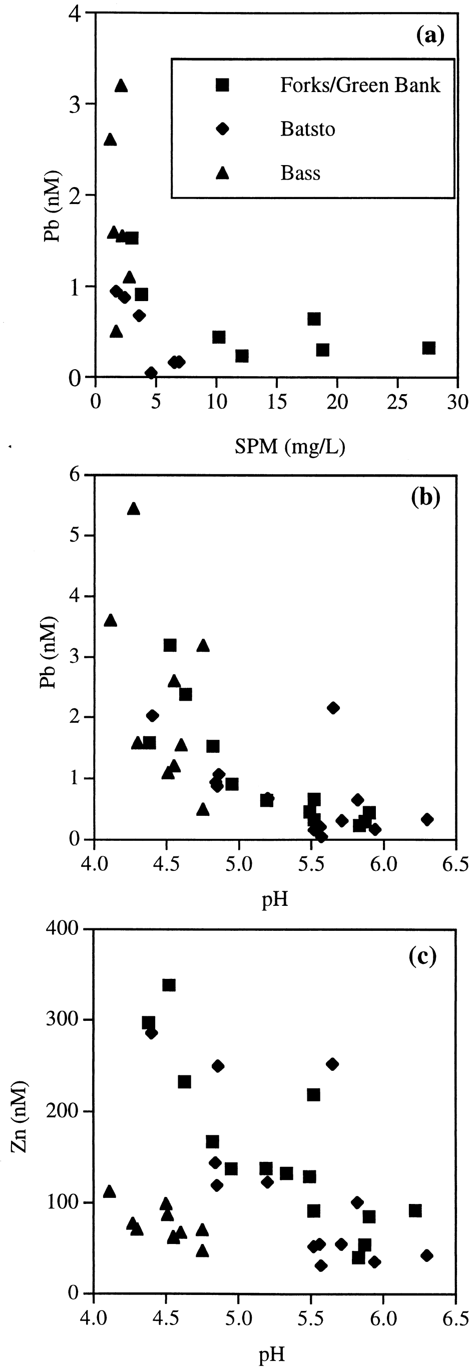

Fig. 7. Relationships of dissolved metals to SPM and pH at three Pinelands stream sites. (a) Pb vs. SPM; (a) Pb vs. pH; (c) Zn vs. pH.

increased throughout the 5 day period, indicating an in-stream chemical response lasting beyond the return to base flow. In addition, SPM decreased about 25% overall, while pH decreased by about 0.2 units over the same period.

Correlations of dissolved Al and Zn to the average discharge of the 72 hr prior to and including the sampling time were highly significant ($p < 0.01$) (Table 1). These short-term relationships are presented graphically in the context of the long-term time series in Figs. 9a and b, respectively. The cluster of short-term points describes a linear relationship greatly restricted in range but reasonably similar in slope to regression for the long-term discharge relationships. We speculate that the chemical response to individual events, occurring over days-weeks and scaled up in magnitude relative to this one, could account for most of the total range in dissolved metal concentrations. It seems likely that dissolved metal maxima associated with a series of closely spaced discharge events could "bridge" a period of at least several weeks, resulting in relatively smooth long-term trends. Following this reasoning, we conclude that dissolved metal concentrations from the long-term time series are representative of discharge conditions over days to weeks preceding the time point, and therefore describe a reasonable record of seasonal variation.

3.3.2. Short-term in-stream effects on dissolved metal concentrations

The short-term sampling at Quaker Bridge, 8 km upstream from the Batsto site (Fig. 1), allows a first-order quantitative estimate of the effects of in-stream processes occurring on short time scales between the two sites. Short-term Quaker Bridge dissolved metals (Fig. 9a, b) displayed a substantially larger and somewhat earlier response than at Batsto. Concentrations of Zn and Al increased three- to four-fold in the two days after the storm, then decreased slightly over the following two days. In order to understand the differences between the sites, Batsto metal concentrations were modeled as the result of Quaker Bridge water propagating downstream through the lake, with the assumption of immediate mixing of incoming river water with the entire volume of lake water, using a 1 hr time step (initial condition concentrations equal to Batsto concentrations on 9/17). Residence time of water between the two sites during this low discharge period is about 46 hr, and is dominated by retention in the lake.

