



The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers

GABOURY BENOIT* and TIM F. ROZAN†

Yale School of Forestry and Environmental Studies, 370 Prospect Street, New Haven, CT 06511, USA

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Abstract—The particle concentration effect (p.c.e.) is an unexpected decline in partition coefficients (K_d) as suspended particulate matter (SPM) increases. This anomaly has been attributed to a variety of causes, but most often to the existence of colloidal forms of the adsorbate, which are included, in error, in the dissolved fraction when calculating K_d . To test this hypothesis we have directly measured colloidal, macroparticulate, and truly dissolved metals (Cd, Cu, Pb, Zn, Fe, Al, Mn, Ag) monthly for one year (6/96–7/97) in four Connecticut rivers having a range of ancillary biogeochemical characteristics. These include factors that are all likely to influence partitioning between dissolved and solid phases, such as DOC, pH, and competing cations. The p.c.e. is clearly evident in these rivers, and explicit consideration of colloidal metals eliminates or reduces this anomaly in nearly all cases. Furthermore, a substantial portion of metals occurs in the colloidal fraction, and the amount of colloidal metals increases with SPM. Both of these conditions are necessary for the colloidal model to explain the p.c.e.. Important differences are observed among rivers and metals, and in some cases systematic decreases in K_d continue even when colloidal metals are taken into account. This additional decrease can be eliminated by excluding large particles having negligible surface complexation sites. When corrections are applied for both colloids and large particles, K_d values become truly constant. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

1.1. Background

Trace metals in solution are generally present well below saturation with respect to precipitation of crystalline or amorphous forms of pure minerals. Instead, the amount of dissolved metals is limited by sorption to particles (Turekian, 1977). Partitioning between solids and solution plays a critical, or even dominant, role in the distribution, transport, behavior, and fate of metals in aquatic environments ranging from sediment pore waters and ground waters to rivers, lakes, and oceans.

Partitioning can be described in terms of detailed surface complexation models (Schindler and Gamsjager, 1972; Stumm et al., 1970) only when adequate site-specific data about SPM surface properties are available. The models have recently been applied to natural sediments (Wen et al., 1998), but reliable extrapolation from one system to another may be difficult unless the solid phase is a nearly pure substance. More commonly, modelers and trace metal geochemists rely on a simple partition coefficient, K_d , defined as:

$$K_d = \frac{(\text{mass of filter-retained metal})/(\text{mass of macroparticles})}{(\text{mass of filter-passing metal})/(\text{volume of water})} = \frac{[Me]_{SPM}/SPM}{[Me]_{filt}} \quad (1)$$

(units = $l \text{ kg}^{-1}$). K_d is site specific, but readily calculable from widely measured parameters. In this formulation, metal in each fraction is normalized to the total quantity of its carrier phase, as

would be done if K_d were a true thermodynamic mass action constant. Use of a simple partition coefficient is perhaps the most appropriate approach when dealing with heterogeneous solids, such as most aquatic suspended particulate matter. Because of its simplicity and nearly universal applicability, K_d remains the most widely used parameter to describe critical partitioning of metals between filtrate and filter-retained fractions in aquatic systems.

Although K_d is a conditional constant, there is no reason to expect it to change systematically with variation in the amount of the partitioning phases, solid and solution (Benoit, 1995). Contrary to this expectation, K_d has been observed to decline across several orders of magnitude with increasing concentrations of suspended particulate matter (SPM) in both marine and freshwater environments (Benoit et al., 1994; Honeyman and Santschi, 1988). This anomaly, the particle concentration effect (p.c.e., O'Connor and Connolly, 1980), might be explained by a variety of causes. Each would have its own unique set of geochemical consequences, and each hypothesized cause can be tested in the field or laboratory by an examination of those effects.

The significance of the p.c.e. depends on its cause. The p.c.e. may be an unintended consequence of the nature of filtration through $0.5 \mu\text{m}$ filters. If so, the p.c.e. anomaly has important ramifications for an important and nearly universal separation methodology, which has been written into pollution regulations having multi-billion dollar consequences (e.g., the Clean Water Act and amendments). Alternatively, the p.c.e. may point to unknown gaps in our fundamental phenomenological understanding of the distribution of metals across all size classes from truly dissolved to macroparticulate, or of the kinetics of exchange between dissolved and sorbed phases. Finally, irrespective of its cause, the p.c.e. can be used as a tool to predict partitioning based on a single, commonly-measured parameter, SPM.

† Present address: College of Marine Studies, University of Delaware, 700 Pilottown Road, Lewes, DE 19958.

Table 1. Ranges of some physical and chemical characteristics of the study sites.

		Quinnipiac	Hammonasset	Naugatuck	Pawcatuck
Conductivity	($\mu\text{mhos/cm}$)	250–490	45–105	44–480	49–370
pH	—	6.8–7.9	6.6–7.1	6.8–7.9	4.8–6.8
ANC	($\mu\text{eq/l}$)	630–1850	60–330	125–520	50–380
SPM	(mg/l)	0.8–18.2	0.6–4.5	0.5–8.3	0.8–5.2
DOC	(mgC/l)	1.6–12.1	1.9–6.0	1.2–4.7	3.2–11.6
Ca^{2+}	(mM)	0.54–0.95	0.04–0.15	0.06–0.46	0.06–0.14

1.2. Competing Models

Several causes might explain the p.c.e., including sorption kinetics (Hering and Morel, 1988; Hering and Morel, 1990; Jannasch et al., 1988; Nyffeler et al., 1984), irreversible adsorption or incomplete desorption (Di Toro and Horzempa, 1982), qualitative variations in surface chemistry (Hamilton-Taylor et al., 1993), filtration artifacts (Horowitz et al., 1992), particle-particle interactions (Di Toro et al., 1986), the presence of a non-aqueous dissolved phase (Voice et al., 1983; Voice and Weber, 1985), and the contribution of trace elements bound to colloids included in the filtrate fraction (Benoit, 1995; Benoit et al., 1994; Honeyman and Santschi, 1989; Morel and Gschwend, 1987). Some of these are more easily investigated in laboratory experiments, while others – especially those related to particle size distributions in nature – need to be tested on the basis of careful field measurements. Such tests were not possible in the recent past, at least for fresh waters, since trace metal data were unreliable (Benoit, 1994). Application of clean methods and ultrafiltration techniques finally allows these hypotheses to be evaluated.

At least three possible causes for the p.c.e. require testing based on field data. One possibility is if occurrences of elevated SPM are linked to episodes of high total metal loading. Suspended sediments are heterogeneous, and can be composed of clay minerals, hydrous iron and manganese oxides, amorphous aluminosilicates, calcite, apatite, various kinds of detrital organic matter, and even viable cells. Furthermore, these substances can exist in morphologically complex forms, and trace components can dominate surface composition if they occur as coatings on more abundant substances. As a consequence, SPM possesses a variety of complexation sites characterized by a range of stabilities with various metals, with sites having lower constants (weak sites) much more abundant than ones with higher constants (strong sites) (Dzombak and Morel, 1990). Assuming reversible reactions, at equilibrium metals should occupy the strongest available sites. Thus, at low sorption densities (Γ ng/mg), metals should occupy the few strongest sites, while at high values of Γ , metals are complexed at progressively weaker sites. Thus, periods of high SPM (if linked to high total metals) would be associated with greater dissolved metal concentrations and lower K_d s under this scenario. This hypothesis can be tested by measuring whether the metal to solids ratio changes systematically with SPM.

A second potential explanation would be if periods of high SPM were tied to greater amounts of larger particles with lower surface area. Coarse particulate matter should have fewer complexation/sorption sites per mass (meq/g), and lower K_d values. This hypothesis is intuitively attractive, since elevated dis-

charge could cause both high SPM and resuspension of larger particles. On the other hand, some studies have not found such a correlation (Sturdevant et al., 1994; Warren and Zimmermann, 1994). One way to test this hypothesis is to measure particle size distributions as a function of SPM. Another is to examine whether decreasing K_d s are caused by decreasing $[\text{Me}]_{\text{SPM}}$ (consistent with dilution by large particles) or by increasing $[\text{Me}]_{\text{filt}}$ (eqn. 1).

Third, conventional filters (i.e., those with nominal pore sizes near $0.5 \mu\text{m}$) do not actually discriminate between dissolved and particle-bound forms of metals since colloidal particles can pass through and be counted with the dissolved fraction. Several recent field studies have supported the possibility that systematic variation of the quantity of colloids (mg/l) with SPM can explain the p.c.e. (Benoit, 1995; Benoit et al., 1994; Booi et al., 1997). It is now widely recognized that colloids play a key role in the behavior of trace substances in aquatic environments (Gustafsson and Gschwend, 1997). The purpose of the current research was to test the hypothesis that the p.c.e. is caused by colloids in rivers by directly measuring the colloidal fraction, i.e. by separating truly dissolved metal from that on particles of all size classes. The same data was used to shed light on the other two possible causes. The study was carried out in rivers, dynamic environments marked by substantial and rapid changes in a broad range of biogeochemical conditions, which provide an especially severe test of the causes of the p.c.e..

