

Role of colloids and fine particles in the transport of metals in rivers draining carbonate and silicate terrains

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Abstract

We have used cross flow filtration (CFF) to determine the pools of fine particulate (0.1–0.45 μm), colloidal (1,000 Dalton to 0.1 μm), and dissolved (<1,000 Dalton) metals in seven rivers that are all relatively rich in organic matter but have differing pH, alkalinity, and ionic strength. The metal content of <0.45- μm filtered river water primarily reflects a mixing of two metal pools with differing elemental compositions: a truly dissolved pool and a colloidal pool. Fine particulate metals contribute <10% of the total metal load of <0.45- μm filtered water. Colloidal metals generally comprise at least the following percentages of the metal load of <0.45- μm filtered water: >50% of Fe, Al, and trace metals; 30% Mn, 25% Ca and Mg; 15% Na and K; and a few percent Si. We believe that these figures are minima because recovery experiments with the CFF apparatus suggest that whilst recoveries of pure metal salt solutions are close to 100%, only 70% of particle-reactive metals are recovered from metal salt solutions spiked with humic acid. We propose that the metal composition of riverine colloids is primarily controlled by element mobility during weathering. In organic-rich soils with low acid-neutralizing capacity, low pH solutions drive the dissolution of aluminosilicates and oxides. Uptake of Al, Fe, and trace metals onto colloidal organic matter helps to maintain low activities of dissolved metals and enhances mineral dissolution. Colloids derived from these soils are thus enriched in Al, Fe, Mn, and trace metals, resulting in high concentrations of these elements in <0.45- μm filtered water. In carbonate-rich soils, rapid neutralization of rainwater by carbonate minerals restricts the mobilization of aluminosilicates and oxides. Compared to colloids from rivers draining silicate terrains, colloids in carbonate-rich systems have higher total loadings of metals, are enriched in alkali and alkaline earth metals, but are depleted in Al, Fe, and trace metals.

Quantifying weathering processes and the subsequent transport of elements to the ocean is a fundamental aim of geochemistry. Although the abundance of dissolved elements has been commonly and pragmatically quantified by filtering water at 0.45 μm , it is well known that sub-0.1- μm colloidal phases, such as organic matter and oxides, interact strongly with dissolved metals (for reviews see Buffle 1988; Stumm 1992, 1993; Gustafsson and Gschwend 1997). Several previous studies suggest that colloids can be important metal carriers in freshwater (e.g., Giesy and Briese 1977; Reuter and Perdue 1977; Hoffmann et al. 1981; Salbu et al. 1985; Tanizaki et al. 1992; Dai and Martin 1995; Ross and Sherrell 1999), and it is likely that the loss of metals from estuarine water is related to the coagulation of colloids (Sholkovitz 1976; Boyle et al. 1977).

This paper reports the results of a study aimed at determining the importance of colloids as metal carriers in a series of rivers of widely varying pH and ionic strength. Cross flow filtration (CFF) is developed as a method of fraction-

ating 0.45- μm filtered water into fine particulate (0.1–0.45 μm), colloidal (1,000 Dalton [Da] to 0.1 μm), and dissolved (<1,000 Da) pools. The results indicate some of the circumstances under which colloids act as important metal carriers and also give some insights into the likely role of colloids in the weathering process.

Sampling and analysis

Water was sampled from seven rivers in NE England and SW Scotland (Fig. 1; Table 1). The main regional rivers are the Tyne and Tweed, which drain areas of often peat-rich uplands overlying a variety of Carboniferous sandstones, shales, and limestones. Samples were also taken from three tributaries of the Tyne: the headwaters of the North Tyne, which drain peat moorlands overlying sandstones, and the River Nent and a small tributary of the Tyne (“Tyne tributary” hereafter) both of which drain areas composed mainly of limestones. As a result of abandoned mine workings, the River Nent is contaminated with Zn and Pb (Macklin and Dowset 1989), which, probably as a result of grazer mortality, has in turn resulted in the formation of an algal bloom in the river (Say and Whitton 1981). Additional samples were taken from the River Luce and Crosswater of Luce in SW Scotland, where peat-rich moorland overlies Ordovician greywackes and siltstones (see Sholkovitz [1976] and Elderfield et al. [1990] for other studies of the metal chemistry of the River Luce; Robson and Neal [1997] for data on the River Tweed).

Ten- to 25-liter samples were drawn from the rivers through polypropylene tubing using a teflon-lined Yamada

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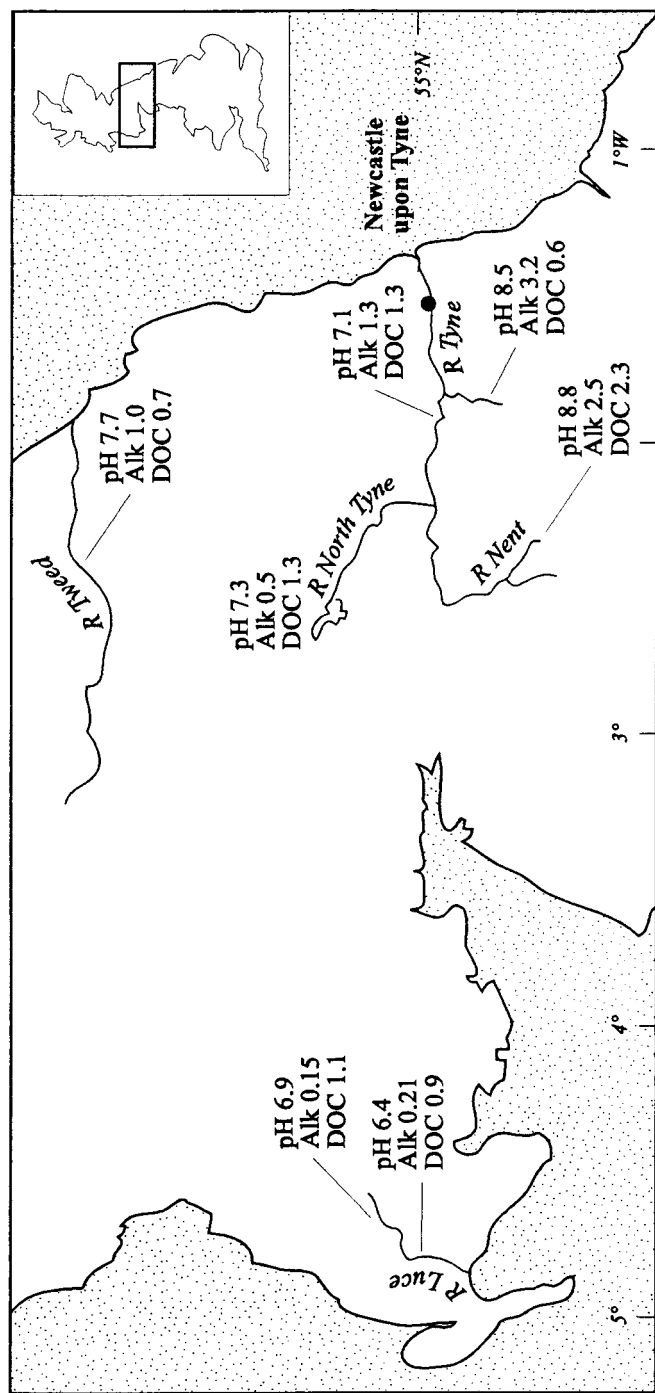


Fig. 1. Sample location map with basic characteristics of waters: DOC (mmol L^{-1}), alkalinity (mmol L^{-1} bicarbonate).

diaphragm pump. The water was filtered directly through 142-mm-diameter, 5- μm and 293-mm 0.45- μm Millipore MF filters mounted on acrylic filter holders and stored in 25-liter high-density polypropylene carboys with fluorinated linings.

