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Interactions between trace elements and dissolved organic matter in the stagnant anoxic deep layer of a meromictic lake

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Abstract

About 80% and more than 90% of the dissolved organic carbon (DOC) in the bottom water of Lake Pavin were isolated, respectively, on Amberlite XAD and Spherodex DEAE resins. Trace element concentrations in the fractions isolated were analyzed by using ICP-MS. Uranium, molybdenum, and antimony were found to be about 40% associated with fulvic and hydrophilic acids adsorbed on XAD resins at pH 2, the metal-organic association being not dissociated. Much higher percentages of the same elements, plus vanadium, were adsorbed on the DEAE resin at the pH of natural water, possibly because of the better preservation of acid labile organic complexes or of the supplementary adsorption of inorganic compounds. Ultrafiltration and dialysis made it possible to exclude colloidal fractions together with much U (78%), Mo (80%), V (55%), and DOC (65%). These elements and many others (including barium) were previously found to be quite reactive at the bottom of the lake, (apparently being scavenged by settling particles, which are mostly diatoms, then dissolved at the sediment-water interface). Conversely, trace elements with a conservative behavior in the bottom layer (such as lithium and cesium) were not found associated with dissolved organic matter (DOM). Barium was not strongly associated with the extractable DOM, which may argue for a direct interaction with inorganic particles or the existence of very labile complexes. Our work suggests the existence of relatively stable (nonacid labile) U and Mo–DOM colloidal associations in the anoxic bottom waters of the lake and their importance in the scavenging of those metals.

Although the general features of the cycling of many metals have been described in numerous lakes (e.g., Kuhn et al. 1994; Sigg et al. 1995; Viollier et al. 1995a, 1997; Hamilton-Taylor et al. 1996), the variety of biogeochemical processes at work in such highly dynamic systems means that the behavior of most trace elements may follow highly complex patterns (Buffle and De Vitre 1994; Hamilton-Taylor and Davison 1995). The stagnant deep layer of meromictic lakes (the monimolimnion), which usually exhibits an accumulation of dissolved elements, is highly suitable for studies of physical and biogeochemical phenomena, especially in anoxic conditions (Balistrieri et al. 1994; Viollier et al. 1995a, 1997; Hongve 1997). In some cases (e.g., Lake Pavin, Massif-Central, France) an approximate steady-state may be reached in the monimolimnion, owing to the depth profiles of chemical species which are stable over several years (Michard et al. 1994). In locations where there is enough water depth between the oxic–anoxic transition zone and the bottom of the lake, a depth zoning of the different processes may be expected. In particular, it may be possible to distinguish between the cycling of elements via precipitation–dissolution of Fe–Mn oxides at the redox boundary and the phenomena at the water-sediment interface (Viollier et al. 1997).

As discussed by Hamilton-Taylor and Davison (1995), it is generally difficult to distinguish between diffusion across the sediment-water interface and dissolution of settling par-

ticles as the source of increasing concentrations of trace elements at the bottom of lakes. Previous modeling of trace element cycling in the anoxic bottom layer of Lake Pavin based on depth profiles, the use of sediment traps, porewater measurements and mass-budget calculations, concluded that many trace elements found in the deep water layer were almost totally released by dissolution of the settling particulate flux at the sediment-water interface (Viollier et al. 1995a, 1997). However, for some elements, upward dispersion through the water column appeared to be hindered within 20 m above the bottom of the lake by one or more selective scavenging processes (Viollier et al. 1995a, 1997), emphasizing the role of sedimentation in trace element regulation in lakes (Sigg 1994). Coprecipitation with amorphous hydrous iron phosphate particles (Buffle et al. 1989) formed at the surface of settling diatoms was suggested as the dominant removal process (Viollier et al. 1997). In the same zone, dissolved organic matter (DOM) appeared to be removed from solution (Viollier et al. 1995a,b).