2. EXPERIMENTAL METHODS

2.1. Sampling Sites

Water samples were collected monthly from four rivers in southern New England: the Naugatuck, Quinnipiac, Hammonasset, and Pawcatuck. These four were selected because they cover a broad spectrum of background chemistry and extent of development (presence of contaminant metals) within a small geographic area (Table 1). Sampling dates covered a range of seasonal conditions and river discharge (Fig. 1). In general, an effort was made to sample the rivers under baseflow conditions, defined here as at least 48 h after the last storm event. Discharge was monitored for the Quinnipiac River alone (USGS gauging station data for Sta. 01196500- Quinnipiac River at Wallingford, CT, Fig. 1), but this site is located near the center of the area studied and should represent qualitatively the other sites as well.

2.2. Sample Collection

Samples were filtered during collection in the field by passage through $0.45 \mu\text{m}$ nominal pore size filters (Millipore™ Durapore®). Care was taken to avoid overloading filters, which can cause a decrease in effective pore size and variable removal of colloidal particles (Horowitz et al., 1996; Shiller and Taylor, 1996). Extensive tests have shown that, for our study sites, a nearly constant size fraction of

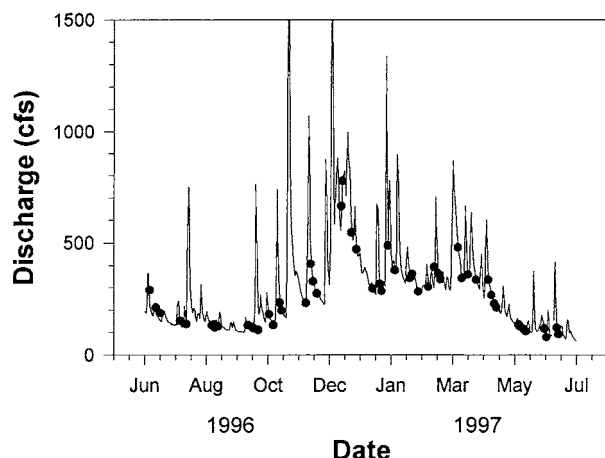


Fig. 1. Discharge of the Quinnipiac River during the study period. The line indicates average daily flow, while filled circles indicate dates when rivers were sampled (one or two each day). Samples were collected during the lowest seasonal flow conditions (i.e., baseflow). Discharge data are plotted only for the Quinnipiac, but the other three rivers should have similar hydrographs.

particles is removed by filtration until back-pressure begins to increase dramatically (near 100 kPa). We also found that the Durapore filters remove an identical size fraction compared to Nuclepore™ screen-type filters, but that the latter begin to clog much sooner, making them impractical for river samples of the requisite volume. After filtration, samples were packed in ice for transport to the laboratory, where they were processed immediately. Ultrafiltration was started within 2 h of sample collection as recommended by Wen et al. (1996).

2.3. Chemical Analyses

Sample collection, processing, and metal analyses (Cd, Cu, Pb, Zn, Ag, Fe, Al, and Mn) were all carried out following strict clean method protocols (Benoit, 1994; Benoit et al., 1997), with all laboratory manipulations performed in a Class 100 clean room. Transverse flow ultrafiltration was conducted with polysulfone hollow-fiber filters of 3,000 M.W. nominal cutoff (Amicon™ model H1P3-20). In previous research (Wang and Benoit, 1996), high-pressure size exclusion chromatography indicated that these same filters separate very close to their rated pore size, at least for the soil colloids studied. Since the selection of 3000 MW is arbitrary, and ultrafilters are not perfect size discriminators, the terms “colloidal” and “truly dissolved” should be understood to be operationally defined in this study.

Ultrafiltration, like all sample manipulations, is subject to a variety of potential artifacts (Buesseler et al., 1996; Buffle and Leppard, 1995; Chen and Buffle, 1996a; Chen and Buffle, 1996b), and care was taken to avoid these to the greatest extent possible. Filters are exhaustively cleaned and conditioned between runs to avoid cross-contamination and metal sorption to the filters (Wen et al., 1996). Mass balances were calculated for all runs, comparing a total 0.45 μm filtered sample to the sum of colloidal and ultrafiltrate fractions, which agreed within $100 \pm 10\%$, except for Fe, which sometimes had a greater difference. To reduce artifacts, samples were ultrafiltered with minimum back-pressure (<30 kPa) and with a concentration factor of 7:1 (Wen et al., 1996). As with conventional filtration, ultrafiltration does not provide absolute size cut-off, and some particles smaller than the nominal value are retained, while some that are larger pass through the ultrafilter (Guo and Santschi, 1996).

Samples for analysis of dissolved metals were preserved with 2 ml concentrated ultrapure HNO_3 per liter of solution to a final pH of 1.5. Particulate samples were extracted with hot concentrated HNO_3 , evaporated to dryness, and redissolved in 0.2% HNO_3 for measurement by

graphite furnace-atomic absorption spectroscopy (GFAAS). Dissolved metals were preconcentrated by chelation with APDC-DDDC and extracted into chloroform (Bruland et al., 1985) then re-extracted into a small volume of acid before measurement by GFAAS. Zinc, Fe, Mn, and Al, metals which generally occurred at higher concentrations, were measured by inductively coupled plasma-atomic emission spectroscopy. DOC, COC (colloidal organic carbon), and truly dissolved organic carbon were measured via high temperature catalytic oxidation on a Shimadzu organic carbon analyzer.

2.4. Data Reduction

The standard partition coefficient, K_d , was calculated by eqn. 1. The colloid-corrected partition coefficient, K_d^c , was calculated according to the following relation:

$$K_d^c = \frac{[Me]_{SPM+CPM}}{[Me]_{diss}} \quad (2)$$

Where $[Me]_{SPM+CPM}$ is the sum of metals captured by 0.5 μm filters and 3000 MW ultrafilters divided by the mass of macroparticles and colloids collected in the same fashion, and $[Me]_{diss}$ is the mass of metals passing the ultrafilter, normalized to the volume of solution. Expanding terms, eqn. 2 can be rewritten as:

$$K_d^c = \frac{([Me]_{SPM} + [Me]_{CPM})/(SPM + CPM)}{[Me]_{diss}} \quad (3)$$

Where $[Me]_{CPM}$ is the mass of metals retained by the ultrafilter, and CPM is the concentration of total colloids retained by the ultrafilter. Macroparticulate mass was determined gravimetrically, while colloidal particulate mass was calculated from the total mass of colloidal C, Fe, Al, and Mn, assuming that they occurred as CH_2O , $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and MnO_2 , respectively. In the rivers tested, most of the colloidal matter was organic, and K_d^c was not sensitive to reasonable changes in the assumed form of C, Fe, Al, and Mn (e.g., Al as various clay minerals).

2.5. Statistical Analyses

Linear regression analyses were carried out with the software package SigmaStat for Windows, ver. 1.0 (Jandel Corp.), which yielded regression slopes, coefficients of determination (R^2), P values, and standard errors of the regression (S.E.). Significance of changes in slope between treatments was determined by comparing the difference in slopes with the combined standard errors. Values of S.E. were added in quadrature (combined error = $[(S.E.1)^2 + (S.E.2)^2]^{1/2}$), as is appropriate for random independent errors (Taylor, 1982). When the ratio of the difference in slope to the combined error is 2.0 or greater, then the difference is significant at the $P = 0.05$ level. In this analysis and elsewhere, except where noted, the criterion for significance was a P value of 0.05, i.e. the probability of concluding that two treatments are different when they are actually the same is $\leq 5\%$. This threshold is arbitrary, but widely used.