In the laboratory, samples were subjected to CFF using a Millipore Pellicon tangential flow system, usually within 2 h of collection. CFF works by continuously pumping water from a sample reservoir tangentially across a membrane with

Table 1. Major element data for 0.45- μm filtered waters.*

River	Sampling date	pH	DOC (mmol L^{-1})	Alkalinity (mmol L^{-1})		Na (mmol L^{-1})	K (mmol L^{-1})	Ca (mmol L^{-1})	Mg (mmol L^{-1})	F (mmol L^{-1})	Cl (mmol L^{-1})	SO_4 (mmol L^{-1})
				HCO ₃	Alk							
Luce	16 Oct 93	6.4	0.9	0.21	0.39	0.015	0.12	0.10	ND	ND	ND	ND
Crosswater of Luce	17 Oct 93	6.9	1.0	0.15	0.33	0.005	ND	ND	<LoD	<LoD	0.03	<LoD
North Tyne (I)	24 Jan 94	7.4	4.0	0.33	0.18	0.012	0.25	0.10	ND	ND	ND	ND
North Tyne (II)	21 Mar 94	7.2	1.1	0.41	0.23	0.018	0.18	0.09	<LoD	<LoD	0.22	0.06
North Tyne (III)	2 Nov 94	7.2	0.9	0.57	ND	ND	ND	ND	ND	ND	ND	ND
North Tyne (IV)	30 Jan 95	7	1.3	0.33	ND	ND	ND	ND	ND	ND	ND	ND
North Tyne (V)	1 May 95	7.8	1.1	0.57	ND	ND	ND	ND	ND	0.02	0.20	0.05
Tyne	7 Dec 94	7.1	1.3	1.23	0.32	0.049	0.28	0.16	ND	ND	ND	ND
Tyne tributary	25 May 94	8.5	0.6	3.20	2.33	0.125	2.05	0.46	ND	ND	2.26	0.36
Nent	5 July 94	8.8	2.3	2.51	0.46	0.065	1.58	0.58	0.03	0.03	0.31	0.76
Tweed	20 Mar 95	7.7	0.6	0.98	0.36	0.022	0.47	0.22	<LoD	<LoD	0.39	<LoD

* DOC, dissolved organic carbon; ND, not determined; <LoD, below limit of detection.

a defined pore size and back to the sample reservoir (Buffle et al. 1992). When, as in this work, CFF is carried out in concentration mode, material larger than the nominal molecular weight limit (NMWL) of the membrane is retained in the sample reservoir, forming the *retentate*. Material finer than the NMWL of the membrane passes through the membrane to form the *permeate*. In our work, an internally lined Procon pump circulated the sample through the CFF system to and from fluorinated polypropylene sample reservoirs. All tubing and connections were made from Teflon. CFF was carried out sequentially, first with 0.1- μm microporous Durapore (polyvinylidene difluoride) membranes and then with polysulphone membranes with a NMWL of 1,000 Da. In each case, two membrane cassettes were used within the acrylic membrane housing, giving a total surface area of 0.924 m². The standard operating conditions for the 0.1- μm membranes used an input pressure of 20 psi and an output pressure of 5 psi. The 1,000-Da membranes required a larger back pressure of 10 psi in order to reduce the sample processing time. This procedure allowed the fractionation of the 0.45- μm filtered river water into a *fine particulate* fraction (0.45–0.1 μm), a *colloidal fraction* (0.1 μm to 1,000 Da), and a *truly dissolved* fraction (<1,000 Da). CFF of a 20-liter sample to half volume at 0.1 μm took approximately 15 min. CFF of 10-liters of the 0.1- μm permeate to half volume using the 1,000-Da membranes took approximately 2 h.

All samples—permeates and retentates from the CFF procedure and aliquots of the <0.45- μm filtered water—were acidified to 1% HNO₃ with distilled Aristar HNO₃ and stored in acid-cleaned polypropylene bottles at 4°C until analysis. Metal concentrations were determined using flame (Na, K, Ca, Mg, Si, some Fe) and graphite furnace (Fe, Mn, Al, Zn, Cu, Ni, Pb) atomic absorption spectrophotometry. Trace metal data for some samples were acquired by inductively coupled plasma mass spectrometry (ICP-MS) using the research instrument at the NERC ICP-MS facility. Anion analyses were performed using a Dionex 4000 Series ion chromatograph and alkalinity was determined by manual titration.

Organic carbon concentrations were determined for the 0.45- μm filtered waters by high-temperature catalytic oxidation. We did not determine the organic carbon contents of ultrafiltered samples and do not accurately know its molecular weight distribution, although Cooper (1995) showed that 30–50% of the organic matter in 0.45- μm filtered River Tyne water was retained by a 1,000-Da filter. In addition, most of the brown coloration occurs in the colloidal fraction, consistent with the likely 2,000–10,000-Da molecular weight of humic material (MacCarthy and Suffet 1989). To avoid confusion over the terminology of “dissolved” and “colloidal” organic carbon we will use the term “organic carbon” to specify the organic carbon that passed through the 0.45- μm filter.

Based on the repeated analysis of (1) natural samples and (2) standard reference materials (CRM-TMDW, the contaminated drinking water standard from the Greyhound Chemical Service, and SLRS-2, river water from the National Research Council of Canada), analytical precision is close to 2% for Na, K, Ca, and Mg; 5% for Si, Al, Fe, and Mn; and 15–20% for Cu, Zn, Ni, and Pb where abundances are in the

5–50-nM range. Comparison with values for the standard reference materials indicates that the accuracy of the analyses is similar to the reported precision.

A range of standard procedures was used to minimize contamination. All acids were Aristar-grade and had been distilled in a subboiling quartz still. All the field sampling equipment was thoroughly rinsed with deionized (Milli-Q 18M Ω) water before use and flushed with 5 liters of river water before collection started. Laboratory work was performed in a positive-pressure clean room with filtered air. Contamination from sampling and storage equipment was minimal, except for Zn, where the blank was as high as 15% of the signal. The data were not corrected for this contamination. We corrected for the acid blanks, which were also small. The more rigorous tests undertaken to assess the performance of the CFF equipment are outlined below.

Cross flow filtration—Several studies have shown that CFF membranes have variable retention and adsorption characteristics for both colloids and metals (Kwak et al. 1977; Whitehouse et al. 1990; Leonard et al. 1994; Buesseler 1996 and references therein; Dai et al. 1998). We therefore undertook a range of experiments to test and optimize the use of our CFF equipment for sampling trace metals. Important issues are contamination, recovery (loss) and, as a result of a buildup of colloidal material close to the membrane interface, breakthrough into the permeate of material greater than the NMWL of the membrane.

Prior to processing each sample, the CFF equipment was rigorously cleaned with alkali, acid, and deionized water. The apparatus was first flushed with 10 liters of deionized water to remove traces of the 2% formaldehyde storing solution. Sodium hydroxide (0.1 M) was then recirculated for 30 min, in order to destroy any residual organic material, then flushed with 20 liters of deionized water. The membranes were then washed three times with distilled Aristar 0.1 M HNO₃, each acid treatment being flushed with 15 liters of deionized water. Finally the apparatus was flushed with a further 20 liters of deionized water.

Maximum levels of contamination from the CFF system were estimated by recirculating 5 liters of deionized water through the system for 30 min. In most cases, levels of contaminants in both the initial deionized water and after circulation through the system are close to or below the limit of detection (around 1 nmol L⁻¹ for most elements) for both the 0.1- μm and 1,000-Da membranes; no corrections were therefore made to the raw data for any element. Small amounts of Fe, Al, and Zn were leached from the 1,000-Da membranes. For Fe and Al, the levels of contamination are small (9 and 4 nmol L⁻¹) compared to the levels measured in the water studied here. The levels of Zn (30 nmol L⁻¹) are within the range of the abundance measured in the 1,000-Da permeates. Since deionized water is a relatively strong solvent, it is likely that the estimated level of Zn contamination is maximal. Nevertheless, the Zn data should be treated cautiously.

Recoveries were determined using a Millipore Minitan CFF system with four 1,000-Da polysulphone membrane plates installed in parallel within the acrylic housing. Solutions of Ca, Fe, Cu, and Pb metal salts were made from

standard metal solutions to concentrations approximating those found in river water (Ca: 20 $\mu\text{mol L}^{-1}$; Fe: 1 $\mu\text{mol L}^{-1}$; Cu: 150 nmol L^{-1} ; Pb: 50 nmol L^{-1}). Some of the solutions were spiked with 10 mg L^{-1} Aldrich Humic Acid to simulate the organic material in natural river water. CFF was carried out to half volume in approximately 2 h. Samples of permeate and retentate were analyzed and recovery factors calculated as

$$\text{Recovery} = \left(\frac{C_p V_p + C_r V_r}{C_i V_i} \right) \times 100, \quad (1)$$

where C is concentration, V is volume, and p, r, and i represent permeate, retentate, and initial. Recoveries above 100% indicate contamination from the CFF system, and recoveries below 100% represent loss of material to the CFF apparatus. Recovery levels do not, however, give information on possible changes in element speciation, such as the formation of colloidal Fe oxyhydroxide, which may result from the filtration process.