The interaction of DOM with authigenic solids (as mentioned by Tipping and Woof 1983, for iron oxides), or the destabilization of colloidal organic matter, can potentially lead to the precipitation of associated trace elements. The existence and the geochemical significance of trace metal–nonvolatile dissolved organic matter associations in natural waters have been relatively well established for Cu (e.g., Mills et al. 1989; Elbaz-Poulichet et al. 1994; Sigg et al. 1995) but occasionally other metals have been found to be affected by this process (Douglas et al. 1986; Yagi 1988; Douglas and Quinn 1989; Balistrieri et al. 1994; Küchler et al. 1994; Martin and Dai 1995; Zeh et al. 1997). In this

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study, DOM-trace metal associations in the anoxic bottom waters of Lake Pavin were investigated to evaluate the role of DOM in trace metal scavenging. DOM fractions and combined trace metals were isolated by using (1) nonionic macroporous resins and weak base anion exchange resins, and (2) in situ dialysis and on-line crossflow ultrafiltration. The combination of these different techniques and the analysis of a large panel of trace elements were used to determine which elements were largely bound to DOM.

Geochemistry of Lake Pavin—Lake Pavin is an oligotrophic meromictic crater lake, 92 m deep, located in the Massif Central area (France). The anoxic permanent deep layer (monimolimnion) contains higher concentrations of almost all compounds except sulphate, nitrate and oxygen than the mixolimnion (0–60 m from the surface). In spite of sublacustrine water inputs, the enrichment of most elements in bottom waters seems mostly to be due to internal cycling (Sholkovitz 1985). Several different reaction zones have been identified in the water column (Viollier et al. 1997). At the oxic–anoxic boundary (60 m from the surface), recycling occurs during Fe–Mn oxides precipitation–dissolution (Hamilton-Taylor and Davison 1995). Reactions of trace metals with sulfides (Hamilton-Taylor et al. 1996) seem mainly to be located below the oxic–anoxic boundary and to be important for U, Mo, Cu, and Co (Viollier et al. 1997). In the bottom layer, coprecipitation of iron and phosphate with a ratio close to that of vivianite (Michard et al. 1994) seems to be the main scavenging mechanism, especially for barium (Viollier et al. 1997), although Ba scavenging by Fe, Mn-oxides, or both at the redox boundary also occurs in Lake Pavin as mentioned elsewhere (Sugiyama et al. 1992). At the water-sediment interface, transient release of metals (Hamilton-Taylor and Davison 1995) seems to be due to transitions between iron phases (iron phosphate to pyrite).

Two groups of elements may be distinguished on the basis of their depth profiles in the bottom 30 m. In each group, profiles look alike and two parameter values can be linearly correlated (Michard et al. 1994; Viollier et al. 1995a). One group contains Cs, Li, Rb, B, Cl, Na, K, Ca, and Mg which are collectively presented by the Cs, Li, and Rb profiles in Fig. 1a–c. These elements behave conservatively in the monimolimnion and diffuse up to the superficial zone of the mixolimnion where an important part leaves the lake with the outlet waters while another part is incorporated into the settling biogenic flux and may be recycled at the water-sediment interface. The other group contains U, Mo, V, Ba, Sb, Al, Cu, La, Ce and Pb. Comparisons with the profiles for the first group elements (e.g., Li, Fig. 1b) indicate the second group elements are removed during upward diffusion. The removal of these elements is also shown by the depth increase of their settling particulate fluxes between 65 and 85 m (Viollier et al. 1997). The concentrations of the second group of elements are also strongly linearly correlated with DOC and iron ($R^2 = 0.96$) in the deepest 20 m of the water column, suggesting these trace elements, DOC and iron may be scavenged together. DOC may be biologically consumed as well. DOM profiles in lakes may be controlled by several factors such as planktonic production and bacterial re-assimilation in the water column (Maurin et al. 1997), pedogenic

organic matter inputs from the watershed (Zumstein and Buffle 1989), coupling with Fe oxide precipitation–dissolution, and sedimentary organic matter decomposition (Tipping and Woof 1983; Hamilton-Taylor et al. 1996). In this study, DOC profiles stable over several years are reported in the bottom layer of Lake Pavin (Fig. 1). The release of DOC may be primarily controlled by the decomposition of particulate organic matter and iron phase transition and dissolution at the bottom of the lake.

