

The role of colloids in tracemetal transport and adsorption behavior in New Jersey Pinelands streams

James M. Ross¹ and Robert M. Sherrell²

Institute of Marine and Coastal Sciences, Rutgers University, 71 Dudley Road, New Brunswick, New Jersey 08901-8521

Abstract

Dissolved and colloidal concentrations of Al, Fe, Mn, Cu, Zn, Cd, and Pb were determined in the Mullica River, New Jersey, and its tributaries on nine occasions between August 1994 and September 1995. Cross-flow filtration (CFF) at a nominal 10 kDa cutoff was used to separate total dissolved (<0.45 μm) riverine metals into colloidal and truly dissolved fractions. Reproducibility tests on full procedural replicates demonstrated CFF's precision and indicated that temporal or spatial differences exceeding 10–15% in colloidal fraction can be resolved using these techniques. For the whole data set, mean colloidal fractions of 0.45- μm filtrates were 65% for Al, 82% for Fe, 29% for Mn, 66% for Cu, 31% for Zn, 46% for Cd, and 88% for Pb. The magnitude of the colloidal fraction followed an elemental order that was largely consistent from site to site and among different sampling dates, despite large variations in total dissolved metal concentrations. The order was very similar to that observed previously in rivers of varying geochemical properties, suggesting that the degree of colloidal association is driven by a metal's affinity for humic materials and is relatively insensitive to other riverine properties such as pH, dissolved organic carbon, and suspended mass. The constancy of this elemental pattern in Pinelands streams suggests that the relative fates of metals during estuarine colloid flocculation may be predictable and temporally stable. Iron behavior was distinct from that of the other elements: colloidal Fe fraction was positively correlated with pH (range, 4.3–7.1) and the colloidal Fe/Al ratio showed clear seasonal variation. The other metals did not exhibit these behaviors, which suggests that their colloidal association was distinct from that of Fe. Colloidal metal/Al ratio for Fe, Pb, and Zn was clearly different from that of >0.45- μm particles; that finding is consistent with the distinct compositions and sources for colloidal and particulate fractions. The distribution coefficient (K_d) for Pb was positively correlated with suspended particulate mass (<10-fold variation) over time at one representative site. This inverse particle concentration effect runs contrary to recent observations in other freshwater and marine systems and suggests that colloidal and particulate size fractions vary independently over the course of the year.

In continental surface waters, trace metals occur in a broad spectrum of physicochemical states. Until recently, metals and other chemical components have been grouped into dissolved and particulate pools, which are operationally defined fractions based on simple membrane filtration. With growing concern about controls on the fate of environmental pollutants and their potential impact on aquatic organisms, the need for a more detailed and mechanistic understanding of metal speciation in rivers and lakes has become increasingly urgent (Erel et al. 1991; Benoit 1995; Rozan et al. 1998). This need has been paralleled by practical advances in direct determination of the physicochemical state of metal species, which may be separated by size above ~ 1 nm. In particular, size separation techniques based on various versions of cross-flow filtration (CFF) have seen rapid advances in the last few years (Buesseler et al. 1996; Guo et al. 1996; Santschi 1996; Sañudo-Wilhelmy et al. 1996; Greenamoyer and Moran 1997; Gustafsson and Gschwend 1997; Kraepiel et

al. 1997; Wells et al. 1998; Benoit and Rozan 1999). These techniques can separate dissolved metals into one or more colloidal phases and a truly dissolved or soluble phase. The colloidal phases are usually defined as being between 1 kDa (very roughly 1 nm) and a semiconventional colloid/particle cutoff of 0.2–1.0 μm . The bulk composition of natural colloidal matter has only begun to be described and quantified, but it is understood to comprise a mixture of clays, hydrous metal oxides, refractory and labile organic matter, and products of phytoplankton (Koiike et al. 1990; Rees and Ranville 1990; Stumm 1992; Wells and Goldberg 1992; Guo and Santschi 1996, 1997; Benner et al. 1997; Rostad et al. 1997; Wells et al. 1998). Much effort has been directed toward understanding the composition and dynamics of marine and estuarine colloidal matter. Colloidal trace metal behavior in freshwater has received less extensive study because limnologists have only recently begun to use techniques developed by oceanographers.

Before the development of CFF, other methods for sub-micron size fractionation were employed in a few colloidal metal studies in rivers and estuaries over the last two decades. The size fractionation of riverine Fe was examined by Boyle and Edmond (1977), who used coagulation by seawater cations combined with traditional membrane filtration to show that most <0.7- μm Fe in New Jersey's Mullica River (one of the sites of this study) existed in colloidal size fractions. Using similar coagulation techniques, later researchers of Scottish rivers found substantial fractions of <0.4- μm Fe and Cu, but lesser fractions of Mn and Cd, in

¹ Present address: Geochemistry Department, Lamont-Doherty Earth Observatory, Palisades, New York 10964.

² Corresponding author

Acknowledgments

We thank Paul Field for assistance with sampling and analytical methods development and Mark Wells and William Landing for advice on cross-flow filtration techniques. Gaboury Benoit, Sergio Sañudo-Wilhelmy, and one anonymous reviewer provided very helpful reviews. This work was supported by the Water Resources Research Institute (USGS) and the Institute of Marine and Coastal Sciences, Rutgers University.

colloidal fractions (Sholkovitz et al. 1978; Sholkovitz and Copland 1981). Laser light-scattering techniques have been employed to show that Mississippi River particulate matter had a mass median diameter of $0.27 \mu\text{m}$, within the operationally defined colloidal size range; clays were found to constitute $>20\%$ and organic carbon $3\text{--}6\%$ of this material (Rees and Ranville 1990). Whitehouse (1990) published one of the first demonstrations of CFF's utility for separating river-water colloidal phases. These investigators determined that the percentages of $<0.45\text{-}\mu\text{m}$ Fe, Al, Mn, Cu, and organic carbon retained by a 10-kDa membrane were significant: $83\text{--}95\%$, $75\text{--}85\%$, $43\text{--}64\%$, $39\text{--}53\%$, and $60\text{--}80\%$, respectively, in two Nova Scotian rivers.

The existence of significant colloidal metal fractions in rivers has a number of implications for the transport and fate of metals within a river and during subsequent estuarine mixing with coastal seawater. First, colloidal metals by definition are transported as efficiently as dissolved metals, but may not be subject to some of the removal mechanisms affecting truly dissolved metals (Gustafsson and Gschwend 1997). Second, metals bound in colloidal phases may be unavailable to biological uptake (Rich and Morel 1990; Wells and Mayer 1991), limiting the transport of potentially toxic metals up the aquatic food web. Third, since colloids may flocculate upon changes in ionic strength or pH, colloiddally bound metals may be removed from the water column in zones of major water chemistry changes, most importantly in estuaries (Boyle and Edmond 1977; Sholkovitz and Copland 1981; Powell et al. 1996). Colloids may serve as a critical intermediary from solution to particulate ($>0.4 \mu\text{m}$) phases, a process termed "colloidal pumping" (Honeyman and Santschi 1991; Wen et al. 1997). Improved prediction of metal behavior in freshwater systems is therefore dependent on understanding metal associations with colloids.

Despite the differences between colloidal and truly dissolved species in behavior and ecological impact, most studies of riverine trace metals have followed the conventional dissolved/particulate scheme, often based on $0.45\text{-}\mu\text{m}$ filtration. Models of trace-metal biogeochemistry based on this simple partitioning necessarily have limited the ability to predict metal behavior in aquatic systems. In addition, applying such models may incorrectly represent transformations of metals between dissolved and particulate forms, generating erroneous estimates of kinetic rate constants for heterogeneous reactions because particle-particle interaction kinetics are not properly considered. A further difficulty is that filtration artifacts limit the precision of the $0.45\text{-}\mu\text{m}$ cut-off and may cause operational size separations that depend on particle quality, filter loading, filtration rate, filter type, and other factors (Horowitz et al. 1992, 1996; Shiller and Taylor 1996).

Recently, researchers have cast a critical eye on such operational uncertainties and have begun using CFF in numerous studies of colloidal metals in coastal and open ocean environments, as well as along estuarine salinity gradients (Baskaran et al. 1992; Benoit et al. 1994; Dai et al. 1995; Martin and Dai 1995; Moran et al. 1996; Powell et al. 1996; Sañudo-Wilhelmy et al. 1996; Greenamoyer and Moran 1997; Wells et al. 1998). However, apart from a few data points typically collected at the freshwater end-member of

estuarine transects, the magnitude and variability of freshwater colloidal metal fractions are sparsely described (Erel et al. 1991; Benoit and Rozan 1999). One reason is that CFF techniques for natural waters are still maturing (Buesseler et al. 1996). Uncertainties about methodological details such as membrane type, system recovery, blanks, true size cutoffs, membrane loading, and reproducibility have so far precluded acceptance of a standard method for determining colloidal species for any aquatic or marine environment (Murkes 1990; Guo and Santschi 1996; Gustafsson et al. 1996; Wen et al. 1996). Indeed, many such factors are likely to be a function of the quality or composition of the colloids, so that operating guidelines established for marine or estuarine systems may not be optimal for freshwaters. In addition, comparisons between different freshwater bodies may be limited as much by the variability in aquatic chemistry from one watershed to another as by differences in CFF hardware or methods. Understanding colloidal metal dynamics in aquatic systems requires better constraints on CFF performance for waters low in ionic strength and high in dissolved organic carbon so that complementary data sets can be rigorously compared to test generalizable hypotheses.

In this study, we pursued this goal by using CFF to determine colloidal fractions of stream-water Al, Fe, Mn, Cu, Zn, Cd, and Pb in the Mullica River and three tributaries in the New Jersey Pinelands. Samples were collected over a full year, allowing a temporal/spatial approach to colloidal metal variability within a single large watershed. We paid special attention to CFF method development and quality control issues, in particular analyte recovery, which has been an important issue in previous studies (Reitmeyer et al. 1996; Sañudo-Wilhelmy et al. 1996; Stordal et al. 1996; Wen et al. 1996). Another important issue was separation reproducibility, a criterion that is largely ignored in studies of natural waters. Second, we examined metal size fractionation in the stream water, examining spatial and temporal consistencies in the relative colloidal versus total dissolved fraction for these metals and providing evidence for differential behavior of colloidal metals. This evidence suggests independent classes of metal-binding colloidal matter. Third, we compiled preliminary evidence for Pb that suggests a relationship between the distribution coefficient and suspended particle concentration that is opposite to the normal particle concentration effect (PCE) often observed in other systems. A companion paper will present a detailed discussion of temporal trends in all metal fractions relative to pH and discharge in these streams (Sherrell and Ross 1999).