Recoveries of pure metal salts of Pb, Cu, and Ca were >90% and 70% for Fe. These values are comparable to those reported by Whitehouse et al. (1990) and Tanizaki et al. (1992), who also found that recoveries of Fe are frequently lower than for other metal ions, perhaps because of the formation of colloidal iron oxyhydroxide. Recoveries of metals from the solutions containing humic acid were noticeably lower than those not containing humic acid: 95% for Ca and 50–60% for Fe, Cu, and Pb. This suggests that the CFF process leads to the preferential loss of metals bound to humic material. Others have concluded that colloidal metals and radionuclides are lost to CFF systems (Kwak et al. 1977; Baskaran et al. 1992; Leonard et al. 1994; Sañudo-Wilhemly et al. 1996; Ross and Sherrell 1999), although the extent of loss may be related to the nature of both the CFF membrane and the colloidal phase (Dai et al. 1998).

Recoveries of major elements and Si for the natural samples are between 95 and 100% for both the 0.1- μm and 1,000-Da membranes. For the minor elements Al, Fe, and Mn, recoveries are mainly between 60 and 100%; for the trace elements Zn, Cu, Pb, and Ni, recoveries are mainly between 60 and 100%, with some values above 100%, indicating contamination or inaccurate analyses. The observation of lower recoveries of those elements most likely to be associated with colloidal phases is consistent with the experimental data, implying the loss of humic-bound metals in the ultrafiltration system. As we have chosen not to correct the data for the potential loss of humic-bound colloidal metals, the measured abundance of colloidal metals should be treated as minima, especially for those metals that bind strongly to humic material (e.g., Fe, Al, Cu, Pb, and Zn; see Tipping and Hurley 1992).

By monitoring the concentration of metals in the permeate during the CFF process, we found that the abundance of metals in the permeate increased when the volume of retentate had reduced to about 25% of its initial volume. Similar results have been reported by Wheeler (1976), Buffle et al. (1992), Dai et al. (1995), and Wen et al. (1996). The calculated proportion of metals associated with the colloidal phase is thus dependent on the extent of CFF. For most of

our samples, retentate volumes were never less than 50% of the initial volume. Although this reduces the fractionation between retained (colloidal) and dissolved (permeate) metals, a more accurate assessment of dissolved metals is achieved, as well as a reduction in sample processing time. In a few cases, much higher concentration factors were used, in which case the proportions of fine particulate and colloidal metal should be taken as minimum values. Overall, the combined effects of (1) adsorption of humic bound metals to the membrane and (2) breakthrough to the permeate of material with a NMWL greater than that of the membrane means that the reported proportions of fine particulate and colloidal metals are minima.

CFF yields two fractions from the initial water sample: the permeate, which contains metals associated with material with a molecular weight less than the NMWL of the membrane, and the retentate, which contains a concentrate of metals associated with material with a molecular weight greater than the NMWL of the membrane and metals associated with smaller material that did not pass through the membrane. The proportion of metals associated with the retained material larger than the NMWL can be calculated as the difference between (1) the actual mass of metal in the retentate and (2) the expected mass of metal in a retentate containing only material larger than the NMWL.

$$\begin{aligned} \text{Metal} > \text{NMWL} \\ &= \left(\frac{[(\text{Me}_r \cdot V_r) - (\text{Me}_p \cdot V_r)]}{\text{Me}_i \cdot V_i} \right) \times 100 (\%) \quad (2) \end{aligned}$$

Me_r , Me_p , and Me_i represent the concentration of metal in the retentate, permeate, and initial (0.45- μm filtered) fractions; V_r and V_i represent the volumes of retentate and initial samples. The masses of metal in the retentate and initial solution are $(\text{Me}_r \cdot V_r)$ and $(\text{Me}_i \cdot V_i)$, respectively. However, the retentate also contains metals that would pass into the permeate with continued filtration and that must be accounted for if the true mass or concentration of colloidal or fine particulate metals is to be accurately assessed. The mass of metal in the retentate that is associated with material smaller than the NMWL of the membrane is $\text{Me}_p \cdot V_r$. The true mass of retentate (colloidal or fine particulate) metal is thus $(\text{Me}_r \cdot V_r) - (\text{Me}_p \cdot V_r)$.

Since the masses and concentrations of colloidal and fine particulate metals are calculated by difference, analytical errors are propagated into the calculation. This is a potentially severe problem for analytes close to the limits of detection. We gained an idea of the level of uncertainty by making duplicate analyses of two samples from the River North Tyne. In one case, two 20-liter samples were collected into separate carboys within a few minutes of each other and were processed and analyzed separately. In the second case, one 20-liter sample was split and processed separately. In both cases, the proportions of colloid-associated metals for each of the samples were very similar for Na, K, Ca, Mg, and Mn and generally within 10% of each other for the remaining elements.

Results and discussion

General geochemistry—The major ion composition of these rivers varies considerably and spans the global average river composition (Table 1; Martin and Meybeck 1979; Martin and Whitfield 1983). Based largely on the geology of their drainage basins, the rivers can be divided into three main categories. (1) Silicate rivers. The Luce, Crosswater of Luce, and North Tyne drain regions of silicate sediments overlain in parts by peat. They have low ionic strengths, low alkalinities, low to moderate pHs, and moderate to high DOC contents. (2) Carbonate rivers. The Nent and Tyne tributary drain carbonate terrains. Compared to the silicate rivers, they have higher ionic strengths, higher alkalinities, and higher pHs but still have DOC contents above the world average (0.5 mmol L^{-1} ; Ertel et al. 1986), perhaps reflecting the peat-rich nature of the soils lining parts of the catchments. The Nent is unusual in that it has a high DOC concentration but lacks the strong brown coloration which typifies humic-rich water. As a result of grazer mortality, zinc contamination in the Nent has led to the proliferation of an alga that contributes to its organic loading (Say and Whitton 1981). (3) Regional rivers. The Rivers Tyne and Tweed, which are two of the main regional rivers, integrate these end-member waters and have intermediate compositions.

The range of concentrations of dissolved Fe, Al, and Mn span, but are generally higher than, the world average values (Martin and Whitfield 1983). There is a general inverse relationship between the abundance of major and minor cations, such that rivers draining limestone-rich regions have higher concentrations of Na, K, Ca, and Mg but lower concentrations of Fe, Al, and Mn. The concentrations of Ni, Cu, Zn, and Pb in the rivers are slightly higher than the world average. High Zn concentrations occur in the contaminated River Nent and the River Tyne, which carries a contribution from the Nent.

Fine particulate metals—Element data derived from the ultrafiltration procedures are given in a Web appendix (<http://www.aslo.org/lo/pdf/vol.46/issue.2/0331a1.pdf>). The proportions of metals in the fine particulate pool ($0.45\text{--}0.1 \mu\text{m}$) are shown in Fig. 2. The proportions are generally small for all the rivers: a few percent Na, K, Ca, Mg, and Si and generally 10% or less Fe, Mn, and the trace metals. Aluminum is exceptional in that four of the samples, from rivers of diverse type, carry significant fractions of fine particulate Al; some also have relatively large amounts of fine particulate Fe. With small amounts of fine particulate Si, these data imply the occurrence of very fine aluminosilicates and possibly Fe oxyhydroxides. In particular, the River Nent has large fractions of fine particulate Fe, Al, Zn, Pb, and Ni, all of which are likely to be oxidation products of the sulfide minerals in abandoned mines and tailings piles.

Colloidal metals—Although we did not analyze a dried colloid concentrate in this study, we believe for several reasons that the dominant colloidal material in these rivers is organic matter. First, the 1,000-Da retentates are very brown, implying the presence of humic material that typically has molecular weights between 2,000–10,000 (MacCarthy and

Suffet 1989; Higgo et al. 1992; Pettersson et al. 1994) and would therefore be retained by the 1,000-Da membrane. Second, organic carbon occurs in millimolar concentrations in $0.45\text{-}\mu\text{m}$ filtrates, whereas Si, Al, and Fe, other phases that may form colloidal particles, occur in micromolar amounts. Third, by using dialysis to remove inorganic salts from a 1,000-Da retentate, Cooper (1995) showed that the organic carbon content of colloidal material in the River Tyne was around 50%—close to literature values for soil and aquatic humic acids (49–58%; Steelink et al. 1988; Schulten and Schnitzer 1993), thus suggesting that the colloidal material was largely organic. Nevertheless, the data do not allow us to easily distinguish between (1) colloidal, inorganic Fe–Al–Mn oxyhydroxides and (2) humic-bound colloidal Al, Fe, and Mn.