Methods

Sampling—Water pumped from a depth of 80 m was either filtered on-line (and acidified in the case of XAD resins) and passed through the resin columns, or forced on-line successively through the crossflow ultrafiltration cell. The devices used were two Millipore Minitan systems (without any metallic fittings) equipped respectively with a 1,000 dalton PLAC filter plate and a 10,000 dalton PLGC filter sheet, both of the regenerated-cellulose type. In situ pumping was preferred in order to preserve sample integrity (e.g., oxygen contamination). PVC tubing (4 and 8 mm i.d. for resin and ultrafiltration experiments respectively) were rinsed with diluted nitric acid, distilled water, and several liters of sample water before installation of the crossflow cells or the filter holder and the columns. Sample flows up to 300 ml min⁻¹ were set in the crossflow cells. Since the void volume of the cells is about 10 ml only, the time of transit of the water in the cell is very short and the sampled water is continuously renewed. Cells fitted with ultrafiltration membranes were cleaned several times by means of successive nitric acid and NaOH (both 0.1 N) rinses, and water, until blank values for DOC were less than 0.1 mg L⁻¹. In the case of the resin experiments, samples were filtered on-line through 47 mm Teflon 2 μ m prefilters and Durapore 0.45 μ m Millipore membranes. About 2 liters of sample were run through the filter units prior to membrane replacement. Comparisons with in situ syringe samplings indicate that transit from 80 m depth in the polymer tubing does not modify the concentrations of DOC and other monitored elements.

For the in situ dialysis, 50-ml 8,000 dalton dialysis bags (Spectrapor 7) filled with oxygen-free MilliRQ water and enclosed within 0.45 μ m membrane bags were suspended at 85 m depth for two days (a time sufficient for free solute concentrations inside the dialysis bags to reach 100% of the outside concentrations).

Resin experiments—On-line acidification utilized 50 times diluted Merck Suprapur nitric acid (final concentration about 0.3 M). A double-head Masterflex peristaltic pump was utilized to mix the sample with acid. An approximate flow rate ratio of 1 : 15 (acid : sample) yielded an experimental pH of 2. Cation exchange resin preacidification may be a possible alternative mean of acidification (Slauenwhite and Wangersky 1996). An array of two columns (PVC) filled with 75 ml Amberlite XAD-8 and XAD-4 resin beads was prepared as described by Aiken et al. (1992). Samples passed first through the XAD-8 column. Degassing (of primarily CH₄ and CO₂) due to pressure drops in the system was observed, but no attempt was made to split samples into liquid and