3. RESULTS AND DISCUSSION

3.1. Confirmation of the P.C.E. and the Colloidal Model

The p.c.e. is clearly evident for the metals Pb, Cd, Cu, Zn, and Ag in the four rivers studied (Figs. 2a–5a, 6). Combining all the data, correlations are robust above the $P = 0.0001$ probability level for each metal. Rivers were intentionally sampled under baseflow conditions, so SPM varied by only a factor of 30. However, using a larger data set that includes storm event sampling for the Quinnipiac River alone, the trend continues for more than two orders of magnitude in SPM. (The storm event samples were not measured for colloidal forms of metals, so they are not included in subsequent analyses.) Slopes

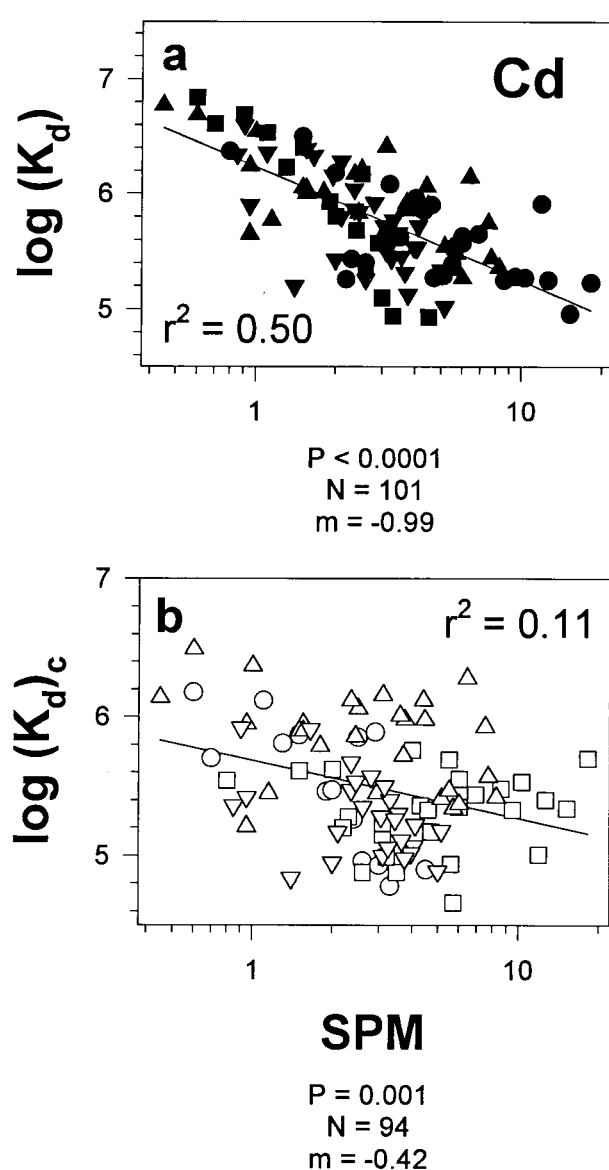


Fig. 2. (a) The p.c.e. is clearly evident for the metal Cd when data are pooled from all sites. Nearly all individual sites also have statistically significant linear regressions for the log-normalized data. Circles are data for the Quinipiac River, squares are the Hammonasset River, triangles are the Naugatuck River, and inverted triangles are the Pawcatuck River. (b) Including colloidal forms of metals in the particulate metal fraction causes the slopes of the lines to flatten and the significance of the regressions to decline for Cd. (According to the colloidal model, the slope of all the regression lines should become zero when plotted in this way.) As shown in Table 2, there is a significant difference between the slopes of the two treatments for Cd.

on the log-log plots are between -0.48 and -0.99 , similar to values reported for other systems, which tend to cluster around -0.7 (e.g., Benoit et al., 1994).

Metals that passed $0.45 \mu\text{m}$ filters were further discriminated with $3,000 \text{ MW}$ ultrafilters, and a substantial portion fell within the colloidal fraction. All sites produced roughly similar results, and yielded the following averaged amounts of colloidal metals expressed as a fraction of the $0.45 \mu\text{m}$ filtrate amount:

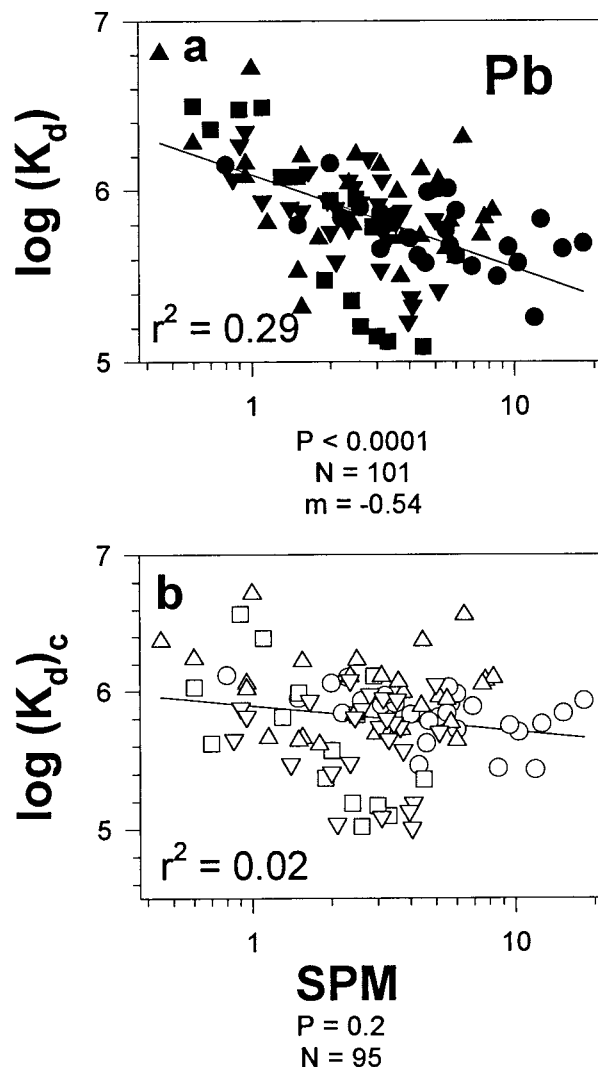


Fig. 3. Same as Fig. 2, but for Pb.

Pb 46%, Cd 32%, Cu 53%, Zn 43%. These values are similar to that for DOC which averaged 50% colloidal in the four rivers. The existence of a large proportion of colloidal metals is necessary if the p.c.e. is caused by colloids.

For Cd, Pb, and Zn, the slopes of the p.c.e. lines approach zero and the strengths of the correlations decline or are eliminated when dissolved forms are differentiated from particulate ones at $3,000$ nominal MW (Figs. 2b, 3b, and 5b, Table 2). Table 2 shows that the differences in slope of the two treatments for Cd, Pb, and Zn are more than two times the combined standard errors, indicating that the changes in slope are statistically significant above the 0.05 probability level. For Cu this is true in two of the four rivers studied (Hammonasset and Naugatuck). The ultrafiltration-induced reduction in the p.c.e. is compelling evidence that colloidal metals passing through $0.45 \mu\text{m}$ filters are an important cause of this effect. At the same time, the failure of ultrafilters to eliminate the p.c.e. completely in all cases implies that other, secondary causes are active as well, or that colloids smaller than 3000 MW play an important role.

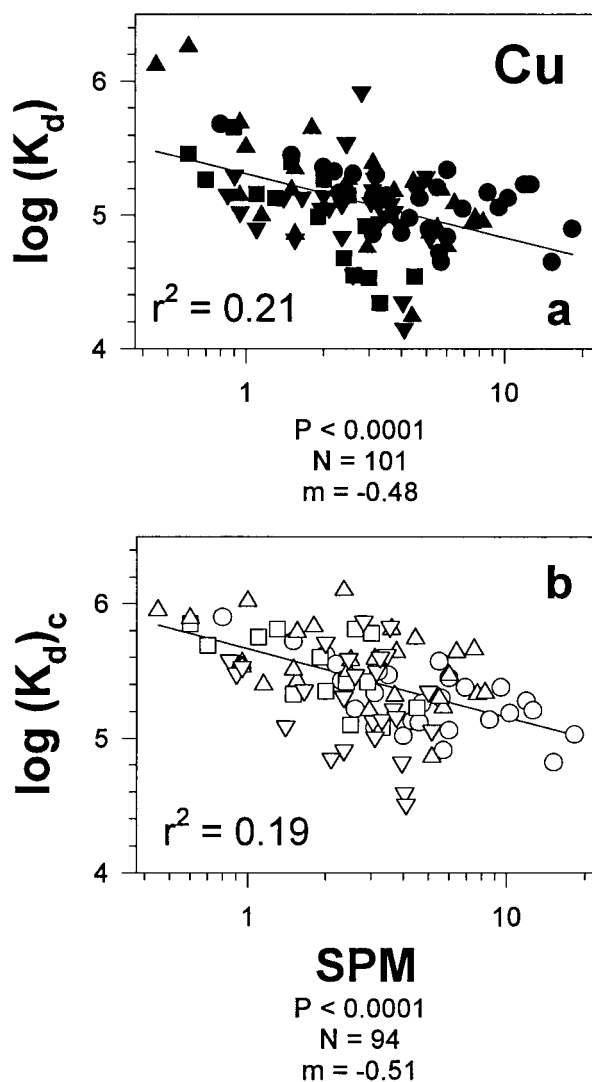


Fig. 4. Symbols same as Fig. 2, but for Cu. The Cu results are largely unaffected by including colloidal forms. This may be because Cu is bound mainly to colloids that pass through the 3,000 MW ultrafilter.