It appears that colloids in the carbonate rivers have higher total metal loadings and strikingly different metal compositions than colloids in silicate rivers (Fig. 3). For each river, Fig. 3 displays the amounts of colloidal Al, Fe, and Mn versus the amounts of colloidal Na, K, Ca, and Mg, normalized in each case to the amount of DOC. Assuming that each river contains similar amounts of DOC with molecular weights above and below 1,000 Da (Cooper's [1995] data for several River Tyne samples suggested an approximate 50:50 mix of organics with NMWLs above and below 1,000 Da), Fig. 3 gives an indication of the metal loadings of the colloidal material. Colloids in carbonate rivers have much lower loadings of Al, Fe, and Mn but higher loadings of Na, K, Ca, and Mg. The two regional rivers have differing characteristics: Tyne colloids have high abundances of alkali, alkaline earth, and transition metals, whereas Tweed colloids are similar to those in the carbonate rivers—enriched in alkalis and alkaline earths but depleted in transition metals.

The proportions of metals associated with the colloidal pool (1,000 Da to $0.1 \mu\text{m}$) are shown in Fig. 4. As discussed previously, these values are minima, especially for those elements that are strongly associated with colloids. Typical proportions of colloidal metals are: a few percent for Si, 15% for Na and K, 25% for Ca and Mg, 30% for Mn, and commonly greater than 50% for Fe, Al, and the trace metals.

Despite the rather small data set, there is some evidence that, compared to the rivers draining silicate terrains, the proportions of colloidal Na, K, Ca, Mg, Fe, Al, and Mn are lower in the carbonate rivers and in the regional rivers, which are compositionally intermediate between the carbonate and silicate rivers. There are insufficient data for the trace metals to comment on differences between each river type. The lower proportions of alkali and alkaline earth metals reflect the higher ionic strength of these rivers and thus the higher abundance of truly dissolved alkali and alkaline earth elements. In contrast, both the absolute amounts and the proportions of colloidal Fe, Al, and Mn are lower in the carbonate rivers.

The proportions of colloidal metals found in these rivers span and, in some cases, extend the range reported in other studies of freshwater systems (see Table 2). Care must be taken in comparing data in different studies, in which membranes with different properties and with different NMWLs were used. Nevertheless, our data support previous findings that, in many rivers, much or most Fe, Al, and Pb is colloidal.

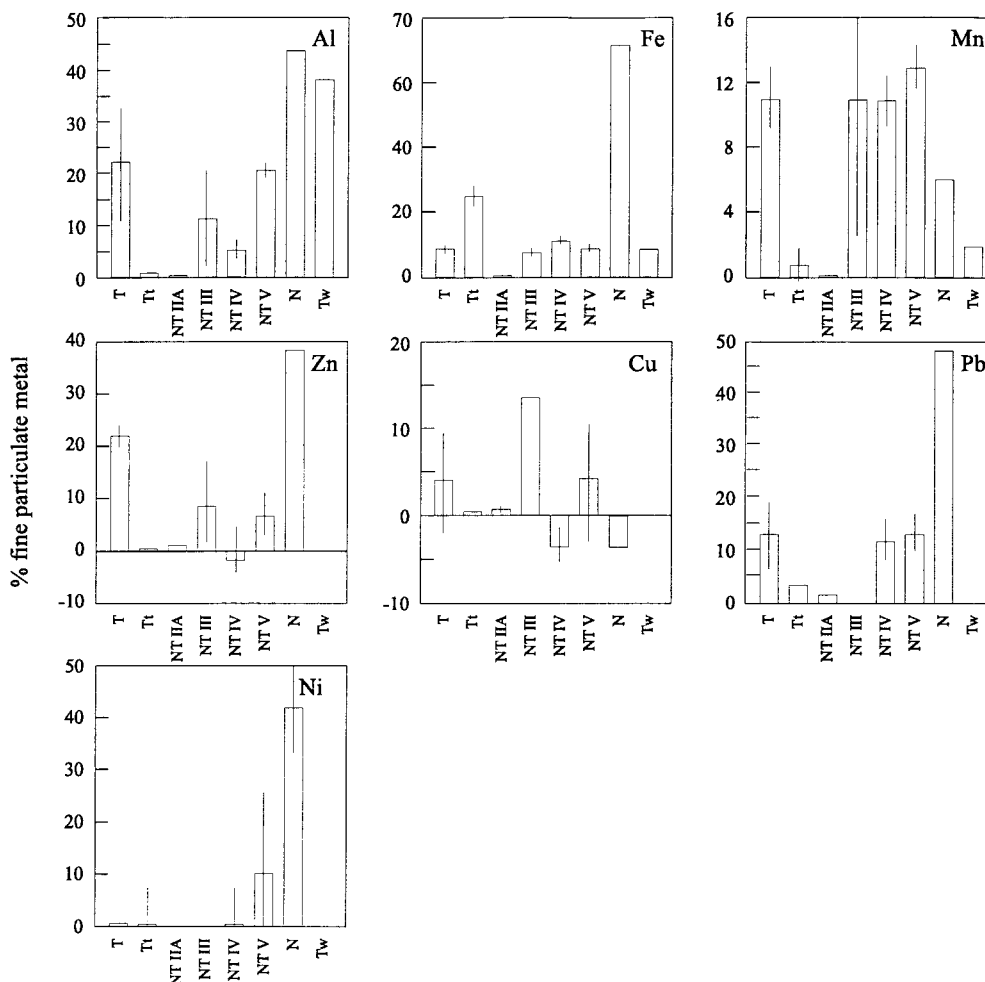


Fig. 2. Percentage of metals associated with the fine particulate ($0.1\text{--}0.45\ \mu\text{m}$) pool. The alkali, alkaline earth metals, and silicon are associated to a limited extent ($<5\%$) with the fine particulate fraction and are not shown. Error bars were determined by a summation of the errors in the replicate metal analyses in the retentate, permeate, and initial sample (see Eq. 2; Potts 1987). Abbreviations for each river are: T, Tyne; Tt, Tyne tributary; NT, North Tyne; N, Nent; Tw, Tweed.

dal, and it is common that up to half the Mn, Cu, and Zn is colloidal. What remains unclear are the reasons for the quite wide range of colloidal metals observed in different rivers. Although our data imply that the nature of the source terrain is one factor, with rivers draining carbonate terrains yielding lower proportions of colloidal metals, other possibilities include the geochemical and biochemical nature of the DOC and also the occurrence and relative importance of colloidal phases other than organic matter.

The proportions of metals associated with the colloidal phase increase in the following order.

$$\text{Si} < \text{Na} < \text{K} < \text{Mg} < \text{Ca} < \text{Mn} \approx \text{Zn} \approx \text{Ni} \approx \text{Cu} < \text{Al} \\ \approx \text{Pb} < \text{Fe}$$

The list supports the probability that most of the colloidal metals are associated with organic matter but does not rule out the occurrence of colloidal inorganic Fe–Al–Mn oxyhydroxides. The order of metals in the list is similar to the

affinity of divalent metals for organic O, S, and N ligands defined by the Irving–Williams series (Irving and Williams 1948); the binding strengths of metals with humic acids modeled by Tipping and Hurley (1992); the stability constants for metal–humic complexes for natural water determined using gel filtration by Mantoura et al. (1978); the stability constants for metal–fulvic complexes measured by Schnitzer and Skinner (1967); and other studies of river and estuarine systems (Sañudo-Wilhelmy et al. 1996; Ross and Sherrell 1999). The main uncertainty between our list and those defined using other techniques is the position of Fe in the series. This depends on whether divalent or trivalent Fe was used as the model ion. In our case, ferric ion is the likely ion, although we do not know whether the Fe occurs independent of organic matter as a colloidal oxyhydroxide or is bound in some way to the organic matter (Picard & Felbeck 1976; Sholkovitz 1976). Silicon is found to be almost totally in the truly dissolved phase, presumably as simple inorganic species such as silicic acids (Leppard 1992).

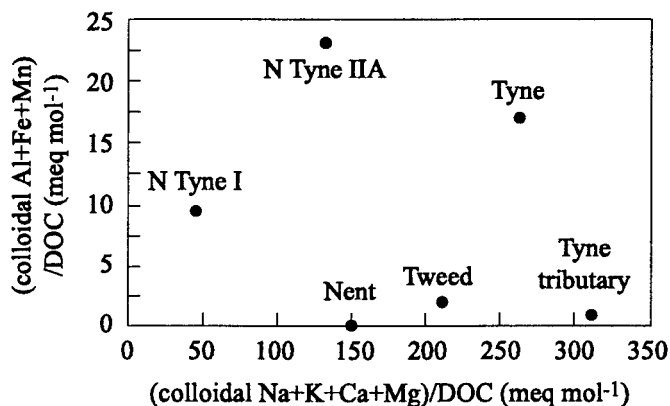


Fig. 3. Colloidal (Al + Fe + Mn)/organic content (OC) versus colloidal (Na + K + Ca + Mg)/OC. OC = <0.45- μ m organic carbon. Metal data are normalized to OC since it is probably the major colloidal phase. Metal chemistry of colloids from carbonate rivers (Nent, Tyne tributary) are very different from those from silicate rivers (North Tyne, Luce, Crosswater of Luce). The two regional rivers (Tweed and Tyne) have differing signatures. The Tyne has high abundances of both sets of elements; the Tweed is like the carbonate rivers.