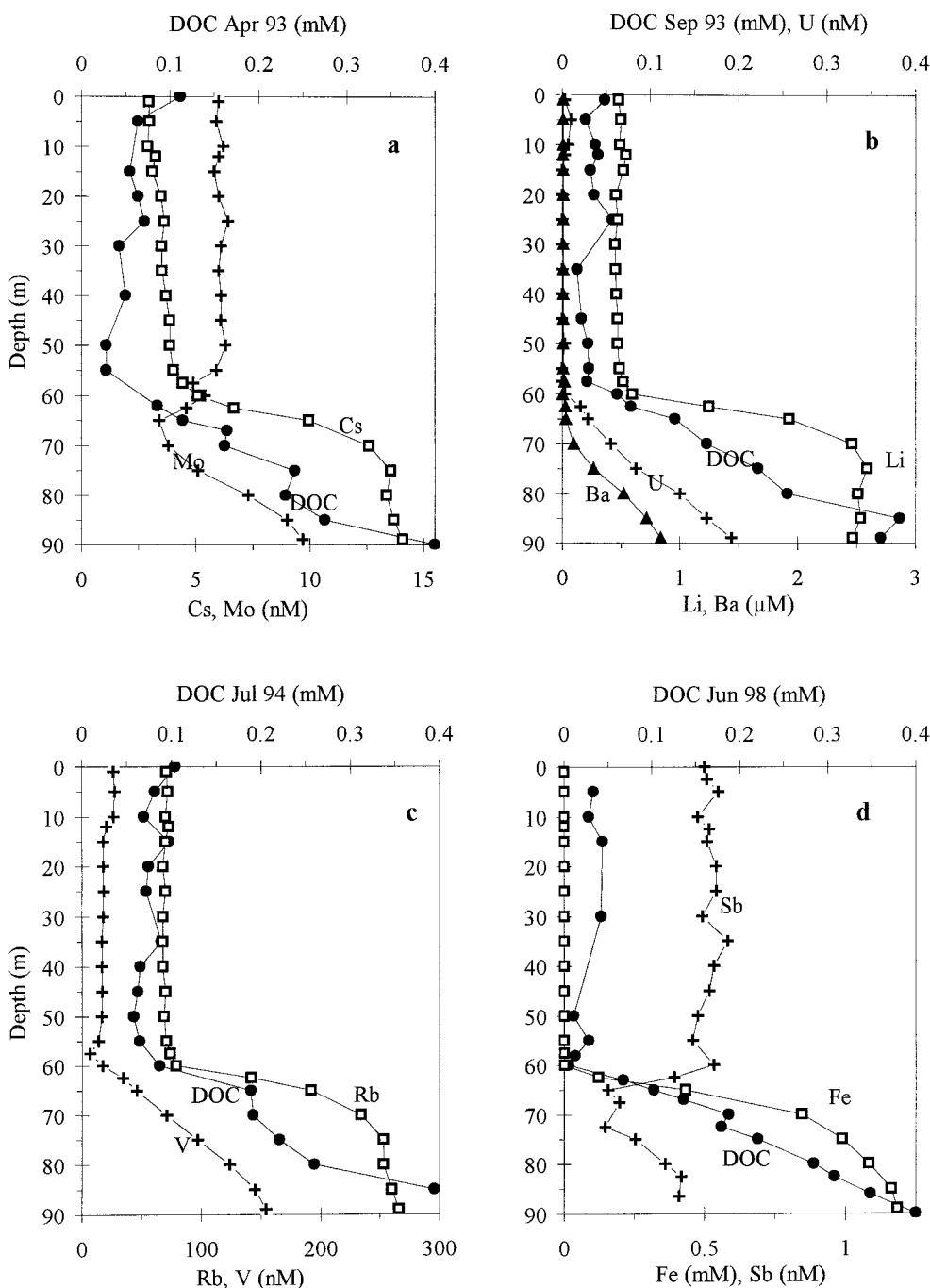


Fig. 1. Profiles of DOC in Lake Pavin in (a) April 1993, (b) September 1993, (c) July 1994, and (d) June 1998. Fe in September 1992; Li, Ba, V, U, Mo, Sb, and Cs in September 1993 (metal data from Michard et al. 1994 and Viollier et al. 1995a).

gaseous phases. Three assays were made in June and July 1994 (XAD-8 column only) and March 1995 (XAD-8, XAD-4 array). The hydrophobic-hydrophilic breakthrough (50% retained) should apply to solutes with a capacity factor (Leenheer 1981; Thurman and Malcom 1981) of about 20 for the two first assays and 100 for the last one. Resins were separately eluted with 0.1 M (two first assays) or 0.05 M (last assay) sodium hydroxide (NaOH with H₂O Merck Suprapur) into polypropylene Falcon tubes. NaOH concentra-

tions were chosen to minimize the experimental background concentrations for trace elements. In 1995, elution with NaOH was preceded by rinsing with 50 ml of 0.01 M HNO₃ to remove the dead volume sample content; DOC binding is favored under those conditions.