Although the model results (Fig. 10a,b) reproduce the monotonic increase in metal concentrations at Batsto, they also show that the difference between Batsto and Quaker Bridge cannot be ascribed solely to mixing with lake water. If the model is modified to allow river water to mix only with the epiliminion, the effective mixing volume of the lake is reduced and the model-data discrepancy becomes even greater. Long-term time series data for dates on which Quaker Bridge site was sampled (Table 3), show that concentrations of metals as well as nutrients (nitrate and silicate) were similar during a high discharge period (3/15/95) but were substantially higher at Quaker Bridge during lower discharge summer and fall periods. These results point to phytoplankton productivity and resultant biological scavenging of metals, occurring mostly in the lake, as the primary process responsible for the differences in Al and Zn concentrations at the two sites. Similar biologically mediated metal removal may occur in all Pinelands streams during the summer months, given sufficient residence time at low discharge. The importance of this process relative to hydrologic controls on seasonal metals variability throughout the study area is difficult to estimate given the available data; additional investigations would be required to quantify the relative roles of in-stream metal removal and discharge-driven source variations within the aquifer.

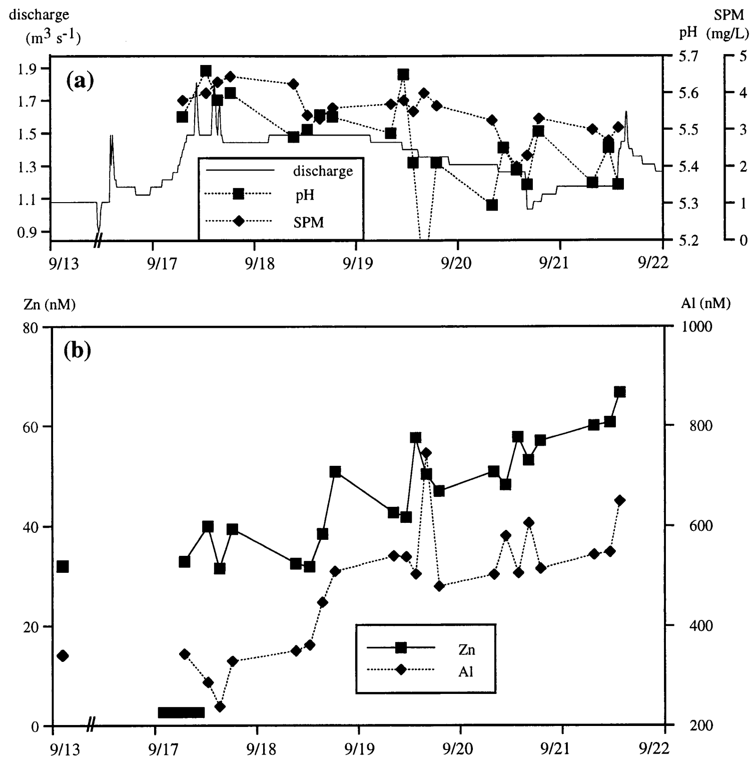

Fig. 8. Time-series data from Batsto site for intensive sampling experiment following rain event on 9/17/95. (a) Discharge, pH and SPM; (b) dissolved Al and Zn. Single data points indicated 9/13 at left of (b) indicate final sampling of long-term time series at this site. Solid bar during 9/17 in (b) indicates approximate duration of rain event.