Materials and methods

Study area—Water samples were collected at four stream sites in the Mullica River's drainage basin in the New Jersey Pinelands. Sampling occurred on nine dates from 15 August 1994 to 13 September 1995. The Pinelands is an area of approximately $3,000 \text{ km}^2$ characterized by sandy soils, numerous wetlands, low relief, and tea-colored, low-pH surface waters. The Mullica is the Pinelands' largest river, with a drainage basin of approximately 900 km^2 . The sampling sites included the main branch of the Mullica at Forks/Green

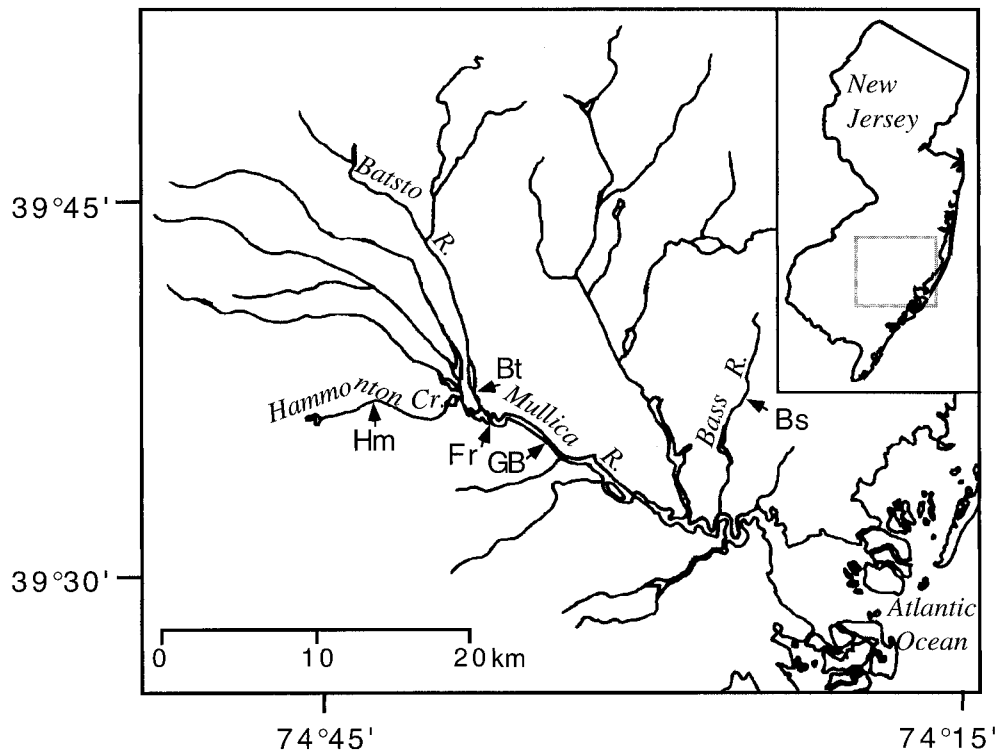


Fig. 1. Map of study area in New Jersey Pinelands. Arrows indicate sampling points at Hammonton Creek (Hm), Batsto River (Bt), Forks (Fr), and Green Bank (GB) on the main trunk of the Mullica River and the sampling point on the Bass River (Bs).

Bank, the Batsto River, a major tributary, and two small streams: Bass River and Hammonton Creek (Fig. 1). The Forks/Green Bank samples were taken from three locations considered equivalent: halfway between Forks and Green Bank in August 1994, at Green Bank in October 1994, and at Forks thereafter. The Batsto and Forks/Green Bank sites mostly drain undeveloped forest, but they are both moderately impacted by agriculture. The Bass drainage basin is protected forest land, while the Hammonton is affected by agriculture and effluent from a sewage treatment plant (Morgan and Philipp 1986). The pH range during the study was 4.27–4.75 (Bass), 4.82–6.22 (Batsto, Forks/Green Bank), and 5.63–7.11 (Hammonton). Further description of the study area and sampling locations is presented elsewhere (Sherrell and Ross 1999).

Sample collection and handling—Great effort was taken 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 deionized, distilled water (ddH₂O). Laboratory filtration and other sample handling was done in a Class 100 clean bench, and plastic gloves were worn during sampling and whenever samples were handled. Duplicate water samples were collected from shore in 250-ml high-density polyethylene (HDPE) bottles held at the end of a nonmetallic pole. After collection, samples were either refrigerated and transported to the lab for preliminary filtration within 12 h (August and October samples) or were filtered immediately after collection in a clean field glove box (all other samples). In both the lab and the

field, samples were vacuum-filtered at 200 mm Hg through 47-mm diameter, 0.45- μ m pore Supor polysulfone filters (Gelman) using polycarbonate filter funnels (Millipore) with silicone O-rings fitted to custom-made vacuum chambers. The 0.45- μ m filtrate was collected in acid-leached HDPE bottles and held at 4°C in the dark pending CFF processing. Although duplicate samples were collected at every sampling, not all duplicates were processed by CFF. The relatively small sample sizes were chosen to limit filtration times in the field as well as total time required for CFF of each sample set. Samples were processed by CFF within 48 h of collection, and most were completed within 24 h. Although long sample holding times can allow the original size partitioning to change (Stordal et al. 1996; Wen et al. 1996), careful cleaning of the CFF apparatus between samples necessitated that some samples be held for longer than optimal periods while all the samples were being processed. We regard the danger of cross-contamination to be at least as important as storage artifacts for 0.45- μ m filtrate. Particulate matter on the membrane was dried, weighed, and saved for later digestion and analysis (Batsto samples only).

Cross-flow filtration—CFF was achieved using a Filtron Minisette system. Components that contacted the sample were made of HDPE (tubing), acrylic (membrane cassette holder, reservoir), Teflon (valves), and C-flex (Cole-Parmer) peristaltic pump tubing. The polyethersulfone membrane had a surface area of 0.07 m² and a nominal molecular-weight cutoff of 10 kDa (~3 nm), corresponding roughly to the lower size limit of high-molecular-weight colloids (Powell

et al. 1996; Guo and Santschi 1997). Before their initial use, all system components were leached in 1 N HCl and rinsed several times with ddH₂O. The CFF was used and stored in a clean room with air filtered by high-efficiency particulate-air filters and under positive pressure.

Approximately 225 ml of the sample filtrate was transferred to the CFF reservoir and recirculated for 1 min at 400–500 ml/min with the permeate outlet clamped closed. The permeate clamp was then opened, the pump speed maintained, and permeate collected until the volume of retentate decreased by a concentration factor of 3–4. Permeate collection rate was 70–120 ml/min. After collection was finished, the permeate clamp was closed and the remaining solution was allowed to recirculate for 1 min at a pump speed of 700–800 ml/min to help dislodge adsorbed colloids from the membrane. The retentate valve was then opened and the remaining solution was collected. Net weights were recorded for the permeate, retentate, and remaining <0.45- μ m sample (~25 ml). These fractions were then acidified to pH 1.5 with double-subboiled distilled ultraclean HNO₃ (prepared in a Teflon PFA still, Savillex) and stored at room temperature until analysis. By established convention (Benoit et al. 1994; Dai et al. 1995; Moran et al. 1996; Sañudo-Wilhelmy et al. 1996; Wells et al. 1998), we termed the resulting fractions total dissolved (<0.45 μ m), colloidal (10 kDa – 0.45 μ m), and truly dissolved (<10 kDa). This terminology is defined operationally. In particular, we acknowledge that significant colloidal fractions for some metals may be found in the nominal size range 1–10 kDa (Powell et al. 1996; Benoit and Rozan 1999). The selection of the 10 kDa membrane was based on comparability with previously published data sets, although it is well known that different types of membranes with the same nominal cutoff can perform quite differently (Gustafsson et al. 1996; Dai et al. 1998). The goal of this study was to isolate a colloidal fraction that was clearly different in composition and geochemical behavior from both the particulate and truly dissolved fractions; other colloidal fractions certainly exist, and results obtained with 3-kDa membranes, for example, would likely be somewhat different in quantitative detail (Benoit and Rozan 1999).

Cross-contamination was a serious concern, since it has been well documented that CFF recovery is often incomplete. The analyte can be trapped by CFF membranes and released into subsequent samples (Reitmeyer et al. 1996; Stordal et al. 1996; Wen et al. 1996). Therefore, a cleaning procedure to minimize this problem was performed after every sample. This procedure consisted of a water rinse to remove residual sample, an HCl wash to mobilize metals adhered to the membrane, and three more water rinses to remove the HCl. Rinses used 500 ml of ddH₂O, which was added to the reservoir and recirculated for 30 s. The HCl wash was done with 500 ml of 0.5 N HCl (reagent grade in ddH₂O), which was recirculated at high speed for 20 min. When the device was stored for more than 12 h, it was loaded with 0.1 N HCl to discourage bacterial growth.

Two lines of evidence indicated that cross-contamination did not occur. First, five test aliquots of ultraclean 0.1 N HNO₃ were processed as samples on three different dates, each following a real sample and the standard cleaning procedure. HNO₃ was used for optimum graphite-furnace atom-

ic absorption spectroscopy (GFAAS) performance and to match the compound used for acidification. The permeate and retentate of each test aliquot were analyzed for Fe, Al, and Mn and found to be below the detection limit for all. Second, permeates (for all metals) and retentates (for Al, Fe, Mn, and Zn) of procedural blanks (ddH₂O processed like real samples) were below analytical detection limits for all sampling dates. That this was true for all metals, including those with low GFAAS detection limits, lends confidence that contamination memory did not occur to any significant extent.

Methods were developed to determine reproducibility, optimize recovery, and quantify the dead volume of the system. In order to test the reproducibility of CFF for replicate subsamples, a 4-liter sample of Batsto water was collected on 20 December 1994 and filtered on 14 January 1995, using a 0.45- μ m Supor cartridge filter, into four separate 1-liter bottles. These bottles were stored at 4°C without acidification until CFF was carried out on three separate dates from 15 January to 1 March 1995. In each filtration, two subsamples from each 1-liter bottle were processed by CFF in succession. The apparatus was cleaned as described above between subsamples. The permeates, retentates, and an aliquot of the <0.45- μ m sample were then acidified and analyzed for Fe, Al, and Mn. Full procedural reproducibility of CFF for duplicate <0.45- μ m samples collected on different dates was also examined; that data is discussed below in Results and Discussion.

Because mass balance calculations often gave significantly less than 100% recovery in preliminary tests of the CFF device, experiments were carried out to quantify metals adsorbed to the membrane, as follows: Approximately 500 ml of ultraclean 0.5 N HCl (subboiled distilled in ddH₂O) was introduced to the system immediately after the sample was run, with no intervening water wash. The acid was recirculated for 10–20 min with the permeate clamp closed, drained through the retentate valve only, then analyzed to determine metals recovered from the membrane.

Dead volume of CFF devices is not usually considered in calculations of colloidal fractions because it is negligibly small relative to typical sample volumes. In our case, however, the dead volume was significant in comparison to the volume of bulk <0.45- μ m sample introduced. Because the system was filled with water when samples were introduced, both permeates and retentates were diluted by a small but significant factor. Dead volume comprised the peristaltic pump tubing, the plumbing of the membrane cassette holder, and the void volume of the cassette itself. Because geometric estimation of these volumes was uncertain, dead volume was quantified by loading the system with a known volume of Mg solution, draining normally, diluting it by processing a known volume of water, and measuring Mg in the water by flame atomic absorption. The dilution of the Mg solution gave a system dead volume of 26.3 ± 0.8 ml. Therefore, all permeate and retentate concentrations reported here have been corrected by a factor of $(V_{\text{sample}} + 26.3)/(V_{\text{sample}})$, where V_{sample} is the volume of sample (in ml) introduced to the CFF reservoir.

Analytical methods—Metals in all aqueous fractions and digests were analyzed by GFAAS on a Hitachi Z-9000 mul-

tiement instrument, which allows elements with similar atomizing temperatures to be run simultaneously using up to four independent optical pathways through the graphite tube. In this study, Al and Mn were analyzed simultaneously, as were Cd and Pb; Fe, Cu, and Zn were analyzed individually. The standard-addition method was used for all samples. To determine analytical precision, a subset of samples was analyzed twice. These duplicates generally agreed to within $\pm 5\%$ for all elements, and often agreed to 2–3%. Accuracy was determined by analysis of SLRS-3 standard river water; measured values matched certified values within the 2-sigma uncertainty. Analyses of duplicate particulate samples agreed to within $\pm 8\%$ for Al, $\pm 10\%$ for Cu, $\pm 5\%$ for Fe, $\pm 10\%$ for Mn, $\pm 8\%$ for Pb, and $\pm 15\%$ for Zn. Cd was below the detection limit of the particulate digestion method (0.02 nM) for all samples analyzed. Reproducibility of CFF-derived solutions is discussed below. Taking preconcentration into account for Cd, Cu, and Pb (as discussed below), detection limits for aqueous fractions were Al, 35 nM; Cd, 0.005 nM; Cu, 0.3 nM; Fe, 35 nM; Mn, 5 nM; Pb, 0.02 nM; and Zn, 1 nM. These detection limits were equivalent to the following percentages of the lowest samples measured (typically the lowest permeate fractions): Al, 50%; Cd, 16%; Cu, 25%; Fe, 100%; Mn, 23%; Pb 100%; and Zn, 12%. However, analyses of most sample fractions exceeded detection limits by a factor of 10 or more.