Assuming that organic matter is an important carrier of metals in these rivers, we used Tipping's (1994) WHAM model to calculate the equilibrium speciation of the waters. WHAM is designed to model humic-rich water and combines several submodels describing solution chemistry, precipitation of iron and aluminum oxyhydroxides, cation exchange on a representative clay, and the adsorption-desorption reactions of fulvic and humic acids. Input parameters include ion concentrations, pH, alkalinity, and concentrations of fulvic and humic acids. Based on Cooper's (1995) data, which suggests that around half the <0.45- μ m organic matter in the River Tyne has a molecular weight in excess of 1,000 Da and is thus likely to be humic in nature, we assumed a 50:50 mixture of humic and fulvic acids and that all Fe is Fe(III). The results (Fig. 5) show that compared to the measured data, the model predicts slightly lower proportions of colloidal alkali and alkaline earth elements plus Mn, about the correct proportion of Al, and higher proportions of colloidal Fe, Cu, Zn, and Pb. The discrepancy for Fe and the trace elements may be expected since we know that the CFF technique underestimates the proportion of colloidal metals. The differences between modeled and measured results for the alkalis and alkaline earth elements are probably real. However, the model very accurately predicts the measured affinity series of metals with colloidal material, supporting the assertion that organic matter comprises a major pool of colloidal metals in these rivers.

Despite the strong circumstantial evidence that organic matter is an important carrier of metals in these rivers, it is certainly not the sole control on either the absolute abundance of metals or the proportion of metals carried by the colloidal fraction. Figure 6 shows the rather weak relationships between total metal concentrations and <0.45- μ m concentrations of DOC. This is expected for the major ions, which occur predominantly as free ions or simple ion complexes. However, it is also true for those metals (Fe, Al, Mn,

trace metals) that are strongly associated with colloidal material in these and other rivers (Pitwell 1974; Giesy & Briese 1977; Reuter & Perdue 1977; Ross and Sherrell 1999; Table 2). The River Nent is unusual in that it is rich in organic matter but has low concentrations of Fe and Al, metals that complex strongly with organic matter and that have been observed in other rivers to be associated with organic carbon (Perdue et al. 1976). Although we cannot be certain about the nature of the organic matter in the River Nent, it was notable that the 1,000-Da retentate from this river was much less brown than those of the other rivers in this study, implying a less humic nature for the organic matter. We therefore speculate that the different geochemical behavior of Fe and Al in the Nent results from the more biological and less humic nature of its organic matter, which appears to have a lesser ability to bind metals.

Figure 7 shows that the percentage of <0.45- μ m metal associated with the colloidal fraction is not well correlated with the abundance of <0.45- μ m DOC. Some of the lowest correlation coefficients are for Fe and Mn, elements known to bind strongly to DOM. Rivers with the lowest proportions of colloidal metals, including strongly binding metals, are the high-pH, high-ionic strength rivers draining carbonate terrains (Fig. 8).

There are several reasons why there might not be a very strong relationship between <0.45- μ m DOC and the proportion of colloidal metals, including the occurrence of free Fe-Mn-Al oxyhydroxides and variations in the nature and molecular weight of the organic matter; neither of these factors are constrained by our data. However, the lower proportions of colloidal metals in the carbonate rivers are not due to the overall ability of organic matter to bind metals since the apparent metal loadings of organic matter in carbonate rivers are higher than those in silicate rivers. Calculated ratios of colloidal metals to DOC are lowest for the silicate rivers: 60 meq mol⁻¹ for North Tyne I, 156 meq mol⁻¹ for North Tyne IIA, 152 meq mol⁻¹ for the Nent, 213 meq mol⁻¹ for the Tweed, 292 meq mol⁻¹ for the Tyne, and 318 meq mol⁻¹ for the Tyne tributary (Fig. 3). The Nent's relatively low colloidal metal content, compared to its ionic strength, suggests a lower average complexation capacity than the organic matter in the other rivers, consistent with a higher proportion of biological organic matter (Say and Whitton 1981).

The low proportions of colloidal Na, K, Ca, and Mg in the higher pH rivers can be explained by the higher total abundance of these elements and their primary occurrence as free ions. It is more surprising that the proportions of colloidal Al, Fe, and Mn are also lower than in the carbonate rivers compared to the silicate rivers. This is counterintuitive since these metals are more strongly adsorbed onto solid phases at higher pH and their oxyhydroxides are less soluble at higher pH. The data imply that neither the abundances nor the relative proportions of colloidal Al, Fe, and Mn in these rivers can be solely explained by an equilibrium partition model between dissolved and colloidal phases. A crossplot (Fig. 3) of the abundance of colloidal Al + Fe + Mn and colloidal Na + K + Ca + Mg indicates that the rivers carry widely varying amounts of colloidal major and minor elements. Two samples from the North Tyne, draining silicate sediments overlain by peat, have high abundances of Al +