3.4. Hydrologic control of dissolved metal variations in Pinelands streams

The evidence presented above suggests that temporally variable hydrologic pathways drive dissolved metals' variability (except Pb) by preferentially flushing distinct portions of the aquifer with varying intensity. In this light, existing theories of mechanisms controlling dissolved Al may be examined for relevance to other metals in the Pinelands. Because of its role in toxicity to fish in acidic waters, the behavior and mobility Al in watersheds has been studied much more extensively than that of Cd, Cu, Pb and Zn. Mobility of Al in soil solution has been shown to be controlled by dissolution equilibrium with gibbsite and other crystalline phases (Johnson et al., 1981; Mulder et al., 1990) and also sorption and organic complexation (Cook et al., 1994; McAvoy, 1989; Mulder et al., 1990; Sullivan et al., 1986). Many studies of small watersheds have shown that episodic increases of dissolved Al are well correlated to increases in acidity and discharge. It has been argued that the chief determinant of dissolved Al in these areas is the hydrologic flow path through the catchments (McAvoy, 1989; Mulder et al., 1990; Swistock et al., 1989). During high-discharge events, increased flow through surface soil horizons flushes Al and H^+ from these zones into streams (Swistock et al., 1989; Turner, 1991; Wigington et al., 1992; Wilson et al., 1991). At low discharge, streams are fed largely by deep groundwater, which is more alkaline, because weathering reactions have consumed H^+, and hence contains less Al.

While it is tempting to apply this model to metals variability in the Pinelands, there are two arguments against the efficacy of this explanation. First and most important, previous research shows that much Pinelands groundwater is acidic (pH = 3.5–4.5) and high in Al (up to 60,000 nM; Lord et al., 1990; Means et al., 1981; Rhodehamel, 1973). If unadulterated groundwater is the dominant source to the stream at low discharge, we should observe maximum, not minimum Al concentrations during these periods. Second, the highly permeable soils of the Pinelands do not retain water as effectively as podzols in upland forests. In addition, the Pinelands have much lower relief than the mountainous areas for which the above model was developed, hence lateral flow and contact time in the upper soil horizons are minimized in this environment.

A more likely means of hydrologic control of dissolved metals in the Pinelands involves processes that occur in wetlands (Morgan et al., 1988). It has been noted previously that H^+, Al, and DOC concentrations are lower in cedar swamp waters than in other Pinelands surface and groundwaters (Johnsson and Barringer, 1993; Turner et al., 1985a). This anomaly has been ascribed to sulfate reduction taking place in these areas (Spratt and Morgan, 1990), which increases alkalinity and hence favors the precipitation of solid-phase Al (M. Morgan, Rutgers University, pers. comm.). Although other metals have not been measured in these swamps, it is likely that many of these metals are also immobilized. Removal of DOC in these areas should lower soluble ligand concentrations, increased pH and solid phase organic carbon should encourage sorption, and the presence of sulfide should lead to metal

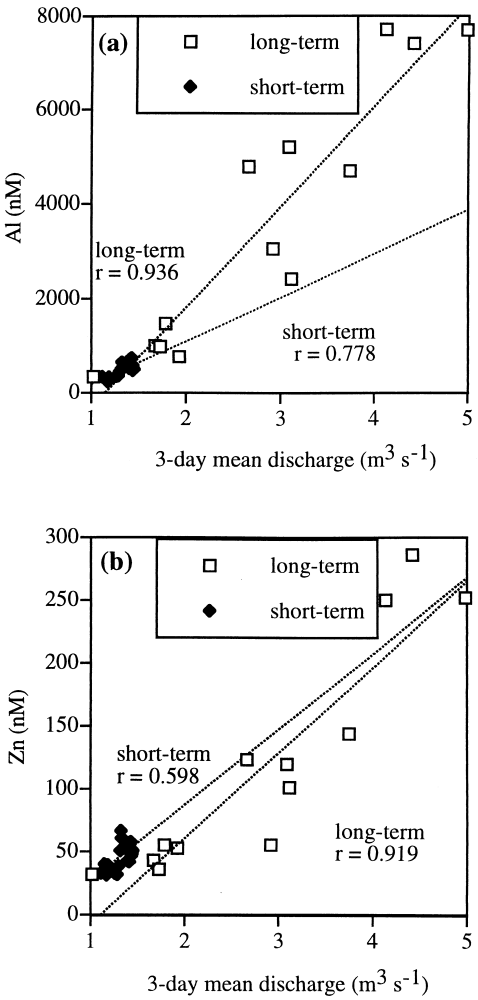

Fig. 9. Relationship of metal concentration to 3 day averaged discharge during long- and short-term time series at Batsto River for (a) Al and (b) Zn.