Before analysis, a 12-ml aliquot of each $<0.45\text{-}\mu\text{m}$ and CFF-permeate fraction was preconcentrated evaporatively by a factor of 20–30 for analyzing Cu, Pb, and Cd. The exact preconcentration factor was determined gravimetrically to $\pm 1\%$ for each sample. 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 infrared lamps. There was no evidence of artifacts such as precipitation resulting from this procedure, and duplicate samples preconcentrated separately gave very similar results (see *CFF Reproducibility*, below). CFF retentates were not preconcentrated, because doing so made them viscous and adhesive enough to compromise pipetting accuracy and GFAAS autosampler performance. Therefore, we obtained no data on Cd, Cu, and Pb in CFF retentates and calculated the colloidal fraction by difference.

For particulate matter digestion, dried filters were cut in quarters using a template and stainless steel scalpel, and two opposite quarters (with the exact fraction determined gravimetrically) were placed in Teflon bombs and digested on a hot plate in a mixture of 400 μl double-subboiled distilled HNO_3 , 400 μl dd H_2O , and 100 μl concentrated HF (Ultrex, J.R. Baker) for 6 h. This mixture was optimized to totally digest particulate material while leaving the filter material relatively intact. The method was modified from a digestion method used previously for oceanic particulate matter (Sherrell 1991; Sherrell and Boyle 1992). After digestion, the solution was diluted with dd H_2O . Blanks were below detection limits for all metals except Zn, for which $\sim 50\%$ blank correction was needed for the lowest sample. Blanks for most other Zn determinations and for all other metals were $<10\%$ of the sample concentration.

Table 1. Percentage of recoveries from cross-flow filtration with and without wash solutions.

Sample	Al (%)		Fe (%)		Mn (%)	
	With-out wash	With wash	With-out wash	With wash	With-out wash	With wash
12/93 Fr/GB 4	89	99	60	93	93	95
10/94 Fr/GB 1	54	73	20	66	97	97
10/94 Fr/GB 2	53	74	39	72	78	82
10/94 Bt 2	74	94	54	97	97	102
10/94 Hm 2	55	89	49	95	101	112
3/95 Bt 1	84	107	56	77	109	125
3/95 Bt 3	86	91	66	86	86	87
Mean	71	90	49	84	94	100

Results and discussion

Cross-flow filtration recovery—Results of mass balance experiments are presented in Table 1, in which recoveries both with and without the subsequent wash are compared. Recovery, expressed as a percentage (R%), is defined by Eqs. 1 and 2:

$$R\% = 100 \times \frac{C_p \times V_p + C_r \times V_r}{C_t \times V_t}, \quad (1)$$

excluding the wash solution, and

$$R\% = 100 \times \frac{C_p \times V_p + C_r \times V_r + C_w \times V_w}{C_t \times V_t}, \quad (2)$$

including the wash solution, where C_p is the metal concentration in the CFF permeate, corrected for dilution by dead volume; V_p , the volume of permeate collected; C_r , the corrected metal concentration in the CFF retentate; V_r , the volume of retentate collected; C_t , the total $<0.45\text{-}\mu\text{m}$ concentration; V_t , the volume of $0.45\text{-}\mu\text{m}$ filtrate entered into the system; C_w , the adjusted metal concentration in the wash solution; and V_w , the volume of the wash solution.

Recoveries, excluding the wash solution, ranged from 53 to 89% for Al, 20 to 66% for Fe, and 78 to 109% for Mn (Table 1). The relatively poor recoveries presumably resulted from metal adsorption to CFF membrane, a problem that has plagued other investigators of metal fractionation in freshwaters, especially in low conductivity, relatively high-DOC waters such as Pinelands streams. Because poor recoveries introduce an uncertainty into calculating the colloidal metal concentration, it was necessary to account for the unrecovered material. Including the HCl wash solutions in the mass balance increased recoveries substantially for Al and Fe: to 73–107% (mean 90%) and 66–97% (mean 84%), respectively, in the seven samples for which wash solutions were analyzed. Mn recoveries, on the other hand, were not significantly greater with the wash solution included (mean = 94% without and 100% with rinse; Table 1). Recoveries in this range are comparable to values considered acceptable for CFF of natural water samples (Powell et al. 1996; Stordal et al. 1996). Because a significant portion of the initially unrecovered Al and Fe was present in wash solutions that

Table 2. Permeate concentrations (nM) and reproducibility of cross-flow filtration process duplicates.

Metal	Sub-sample	C _{tot} dis	C _p 1	C _p 2	% difference	% colloidal
Al	a	4,889	4,435	4,694	5.7	6.6±2.6
	b	5,456	2,870	2,675	7.0	49.2±1.8
	c	7,644	5,837	5,797	0.7	23.9±0.3
	d	4,667	2,765	2,306	18.1	45.7±4.9
Fe	a	4,647	2,588	2,945	12.9	40.5±3.8
	b	2,249	478	459	4.1	79.2±0.4
	c	6,061	3,829	3,283	15.4	41.3±4.5
	d	4,654	505	436	14.7	89.9±0.7
Mn	a	297	291	304	4.4	-0.2±2.2
	b	324	257	245	4.8	22.5±1.9
	c	302	249	247	0.8	17.9±0.3
	d	310	229	214	6.8	28.5±2.4

C_{tot} dis = total dissolved (<0.45 μm) concentration.

C_p 1 and C_p 2 = permeate concentrations from duplicate CFF filtrations of the same <0.45 μm sample.

contacted the retentate side only, we concluded that most of the total unrecovered Fe and Al was reversibly adsorbed to the retentate side of the membrane. It was not clear whether this material was larger or smaller than the pore size; that is, whether it should have been included in the retentate or permeate fraction. It has been reported that material smaller than the nominal pore size may adsorb to CFF membranes and may thus be included, by retentate-side rinsing, in the larger size fraction (Guo and Santschi 1996; Gustafsson and Gschwend 1997; Wen et al. 1996). However, the fact that Mn had the best recoveries and that truly dissolved Mn concentrations were close to total dissolved concentrations (data presented below) suggests that CFF-permeable Mn was not adsorbed to the membrane. Although interactions with the membrane depend on individual chemical properties of each metal, we assumed from the above evidence that the material unrecovered in normal use (which did not include analysis of wash solutions) should be ascribed to the retentate as part of the colloidal fraction. The same applied to Cu, Cd, and Pb, which were analyzed in the permeate only. Hence, we calculated the colloidal concentration by difference, as follows:

$$C_c = C_{td} - C_p \quad (3)$$

$$C_p = C_{tru} \quad (4)$$

$$\%Coll = (C_{td} - C_p)/(C_{td}), \quad (5)$$

where C_c is the colloidal concentration; C_{td} , the total dissolved concentration; C_p , the corrected permeate concentration; C_{tru} the truly dissolved concentration; and %Coll, the percent of C_{td} in the colloidal fraction. Similar findings have led to the same method of quantification in previous studies (Dai et al. 1995); any systematic error resulting from this method would favor overestimation of the colloidal fraction.

Cross-flow filtration reproducibility—Reproducibility of CFF separations for natural samples has been examined only sporadically in the literature, possibly because large volumes are typically processed and the effort of processing duplicates is high (Baskaran et al. 1992; Dai et al. 1995; Guo and Santschi 1996). To better quantify the precision of CFF separations in our samples, we investigated reproducibility by comparing both process duplicates (aliquots of the same <0.45-μm solution) and field duplicates (separate <0.45-μm solutions filtered independently from duplicate sampling bottles). Percentage differences between permeate concentrations of process duplicates were 5.7–18.1% for Al, 4.1–15.4% for Fe, and 0.8–6.8% for Mn (Table 2). These differences translated to absolute differences about the mean resulting %Coll values of ±0.3–4.9, ±0.4–4.5, and ±0.3–2.4 percentage points for Al, Fe, and Mn, respectively. Note that the differences between first and second aliquots are not systematic, indicating that the normal cleaning protocol reset the membrane and prevented memory problems. By comparison, field-sampling duplicates of <0.45-μm fractions agreed to within ±4% for Al, ±6% for Cd, ±15% for Cu, ±8% for Fe, ±5% for Mn, ±10% for Pb, and ±6% for Zn.

The %Coll values for 10 pairs of filtered field-duplicate samples are compared in Table 3. These were the only pairs in which both duplicates were processed by CFF. Differences in %Coll for Al and Fe in duplicate samples were generally less than 10 percentage points for every pair. Differences in %Coll for the other metals were generally less than 15 percentage points. Differences greater than 20 points were almost always due to major differences (>30%) in C_p values.

Table 3. Absolute differences (%) in colloidal metals for full procedural duplicate samples.

Sample	Al	Fe	Mn	Cd	Cu	Pb	Zn
10/17/94 Bass	1.2	1.1	16.9	14.8	25.6	7.1	7.2
10/17/94 Batsto	1.0	1.5	6.3	16.2	20.6	53.9*	13.6
10/17/94 Fr/GB	11.9	2.1	20.6	ND	10.1	ND	12.5
10/17/94 Hammonton	0.8	1.5	8.4	11.8	5.1	0.4	17.8
12/20/94 Bass	2.0	8.9	0.4	10.0	ND	2.6	8.0
12/20/94 Batsto	24.5*	4.5	27.9*	36.2*	8.6	14.3*	15.6*
12/20/94 Hammonton	4.0	2.9	10.8	0.1	1.7	0.6	ND
6/7/95 Batsto	3.3	1.1	25.4	11.1	3.0	15.8	14.4
7/18/95 Batsto	3.3	3.0	4.7	16.2	51.0*	0.0	7.8
9/13/95 Batsto	3.8	9.1	6.3	9.4	14.1	0.0	3.5
Mean	5.6	3.6	12.8	14.0	15.5	10.5	11.2

* Difference due to a large (>30%) difference in corrected permeate concentration. ND, not determined.

Of the 66 sample replicate/metal comparisons listed in Table 3, 7 displayed this relatively poor CFF reproducibility, and 5 of these occurred with the 20 December 1994 Batsto sample for Al, Mn, Zn, Cd, and Pb. We concluded that, of the 10 sample pairs used to check reproducibility, the CFF separation was acceptably reproducible for all but one. The uncertainty in processing duplicates was similar to that of full field-sampling duplicates for Al and Fe (<6% in %Coll; Tables 2 and 3), indicating that the CFF procedure and analytical error accounted for most of the overall uncertainty in %Coll. Therefore, reproducibility of <0.45- μ m filtration contributed little additional uncertainty for these elements but appeared to contribute significantly to overall %Coll Mn uncertainty.

These two sets of data demonstrate that reproducible CFF permeate concentrations and resultant %Coll values can be achieved on real samples with our procedure, and that reproducibility uncertainties are generally small relative to spatial/temporal variations. Reasons for this consistency may include our practice of analyzing composite permeates, rather than a temporal aliquot of the permeate stream, and our adherence to a narrow range of concentration factor (CF) for all sample processing. While others report little dependence of %Coll on CF over CF = 2–10 for the Filtron membrane (Buesseler et al. 1996; Wells et al. 1998), clear dependence has been demonstrated for other CFF units over CF = 2–5 (Gustafsson et al. 1996; Wen et al. 1996). Theoretical and experimental work demonstrates that the magnitude of this effect, as well as the operationally effective size cutoff, depends on ionic strength and the three-dimensional configuration of macromolecules (Kilduff and Weber 1992). Performance of a particular membrane type in one aquatic or marine environment may not accurately predict its performance in another. Because we were certain that our CFF system did not introduce measurable contamination, we concluded that absolute differences in %Coll exceeding 10–15 percentage points reflected real differences in metal size-fractionation, not CFF artifacts.