Adsorption on weak base anion-exchange resins was conducted in March 1995 with an 80-ml column of DEAE-Spheredex[®] macroporous resin (Bioseptra, France) which supports high flows (up to 70 ml min⁻¹). The average

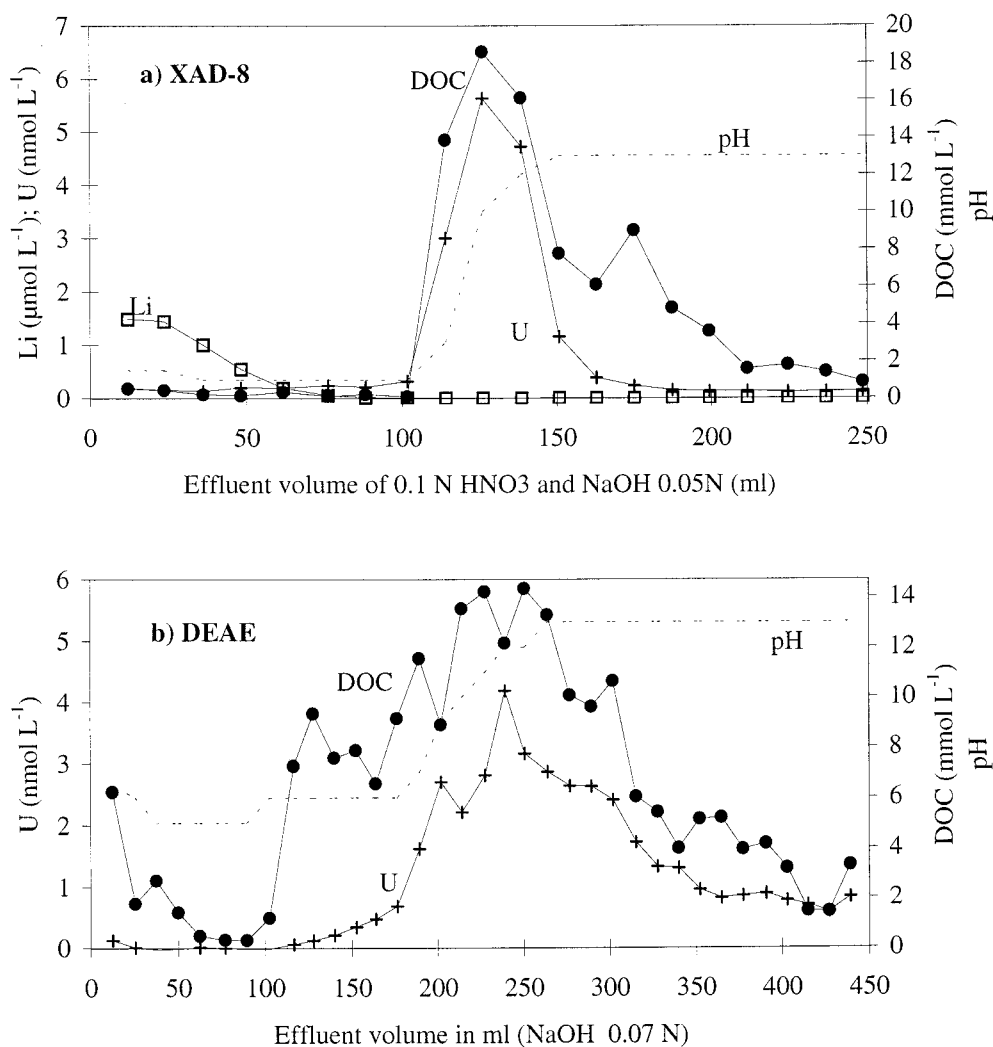


Fig. 2. Elution curves of DOC, U, and Li from (a) the XAD-8 and (b) the DEAE columns.

amount of ionizable groups is about $100 \mu\text{eq ml}^{-1}$. The volume of the sample was limited to 5.7 liters so as not to exceed the exchange capacity of the column (Miles et al. 1983). The water was pumped and filtered as described above but with no acidification. Elution was made with 50 ml MilliRQ water, then 0.07 M NaOH.