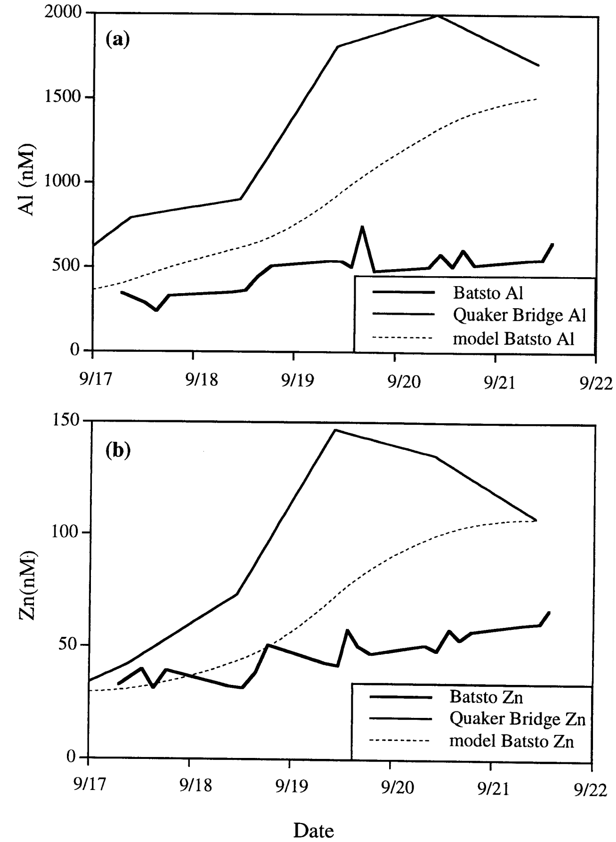

Fig. 10. Comparison of simultaneous short-term sampling at Batsto and Quaker Bridge sites to mixing model results for (a) Al and (b) Zn. See text for model description.

precipitation. It is for these reasons that wetlands in other regions have been shown to be effective sinks of dissolved Cd, Cu, and Zn (Eger and Lapakko, 1989; Gambrell, 1994; Karathanasis and Thompson, 1993).

Hydrologic control of streamwater metals by bordering wetlands could occur through at least two different processes. First, the shorter residence time of recharging water in swamps at high discharge would decrease the extent of removal, consistent with observations. Second, at high discharge, recharging water may follow unique pathways and overflow or bypass wetlands entirely, thereby supplying the stream with "unprocessed," low-pH, metal-rich water. The efficacy of these mechanisms will require further research targeting wetland chemistry and hydrology in relation to that of contiguous streams.

3.5. Flux of Dissolved Metals to the Estuary and Coastal Ocean

The pronounced temporal variability of metal concentrations and the positive correlations to discharge means that riverine metal fluxes (discharge times concentration) undergo very large seasonal cycles and shorter term variations. Metal flux varies over 100-fold for Zn and Cd, and over 200-fold for Pb, from the day of highest flux (1/30/94) to the day of lowest (9/13/95). Estimated seasonal fluxes of winter 1994–95 (determined by averaging daily fluxes of sampling dates during that season) exceed estimated fluxes of summer 1994 by 4.1, 7.8, and 5.5 times for Zn, Pb, and Cd, respectively.