Pooling all the data yields a large N and very robust statistics, but it misses some of the variety among rivers and metals. With four metals and four rivers there are sixteen possible river-metal combinations. (Due to the very low concentrations of Ag found in natural waters, colloidal forms of Ag were not determined, so calculation of K_d^c was not possible for this metal. The major metals Al, Fe, and Mn, are discussed separately later.) Some of these sixteen individual cases contrast with the broader trends. For example, for the Pawcatuck River, Cu and Zn did not exhibit the p.c.e. (correlations not significant at the 0.05 probability level or better. The other 14 cases are all significant at the $P = 0.02$ level or better.) In 12 cases, the exclusion of colloids from the dissolved fraction caused a decrease in the slope of the correlation between K_d and SPM. Because of the relatively small sample size for individual rivers, standard errors of regression slopes were comparatively large. Still, in half of the sixteen cases the decline in slope was

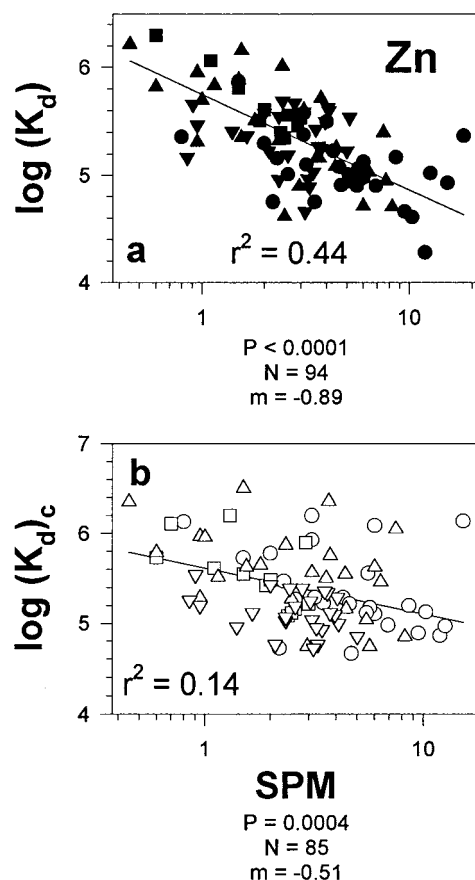


Fig. 5. Same as Fig. 2, but for Zn.

statistically significant at the $P = 0.10$ probability level, and five of these were significant at the $P = 0.05$ level.

3.2. Tests of Other Models

3.2.1. Does metal loading increase with SPM?

The current data can be used to test the hypothesis that the p.c.e. is caused by increased metal loading and consequent filling of weaker surface complexation sites. For the combined data, there is not a significant positive relationship between metal loading and SPM for any metal. On the other hand, for both the Hammonasset and Pawcatuck considered individually, there are strong *negative* correlations between metal loading and SPM. This means that, for these two rivers, as SPM increased there tended to be more particulate matter available per mass of metal. If anything, under these conditions one would expect a higher occupancy of scarcer strong surface complexation sites with increasing SPM. Overall, this data clearly does not support the hypothesis that the p.c.e. results from increasing competition for strong sites at high SPM concentrations.

3.2.2. Filter overloading

Another possible explanation for the p.c.e., associated with filtration artifacts, can be discounted outright, since the pro-

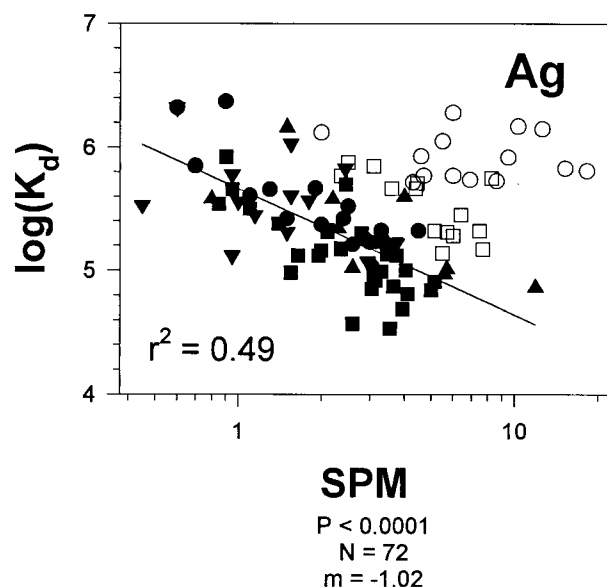


Fig. 6. The p.c.e. for Ag is strongly expressed by the four rivers (solid symbols) once data from the contaminated downstream stations on the Quinnipiac and Naugatuck Rivers (open symbols) are removed. At these sites, Ag inputs in secondary sewage effluents may not equilibrate among all size classes rapidly. Colloidal forms of Ag were not measured at any site.

posed cause leads to the opposite of the expected effect. Recent studies show that for some elements, especially Fe, Al, and Mn, much of the metal occurs in the form of colloids, which are removed with increasing efficiency as filters are progressively overloaded (Horowitz et al., 1996; Shiller and Taylor, 1996). Trace metals associated with these major metals should exhibit similar behavior. Since filter loading is likely to increase with SPM, a systematic decrease in filtrate (dissolved) metal should occur with increasing SPM. This trend would cause the opposite of the p.c.e..

Table 2. Slope of regressions, standard errors, and significance evaluation for Figs. 2–5.

		Slope	Std Error	t*
Cd	K_d	-0.99	0.100	-3.6
	K_d^c	-0.42	0.123	
Cu	K_d	-0.48	0.095	-0.1
	K_d^c	-0.46	0.099	
Pb	K_d	-0.54	0.086	-2.9
	K_d^c	-0.15	0.105	
Zn	K_d	-0.89	0.105	-2.2
	K_d^c	-0.51	0.137	

*Difference in slope divided by combined error. A value of 2 implies a 95% probability of significant difference, while 3 corresponds to a 99.7% probability.

3.2.3. Dilution of SPM by inert “mega-particles”

Another possible explanation is dilution of the solids pool at high SPM by particles having few complexation sites (Fig. 7, case I). These could be large “mega-particles” and thus have small specific surface area (as illustrated), or they could be composed of materials with intrinsically low abundance of sorption sites (e.g., quartz). This explanation does indeed seem to be an important contributing cause of the p.c.e. in these rivers. Evidence is provided by statistically significant negative correlations between sorption density (Γ , ng/mg) and SPM on log-log plots, which are observed in the majority of cases. Specifically, 74% of all possible metal-river pairings (five metals $\times$ seven river sites) had correlations that were significant at the 0.05 probability level or better. If added particles carry no metals ($\Gamma_{\text{new}} = 0$) and also adsorb none from river water (case I), then:

$$\Gamma = \Gamma_0 \times \frac{SPM_0}{SPM} \quad (4)$$

$$\Gamma = (\Gamma_0 \times SPM_0) \times SPM^{-1} \quad (5)$$

$$\log(\Gamma) = k - 1.0 \times \log(SPM) \quad (6)$$

So, in case I, the slope of the line should be -1.0 . In fact, in 10 of the 26 cases where a correlation is evident, the slope is different from -1.0 by less than one times the standard error of the regression, and in an additional 8 cases it is within two times the S.E.. (Case I behavior is not ruled out as a *contributing* cause in the remaining cases.) Slopes of -1 are evidence that the decline in the proportion of particulate metal is often the result of addition of nearly inert particles that are almost free from metals. Further evidence is provided by calculated values of K_p , the partition coefficient for macroparticles interacting with truly dissolved metals (i.e., those in the <3000 MW size fraction). For case I, K_p should decline as SPM is added. For the four metals for which data are available (Cd, Cu, Pb, and Zn), $\log(K_p)$ declined with $\log(SPM)$, with slopes ranging from -0.6 to -0.9 .

Negative correlations between sorption density and SPM could result from an alternative process: addition of macroparticles having surface characteristics comparable to ambient SPM, but with lower initial Γ (Fig. 7, case II). But this explanation does not cause slopes of -1.0 (for log-log plots of Γ against SPM), or K_p values that decline with increasing SPM. This is evidence that the decline in the proportion of particulate metal is often the result of addition of inert particles rather than normal sorption behavior of a single class of particles that are similar to ambient macroparticles.

3.3. Modeling the P.C.E. in the Hammonasset River: The Role of Colloids and Mega-Particles

3.3.1. A significant role for both colloids and mega-particles

The Hammonasset River has a relatively homogeneous, lightly developed watershed. In this system, samples at any time reflect a mix of sources that are relatively similar in nature and that have reacted and been transported under comparable environmental conditions. Probably for this reason, correlations in the data tended to be strongest and most consistent for this