Elemental consistencies in colloidal metal fraction across all sites—Total dissolved, colloidal, truly dissolved, and %Coll metal data for all sampling sites over the test period were measured or calculated by Eqs. 3–5 above (Table 4; complete data set available from the authors upon request). Distributions of %Coll values for Al, Cd, Cu, Fe, Mn, Pb, and Zn at the four sites over eight sampling dates from 15 August 1994 to 13 September 1995 are presented in Figure 2 in the form of box plots that indicate the median and the 10th, 25th, 75th, and 90th percentiles. These plots illustrate overall elemental patterns of %Coll fraction that are consistent among the sampling sites. These values can be compared to previously published elemental order, as well as absolute differences in colloidal fraction, to determine whether geochemically consistent trends for river waters emerge.

Comparing the temporal median of %Coll values for each stream, we observed that the elemental order of %Coll values was nearly conserved, despite substantial differences in metal sources, pH, metal concentrations, and the absolute values of the colloidal fractions (Fig. 2a–d). In most cases,

the colloidal fractions in order from greatest to smallest were Pb > Fe > Al > Cu > Cd > Zn \approx Mn. Exceptions to this rule were slight: Adjacent metals exchanged ordinate positions for some sites (e.g., Fe > Pb at Hammonton) and ranges of variation in %Coll were consistently larger for some elements (e.g., Zn > Pb). Median values for %Coll from Pinelands streams fell into three recognizable groups: 58–95% for Fe, Al, and Pb; 16–51% for Zn and Mn; and intermediate values for Cd and Cu. These trends suggested a broadly consistent relative colloidal partitioning for these metals, even across fairly large changes in stream water chemistry and pH. This order was maintained, generally, for each time point at a single location as well. Figure 3 shows %Coll for each metal for each sampling date at Batsto. The temporal trends in colloidal fraction showed that most metals varied in concert, maintaining the elemental order as %Coll shifted temporally, suggesting that changes in colloidal abundance caused the interelement covariation in colloidal fraction. The major exception to this rule was Cu, which broke the elemental order for individual dates, showing size fractionation behavior independent of other metals. The reason for Cu's apparently anomalous behavior is not presently understood.

For the most part, the relative size-fractionation of metals observed in this study was consistent with the small body of published freshwater colloidal metal data, most of which was obtained using 10 kDa CFF membranes as part of one-time estuarine transects that extended to one or a few freshwater end-member samples. Fe has been strongly associated with the colloidal fraction in all rivers previously studied: Total dissolved Fe was 83–95% colloidal in two Nova Scotian rivers (Whitehouse 1990); >65% colloidal in the Ochlockonee River, Florida (Powell et al. 1996); 82% colloidal in the Silone Channel, Italy (Martin and Dai 1995); 89–97% colloidal in two Russian rivers, the Ob and the Yenisey (Dai and Martin 1995); 84–88% in the San Joaquin and Sacramento Rivers (Sañudo-Wilhelmy et al. 1996); and 69% in the Garonne River (Kraepiel et al. 1997). These data underscore the widespread importance of Fe oxyhydroxide/organic colloids, which have long been recognized as the dominant Fe phase in rivers (Boyle and Edmond 1977; Sholkovitz and Copland 1981; Mayer 1982; Fox 1988). Similarly, 75–85% of total dissolved Al was colloidal in two Nova Scotian rivers (Whitehouse 1990) and 99% in the San Joaquin and Sacramento Rivers (Sañudo-Wilhelmy et al. 1996). These are the only literature values for colloidal Al, to our knowledge. The predominantly colloidal nature of Al is expected; that metal is present in freshwaters both as clays and as organic complexes that extend to the colloidal size range (Turner et al. 1985; Stevenson and Vance 1989; Rees and Ranville 1990; Stumm 1992). Mn generally exhibits smaller colloidal fractions than Fe and Al but shows more variation among streams and sampling times. The colloidal Mn fraction was 43–64% in Nova Scotian rivers (Whitehouse 1990), 30% in the Ochlockonee (Powell et al. 1996), 24% in the Silone Channel (Martin and Dai 1995), 20% in the San Joaquin and Sacramento Rivers (Sañudo-Wilhelmy et al. 1996), and only 5% in the Garonne (Kraepiel et al. 1997). Its relatively small colloidal fraction, compared to Al and Fe, is consistent with Mn speciation, which favors the free ionic

Table 4. Cross-flow filtration data summary for all sites and sampling dates (15 Aug 94–13 Sep 95). Metal concentrations are expressed in nM.

Metal	Variable†	Bass*		Batsto		Forks/Green Bank		Hammonton		All sites and dates	
		Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean
	pH	4.55	4.54	5.54	5.40	5.68	5.54	6.45	6.38		
Al	Ctot dis	2,761	3,234	2,263	2,667	2,493	3,161	3,084	4,080	2,857	3,321
	Ctru dis	1,049	1,274	1,483	1,366	713	1,452	378	1,114	796	1,347
	Ccoll	1,869	1,960	888	1,302	1,780	1,710	2,810	2,965	1,813	1,974
	% Coll	63.3	61.5	57.2	55.2	65.1	62.1	84.8	81.2	64.7	64.1
Fe	Ctot dis	3,031	4,530	2,881	3,080	4,674	5,203	2,621	3,773	3,766	4,249
	Ctru dis	1,156	1,306	1,098	915	578	1,397	158	344	646	1,019
	Ccoll	2,565	3,224	1,962	2,615	3,861	3,806	2,849	3,506	3,023	3,248
	% Coll	62.8	67.8	70.0	73.9	86.1	79.5	94.6	93.0	82.4	78.4
Mn	Ctot dis	115	119	260	250	263	250	503	667	243	319
	Ctru dis	89	83	183	177	190	186	363	406	159	213
	Ccoll	35	36	51	73	56	64	139	262	62	106
	% Coll	25.8	31.6	21.1	27.8	23.5	27.1	34.5	35.0	28.6	29.8
Cu*	Ctot dis	4.2	4.2	3.9	3.2	7.9	9.0	53.2	59.1	7.6	22.8
	Ctru dis	2.0	2.0	1.1	1.5	2.5	2.8	16.4	22.0	2.8	8.4
	Ccoll	2.3	2.3	1.8	1.7	5.9	6.2	31.4	37.2	5.3	14.4
	% Coll	56.1	56.1	54.9	47.6	71.2	66.5	64.5	63.4	65.8	58.7
Zn	Ctot dis	70	69	55	77	92	101	352	324	92	142
	Ctru dis	58	50	54	52	68	76	146	180	68	90
	Ccoll	17	18	24	25	22	25	123	144	29	52
	% Coll	20.9	28.3	30.3	33.2	20.6	29.0	50.8	43.3	30.6	32.8
Cd	Ctot dis	0.24	0.25	0.23	0.25	0.24	0.29	0.78	0.83	0.27	0.40
	Ctru dis	0.17	0.14	0.17	0.15	0.12	0.20	0.36	0.46	0.18	0.24
	Ccoll	0.10	0.12	0.11	0.10	0.10	0.09	0.41	0.37	0.11	0.17
	% Coll	38.5	45.2	45.8	38.5	26.6	37.1	53.2	47.9	45.7	41.5
Pb	Ctot dis	1.57	2.15	0.26	0.42	0.44	0.63	2.95	3.06	1.02	1.56
	Ctru dis	0.20	0.40	0.07	0.11	0.03	0.09	0.37	0.54	0.14	0.30
	Ccoll	1.44	1.75	0.17	0.31	0.36	0.53	2.38	2.52	0.81	1.29
	% Coll	81.7	80.5	84.4	79.5	91.1	90.3	88.5	83.8	87.9	81.9

* Cu determined for first two time points only at Bass River site.

† Ctot dis, total dissolved concentration; Ctru dis, truly dissolved concentration; Ccoll, colloidal concentration; % Coll, percentage of Ctot dis that is in the colloidal size fraction.

form or small complexes in freshwaters (Raspor 1980; Sholkovitz and Copland 1981; Laxen et al. 1984; Sigg 1987). Published Cd size-fractionation data also show smaller colloidal fractions than Al and Fe: 42.9% of total dissolved Cd was colloidal in the Silone Channel, 38.1% in the Rhone (Dai et al. 1995), 45–75% in the Ob and Yenisey (Dai and Martin 1995), 49–67% in the Ochlockonee (Powell et al. 1996), not measurable in the San Joaquin and Sacramento Rivers (Sañudo-Wilhelmy et al. 1996), and 61% in the Garonne (Kraepiel et al. 1997). The very limited riverine colloidal database for Zn shows 34% for the Garonne (Kraepiel et al. 1997), very similar to our 34% mean, but only 2% for the San Joaquin and Sacramento Rivers (Sañudo-Wilhelmy et al. 1996). Although these comparisons suggest that some generalities might be drawn with regard to absolute colloidal metal fractions in rivers, the magnitude of temporal variation for the Pinelands streams suggests that seasonal or discharge-related changes in colloidal abundance and composition, little explored in other systems, might complicate river-to-river comparisons.

Our finding that total dissolved Pb fractionates strongly

into the colloidal size range is consistent with this element's particle-reactive nature (Sigg 1987). Further, Pb forms strong complexes with natural organic matter (Windom et al. 1985; Martin and Dai 1995), of which a significant fraction occurs in the colloidal size range (Guo et al. 1996; Santschi 1996; Benner et al. 1997; Guo and Santschi 1997; Gustafsson and Gschwend 1997). However, published colloidal Pb fractions, both from the Silone Channel (49% colloidal [Martin and Dai 1995]) and the Ob and Yenisey (22.4–52.0% colloidal [Dai and Martin 1995]), are significantly lower than our overall mean value of 82%. Both of these systems have lower total dissolved Pb than the Mullica (Ob, Yenisey: 0.02–0.08 nM; Silone: 0.31 nM); colloids may be partially responsible for stabilizing a relatively high <0.45- μ m Pb concentration in the Mullica. However, relative colloidal fractions must be compared with caution because individual CFF devices and operating conditions may have substantially different size-separation characteristics even at the same nominal cutoff size (Buessler et al. 1996; Gustafsson et al. 1996; Dai et al. 1998).