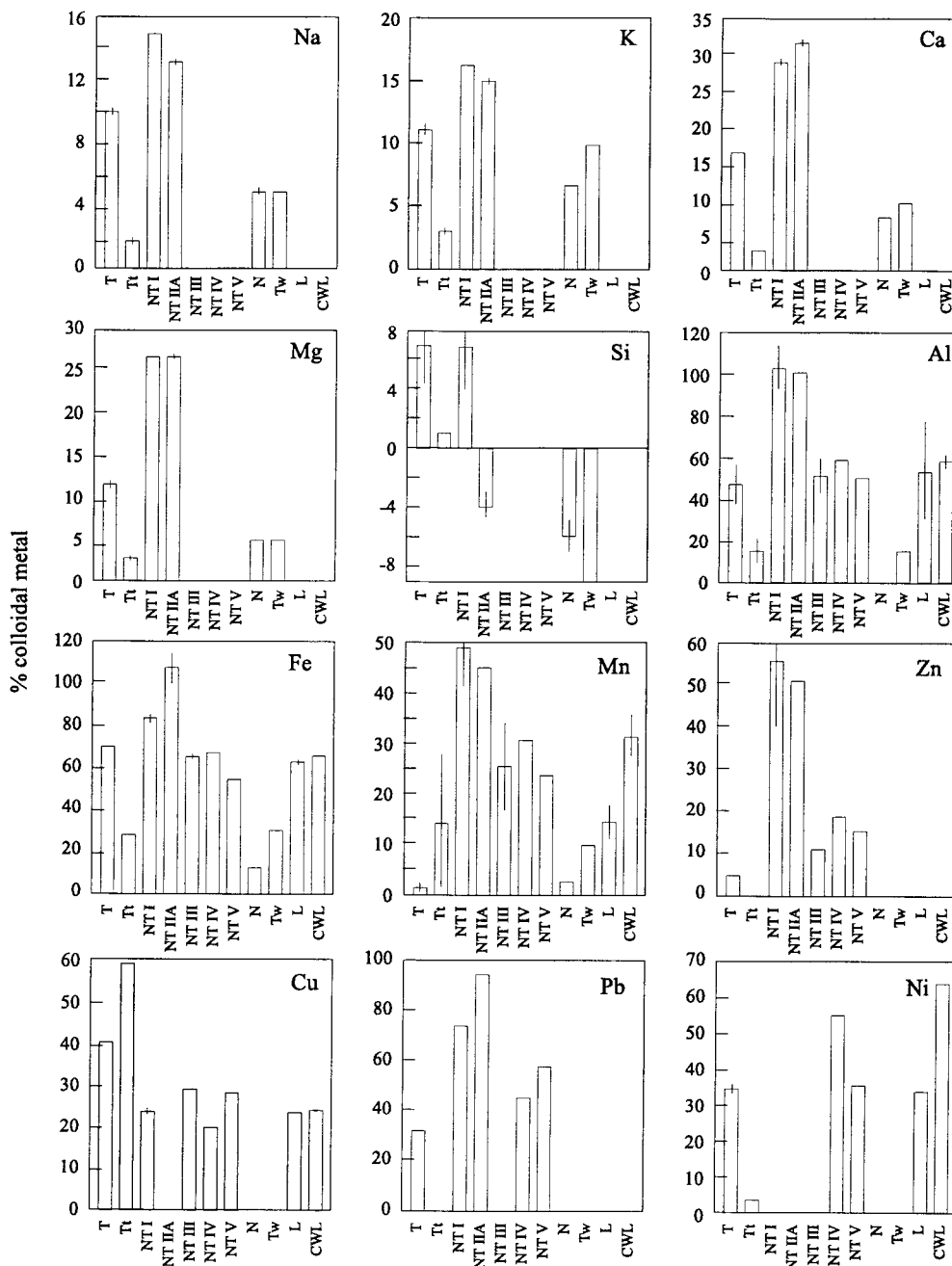


Fig. 4. Percentage of metals associated with the colloidal (1,000 Da to $0.1 \mu\text{m}$) pool. North Tyne II and Luce samples were duplicated. Error bars were determined by a summation of the errors in the replicate metal analyses of the metal concentrations in the retentate, permeate, and initial sample (see Eq. 2; Potts 1987). Error bars are not included where replicates were not determined. Abbreviations for each river are: T, Tyne; Tt, Tyne tributary; NT, North Tyne; N, Nent; Tw, Tweed; L, Luce; CWL, Crosswater of Luce.

Fe + Mn and low abundance of Na + K + Ca + Mg. In particular, North Tyne (I), which was collected during a period of snowmelt and thus had a strong input of surface runoff, has very high DOC and a low abundance of alkalis. The Nent, Tyne tributary, and Tweed are higher pH, higher ionic strength rivers that have greater abundances of colloidal alkalis but very low abundances of colloidal Fe, Al, and

Mn. The Tyne has high colloidal abundances of *all* the elements. In summary, the rivers in this study (North Tyne I excepted) have generally similar DOC concentrations but variable proportions of colloid-associated metals.

Synthesis—Synthesis and explanation of our data set needs to account for the following observations. (1) The

Table 2. Percent colloidal minor and trace metals in 0.45- μm filtered water. Colloidal metals are defined as those retained by a 1,000-Da or 10-kDa membrane.*

River/region	% colloidal metal [†]						
	Fe	Al	Mn	Cu	Zn	Pb	Ni
Northern Britain ¹	30–100	15–100	10–50	20–60	5–50	30–90	3–60
Nova Scotia ²	83–95	75–85	43–64	ND	ND	ND	ND
Ochlockonee (Florida) ³	>65	ND	30	ND	ND	ND	ND
Silone Channel (Italy) ⁴	82	ND	24	ND	ND	49	ND
Ob/Yenisey (Russia) ⁵	89–97	ND	ND	ND	ND	22–52	ND
San Joaquin/Sacramento ⁶	84–88	99	20	ND	2	ND	ND
Garonne ⁷	69	ND	5	ND	34	ND	ND
New Jersey Pinelands ⁸	63–96	55–85	25–35	48–71	20–50	80–91	ND

* References are: ¹ This study; ² Whitehouse et al. 1990; ³ Powell et al. 1996; ⁴ Martin et al. 1995; ⁵ Dai and Martin 1995; ⁶ Sañudo-Wilhelmy et al. 1996; ⁷ Kraepiel et al. 1997; ⁸ Ross and Sherrell 1999.

[†] ND, not determined.

<0.45- μm fractions of low-pH, low-alkalinity, and low-ionic strength rivers draining silicate terrains are enriched in Al, Fe, and Mn. The fraction of colloidal metals is higher in all cases compared to rivers draining carbonate terrains. (2) The <0.45- μm fractions of high-pH, high-alkalinity, high-ionic strength rivers draining carbonate terrains are enriched in Ca, Mg, Na, and K but are depleted in Al, Fe, and Mn. Although the absolute amounts of colloidal Ca, Mg, Na, and K are greater than those in the silicate rivers, lower proportions of these elements are associated with colloidal material. Both the absolute and relative amounts of colloidal Al, Fe, and Mn are lower in these rivers compared to the silicate rivers. (3) Regional rivers display geochemical characteristics intermediate between those of the silicate and carbonate rivers that feed them. There is little evidence for the displacement of minor elements from colloids by major elements. (4) The abundance of DOC has little influence on the abundance of major elements in <0.45- μm filtered river water and only a modest influence on the abundance of minor and trace elements. The proportions of elements in <0.45- μm filtrates show modest to good correlations with DOC.

We believe that the metal composition of colloids in these rivers is primarily a reflection of element mobility during the weathering process, with the additional influence of precipitation and partition reactions along the groundwater/river

flow path. Rainfall in this region of northern Britain currently has a pH of around 4.8. Rivers with high loadings of colloidal Al, Fe, and Mn drain peat-rich, acidic soils with low acid-neutralizing capacities. At low pH, Al, Fe, and Mn are more readily leached into solution. We have used the thermodynamic solubility–speciation–reaction path model, Geochemists Workbench[®] (Bethke 1996), to explore the likely abundance of Al, Fe, Mn, and Si resulting from the reaction of local rainwater with a reasonable mineral assemblage of quartz, kaolinite, ferric hydroxide, and the Mn oxide mineral bixbyite. In the model, we suppressed the precipitation of the iron minerals nontronite, hematite, and goethite and the manganese minerals todorokite, birnessite, and pyrolusite. The formation of these minerals is likely to be kinetically hindered at the timescales and temperatures relevant to these river systems. The results are given in Table 3, along with the results of similar models run to explore the apparent saturation state of 0.1- μm and 1,000-Da filtrates of the river waters for which we have sufficient data to adequately constrain the model. The model assumes thermodynamic equilibrium between minerals and water and does not account for the uptake of metals by colloidal phases. Although the model can only approximate the real river system, it nevertheless allows us to explore the likelihood that river chemistry is controlled by equilibrium processes and the extent to which colloidal material may be enhancing the ability of the waters to transport metals.

For the North Tyne, a silicate river, the abundances of operationally defined (i.e., <1,000 Da) dissolved iron, silicon, and manganese appear to be close to inorganic, thermodynamic equilibrium with the imposed mineral assemblage. The 1,000-Da filtrates, however, are highly supersaturated with respect to kinetically inhibited minerals such as hematite, goethite, nontronite, and todorokite. The equilibrium abundance of aluminum is about one order of magnitude lower than that observed in the 1,000-Da filtrate, implying a kinetic constraint on precipitation, the occurrence of polymeric Al, or both. The situation for the 0.1- μm filtrate is very different. Although silica is close to the expected equilibrium value, the abundance of particle-reactive elements is much greater than the equilibrium values: 300 times greater for Al, 100 times greater for Fe, and 7 times greater

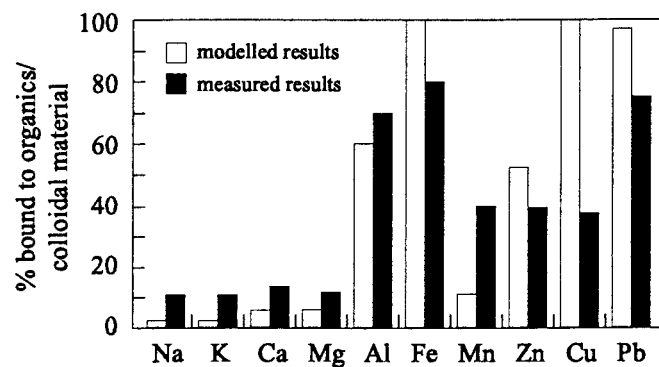


Fig. 5. Comparison of measured proportions of colloidal metals in the North Tyne and those predicted by WHAM (Tipping 1994) to be associated with humic and fulvic material.