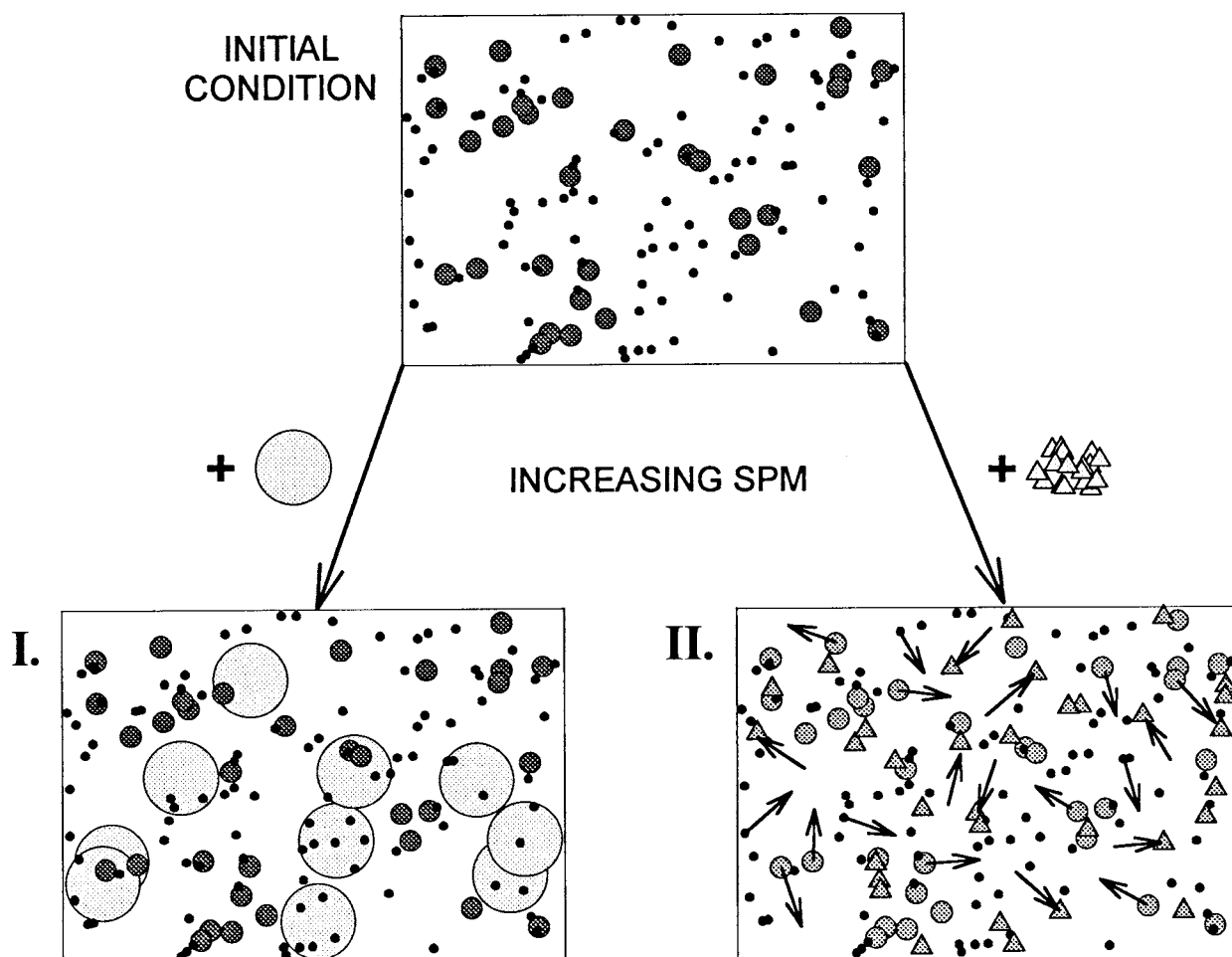


Fig. 7. Schematic diagram illustrating the possible causes of the negative correlation between Γ (metal sorption density on particles) and SPM. When SPM is low (initial condition), it includes macroparticles that are larger than the pores of standard 0.5 mm filters along with colloids that pass through the filters. (In this and subsequent panels, each size class is shown, for simplicity, as being monodisperse. In fact, there is likely to be a range of sizes in both the macroparticulate and colloidal fractions. The sorption density, Γ , on each size class is represented by the intensity of gray shading.) Addition of SPM can occur in a range between two endmembers represented by panels I and II. In I, added macroparticles have very few sorption sites per mass either because they are large and have a low specific surface area, are composed of materials that do not sorb metals, or for other reasons. There is no shift in the equilibrium other than a dilution of the macroparticulate mass. In this case, the average Γ and the macroparticulate partition coefficient (K_p) should both decline on a one-for-one basis with the added mass. This was true for about half the river-metal combinations. In II, added SPM (represented by triangles) has a density of sorption sites similar to that of ambient macroparticles. Metals exchange with solution in order to reach a new equilibrium. If the added SPM initially carries less metal than the ambient macroparticles, the average Γ declines, as was observed in the rivers studied. However, addition of type II macroparticles is not consistent with commonly observed slopes of -1 or the decrease in K_p with increasing SPM.

river. Usually, characteristics that did covary had their highest correlation coefficients and occurred across more metals in the Hammonasset than in other rivers (Table 3). In particular, colloidal metals increased with SPM, consistent with the colloidal model.

In the Hammonasset River, colloidal and dissolved forms of metals correlate with various size fractions of solids from macroparticulate (SPM) to colloidal (CPM) to truly dissolved (DOC). (The latter fraction includes large molecular weight material, some of which arguably might belong in the colloidal pool.) The solids also correlate among themselves. Together these results suggest that systematic relations exist across all

size fractions from macroparticulate to truly dissolved. The data support the notion of dynamic self-regulation of size distribution, across seasons and changes in discharge, through interaction and competition among processes of aggregation (Brownian, shear, and differential settling types), disaggregation, and generation of new particles. Table 3 also indicates that some parameters correlate well with temperature, which we believe to be a consequence of seasonal changes in biogeochemical cycling in this river.

The clearly expressed links among the functional parts of this river-watershed system make it especially well suited for modeling. As noted before, the p.c.e. is very clearly evident in

Table 3. Values of r^2 for correlations among various trace metal fractions and chemical and physical characteristics of the Hammonasset River.

Dependent variable	Independent variable		Pb	Cd	Cu	Zn	Ag
log(K_d)	log(SPM)		0.78	0.86	0.66	0.75	0.58
Metal load	SPM	—	0.57	0.52	0.49	0.47	0.56
Colloidal Me	DOC	—	0.57	0.45	0.29	0.05	—
Colloidal Me	CPM	—	0.38	0.01	0.32	0.01	—
Colloidal Me	SPM	—	0.76	0.57	0.31	0.00	—
Dissolved Me	DOC	—	0.56	0.72	0.70	0.01	0.19
Dissolved Me	SPM	—	0.54	0.77	0.72	0.02	0.31
Me on Particles	SPM	—	0.79	0.68	0.43	0.47	0.42
Truly Dissolved Me	SPM	—	0.34	0.71	0.72	0.43	0.31
CPM	SPM	0.58	—	—	—	—	—
DOC	SPM	0.70	—	—	—	—	—
CPM	DOC	0.59	—	—	—	—	—
DOC	T	0.63	—	—	—	—	—
SPM	T	0.71	—	—	—	—	—
ANC	T	0.67	—	—	—	—	—

In most cases $N = 15$, and the 95% confidence level ($P = 0.05$) corresponds to $r^2 = 0.26$. The correlations of metal load, metal on particles, and K_d with SPM are negative, all others are positive.

the Hammonasset, as it is in the other rivers (Figs. 8a, 9a). Explicitly including colloidal metals in the particulate fraction causes the slope of the regression between K_d and SPM to decline significantly and the strength of the correlation to be reduced substantially (Figs. 8b, 9b). Nevertheless, a dependence of K_d on SPM remains. A further correction can be applied, accounting for the decrease in metal concentration on particles as SPM increases, a phenomenon which we have attributed to dilution of SPM by large particles having few surface complexation sites (e.g., quartz grains). The simplest model is to assume that the increase in SPM is caused by resuspension of a class of particles, which we term “mega-particles”, having no binding sites. This dilution can be quantified via the correlation between metal concentrations on macroparticles and SPM, and the effect of mega-particles can be subtracted. When this correction alone is done for the Hammonasset River (Figs. 8c, 9c), the slopes and correlation strengths decline, but a significant relationship still exists between K_d and SPM. This suggests that both the presence of colloidal metals and large unreactive mega-particles contribute to the p.c.e. in rivers. Only when both the influence of colloids and mega-particles are considered simultaneously is a significant correlation eliminated completely (Figs. 8d, 9d). For the Cd data, the changes in slope for all three treatments is statistically significant above the 0.01 probability level. For Pb, the changes are significant above the 0.05 probability level except for the difference in slope between K_d and K_d^c which is significant at the 0.10 level.

Spurious correlations can result when trends in normalized data are sought as a function of the normalizing parameter, as here (Fig. 10) where the ratio $[Me]_{part}/SPM$ is plotted against SPM (Berges, 1997). In the present instance, a real effect is clearly evident; an expected increase in $[Me]_{part}$ with SPM is not found. The resultant correlations between $[Me]_{part}/SPM$ and SPM are a convenient mathematical way of capturing this phenomenon and describing it for modeling purposes. The same correlations evident for the Hammonasset River are seen in the other three rivers, though not with the same frequency. This we attribute to the more highly developed and heteroge-

neous nature of their respective watersheds. They include dense urban areas, secondary sewage treatment plants, permitted industrial discharges, and historically contaminated sediments and floodplains (Benoit, 1994; Benoit and Rozan, 1996; Rozan et al., 1994). Samples collected from these other rivers at any point represent a blend of source waters (e.g., uncontaminated groundwater, urban runoff, treated sewage effluent, etc.) that has had an opportunity to mix and react for only a few hours, the residence time of water in the rivers. If equilibrium is not achieved rapidly, then this combination of source chemistries can introduce significant scatter into any trends that might otherwise be present.