The order of relative colloidal fraction we found, Pb >

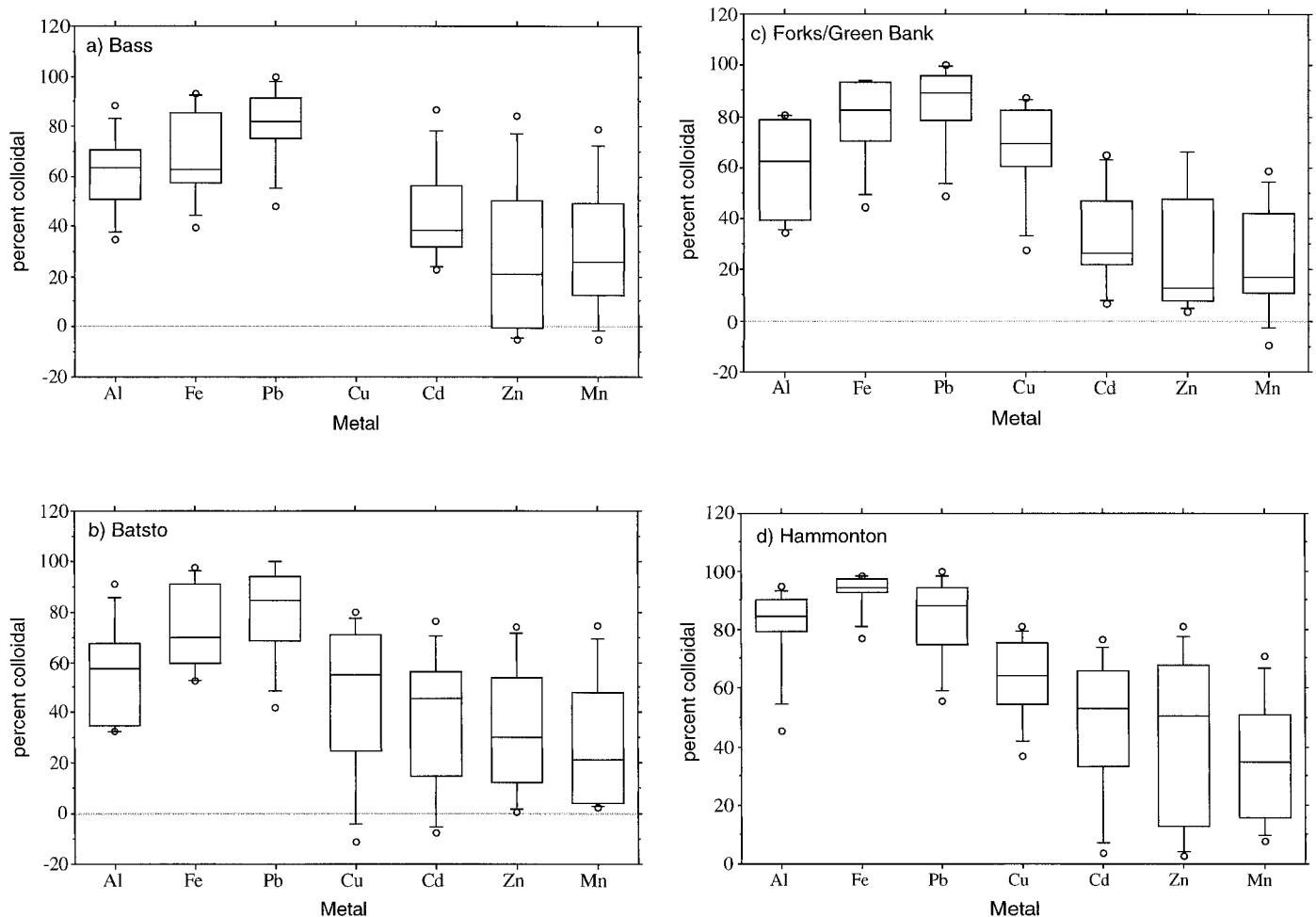


Fig. 2. Box-and-whisker plots showing the distribution of percent-colloidal values at all sites for all metals. The middle line shows the median, the box shows the 25th and 75th percentiles, and the whiskers show the 10th and 90th percentiles. Small circles show the extreme data points. Negative values indicate slightly higher measured values for permeates than for total dissolved samples, generally within measurement precision. Colloidal Cu was determined for only two time points at Bass River, so that data was omitted from this figure.

$Fe > Al > Cu > Cd > Zn \approx Mn$, is very similar to that obtained in a recent estuary study of two California rivers feeding San Francisco Bay (Sañudo-Wilhelmy et al. 1996). The comparable order for freshwater riverine end-members in that study was $Al > Fe > Mn > Cu > Zn > Cd$ (Pb was not determined). The California study used the same CFF apparatus and 10 kDa membrane employed in this study but processed 20 liters of water for each sample, while we processed only 0.23 liter per sample. The geochemical consistency of the results, despite disparate operational approaches, suggests that it may be possible to write general rules about the relative colloidal associations of metals, even in rivers that otherwise have quite different properties. The only major difference between the elemental order of colloidal fractions in these two systems is that colloidal Mn is relatively more important, and Cd less important, in the California rivers. Our elemental order was also similar to the stability sequence of humic-metal complexes ($Fe > Al > Cu > Zn > Mn \approx Cd$) and to the coagulation removal sequence associated with humic materials, as deduced from experimental estuarine mixing experiments (Sholkovitz

1978). Overall, both our results and those from the San Francisco rivers (Sañudo-Wilhelmy et al. 1996) suggest that the colloidal fraction's importance is related to the elements' reactivity for humic substances. Further comparisons of colloidal metal fractions in riverine systems may provide additional insights if the <10 kDa colloidal fraction is also examined, as in the recent work of Wen et al. (1999).

The consistent elemental differences in colloidal fraction may affect the behavior of the metals in two ways. In the river, the colloidal fraction may enhance transport by limiting the free ions available for biological uptake or for adsorption to solid phases either on the river bed or suspended in the water. On the other hand, metal removal in the low-salinity region of the estuary is known to be driven by flocculation of part of the colloidal pool. Recent estuarine studies suggest that colloidal metals may be removed to varying degrees, often showing behavior independent of both Fe and organic carbon removal, because individual metals associate with distinct subfractions within the colloidal pool (Dai and Martin 1995; Sañudo-Wilhelmy et al. 1996; Kraepiel et al. 1997). Our results predict a relatively modest removal, or

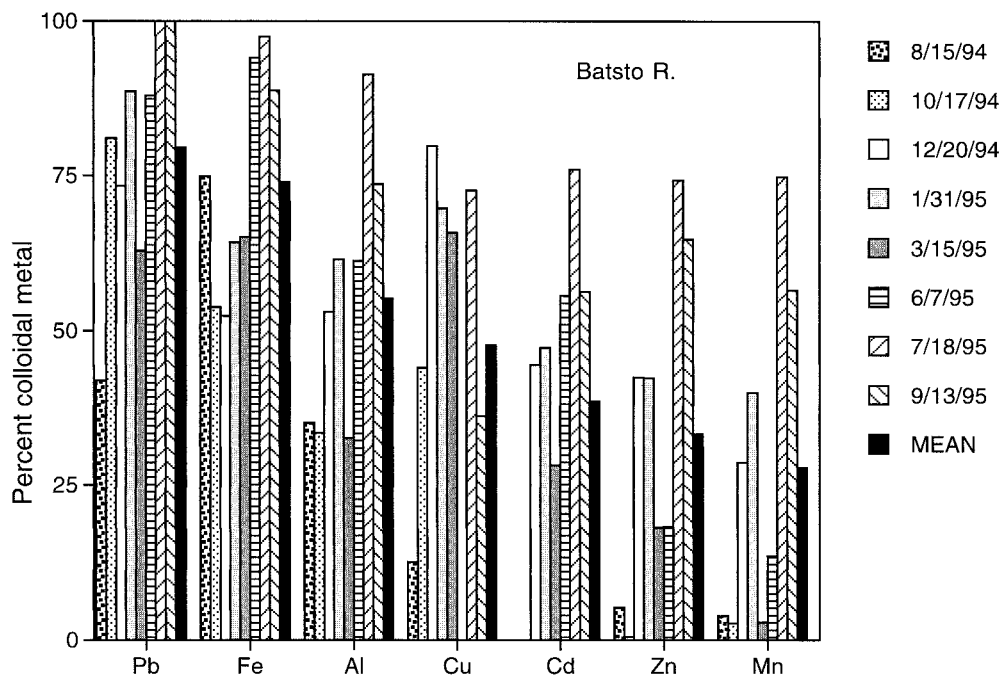


Fig. 3. Percent-colloidal fractions for seven metals on eight sampling occasions at the Batsto River.

perhaps a desorptive input, of $<0.45\text{-}\mu\text{m}$ Mn and Zn and intense removal of $<0.45\text{-}\mu\text{m}$ Fe and Pb. This prediction matches metal-removal patterns in the San Francisco Bay estuary, where the order of freshwater colloidal fractions was very similar and conservative mixing of colloidal Mn and Zn was observed within the estuary (Sañudo-Wilhelmy et al. 1996).

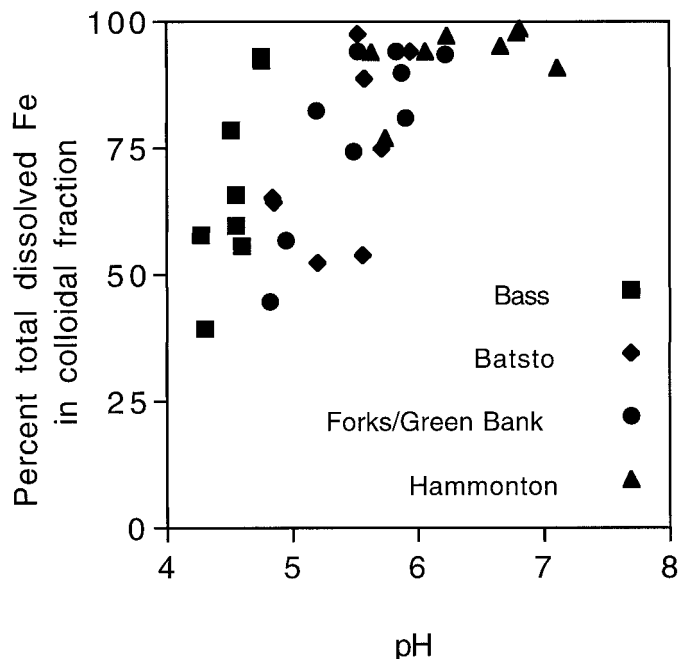


Fig. 4. Percent-colloidal Fe vs. pH for all sampling sites and dates.

Colloidal metals and pH—Of the seven metals, Fe showed the most striking differences in size-fractionation among streams. The median Fe percent-colloidal value increased from Bass to Batsto to Forks/Green Bank to Hammonon, following an increase in median pH. At Hammonon Creek the range of values, 13 percentage points, was the smallest and the median, 95%, the highest of any metal at any site. Furthermore, there was a significant direct relationship between pH and %Coll Fe (Fig. 4) for composite stream water data ($P < 0.01$, $R = 0.69$). This relationship appears broadly consistent with inorganic Fe solubility equilibria, which dictate that the concentration of dissolved ferric Fe is controlled by the solubility of colloidal ferric hydroxide in this pH range (Fox 1988). Truly dissolved Fe data from different streams, however, showed the situation to be more complicated. Although the mean truly dissolved Fe at Batsto ($\sim 1,000$ nM; Table 4) agreed with predicted ferric Fe concentration at this pH (~ 5.5), truly dissolved Fe at Bass (mean pH ~ 4.5) and Hammonon (mean pH ~ 6.4) was an order of magnitude below that predicted by inorganic equilibria at their respective pH (Table 4). For example, the highest pH samples (pH ≈ 7 , at Hammonon) gave a calculated truly dissolved concentration of 30–80 nM, while inorganic equilibria predicted several hundred nM (Fox 1988). These low values suggest that Fe is also bound by organic matter, including >10 kDa humics. It is therefore possible that the correlation between %Coll Fe and pH reflects a relationship partly driven by pH-correlated changes in the abundance of colloidal humic materials, or it may indicate that Fe–organic complexes are partially dissociated in the lower pH range we measured.

In San Francisco Bay estuary, Sañudo-Wilhelmy et al. (1996) argued for colloidal humic materials as the principle

Table 5. Correlation of pH with percentage of colloidal metal (*R*).