This strong seasonality in flux is likely reflected in metal distributions in the estuary and proximal coastal ocean. For example, a rough estimate of this effect for Zn can be made by assuming that all streams in the Pinelands watershed have similar Zn concentrations and discharge proportional to drainage basin area, and that there is no net removal or addition of dissolved Zn in the estuarine mixing zone. We estimate tidally forced dilution of one day's flux into a volume of seawater 3 km by 1 km by 10 m deep. The flux at high discharge would result in a $\approx$20 nM increase in Zn within this coastal water volume, while the low discharge flux would provide an increase of only 1.4 nM. The high discharge increase is significant relative to typical average coastal ocean Zn concentrations of $\approx$15 nM (R. Sherrell, unpubl. data). While these levels are not expected to be toxic, they would be important to the overall trace nutrient status of phytoplankton during the spring bloom, which is coincident with the typical discharge peak in early

Table 3. Comparison of Batsto and Quaker Bridge metals and nutrients for three sampling dates.

Date	3/15/95			7/18/95			9/13/95		
Analyte	Batsto	Quaker Br.	% diff.[a]	Batsto	Quaker Br.	% diff.[a]	Batsto	Quaker Br.	% diff.[a]
Al (nM)	4709	4904	4.1	773	1993	88.2	340	617	57.9
Zn (nM)	144	157	8.6	51	100	64.9	30	34	12.5
SiO2 (μM)	71.8	72.6	1.1	65.7	83.7	24.1	78.4	96.3	20.5
NO3 (μM)	9.8	11.6	16.8	3.1	4.5	36.8	0.8	6.2	154.3
SPM (mg/L)	1.7	2.4	34.1	6.5	7.1	8.8	4.6	4.7	2.2
pH	4.84	4.96	2.4	5.52	5.62	1.8	5.57	5.29	−5.2

[a] (Quaker Bridge-Batsto)/mean × 100%.

spring. For example, high dissolved Zn concentrations are expected to suppress phytoplankton Cd assimilation through competitive uptake interactions (Sunda and Huntsman, 1998). The Mullica outflow is therefore likely to be a good small-scale example of temporally variable effects of a metal-rich river on phytoplankton ecology and trophic transfer of metals in proximal coastal ocean waters.

3.6. Atmospheric Sources for Anthropogenic Metal Inputs to Pinelands Streams

Because high-quality trace metal data are relatively scarce for river waters (Benoit, 1994; Nelson and Campbell, 1991; Windom et al., 1991; Shiller, 1997; Shafer et al., 1997), it is important to consider mean concentrations from this data set in relation to other reliable world river data and to other published data for Pinelands streams. While dissolved Cd in Pinelands streams is moderately elevated relative to most other rivers (both polluted and pristine), and Cu is lower than most, Zn and Pb are at least 10-fold higher than most other rivers, and are matched only by the most impacted rivers, e.g., the Plastic and the Po (Table 4). Comparison with previous measurements in Pinelands streams suggests that most previous determinations of Cu, Cd and Pb were compromised by contamination, while previous Zn determinations are probably correct. Mullica River dissolved Zn (40 nM) tabulated by Shiller (1985), is based on a sample collected in August 1983 at pH 5.81. This is consistent with the low summer values we found, and therefore underestimates the annual mean concentration.

The high concentrations of Zn and Pb in Pinelands streams is surprising because point-source anthropogenic inputs are rare in this system. A possible explanation is a combination of significant atmospheric deposition from anthropogenic sources in nearby urban centers and the Pinelands' acidic and relatively unreactive soils. This combination of factors has been invoked to explain Zn concentrations in southern Swedish streams that are four times higher than those in northern Sweden (Johansson et al., 1995). To examine the magnitude of this input relative to Pinelands streamwater concentrations, metal fluxes from the Batsto and Bass drainage basins were compared to atmospheric fluxes, based on two deposition estimates, one from Lewes, Delaware, 100 km south of the Pinelands, and the other from Ontario (Church and Scudlark, 1991; Lazerte et al., 1989). The results (Table 5) demonstrate that atmospheric and riverine fluxes of Zn are reasonably similar, while atmospheric fluxes of Cu, Pb, and Cd are all substantially larger than riverine fluxes out.