3.3.2. Direct measurement of macroparticulate size distribution

We further investigated the apparent importance of mega-particles in causing part of the p.c.e. by directly measuring the SPM size distribution over the course of one rainstorm on the Quinnipiac River (18 September 1997). The size distribution was elucidated with graded filters (Millipore MF) having nominal pore sizes of 0.45, 0.8, 1.2, 3.0, and 8.0 μm . While filters may not provide completely faithful size distributions, they do at least supply qualitative profiles. During the storm there was a large and steady increase in total SPM from 8.6 to 22.9 mg/l (Fig. 11a). The proportions of suspended matter mass in each measured size fraction shifted at the start of the storm, with larger sizes increasing compared to smaller ones (Fig 11b). Proportions for most size classes were largely constant after the first hour of the 5 h period examined, though the $>8 \mu m$ fraction continued to increase for 3 h. Overall, the results provide only qualified evidence for dilution by mega-particles, consistent with some previous studies (Sturdevant et al., 1994; Warren and Zimmermann, 1994). However, the measured variations reflect a single storm event rather than the seasonal changes under baseflow conditions that were monitored in the rest of this study. The data also do not provide information on changes in size distribution within the size class larger than 8.0 μm , where most of the total SPM was found in this one experiment. The data are also for a river (Quinnipiac)

Hammonasset Cd

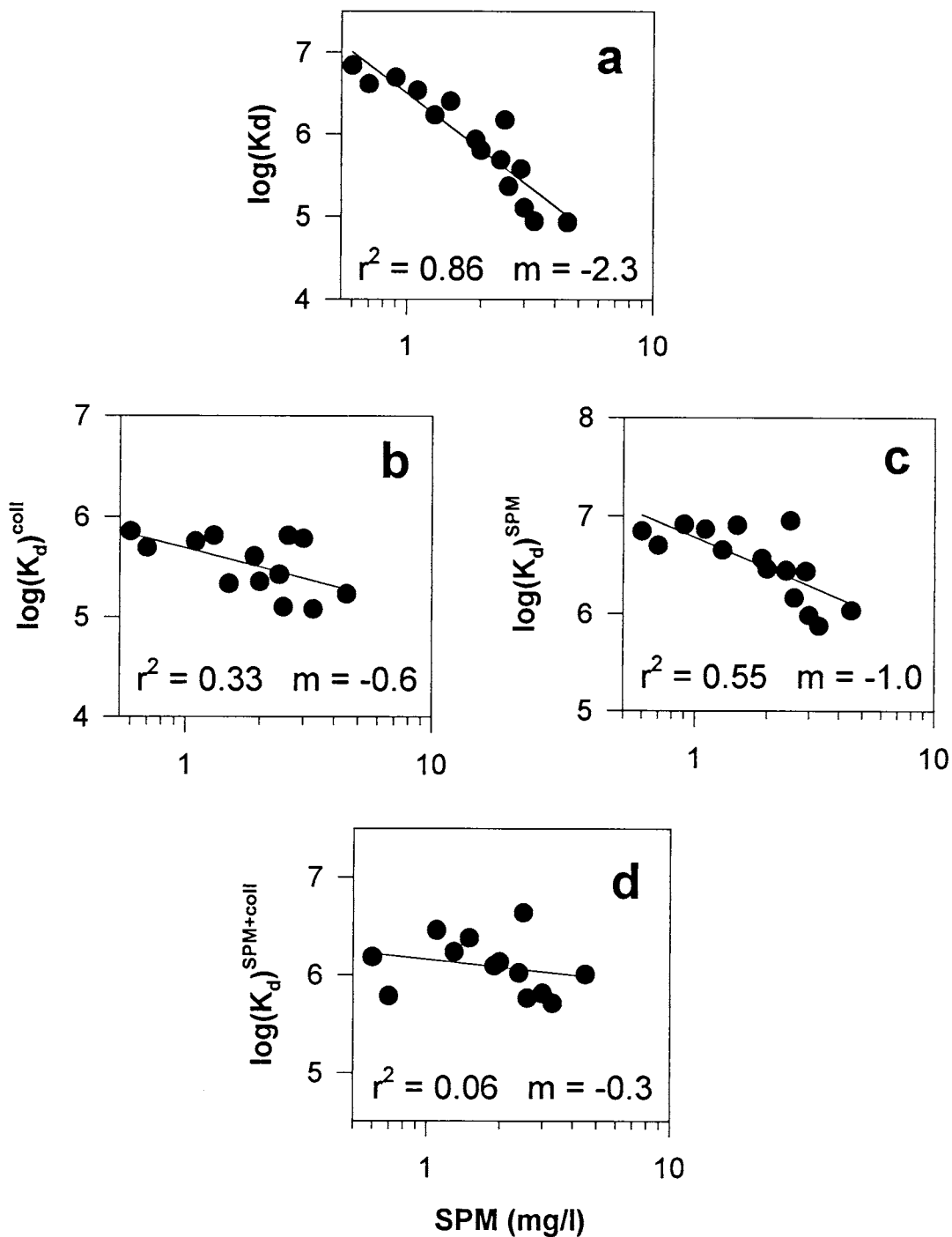


Fig. 8. (a) The p.c.e. is clearly evident in the Hammonasset River, a small system with a homogeneous and lightly developed watershed. (b) Explicitly accounting for colloids greatly diminishes but does not eliminate the p.c.e.. (c) Accounting for non-reactive particles that contain little metal and are presumably large also reduces but does not eliminate the p.c.e.. (d) Simultaneously correcting for the influence of colloids and large particles completely eliminates the p.c.e. and makes K_d s become constant across the full range of SPM.

Hammonasset Pb

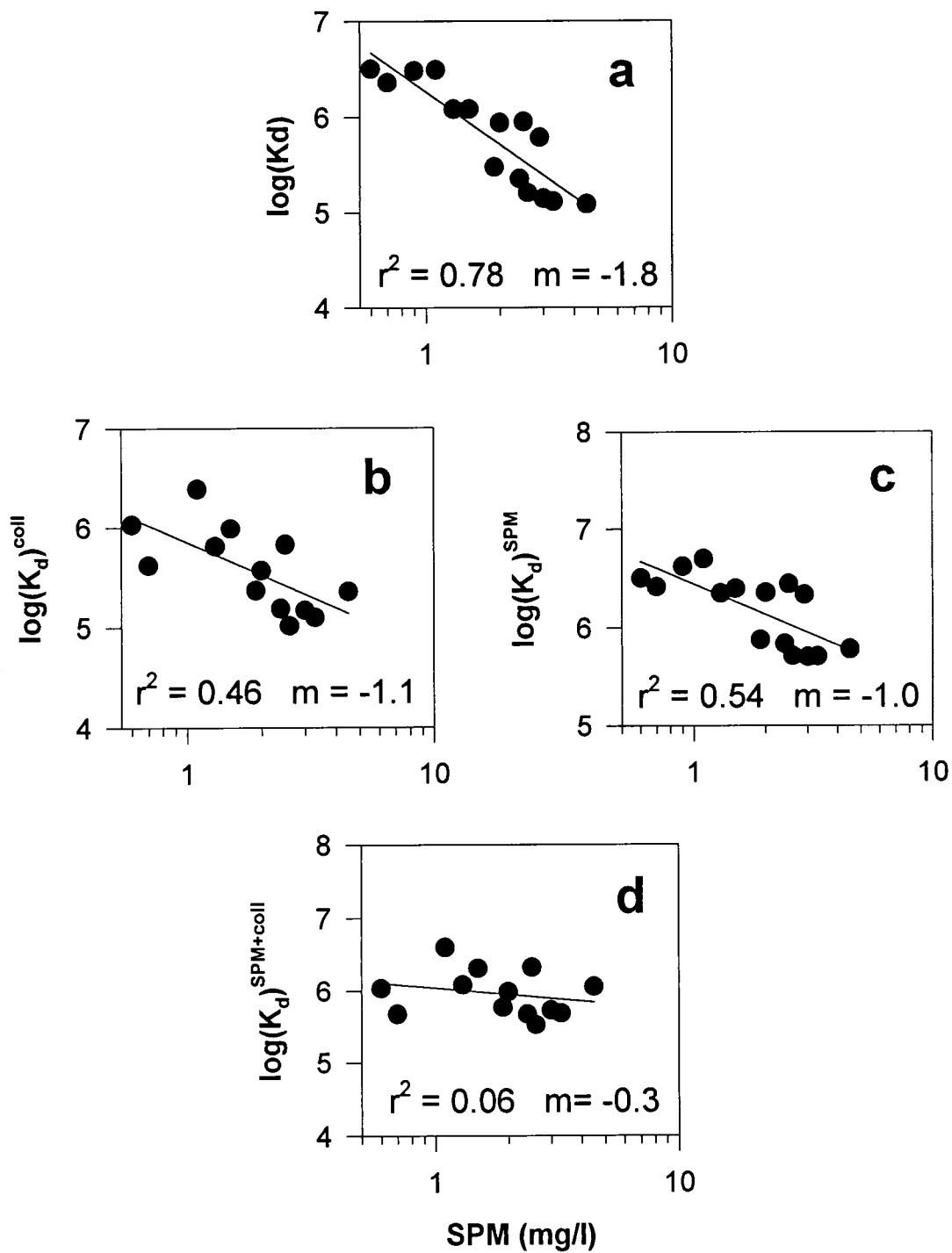


Fig. 9. Same as Fig. 8, but for Pb.