For both resin types, eluates were collected sequentially in series of 15-ml vials and pH was measured (pH test paper). After acidification with nitric acid, the series of test tubes were analyzed for DOC using a high-temperature catalytic oxidation method (Carlo Erba 140 TCM, Albéric et al. 1996) and trace elements using ICP-MS (Viollier et al. 1995a). Sequential collection and analysis of the eluate were used in order to potentially separate different types of DOM retained by the resins and to better appreciate DOC-trace element relationships (Fig. 2).

Blank values for selected elements are displayed in Table 1 and compared to sample values. The ultrafiltrate blank is Milli-Q water passed through the membranes (which were previously cleaned several times as described above). Blank levels are as a rule satisfactory except for Al and Cu, the

latter data being discarded. The XAD-8 blank represents the trace element content of the alkaline eluate after three cleaning cycles with nitric acid and sodium hydroxide (0.1 N). Values were always very small compared to concentration in the sample eluates (see Table 1).

Results

DOC and metals retention on resins—Figure 2a shows typical pH and DOC concentration changes during elution for experiments with XAD resins. Elution of organic matter proceeds by neutralizing DOM acidic functions.

The ratio of the amount of DOC released during elution from a given column to the total amount introduced is plotted in Fig. 3. As expected, a large percentage of DOC present in the bottom layer of Lake Pavin could be isolated and concentrated on XAD resins. About 54% and 26% of DOC were found to be retained at pH 2 on XAD-8 and XAD-4 resins respectively (Fig. 3a,b), totalling 80%. Quite a similar DOC proportion (about 90%) was adsorbed on the anion-

Table 1. Comparison between sample concentrations and blank levels.

Element nmol L ⁻¹	Bulk water < 0.45 μm	Ultrafiltrate blank	XAD-8 eluate (peak values)	XAD-8 blank NaOH eluate
Li	2,500	80	—	2
V	150	2	2,366	1
Co	90	2	609	1
As	120	<1	5,129	1
Rb	250	7	—	1
Sr	880	30	—	—
Mo	9	2	670	1
Cs	13	1	—	<0.1
U	0.17	<0.04	6	0.02
Ba	700	30	300	1
B	800	—	62	20
Sb	0.4	—	38	0.1
Cr	30	—	577	5
Al	51	100	1,365	107
Zn	20	—	149	3
Ni	20	—	472	2
Cu	2	15	114	1
Cd	0.1	—	2	0.1
La	0.2	—	1	0.02
Pb	2	—	56	0.02
DOC (μmol L ⁻¹)	400	1	18,600	175

exchange (DEAE) resin, at the natural pH of the water (Fig. 3c).

Li decreased during the first part of the elution (Fig. 2a), corresponding to the flushing of the dead (void) volume of the column. Similar decreases were recorded for B, Rb, Cs, Ba, Fe, and Mn, which did not show any significant affinity for either XAD resins or the DOM retained by them. Many other trace elements (U, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Sb, La, Ce, W, and Pb) showed an elution curve similar to DOC, although according to elements, the fraction retained by the column and involved in the coelution with DOC ranged from a few percent to up to 40% (only data for U are plotted in Fig. 2). For a given element, quantification of its association with organic matter is displayed as the ratio of the quantity eluted with DOC to the total amount introduced into the column array. Results are summarized in Fig. 3. Although information given by the three XAD experiments was qualitatively similar, quantitative results are based on the third experiment only (March 1995) because of a better control of blank values for the whole panel of elements. For some elements (i.e., Co), a certain proportion of the quantity introduced into the columns seemed not to elute totally from the XAD-4 resin. It was impossible to determine whether this quantity corresponded to free metal sorption which might elute with strong acid (as in Wan et al. 1985), to very hydrophobic organic complexes not eluted by the dilute alkaline solution (Aiken et al. 1992), or simply to precipitation of hydroxides. Results in Fig. 3 account only for the fraction which coelutes with DOC in the alkaline medium. The elements involved in the retention on the XAD column array (XAD-8 + XAD-4) are mainly U (40%), Mo, Sb (35%), Cr (25%), and As (20%). Other elements in Fig.