Site	Zn	Al	Fe	Mn	Cu	Cd	Pb
All streams	0.188	0.482	0.686	0.092	-0.090	0.077	0.105
Bass	0.522	0.462	0.800	0.564		0.316	0.153
Batsto	-0.134	0.179	0.559	-0.019	-0.787	-0.021	0.083
Forks/Green Bank	0.153	0.646	0.828	0.269	-0.251	0.325	0.327
Hammonton	-0.018	0.425	0.455	-0.100	-0.109	-0.043	-0.145

carrier of colloidal Fe because of evidence for humic substances' high affinity for Fe relative to other metals and because of the behavior of Fe in estuarine mixing zones. Conversely, Benoit and Rozan (1999) argued recently for a dominant nonorganic Fe form in Connecticut rivers because

the size distribution of $<0.45\text{-}\mu\text{m}$ Fe was very different from that of organic matter. The latter argument depends on size distribution relationships between bulk organic matter and the Fe-binding humic subfraction. Our data appear to be consistent with a variable mixture of both organic and inorganic forms of colloidal Fe.

For the other metals, %Coll was poorly correlated with pH when the full data set was considered. Correlation coefficients rarely exceeded $R = 0.5$ and switched sign between streams (Table 5). Correlations were significant only for Al and Fe, and the Fe-pH correlation was stronger for all streams than the Al-pH correlation. These data hint at a Fe colloidal fraction that was broadly dependent upon pH-driven solubility changes and that acted independently of the colloidal fractions of the other metals. Processes that control colloidal and dissolved Fe may apply to Al as well, at least in these streams, where refractory clays may not dominate colloidal Al. The partitioning of Cu, Cd, Zn, Pb, and Mn between colloidal and truly dissolved forms was not simply related to pH. It was likely influenced by other factors such as temporal changes in the composition of the dissolved organic matter, with metals' affinity for humic substances playing a dominant role.

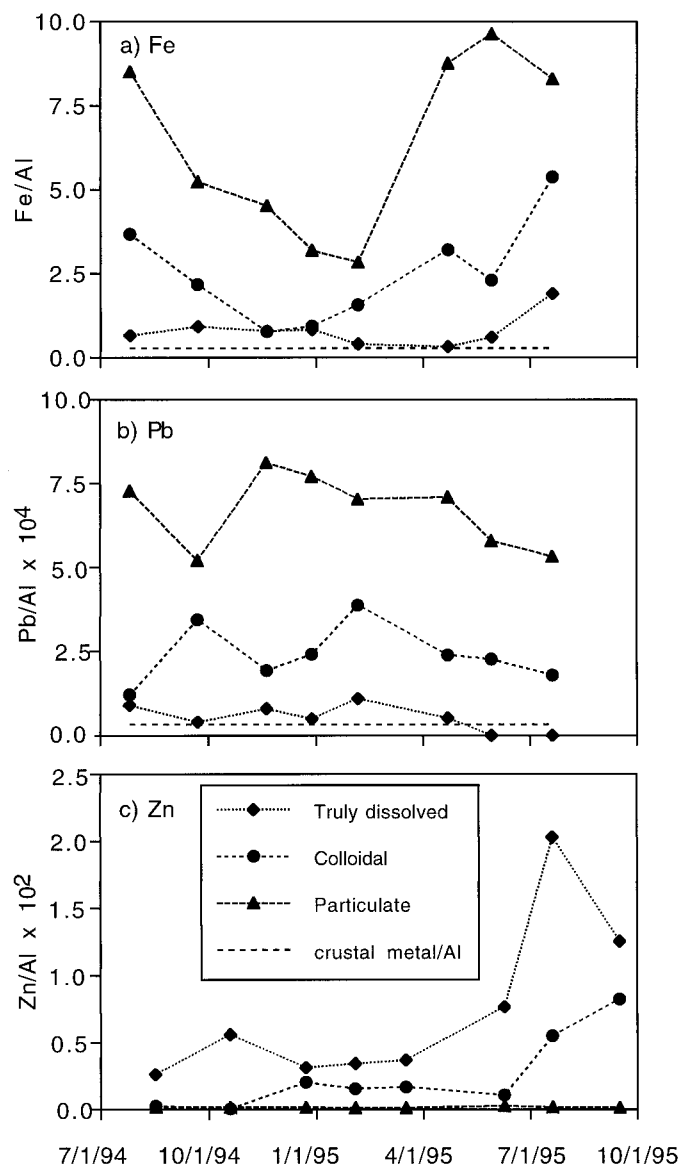


Fig. 5. Ratios of Fe, Pb, and Zn to Al, showing differences in relative trace-metal composition of three size fractions for time-series samples from the Batsto River. Dashed line indicates average crustal metal/Al ratio (Wedepohl 1995).

Trace metal composition of the colloidal fraction—One of our primary interests in this study was to investigate the composition of riverine colloids and their compositional relationship to the particles. To this end, we assessed the relative apportionment of metals to the various size fractions by calculating ratios of Fe, Pb, and Zn to Al in the truly dissolved, colloidal, and particulate size fractions for eight time-series samples collected at Batsto, a representative site (Fig. 5). Using such ratios served two functions: 1) it allowed composition in different size fractions to be easily compared, and 2) changes in the operational characteristics for this temporally variable system, which would be reflected in absolute values of each fraction, were normalized in the ratios. Al was chosen as the normalizing metal because it was one of the most abundant in all fractions and it varied predictably with other metals in the total dissolved fraction. Admittedly, the choice of Al was somewhat arbitrary. It would have been preferable to normalize to the total mass of material in each fraction; however, mass data was only available in the particulate fraction.

An important question for this study was the degree of coherence in composition and implied source for particulate and colloidal fractions. Differences in metal/Al ratios between co-occurring particulate and colloidal fractions would suggest independent sources, while rapid aggregation/disaggregation exchanges between these size fractions, implied

by the colloidal pumping hypothesis, would predict similar composition.

The relative distributions of metals over the size fractions are clearly shown in Figure 5. Because Fe/Al ratios were consistently greater in the particulate fraction than in the colloidal fraction, and consistently greater in the colloidal than the truly dissolved fraction (Fig. 5a), we concluded that the total riverine burden of Fe was more strongly distributed into the larger size fractions than Al is. Similarly, Pb was also more strongly distributed into the larger size fractions (Fig. 5b). Zn, on the other hand, was less strongly distributed into the larger fractions than Al, and hence less than Fe and Pb. These relationships were consistent throughout the year over a >10-fold range in absolute metal concentrations (Table 4; Sherrell and Ross 1999).

The size-composition relationships in Figure 5 were consistent with distinct trace-metal compositions for each fraction, with metal/Al ratios changing monotonically with size fraction. For most sampling dates, the colloidal metal/aluminum (Me/Al) ratio was intermediate between the particulate and truly dissolved fractions, but clearly distinct from both. The consistently different composition of >0.45 μm and colloidal solids suggested that they have independent sources and were not closely related by mass exchanges between colloids and larger particles. These compositional results indicate that if significant colloid aggregation occurred within the hydraulic residence time of the stream, its contribution to overall particulate mass was too small to dominate the composition of the >0.45- μm material. Furthermore, the intermediate position of the colloidal fraction between truly dissolved and particulate fractions suggests that further investigation of smaller colloidal sizes might reveal compositional characteristics for small colloids (e.g., fulvics) that are intermediate between our <10 kDa and truly dissolved Me/Al values. The compositional distinctions among all size fractions suggest that colloidal pumping (Honeyman and Santschi 1989) may have little relevance within the hydraulic residence time of this system.

The temporal progression of Fe/Al ratios in both particulate and colloidal fractions showed a distinct seasonal pattern, while those of Pb/Al and Zn/Al were smaller and more random (Fig. 5). The pattern of higher Fe/Al in summer than in late fall and winter was also observed at the other three sites (not shown). Indeed, this was one of the few clear seasonal signals in the colloidal metals data. A possible source was microbial catalysis of Fe oxyhydroxide formation, which occurs in the stream beds and stream-bordering wetlands in the Pinelands and which increases during warmer months (Crerar et al. 1981; Means et al. 1981). It is interesting to note that the truly dissolved Fe/Al was more constant with time, suggesting that microbial activity, if important, mostly affected composition of the larger size fractions. Alternatively, both Fe and Al may have been associated with small-molecular-weight fulvics within our <10 kDa fraction, and the Fe/Al ratio was stabilized by this association.

The temporal Pb/Al and Zn/Al data showed no clear seasonal patterns. This evidence for variable Zn/Fe and Pb/Fe suggests that colloidal Fe hydroxide may not be the dominant carrier phase for other metals in this system. Instead,

organic colloids may bind these other metals, as has been observed in other rivers and estuaries (Dai and Martin 1995; Sañudo-Wilhelmy et al. 1996; Stordal et al. 1996), while organic matter associations with colloidal Fe are formed independently.

We must point out that refractory clays do not dominate the colloidal metal composition in Pinelands streams, as they do in rivers of the San Francisco Bay estuary (Sañudo-Wilhelmy et al. 1996). In the Pinelands streams, Me/Al ratios in all particulate and colloidal fractions exceeded that of crustal values (Wedepohl 1995) by factors of 4 (Zn/Al in particles) to 33 (Pb/Al in particles). Therefore, it is likely that Zn and Pb have substantial, if not overwhelming, anthropogenic components associated with organic carrier phases but not with refractory weathering products. This is interesting because direct industrial inputs to this system are almost nil; pollutant sources are likely to comprise relatively limited residential and agricultural contributions, as well as long-term and potentially important atmospheric inputs derived from nearby urban areas (Sherrell and Ross 1999). The processes that govern the transport of particulate and colloidal solids in this system likely control the transport of many pollutant metals as well.

An inverse particle concentration effect for Pb?—The colloidal metals data shed light on the temporal variation of the dissolved/particulate partitioning of Pb, a central determinant of its transport pathways in a riverine system. Such partitioning is usually quantified by K_d (the partition coefficient = metal/[mass of particle] divided by metal/[mass of solution]). We examined preliminary evidence for the dependence of K_d for Pb on suspended mass, which is opposite to the normal PCE observed in most previous studies. The results have implications for seasonal changes in the Pb-binding capacity of particles and colloids; they suggest decoupling between sources of >0.45- μm particles and >10-kDa colloids.

Over the past few years, empirical support has been mounting for the broad validity of the PCE, with examples for inorganic and organic species in marine and estuarine environments (Morel and Gschwend 1987; Honeyman and Santschi 1992; Benoit et al. 1994; Smith and Flegal 1994; Moran et al. 1996; Sañudo-Wilhelmy et al. 1996), in controlled laboratory experiments (DiToro et al. 1986; Honeyman and Santschi 1988), and recently in fresh continental waters (Balistreri et al. 1994; Benoit 1995; Benoit and Rozan 1999). One of the freshwater studies found a highly significant PCE ($P < 0.001$) for Al, Fe, Pb, Cu, Zn, and Ag based on a large data set that included several polluted and pristine freshwater bodies and spanned three orders of magnitude in suspended particulate mass (SPM; Benoit 1995). Most comparable to our study is a recent time-series investigation of four Connecticut rivers in which the observed normal PCE was eliminated in most cases by explicitly including the colloidal with the particulate fractions and accounting for seasonal changes in the contribution of large, relatively unreactive particles (Benoit and Rozan 1999).