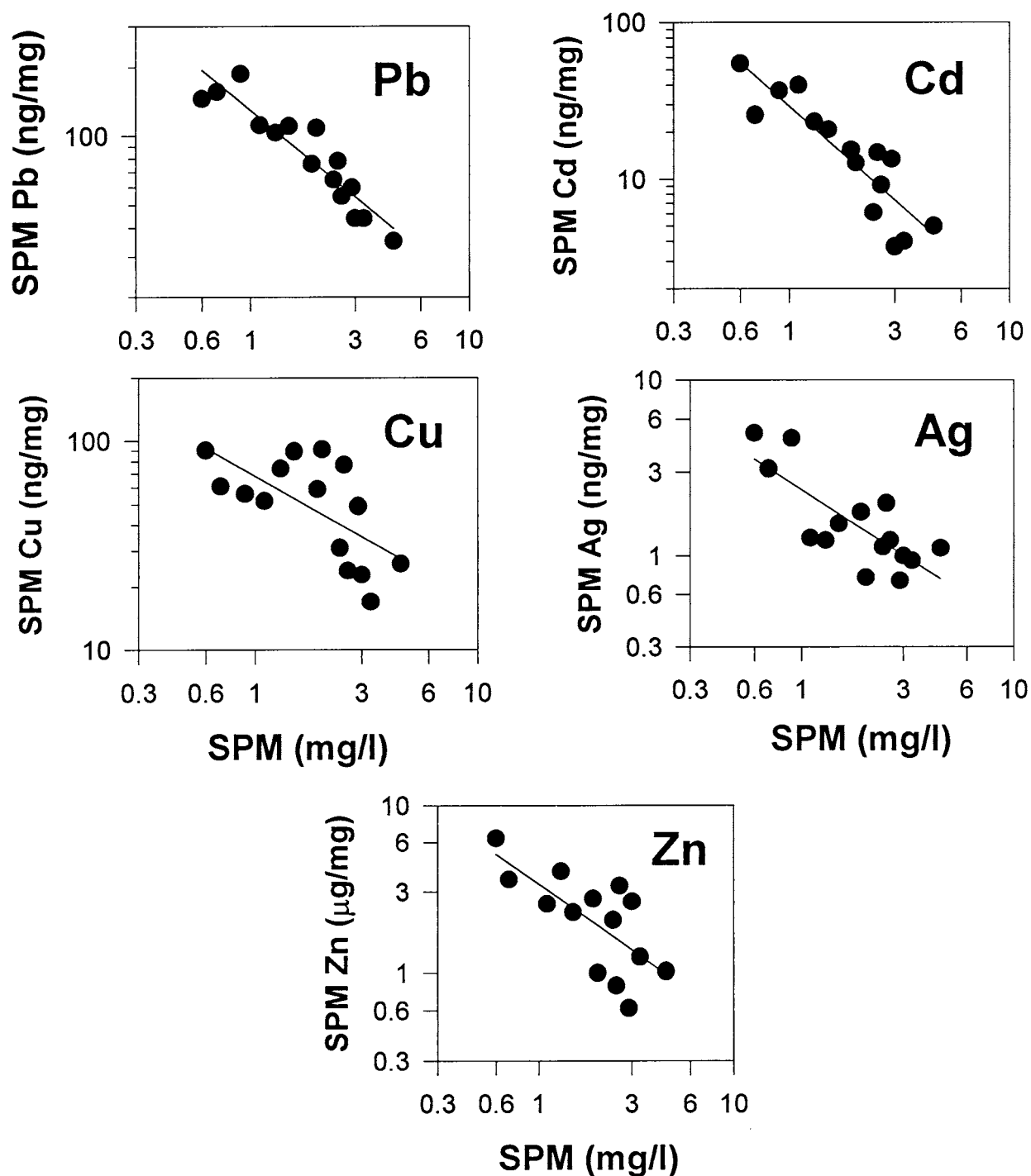


Fig. 10. Concentration of metals on particles as a function of total SPM in the Hammonasset River. The decline is consistent with dilution of SPM by a class of particles that have few surface complexation sites and are low in exchangeable metals, such as would be the case for very large particles.

other than the one we modeled (Hammonasset). In the Quinnipiac River, statistically consistent declines in $[Me]_{SPM}$ with SPM occurred in only 40% of the cases, not 100% as in the Hammonasset.

3.4. Colloid Composition and Major Metals: Fe, Al, and Mn

The particulate trace metals Ag, Cd, Cu, Pb, and Zn occur mainly as surface complexes and minor inclusions in minerals,

so they contribute an insignificant fraction of the total mass of SPM and colloids. The more abundant metals Fe, Al, and Mn can form a major portion of oxyhydroxide precipitates and silicates, especially clay minerals. On average in the SPM we measured, Fe, Al, and Mn contributed a substantial portion of the total dry mass (10.3, 5.4, and 0.7%, respectively, based on assumptions about metal forms described under Methods).

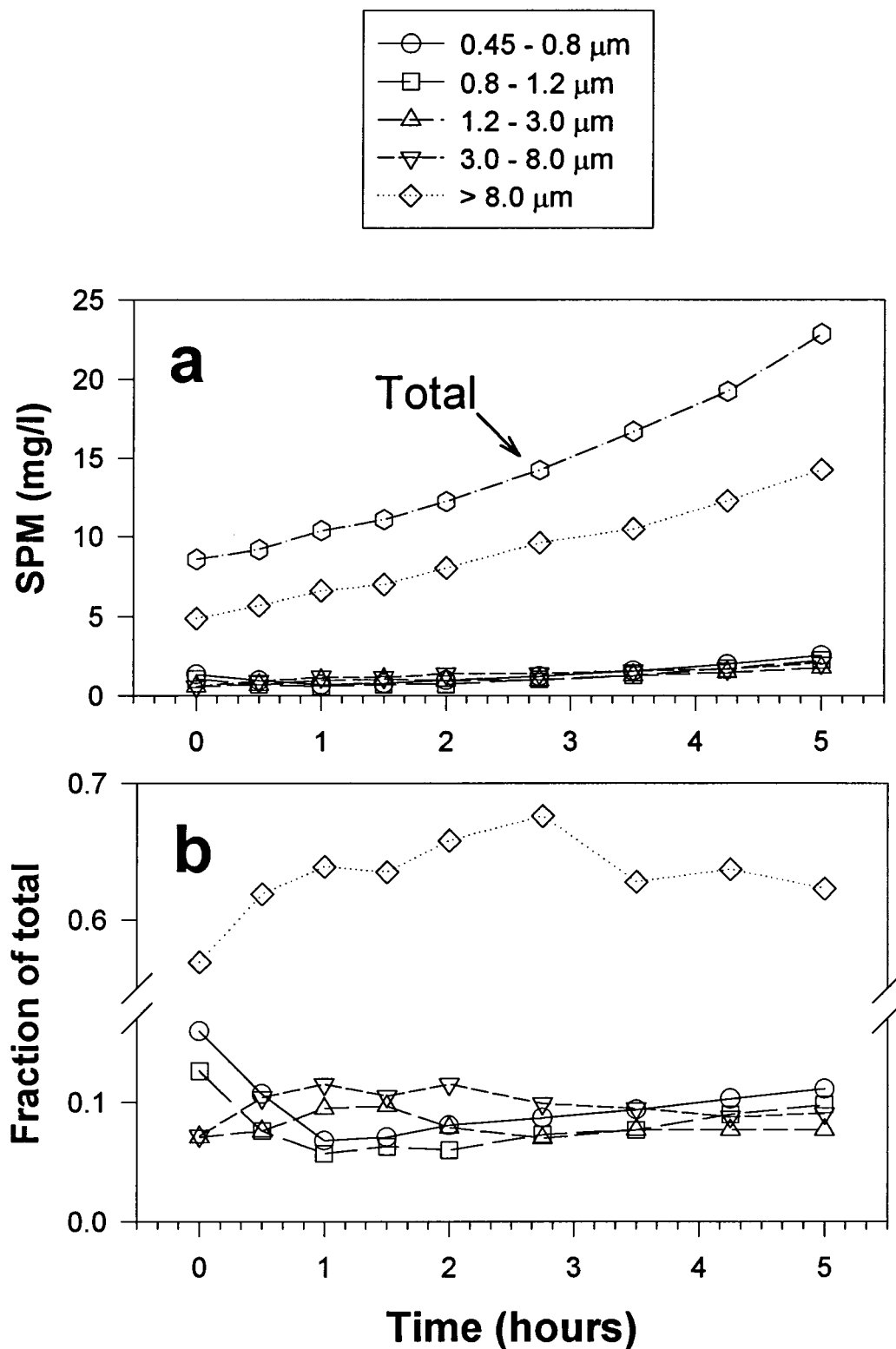


Fig. 11. SPM size distribution for the Quinnipiac River during a storm on 18 September 1997. (a) Total SPM increased from 8.6 to 22.9 mg/l over a period of 5 h, and this appears to be mainly the result of particles larger than 8 μm . (b) Replotting data as a fraction of total SPM shows that larger size classes did increase compared to smaller ones. The proportion of the largest particles increased for the first 3 h of the storm, though it was constant towards the end of the period.