3a and 3b are less than 20% extractable simultaneously with DOC.

During the DEAE experiment, the elution curve was less smooth and tailing is noticeable (Fig. 2b). Most of the trace elements surveyed coeluted with DOC in the central section except U and Sn, which also coeluted in the tail. The extent of association with DOC on the resin (Fig. 3c) was worked out as mentioned above. However, the breakthrough of several elements (Cr, Ni, Cu, Zn, La, Pb, and DOC) was noticed before the end of the experiment, indicating that the fractions are underestimated. More than 90% of Mo and V was extracted by the resin, about 60% of Sb, U, and Ce, and between 40% and 50% of As and Cr. Li, Mn, Fe, Rb, Cs, B, and Ba shown almost no affinity for the resin.

Dialysis and ultrafiltration—Ratios of inner dialysis bag concentrations to outside free water concentrations (0.2 μm filtered) are shown in Fig. 4a. Among tested elements, only V and Mo show a net decrease in the <8,000 dalton fraction. Results for crossflow ultrafiltration are shown Fig. 4b and 4c. Besides V and Mo, DOC, and U are significantly depleted in the <10,000 dalton fraction and even more in the <1,000 dalton fraction. Between 50% and 80% of these elements are found in the fraction higher than 1,000 daltons.

Discussion

The XAD extraction method used operationally divides dissolved organic matter between hydrophobic fractions and hydrophilic fractions by adsorption on polymeric nonionic resins (Leenheer 1981). According to Thurman and Malcom (1981) aquatic humic substances are contained in the hydrophobic acid fraction that is the portion of DOC that sorbs on a column of XAD-8 resin at pH 2, and is eluted at pH 13. This fraction is composed primarily of aquatic fulvic acid. The hydrophilic acid fraction is defined as the portion of DOC contained in the XAD-8 effluent at pH 2 that sorbs on a column of XAD-4 resin, and is eluted at pH 13 (Aiken et al. 1992). The DEAE resin extraction method is used to isolate organic acids from natural waters at neutral pH values (Miles et al. 1983; Petterson et al. 1994). Interactions between solutes and the weak anion exchange material isolate both aquatic humus and hydrophilic acids.

XAD resins cannot be used to quantify in situ association of metals with organic matter at pH of natural waters because of the residual inorganic ion-exchange capacity of XAD resins at neutral pH values (Mackey 1982) and the rapid breakthrough of metals caused by DOM (Wan et al. 1985). Nevertheless, these resins have been used to concentrate free metals at neutral pH after isolation of hydrophobic DOM at acid pH (Wan et al. 1985). On the other hand, since labile metal-humates may dissociate at acid pH, isolation of hydrophobic DOM with XAD resins according to the method we used may favor isolation of non acid-labile organic complexes (Wan et al. 1985; Hiraide et al. 1987). A similar protocol was previously used to study humic-arsenic association in soils (Gustafsson and Jacks 1995). Precipitation of humic acids at acid pH may however reduce metal solubility (Sholkovitz and Copland 1981). DEAE resins are assumed to retain both hydrophobic and hydrophilic acid organic