On the basis of this rough comparison, we speculate that atmospheric deposition may be a significant source of metals to Pinelands streams. The apparent low retention of Zn implied by this comparison is consistent with its small particulate fraction in the streams, relative to the other metals. The other metals show ratios of atmospheric to riverine flux (using the more proximal Church and Scudlark atmospheric data) of 4.4, 4.4 and 13 for Cd, Cu and Pb, respectively, suggesting that the order of fractional metal retention in this watershed is Pb $>$ Cd $\approx$ Cu $>$ Zn. Previously, it was suggested that the primary source of metals to streams in this area was weathering of metal-rich glauconite deposits of the late Cretaceous and early Tertiary which are exposed 10 km west of the Pinelands (Means et al., 1981). If atmospheric inputs stored in upper soil horizons dominate instead, the high concentrations of Zn, Cd and Pb may reflect anthropogenic inputs of the last century. Pinelands soils may have retained sufficient accumulated atmospheric flux to maintain high streamwater concentrations for many years into the future, even after pollutant loading is reduced. A properly located and interpreted sediment record from this environment would be useful for reconstruction of historical changes in metal concentrations in Pinelands surface waters, and could be compared to recent lake core records from New York City (Chillrud et al., 1999).

4. CONCLUSIONS

1. Dissolved concentrations of Al, Cd, Cu, Pb and Zn are positively correlated to discharge in streams of the western portion of the Pinelands streams, New Jersey. As a result, concentrations are highly variable, both on an event basis and in consistent seasonal trends.

2. Although pH varies inversely with discharge, pH appears to be a parallel dependent variable, and does not appear to control directly the temporal variations in most dissolved metals. Metal concentrations in Bass River, which has a lower and less variable pH than the somewhat more impacted rivers to the west (e.g., Batsto R.), are somewhat lower for Cd, Cu and Zn, indicating that source magnitude, and not pH per se seems to control differences in dissolved metals between streams.

3. Dissolved Pb was the only metal which appeared to depend on pH- and SPM-related changes in solution/particle partitioning from site to site. Particulate concentrations are significantly lower than dissolved for the other metals. Instream processes therefore have only secondary effects, and do not in general explain the temporal/spatial variability for metals other than Pb.

Table 4. Comparison of trace metals in world rivers and Pinelands streams.

Data set	River	Notes	Cu		Zn		Cd		Pb	
			nM	μg/L	nM	μg/L	nM	μg/L	nM	μg/L
World Rivers										
Lazerte et al., 1989	Plastic, Ont.	1	11	0.70	276.0	17.9	1.2	0.134	3.1	0.642
Windom et al., 1991	Satilla, GA		8	0.51	60.0	3.9	0.15	0.017	0.03	0.006
Johansson et al., 1995	Swedish streams				170.0	11.1	0.4	0.045		
Shiller, 1985	Atchafalaya, LA				2.8	0.2				
	Delaware@Trenton				60.0	3.9				
	Mississippi@Baton Rouge				2.8	0.2				
	Negro, Brazil				10.5	0.7				
	Atabapo, Venezuela				5.0	0.3				
Shiller & Boyle, 1987	Mississippi@St. Francisville		22.7	1.44	3.2	0.2	0.14	0.016		
Benoit, 1995	Quinnipiac, CT						0.05	0.056	0.91	0.188
Benoit, 1995	Bear Brook, NH								0.04	0.008
Martin et al. 1993	Lena, Russia		9.7	0.62	5.3	0.3	0.05	0.006	0.08	0.017
Dai & Martin, 1995	Yenisey, Russia		25.5	1.62			0.014	0.002	0.03	0.006
Pettine et al., 1994	Po, Italy		32.6	2.07	70.5	4.6	0.701	0.079	1.21	0.250
Windom et al., 1991	17 E coast rivers	2	17	1.08	13.0	0.8	0.1	0.011	0.11	0.023
Pinelands Streams										
Means et al., 1981	Upper Mullica R.	1	14.2	0.90	147.0	9.6	1.3	0.146	8.3	1.718
Swanson and Johnson, 1980	McDonalds Br.	1	25	1.59			<0.9	0.101	18	3.726
Shiller, 1985	Mullica R.				40.5	2.6				
Yan, 1989	Mullica R.		120	7.62	180.0	11.7				
Turner et al., 1985a, b	McDonalds Br.								2.4	0.497
This Study	Bass R.		4.9	0.31	79.0	5.1	0.28	0.031	3.0	0.621
This Study	Batsto R.		4.6	0.29	149.0	9.7	0.39	0.044	1.0	0.207
This Study	Forks/Green Bank		11.1	0.70	196.0	12.7	0.54	0.060	1.5	0.311
This Study	Hammonton Cr.		50.4	3.20	289.0	18.8	0.78	0.087	2.7	0.559