Metals were only half as abundant in colloids, with 4.5, 1.6, and 0.4% of colloidal mass contributed by oxyhydroxides of the three metals. The remainder in each case is mainly organic matter (OM). Within the 0.45 μm filtrate fraction, the metals tended to occur preferentially as colloids (as opposed to in true solution) in the order $\text{Fe} \gg \text{Al} > \text{Mn}$. Colloidal Fe amounted to more than 8 times truly dissolved Fe, while for Al, Mn, and organic matter the ratios were 1.9, 0.45, and 1.0. The near total absence of truly dissolved Fe is probably a consequence of the extreme insolubility of $\text{Fe}(\text{OH})_3$. At pH 7, the equilibrium concentration of Fe^{3+} with amorphous $\text{Fe}(\text{OH})_3$ is $10^{-17.8}$ M, and that of the most abundant ferric iron species at this pH ($\text{Fe}(\text{OH})_2^+$) is $10^{-9.5}$ M. Fox (1988) found that colloidal ferric hydroxide can have an even higher solubility, approaching 10^{-7} M (for $\text{Fe}(\text{OH})_2^+$) at this pH. Whatever value is most appropriate, truly dissolved iron should be present at vanishingly low concentrations in these rivers. What little Fe did pass through our ultrafilters may have been present as very-fine colloidal $\text{Fe}(\text{OH})_3$, dissolved complexes with DOC (Sholkovitz and Copland, 1981), or Fe^{2+} that had not yet oxidized to Fe^{3+} . Reduced Fe and Fe bound to EDTA may be especially abundant downstream from sewage treatment plants (manuscript in preparation). The greater tendency of Mn to be present in true solution may be related to the high solubility of Mn^{2+} and the well-known slow oxidation kinetics of $\text{Mn}(\text{+II})$ to insoluble $\text{Mn}(\text{+IV})$ (Davison, 1993; Diem and Stumm, 1984; Millero et al., 1987).

It is interesting that the size distribution of filtrate Fe (11% truly dissolved) is so different from that of the organic matter (49% truly dissolved) that makes up the bulk of the material passing 0.45 μm filters. Past studies have shown that riverine Fe is colloidal and have suggested that its form is mixed iron oxides and organic matter (Boyle et al., 1977; Sholkovitz and Copland, 1981). Usually, the colloids coagulate and are removed in estuaries because of elevated concentrations of cations, though this does not occur in every river (Shiller and Boyle, 1991). The precipitate that so forms contains only minor amounts of carbon (Boyle et al., 1977). This and the very dissimilar size distributions we measured for Fe and DOC suggest that the Fe may actually be present in a colloidal form that is largely non-organic (e.g., relatively pure oxyhydroxides), a conclusion consistent with the findings of Fox (1988). Organic matter may be only loosely associated with the Fe colloids, acting to peptize them, but not binding Fe in 1:1 complexes. The high tendency of iron to occur as colloids is also evident in conventional filtrations conducted by us and others (Horowitz et al., 1996; Shiller and Taylor, 1996). Overloading 0.45 μm filters causes their effective pore size to decline markedly, eventually leading to nearly complete blockage of Fe from the filtrate fraction.

The dissimilarity of major metals (Fe, Al, and Mn) and trace metals causes differences in their behavior in aquatic systems. In particular, since major metals form amorphous and crystalline solids, they are present in suspended particles largely in forms that cannot readily exchange with solution, unlike the trace metals which exist mainly as relatively labile surface complexes. Thus, the major metals did not exhibit the p.c.e., except for Fe in four of seven sites and Mn in one. In all of these instances the regression of the K_d -SPM line became non-significant when colloidal metals were properly counted

with the particulate fraction, though the scatter in the data became very large. In these cases, the unexpected p.c.e. behavior may occur because some of the Fe and Mn is present on particles in relatively labile forms.

3.5. Relation of Metals and DOC

More than 90% of the colloidal mass is organic matter, and there is an additional quantity of truly dissolved organic carbon that is about equal to the colloidal portion. The majority of both of these fractions is probably humic and fulvic acids of soil origin. In separate research involving electrochemical measurements, we have quantified the metal complexing characteristics of naturally-occurring truly dissolved and colloidal organic matter in these rivers and found that it has a major influence on trace metal speciation. Therefore, it seems likely that the association of metals with colloids documented in this study is a consequence of metals binding to humic and fulvic substances. At the same time, the partition coefficient, K_d , is a bulk parameter and its use requires no knowledge of the composition of macroparticles and colloids involved.

Previous investigators have found a simple proportionality between filtrate metals and DOC (LaZerte, 1991; Shafer et al., 1997), and our data support this relation in some cases, but not most. For the five trace metals, 31% of the metal-river combinations had significant correlations ($P < 0.05$) between the two parameters, and this was true most often for Cu (71%) and Pb (57%). Cadmium showed a positive relationship in only 29% of cases, while filtrate Ag and Zn never correlated significantly with DOC. Presumably, the correlations occur because higher concentrations of DOC bind the metals and keep them in solution. However, the current research shows that so-called dissolved metals and DOC both represent a mixture of colloidal and truly dissolved forms, which will tend to confound simple conclusions based on size discrimination at 0.45 μm .

3.6. Data Limitations and Challenges of Biogeochemical Investigations of Rivers

This research was intentionally designed to capture a wide variety of riverine biogeochemical conditions in order to maximize the generality of its conclusions. The data presented here show that large differences can occur among rivers, even within a restricted geographical range. A challenge for the future will be to document and explain that diversity. In particular, rivers with heterogeneous land uses within their watershed may be subject to variability that masks simple relations among biogeochemical variables. Even a single river may undergo substantial temporal variability due to changing hydrological flow paths between baseflow and storm conditions.

In this investigation, the distinction between colloids and true solution was operationally determined on the basis of the functioning of nominally 3,000 MW ultrafilters. As has been pointed out elsewhere (Gustafsson and Gschwend, 1997), a chemically relevant lower size limit is one where colloids continue to provide an environment that is distinctly different (e.g., electrostatically) from bulk solution. No single universally-applicable limit exists, but it changes from one system to another depending on the local nature of colloids present and the adsorbate under consideration. At present there is no routine

method that can be used to make this chemocentric distinction (*sensu* Gustafsson and Gschwend), and even ultrafiltration remains largely a research-level technique. In the current research, the success of 3,000 MW ultrafiltration (combined with explicit consideration of mega-particles) to generate constant K_d values provides strong circumstantial evidence that the boundary between colloids and true solution has been appropriately drawn. Use of an even smaller size limit (e.g., 1,000 MW) might have been more appropriate in some cases. For example, the p.c.e. for Cu in the Quinnipiac and Pawcatuck rivers might have been eliminated, and truly dissolved Fe might have been reduced even further. That conjecture could be tested by ultrafiltration through a range of pore-size membranes in future research.

4. CONCLUSIONS

The p.c.e. was strongly manifested for Pb, Cd, Cu, Ag, and Zn in four Connecticut rivers spanning a range of background biogeochemical conditions and watershed land uses.

A substantial amount of all metals measured occurred as colloidal forms. Discriminating dissolved from particulate fractions at 3,000 MW rather than 0.45 μm significantly reduced the p.c.e. in virtually all cases. These two facts are strong evidence that the p.c.e. is caused by the existence of colloidal metals that are included in error with the dissolved fraction.

In most cases, the concentration of metals on particles declined significantly with increasing SPM. This is attributed to an increasing quantity of particles that carry almost no metal and which do not react rapidly with the dissolved phase. A simple model is if these are large particles with low specific surface areas and surface complexation site densities. We term these "mega-particles".

Explicitly accounting for mega-particles eliminated some but not all of the p.c.e.. Simultaneously considering the effect of colloids and mega-particles caused K_d values to become true constants over the range of conditions measured.

The major metals Fe, Al, and Mn also all existed to a significant extent in colloidal forms. Iron had an especially great tendency to occur in the colloidal size fraction. The evidence supports the hypothesis that Fe is present as a colloid that is nearly purely inorganic, such as an amorphous oxyhydroxide.

The data support 3,000 MW as an appropriate boundary for discriminating the lower size limit of colloidal particles in these rivers, though an even lower limit might be warranted in the case of some metals in some rivers.

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