The colloid model, the most widely accepted mechanism invoked to explain the PCE (Morel and Gschwend 1987; Honeyman and Santschi 1989, 1991; Benoit 1995; Santschi et al. 1997), assumes that solution which passes a 0.45- μm

filter includes both colloidal and truly dissolved metals, implying that proper separation of these forms would eliminate the observed effect. Accordingly,

$$K_d = \frac{K_{\text{part}}}{1 + K_{\text{coll}} \times \text{SCM}}, \quad (6)$$

where K_d is the conventional distribution coefficient operationally defined by 0.45- μm filtration, and K_{part} and K_{coll} are the true equilibrium adsorption constants for metal associated with $>0.45\text{-}\mu\text{m}$ particles and colloids, respectively (comparable to K_d , but with truly dissolved metal concentration in the denominator). SCM is the suspended colloidal mass, analogous to SPM. If $K_{\text{coll}} \times \text{SCM} \gg 1$ (generally true), then Eq. 6 reduces to

$$K_d = \frac{K_{\text{part}}}{K_{\text{coll}}} \times \frac{1}{\text{SCM}}. \quad (7)$$

In this case, K_d is strictly proportional to SCM^{-1} , since K_{part} and K_{coll} are assumed to be true constants. In addition, there is empirical and theoretical evidence that, at equilibrium, SCM is related to SPM by the following power law:

$$\text{SCM} = k(\text{SPM})^x \quad (8)$$

where $k > 0$ and $x = 0.5\text{--}1.0$ (Gschwend and Wu 1985; Honeyman and Santschi 1989; Benoit et al. 1994). Hence, combining Eqs. 7 and 8, K_d is related to SPM by a power-law relationship with a negative exponent, explaining the normal PCE wherein K_d decreases with increasing SPM. Conversely, if $K_{\text{coll}} \times \text{SCM}$ is $\ll 1$, then K_d will be constant ($= K_{\text{part}}$). Under no circumstance does this theory allow for an increase in K_d with increasing SPM.

In the six Batsto River samplings for which we have SPM values, K_d for Pb increased with increasing SPM, violating the assumptions of the colloid model (Fig. 6). This apparent inverse PCE, which was also present for Al but less clear for Zn and Cu (not shown), could have resulted from at least three different causes, two of them fundamental to the fluvial geochemistry of the Batsto River, and one an operational artifact:

(1) The relationship between SCM and SPM may not be described by Eq. 8; these two properties may instead be negatively correlated. If true, this would imply that SCM and SPM have independent sources and are not strongly related by colloidal pumping processes (Nyffeler et al. 1984; Jannasch et al. 1988; Honeyman and Santschi 1989), which should result in relationships following Eq. 8.

(2) K_{part} and/or K_{coll} may not be true constants, but instead may be seasonally variable because particulate and/or colloidal matter varies in composition and density. If SCM is related to SPM by the relationship normally assumed (Eq. 8), the effect of the summertime increase in SPM would have to be overwhelmed by a large increase in K_{part} and/or decrease in K_{coll} , so that observed K_d would be greater in summer than in winter.

(3) Increased filter loading under high-SPM summertime conditions (with \sim constant filtration volume throughout the year) may cause colloidal Pb to be trapped with the nominal $>0.45\text{-}\mu\text{m}$ fraction, leading to low %Coll values, low truly dissolved Pb, and higher apparent K_d . This effect can only

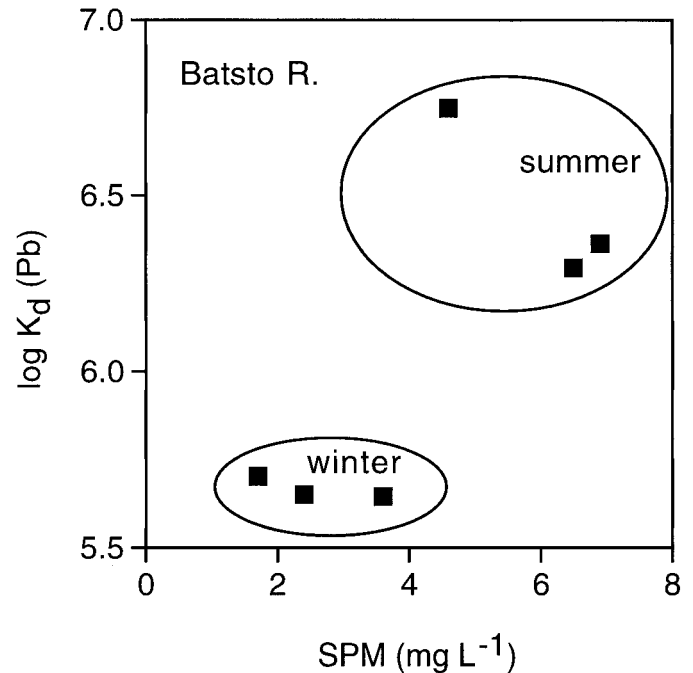


Fig. 6. Distribution coefficient (K_d) for Pb vs. total suspended matter (TSM) for six Batsto occupations from 20 December 1994 to 13 September 1995.

occur if colloidal metal is a large fraction of the total dissolved metal, as it is for Pb. We feel this explanation is unlikely for two reasons. First, %Coll is somewhat higher in summer (88–100% vs. 63–89%), suggesting that colloids were not preferentially removed by the filtration process. Second, the relatively small volumes filtered (250 ml) minimized the effect of filter loading, and the tortuous-path filters we used are less prone to loading artifacts than sieve filters such as track-etch membranes (Horowitz et al. 1992, 1996; Shiller and Taylor 1996).

Unfortunately, the available data do not allow a definitive evaluation of the importance of Mechanisms 1 and 2. It is instructive, nevertheless, to consider briefly each mechanism in order to assess their plausibility and determine additional measurements required to distinguish their relative roles. Mechanism 1 invokes a temporal anticorrelation between SCM and SPM, which might result from the flushing of water enriched in dissolved (including colloidal) organic matter from shallow groundwater reservoirs and wetlands during the winter/spring high-flow period, with relatively little concomitant increase in SPM. This watershed has low relief, porous soils, and is mostly forest. Hence, there is little direct input of eroded soil particles into streams, even during periods of high flow. In addition, shorter hydraulic residence times during high discharge could kinetically limit the aggregation/disaggregation processes that drive the colloidal pumping mechanism leading to theoretical relationships expressed by Eq. 8 (Nyffeler et al. 1984; Jannasch et al. 1988; Honeyman and Santschi 1989). Mechanism 1 cannot be evaluated fully because good estimates for SCM are lacking.

Evaluation of Mechanism 2 is also hampered by poor constraints on SCM, which makes estimates of K_{coll} highly un-

certain. However, K_{part} can be determined; it is about an order of magnitude higher in summer, on average, than in winter ($2.5 \pm 0.6 \times 10^7$ vs. $2.3 \pm 1.4 \times 10^6$, mean \pm SD, for December–March and June–September, respectively). If we assume that K_{coll} is constant and (contrary to Mechanism 1) that SCM is simply proportional to SPM ($x = 1.0$ in Eq. 8), then the calculated K_{d} would be higher in summer by the ratio of the change in K_{part} (~ 11) to that in SPM (~ 2.5); that is, by a factor of about 4. The increased summertime K_{part} , therefore, could account for most of the seasonal change in K_{d} (about seven times higher in the summer; Fig. 6). Unfortunately, seasonal variations in K_{coll} are presently unknown. Compositional differences between particulate and colloidal fractions, demonstrated in the previous section, open the possibility that the Pb-binding affinities of these two size fractions may indeed vary independently. On the other hand, increased biological activity and longer hydraulic residence times in summer might contribute to changes in the composition of both size fractions, with increases in the number or strength of Pb-binding sites in each, which diminishes the importance of Mechanism 2. We conclude that, although a seasonal change in $K_{\text{part}}/K_{\text{coll}}$ appears plausible, quantitative arguments along these lines depend on several unconstrained variables and are therefore speculative.

Regardless of the relative importance of these two proposed mechanisms, the weight of our data suggests that the aquatic chemical environment in these streams may be fundamentally different in summer than in winter. These differences may result from temporal variations in hydrologic flow paths, metal sources, water residence time, and biological productivity. Thus, it may be fallacious to ascribe all the temporal data to a single set of controlling mechanisms. Figure 6 shows that within each three-point cluster of winter and summer data points, a small normal PCE is evident. Although the dataset is small and changes in SPM are modest within each season, further study might reveal more typical PCE effects within individual seasons characterized by distinct mean K_{d} 's. Future studies of the PCE and related phenomena in the Pinelands or elsewhere will require reasonably accurate estimates of SCM, careful determinations of the metal complexing capacity of different size fractions, and additional constraints on spatial/temporal changes in the particle size spectrum.

References

- BALISTRERI, L. S., J. W. MURRAY, AND B. PAUL. 1994. The geochemical cycling of trace elements in a biogenic meromictic lake. *Geochim. Cosmochim. Acta* **58**: 3993–4008.
- BASKARAN, M., P. H. SANTSCHI, G. BENOIT, AND B. D. HONEYMAN. 1992. Scavenging of thorium isotopes by colloids in seawater of the Gulf of Mexico. *Geochim. Cosmochim. Acta* **56**: 3375–3388.
- BENNER, R., B. BIDDANDA, B. BLACK, AND M. MCCARTHY. 1997. Abundance, size distribution, and stable carbon and nitrogen isotopic compositions of marine organic matter isolated by tangential-flow ultrafiltration. *Mar. Chem.* **57**: 243–264.
- BENOIT, G. 1995. Evidence of the particle concentration effect for lead and other metals in freshwaters based on ultraclean technique analysis. *Geochim. Cosmochim. Acta* **59**: 2677–2687.
- , S. D. OKTAY-MARSHALL, A. CANTU, E. M. HOOD, C. H. COLEMAN, M. O. CORAPCIOGLU, AND P. H. SANTSCHI. 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Mar. Chem.* **45**: 307–336.
- , AND T. F. ROZAN. 1999. The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. *Geochim. Cosmochim. Acta*. In press.
- BOYLE, E. A., AND J. M. EDMOND. 1977. The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta* **41**: 1313–1324.
- BUESSELER, K. O., J. E. BAUER, R. F. CHEN, T. I. EGLINTON, Ö. GUSTAFSSON, W. LANDING, K. MOPPER, S. B. MORAN, P. H. SANTSCHI, R. VERNON CLARK, AND M. L. WELLS. 1996. An intercomparison of cross-flow filtration techniques used for sampling marine colloids: Overview and organic carbon results. *Mar. Chem.* **55**: 1–31.
- CRERAR, D. A., J. L. MEANS, R. F. YURETICH, M. P. BORCSIK, J. L. AMSTER, D. W. HASTINGS, K. E. KNOX, K. E. LYON, AND R. F. QUIETT. 1981. Hydrogeochemistry of the New Jersey Coastal Plain, 2: Transport and deposition of iron, aluminum, dissolved organic matter, and selected trace elements in stream, ground- and estuary water. *Chem. Geol.* **33**: 23–44.
- DAI, M., K. O. BUESSELER, P. RIPPLE, J. ANDREWS, R. A. BELSTOCK, Ö. GUSTAFSSON, AND S. B. MORAN. 1998. Evaluation of two cross-flow ultrafiltration membranes for isolating marine organic colloids. *Mar. Chem.* **62**: 117–136.
- AND J. M. MARTIN. 1995. First data on trace level and behavior in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia. *Earth Planet. Sci. Lett.* **131**: 127–141.
- , AND G. CAUWET. 1995. The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu, and Ni) in the Rhone delta (France). *Mar. Chem.* **51**: 159–175.
- DITORO, D. M., J. D. MAHONY, P. R. KIRCHGRABER, A. L. O'BYRNE, L. R. PASQUALE, AND D. C. PICCIRILLI. 1986. Effects of non-reversibility, particle concentration, and ionic strength on heavy metal sorption. *Environ. Sci. Technol.* **20**: 55–61.
- EREL, Y., J. J. MORGAN, AND C. C. PATTERSON. 1991. Natural levels of lead and cadmium in a remote mountain stream. *Geochim. Cosmochim. Acta* **55**: 707–719.
- FOX, L. E. 1988. The solubility of colloidal ferric hydroxide and its relevance to iron concentrations in river water. *Geochim. Cosmochim. Acta* **52**: 771–777.
- GREENAMOYER, J. M., AND S. B. MORAN. 1997. Investigation of Cd, Cu, Ni and ^{234}Th in the colloidal size range in the Gulf of Maine. *Mar. Chem.* **57**: 217–226.
- GSCHWEND, P. M., AND S.-C. WU. 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environ. Sci. Technol.* **20**: 90–96.
- GUO, L., AND P. H. SANTSCHI. 1996. A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater. *Mar. Chem.* **55**: 113–127.
- AND ———. 1997. Isotopic and elemental characterization of colloidal organic matter from the Chesapeake Bay and Galveston Bay. *Mar. Chem.* **59**: 1–15.
- , ———, L. A. CIFUENTES, S. TRUMBORE, AND J. SOUTHON. 1996. Cycling of high-molecular-weight organic matter in the Middle Atlantic Bight as revealed by carbon isotopic (^{13}C and ^{14}C) signatures. *Limnol. Oceanogr.* **41**: 1242–1252.
- GUSTAFSSON, O., K. P. BUESSELER, AND P. M. GSCHWEND. 1996. On the integrity of cross-flow filtration for marine organic colloids. *Mar. Chem.* **55**: 93–111.
- AND P. M. GSCHWEND. 1997. Aquatic colloids: Concepts,