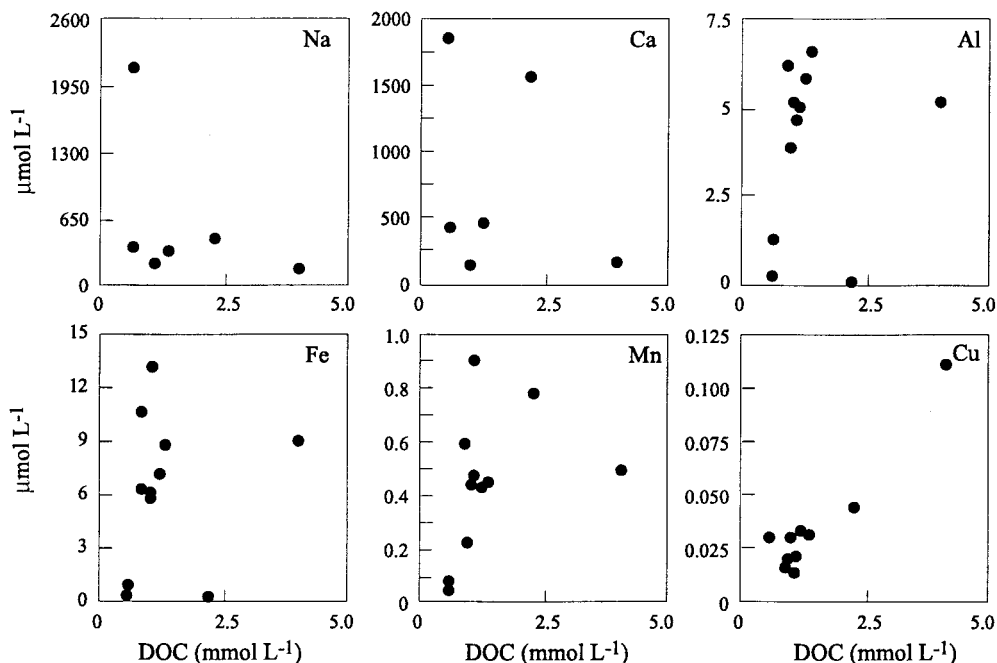


Fig. 6. Metal concentrations versus DOC for $<0.45\text{-}\mu\text{m}$ filtered water. The concentrations of major elements are independent of the organic content of these rivers. The abundance of minor and trace elements is influenced but not solely controlled by organic content.

for Mn. For Al and Fe, the values are very close to the equilibrium values for rainwater of pH 4.8 (Table 3).

We interpret these results as indicating that mineral dissolution in the acid soils results in abundances of dissolved elements that are largely controlled by the pH of rainwater; the low acid-neutralizing capacity of the soils (CLAG 1994) means that low pH values can be maintained long enough to drive the weathering system close to equilibrium with respect to a mineral assemblage typical of weathering silicate rocks (e.g., quartz–feldspar–kaolinite–gibbsite–Fe/Mn oxides/oxyhydroxides). Abundances of alkali and alkaline earth elements remain low due to low availability. Increases in pH should drive the precipitation of Fe–Mn–Al oxides, hydroxides, and silicates or, if precipitation kinetics are too slow, will result in high levels of supersaturation. The high levels of Fe/Mn/Al supersaturation in $0.1\text{-}\mu\text{m}$ filtered river water may thus be apparent rather than real; the “excess” Al, Mn, and Fe is in fact present as inorganic colloids and/or bound to colloidal organic matter, which is not included in the equilibrium model. Binding of metals to colloidal organic matter will maintain lower activities of truly dissolved ions (note the low and similar concentrations of Al, Fe, and Mn in the $1,000\text{-Da}$ permeates of *all* the rivers) and will drive further dissolution of aluminosilicate and oxide minerals. In contrast, the abundance of dissolved silica is controlled largely by simple dissolution of the mineral assemblage.

In carbonate soils, acidic rainwater will be quickly neutralized by reaction with carbonates. Since the concentrations of silica are similar in both silicate and carbonate rivers, we believe that the lower levels of Al, Fe, Mn, and trace metals do not reflect restricted availability due to a lack of minerals containing these elements. Rather, these elements will not be significantly mobilized into solution and will never be sig-

nificantly available for binding into colloidal organic matter. Colloids in rivers draining limestone regions are thus relatively enriched in alkalis and alkaline earth elements and depleted in Al, Mn, Fe, and trace metals. For the Tyne tributary, the $1,000\text{-Da}$ filtrate is close to equilibrium for Fe, Mn, and Si, with minor supersaturation for Al. For the same elements, the $0.1\text{-}\mu\text{m}$ filtrate shows levels of supersaturation between 2 and 10, levels that are explicable by the occurrence of humic-bound metals, as well as the occurrence of modest levels of inorganic colloids. The composition of the $0.1\text{-}\mu\text{m}$ Nent filtrate is close to equilibrium for Si, Al, Fe, and Mn, despite its high organic loading. Again, this indicates that the biological organic material in the Nent has a low metal complexation capacity and is not significantly involved in the transport of metals in that river.

Ultimately, the silicate and carbonate rivers mix to form regional rivers. Based on data from the River Tyne, it appears that the metal content of colloids in regional rivers primarily reflect a mixing of colloids from both river types, with relatively few secondary ion exchange reactions. The Tyne, which draws water from rivers with both carbonate and silicate catchments, has high colloidal abundances of both alkalis *and* minor elements, suggesting that (1) the alkalis do not readily displace minor elements from colloidal organic matter at the concentrations seen in these rivers and (2) the Tyne continues to carry the inorganic Al–Fe–Mn colloids generated, for example, in the North Tyne catchment. This is intuitively reasonable since (1) the pH values of the regional rivers remain high (promoting sorption/precipitation) and (2) the capacity of the total colloid population to sorb metals has not been exceeded (low total metal contents of colloids in silicate rivers). The data for the Tweed may be similarly interpreted. In the $1,000\text{-Da}$ filtrate, equilibrium

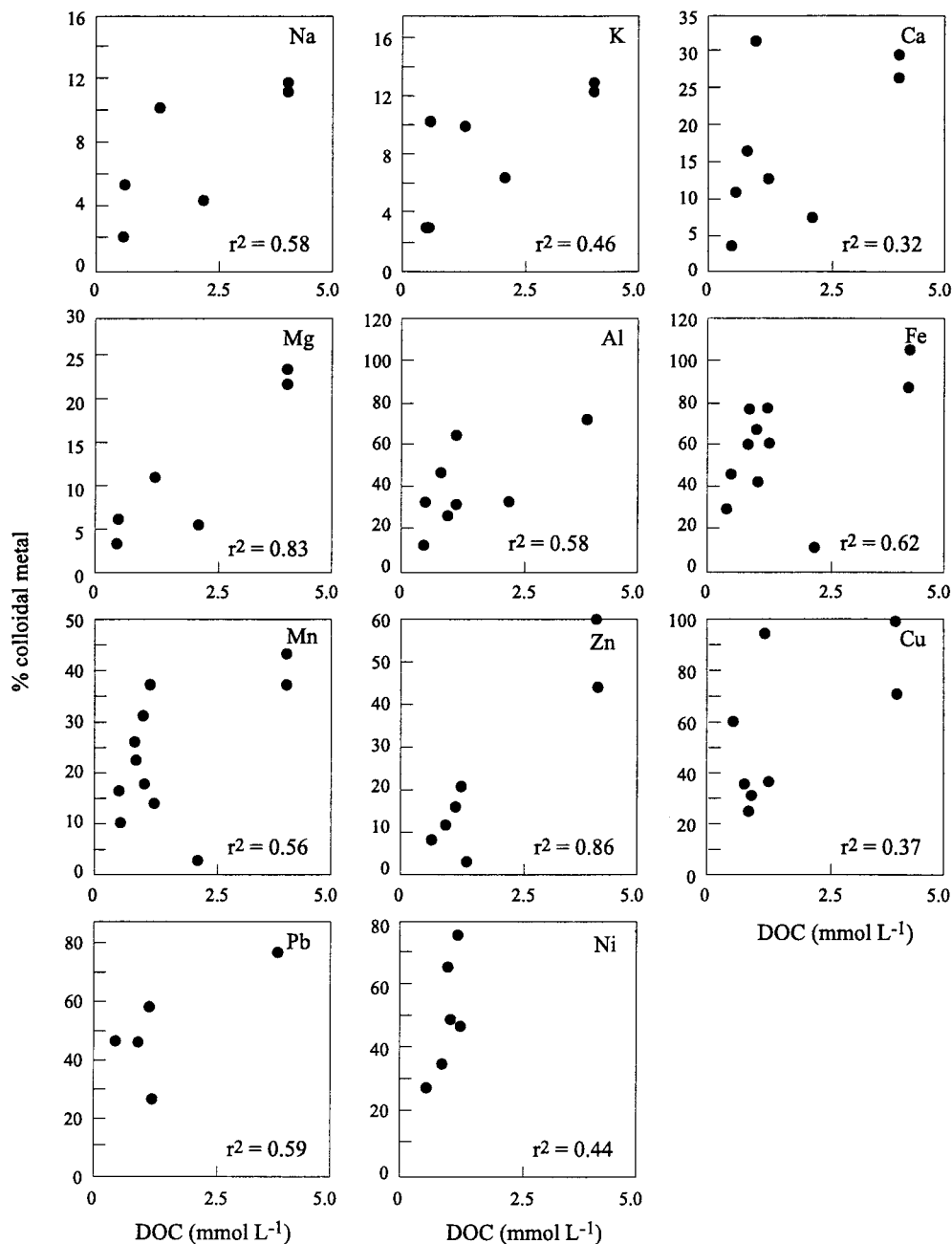


Fig. 7. Proportions of colloidal metals versus DOC.

levels of Si occur, with very modest levels of supersaturation for Al and Fe. In the 0.1- μm filtrate, Si is again at thermodynamic equilibrium, whereas the levels of Al, Fe, and Mn are around one order of magnitude above the equilibrium values. These levels of oversaturation can be explained by uptake of metals onto colloidal organic matter, although the occurrence of inorganic colloids cannot be ruled out.