1 = unfiltered, 2 = unweighted mean.

4. It is suggested that dissolved metal concentrations are primarily under hydrologic control (with in-stream sorption/desorption affecting Pb). High discharge promotes hydrologic flushing of metal-rich low-pH shallow groundwater, and reduces water residence time in stream-bordering wetlands, which act as important metal removal zones at low discharge.

5. Simultaneous sampling at upstream and downstream locations during several days following a major rainstorm revealed that metal concentrations continued to rise for several days after the discharge peak, providing a mechanism for seasonal trends in metals as a result of high concentrations which bridge between frequent and intense discharge events in winter/spring. Fluxes of Al and Zn, as well as nutrients phosphate and nitrate, were substantially lower at the downstream site, suggesting that short-term removal, probably a result of biological activity occurring in an intervening impoundment, can further decrease dissolved metals in warm, low-discharge months.

6. The strongly seasonal nature of metals fluxes in the main Pinelands river (Mullica) suggests that delivery of metals to the estuary and nearby coastal ocean is up to two orders of magnitude greater during high spring discharge periods, relative to low summer baseflow. In particular, springtime ebb tides could substantially alter Zn concentrations within a few km of the coastal ocean.

7. Estimates of recent, largely anthropogenic, atmospheric

Table 5. Comparison of Pinelands riverine flux to watershed atmospheric flux.

Metal	Dissolved riverine flux (kg/yr)	Total riverine flux (kg/yr)	Total atmospheric flux (kg/yr), after Church and Scudlark, 1991	Total atmospheric flux (kg/yr), after Lazerte et al., 1989
Batsto				
Cd	4.3	4.3	19	16
Cu	29	39	173	218
Pb	20	54	720	450
Zn	980	1010	1150	730
Bass				
Cd	0.38	N/D	2.3	1.9
Cu	3.9	N/D	21	26
Pb	7.8	N/D	85	54
Zn	64	N/D	137	87

N/D = not determined.

inputs for Cu, Zn, Cd and Pb suggest that streamwater flux for these metals can be satisfied by direct atmospheric input. In the absence of significant watershed point sources, metals concentrations in Pinelands streamwaters, among the highest measured in world rivers, may be influenced by present and historical atmospheric pollutant input from this densely populated region of the Northeast United States. Comparison of atmospheric and riverine fluxes suggests that Zn is poorly retained, while upper soil reservoirs of Cd, Cu and Pb could supply riverine dissolved metals for many years, even if atmospheric inputs were curtailed.

Acknowledgments—We thank Paul Field for assistance with sampling and analytical methods. Pat Brady and two anonymous reviewers provided very helpful reviews on an earlier version of this manuscript. This work was supported by the Water Resources Research Institute (USGS) and the Institute of Marine and Coastal Sciences, Rutgers University.

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