- definitions, and current challenges. *Limnol. Oceanogr.* **42**: 519–528.
- HONEYMAN, B. D., AND P. H. SANTSCHI. 1988. Metals in aquatic systems. *Environ. Sci. Technol.* **22**: 862–871.
- AND ———. 1989. A Brownian-pumping model for oceanic trace metal scavenging: Evidence from Th isotopes. *J. Mar. Res.* **47**: 951–992.
- AND ———. 1991. Coupling adsorption and particle aggregation: Laboratory studies of “colloidal pumping” using Fe-59-labeled hematite. *Environ. Sci. Technol.* **25**: 1739–1747.
- AND ———. 1992. The role of particles and colloids in the transport of radionuclides and trace metals in the ocean, p. 379–423. *In* J. Buffle and H. P. Leeuwen. [eds.], *Environmental particles*. Lewis.
- HOROWITZ, A. J., K. A. ELRICK, AND M. R. COLBERG. 1992. The effect of membrane filtration artifacts on dissolved trace element concentrations. *Water Res.* **26**: 753–763.
- , K. R. LUM, J. R. GARBARINO, G. E. M. HALL, C. LEMIEUX, AND C. R. DEMAS. 1996. Problems associated with using filtration to define dissolved trace element concentrations in natural water samples. *Environ. Sci. Technol.* **30**: 954–963.
- JANNASCH, H. W., B. D. HONEYMAN, L. S. BALISTRERI, AND J. W. MURRAY. 1988. Kinetics of trace element uptake by marine particles. *Geochim. Cosmochim. Acta* **52**: 567–577.
- KILDUFF, J., AND WEBER, W. J., JR. 1992. Transport and separation of organic macromolecules in ultrafiltration processes. *Environ. Sci. Technol.* **26**: 569–577.
- KOIKE, I., S. HARA, K. TERAUCHI, AND K. KOGURE. 1990. Role of sub-micrometre particles in the ocean. *Nature* **345**: 242–244.
- KRAEPIEL, A. M. L., J.-F. CHIFFOLEAU, J.-M. MARTIN, AND F. M. M. MOREL. 1997. Geochemistry of trace metals in the Gironde estuary. *Geochim. Cosmochim. Acta* **61**: 1421–1436.
- LAXEN, D. P. H., W. DAVISON, AND C. WOOF. 1984. Manganese chemistry in rivers and streams. *Geochim. Cosmochim. Acta* **48**: 2107–2111.
- MARTIN, J. M., AND M. DALI. 1995. Significance of colloids in the biogeochemical cycling of organic carbon and trace metals in the Venice Lagoon (Italy). *Limnol. Oceanogr.* **40**: 119–131.
- MAYER, L. M. 1982. Aggregation of colloidal iron during estuarine mixing: Kinetics, mechanism, and seasonality. *Geochim. Cosmochim. Acta* **46**: 2527–2535.
- MEANS, J. L., R. F. YURETICH, D. A. CRERAR, D. J. J. KINSMAN, AND M. P. BORCSIK. 1981. Hydrogeochemistry of the New Jersey Pine Barrens. New Jersey Department of Environmental Protection.
- MORAN, S. B., P. A. YEATS, AND P. W. BALLS. 1996. On the role of colloids in trace metal solid-solution partitioning in continental shelf waters: A comparison of model results and field data. *Cont. Shelf Res.* **16**: 397–408.
- MOREL, F. M. M., AND P. M. GSCHWEND. 1987. The role of colloids in the partitioning of solutes in natural waters, p. 405–422. *In* W. Stumm. [ed.], *Aquatic surface chemistry: Chemical processes at the particle-water interface*. John Wiley and Sons.
- MORGAN, M. D., AND K. R. PHILIPP. 1986. The effect of agricultural and residential development on aquatic macrophytes in the New Jersey Pine Barrens. *Biol. Conserv.* **35**: 143–158.
- MURKES, J. 1990. Fundamentals of cross-flow filtration. *Separ. Purif. Methods* **19**: 1–29.
- NYFFELER, U. P., Y.-H. LI, AND P. H. SANTSCHI. 1984. A kinetic approach to describe trace element distribution between particles and solution in natural aquatic systems. *Geochim. Cosmochim. Acta* **48**: 1513–1522.
- POWELL, R. T., W. M. LANDING, AND J. E. BAUER. 1996. Colloidal trace metals, organic carbon and nitrogen in a southeastern U.S. estuary. *Mar. Chem.* **55**: 165–176.
- RASPOR, B. 1980. Distribution and speciation of cadmium in natural waters, p. 147–236. *In* J. O. Nriagu [ed.], *Cadmium in the environment, part I: Ecological cycling*. John Wiley and Sons.
- REES, T. F., AND J. F. RANVILLE. 1990. Collection and analysis of colloidal particles transported in the Mississippi River, U.S.A. *J. Contam. Hydrol.* **6**: 241–250.
- REITMEYER, R., R. T. POWELL, W. M. LANDING, AND C. I. MEASURES. 1996. Colloidal aluminum and iron in seawater: An intercomparison between various cross-flow ultrafiltration systems. *Mar. Chem.* **55**: 75–91.
- RICH, H. W., AND F. M. M. MOREL. 1990. Availability of well-defined iron colloids to the marine diatom *Thalassiosira weissfloggi*. *Limnol. Oceanogr.* **35**: 652–662.
- ROSTAD, C. E., J. A. LEENHEER, AND S. R. DANIEL. 1997. Organic carbon and nitrogen content associated with colloids and suspended particulates from the Mississippi River and some of its tributaries. *Environ. Sci. Technol.* **31**: 3218.
- ROZAN, T. F., N. PARRETT, AND G. BENOIT. 1998. Identifying specific trace metal-EDTA complexes in river water using differential pulse cathodic stripping voltammetry. *EOS Trans. Am. Geophys. Union (suppl.)* **79**: S140.
- SANTSCHI, P. H. 1996. Colloids in marine environments: Composition, origin and apparent turnover times, p. 166. *Proceedings of the AGU/ASLO Ocean Sciences Meeting, San Diego, CA.*
- , J. J. LENHART, AND B. D. HONEYMAN. 1997. Heterogeneous processes affecting trace contaminant distribution in estuaries: The role of natural organic matter. *Mar. Chem.* **58**: 99–125.
- SANUDO-WILHELMY, S. A., I. RIVERA-DUARTE, AND A. R. FLEGAL. 1996. Distribution of colloidal trace metals in the San Francisco Bay estuary. *Geochim. Cosmochim. Acta* **60**: 4933–4944.
- SHERRELL, R. M. 1991. Collection of oceanic SPM for trace metal analysis using a new in situ pump, p. 285–294. *In* D. C. Hurd and D. W. Spencer [eds.], *Marine particles: Analysis and characterization*, Geophys. Monograph Ser., vol. 63. AGU.
- AND E. A. BOYLE. 1992. The trace metal composition of suspended particles in the oceanic water column near Bermuda. *Earth Planet. Sci. Lett.* **111**: 155–174.
- AND J. M. ROSS. 1999. Temporal variability of trace metals in New Jersey Pinelands streams: Relationships to discharge and pH. *Geochim. Cosmochim. Acta*. In press.
- SHILLER, A. M., AND H. E. TAYLOR. 1996. Comment on “Problems associated with using filtration to define dissolved trace element concentrations in natural water samples.” *Environ. Sci. Technol.* **55**: 3241–3251.
- SHOLKOVITZ, E. R. 1978. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co, and Cd during estuarine mixing. *Earth Planet. Sci. Lett.* **41**: 77–86.
- AND D. COPLAND. 1981. The coagulation, solubility, and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co, and humic acids in a river water. *Geochim. Cosmochim. Acta* **45**: 181–189.
- SIGG, L. 1987. Surface chemical aspects of the distribution and fate of metal ions in lakes, p. 319–349. *In* W. Stumm [ed.], *Aquatic surface chemistry*. John Wiley and Sons.
- SMITH, G. J., AND A. R. FLEGAL. 1994. Temporal and spatial variations in the cycling of silver within San Francisco Bay estuarine waters. *Estuaries* **16**: 547–558.
- STEVENSON, F. J., AND G. F. VANCE. 1989. Naturally occurring aluminum-organic complexes, p. 117–145. *In* G. Sposito. [ed.], *The environmental chemistry of aluminum*. CRC Press.
- STORDAL, M. C., G. A. GILL, L.-S. WEN, AND P. H. SANTSCHI. 1996. Mercury phase speciation in the surface waters of three Texas estuaries: Importance of colloidal forms. *Limnol. Oceanogr.* **41**: 52–61.
- STUMM, W. 1992. Chemistry of the solid-water interface: Processes

- at the mineral-water and particle-water interface in natural systems. John Wiley and Sons.
- TURNER, R. S., A. H. JOHNSON, AND D. WANG. 1985. Biogeochemistry of aluminum in McDonalds Branch Watershed, New Jersey Pine Barrens. *J. Environ. Qual.* **14**: 314–323.
- WEDEPOHL, K. H. 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* **59**: 1217–1232.
- WELLS, M., AND E. D. GOLDBERG. 1992. Marine submicron particles. *Mar. Chem.* **40**: 5–18.
- , P. B. KOZELKA, AND K. W. BRULAND. 1998. The complexation of 'dissolved' Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI. *Mar. Chem.* **62**: 203–217.
- AND L. M. MAYER. 1991. Variations in the chemical lability of iron in estuarine, coastal and shelf waters and its implications for phytoplankton. *Mar. Chem.* **32**: 195–210.
- WEN, L.-S., P. SANTSCHI, G. GILL, AND C. PATERNOSTRO. 1999. Estuarine trace metal distributions in Galveston Bay: Importance of colloidal forms in the speciation of the dissolved phase. *Mar. Chem.* **63**: 185–212.
- , ———, AND D. TANG. 1997. Interactions between radioactively labeled colloids and natural particles: Evidence for colloidal pumping. *Geochim. Cosmochim. Acta* **61**: 2867.
- , M. C. STORDAL, D. TANG, G. A. GILL, AND P. H. SANTSCHI. 1996. An ultraclean cross-flow filtration technique for the study of trace metals phase speciation in sea water. *Mar. Chem.* **55**: 129–155.
- WHITEHOUSE, B. G. 1990. Cross-flow filtration of colloids from aquatic environments. *Limnol. Oceanogr.* **35**: 1368–1375.
- WINDOM, H. L., R. G. SMITH, AND M. MAEDA. 1985. The geochemistry of lead in rivers, estuaries and the continental shelf of the southeastern United States. *Mar. Chem.* **17**: 43–56.

Received: 18 August 1998

Accepted: 26 February 1999

Amended: 10 March 1999