The role of colloidal organic matter in the weathering process cannot be accurately established with our data. In carbonate terrains, binding of Ca and Mg onto colloidal organic matter will marginally increase the equilibrium concentration of these elements. In silicate terrains, uptake of Al and Fe onto colloidal organic matter will, in principle, substantially

increase the equilibrium concentration of these elements and thus enhance the dissolution of oxides and aluminosilicates. However, ultrafiltration alone does not distinguish colloidal inorganic and organic Fe and Al, so we cannot be certain that metal binding to organic matter has enhanced weathering rates. In agreement with previous studies (e.g., Ross and Sherrell 1999), our data do however indicate that the *transport* of Fe, Al, Mn, and trace metals in rivers draining terrains with low acid neutralizing capacities is substantially achieved by colloids. The process is thus of widespread importance: acid rain studies have shown that large areas of the northeastern United States, Canada, Scandinavia, and northern and western Britain have soils with low acid-neu-

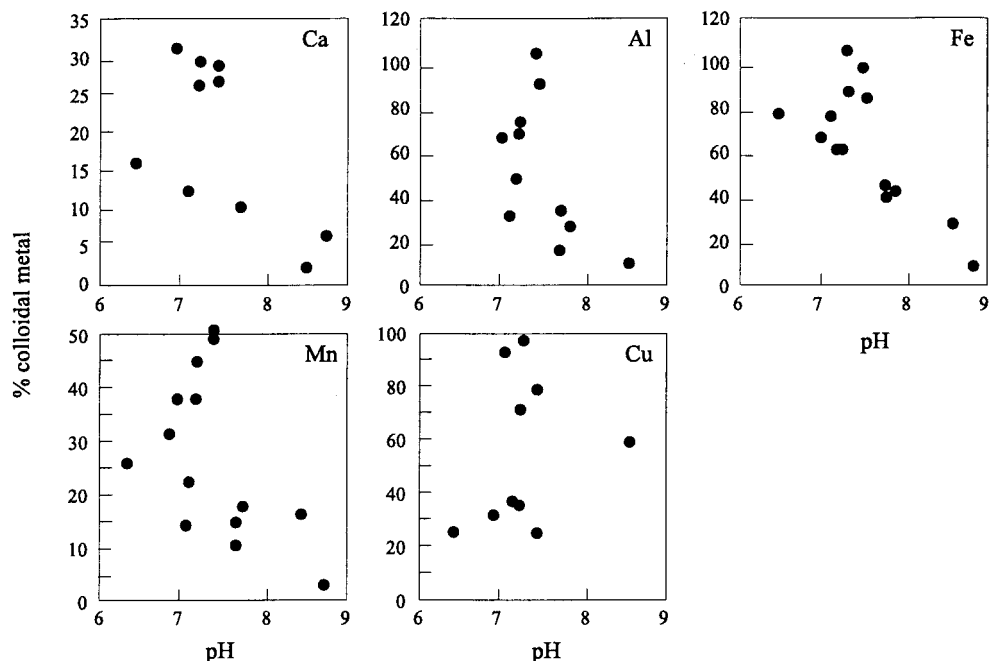


Fig. 8. Percentages of colloidal metals as a function of pH. Ca is shown as an example of a major ion, which all display similar behavior.

tralizing capacities and, in some cases, high organic loadings. For example, the mean pH and organic carbon content of upland British waters are 6.6 and 5.2 mg L⁻¹, respectively (CLAG 1994, 1995). Ultimately, these colloids will flocculate during estuarine mixing (e.g., Sholkovitz 1976; Boyle et al. 1977).

Concluding remarks—CFF provides a reasonably clean and efficient method of fractionating metals in river water into colloidal, fine particulate, and dissolved pools. However, the pool of colloidal metals is probably underestimated by the 1,000-Da polysulphone membranes we used. We observed little or no loss of fine particulate metals using a 0.1- μ m Durapore membrane.

Fine particles are a small pool of metals in these rivers. In contrast, colloids contribute significant fractions of many

metals in <0.45- μ m filtered water, especially those draining silicate terrains: >50% of Al, Fe, and trace metals; 30% Mn, 25% Ca and Mg; 15% Na and K; and a few percent Si. The metal content of <0.45- μ m filtered river water therefore reflects a mixing of two metal pools with differing elemental compositions: a truly dissolved pool and a colloidal pool.

We propose that the metal content of riverine colloids is primarily controlled by element mobility during the weathering process. In organic-rich, acidic soils, low pH solutions drive the dissolution of aluminosilicates and oxides. Uptake of Al, Fe, and trace metals onto colloidal organic matter maintains low activities of dissolved metals and enhances mineral dissolution. Colloids derived from these soils are enriched in Al, Fe, Mn, and trace metals, allowing high concentrations of these elements to develop in <0.45- μ m filtered water. Weathering rates of aluminosilicate minerals will

Table 3. Measured concentrations of metals in 1,000-Da and 0.1- μ m filtrates (in italics) plus equilibrium values predicted using the speciation-solubility-reaction path code, Geochemists Workbench[®]. Model constraints are given in the text. Values for rain assume an initial composition typical of northern England.*

	Metal concentration (μ mol L ⁻¹)							
	Al		Fe		Mn		Si	
	Measured	Equilibrium	Measured	Equilibrium	Measured	Equilibrium	Measured	Equilibrium
Rain, pH 4.8		2.48		7.41		28.9		55.6
N Tyne II 1000 Da	<i>0.15</i>	0.02	<i>0.11</i>	0.11	<i>0.04</i>	0.04	<i>33.3</i>	33.3
N Tyne II 0.1 μ m	<i>5.00</i>	0.02	<i>11.1</i>	0.11	<i>0.74</i>	0.11	<i>34.8</i>	34.8
Tweed 1000 Da	<i>0.07</i>	0.03	<i>0.37</i>	0.11	<i>0.11</i>	0.01	<i>75.6</i>	56.3
Tweed 0.1 μ m	<i>0.26</i>	0.03	<i>1.48</i>	0.33	<i>0.11</i>	0.01	<i>73.3</i>	56.3
Nent 0.1 μ m	<i>0.04</i>	0.02	<i>0.02</i>	0.02	<i>0.04</i>	0.03	<i>60.7</i>	56.3
Tyne trib. 1000 Da	<i>0.06</i>	0.02	<i>ND</i>	0.11	<i>0.05</i>	0.04	<i>99.3</i>	56.3
Tyne trib. 0.1 μ m	<i>0.22</i>	0.02	<i>0.59</i>	0.11	<i>0.07</i>	0.04	<i>106.3</i>	56.3

* ND, not determined.

be high, driven by the low pH solutions and enhanced by the uptake of Al and Fe by colloids. As the pH of the water increases, inorganic colloids may precipitate and form a major transport path over long distances.

In carbonate-rich soils, rapid neutralization of rainwater by carbonate minerals restricts the mobilization of aluminosilicates and oxides. Colloids in these systems will be enriched in alkali and alkaline earth metals but depleted in Al, Fe, and trace metals.

The distribution of major elements between colloidal organic and dissolved phases appears to be controlled by equilibrium partition. This is implied by the WHAM model, which quite successfully describes the extent of metal association with colloids in these rivers. The probable occurrence of inorganic Al-Fe-Mn colloids makes it less easy to determine to what extent these elements partition between solution and colloidal organic matter.

Since most elements adhere more strongly to colloids at higher pH, mixing of river waters derived from carbonate-rich soils and acidic, organic-rich soils will yield a pool of colloidal metals that will maintain high abundances of particle-reactive elements but may lose a fraction of the alkalis and alkaline earths. The loss of alkalis and alkaline earths may not be easily detected because they are likely to dominate the total pool of colloidal metals.

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