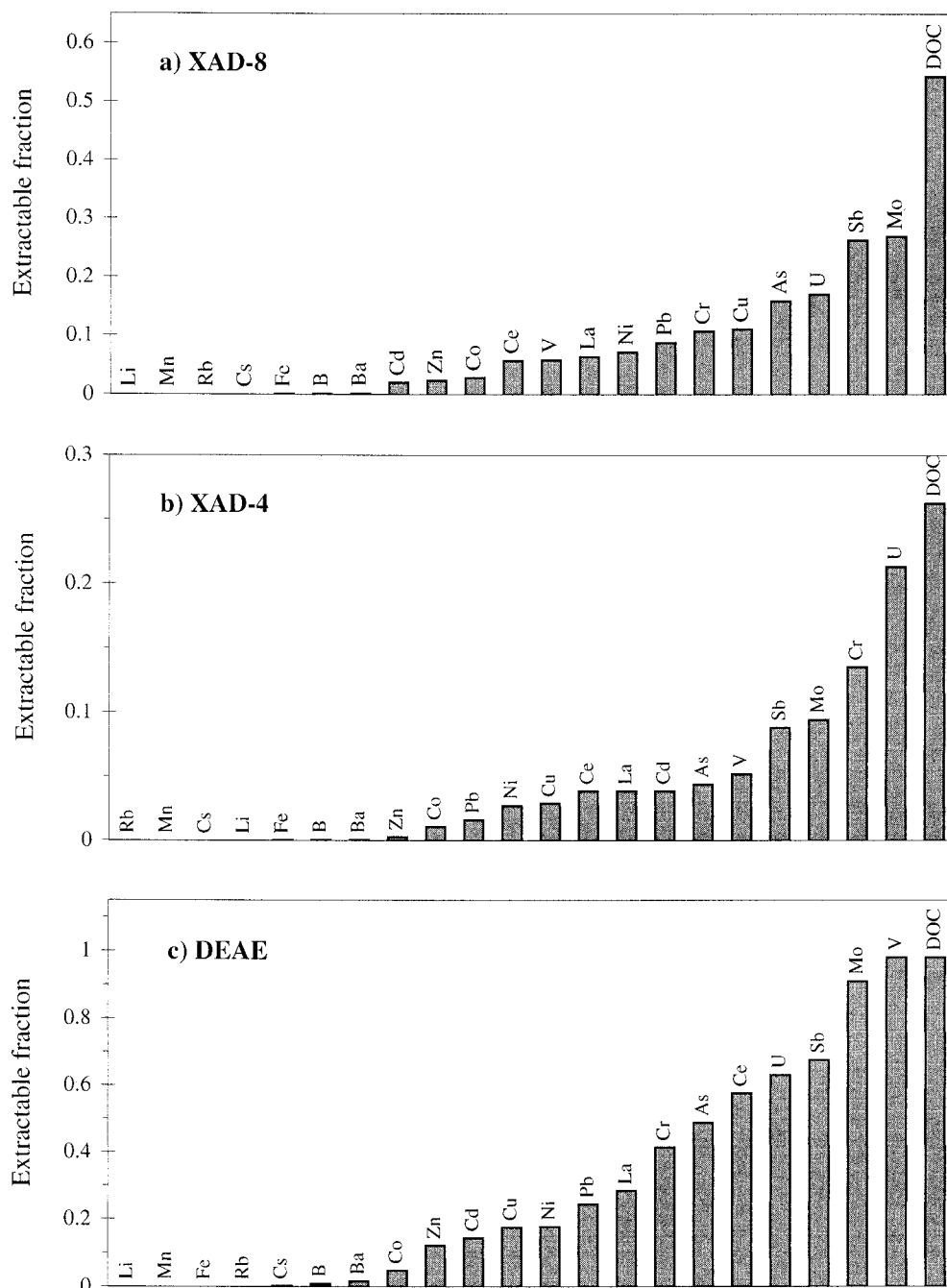


Fig. 3. Fraction of total dissolved element adsorbed on the resin and "coeluted" with DOC (ratio of the amounts collected by the columns to the total amounts introduced into the columns). (a) XAD-8, (b) XAD-4 (XAD-8 and XAD-4 columns serially fitted), (c) DEAE.

compounds as well as associated elements and also inorganic metal anions (Hiraide et al. 1987) at the pH of natural waters.

Consequently, the results obtained with the XAD resins suggest a stable association between aquatic humics and U, Mo, Sb. The same elements plus V are also highly extractable with the DEAE resin which may have preserved the fast reacted compounds from dissociation under acid conditions. However, DEAE resins may not only reflect the as-

sociation of metals to organic matter, since inorganic anions such as oxyanions can also exchange at the surface of the resin (e.g., V, Mo, U, As, Cr). An in situ association of U, V, and Mo with organic macromolecules or colloids is supported by the results of the dialysis and ultrafiltration experiments, which have no pH or resin effects. The agreement between results obtained by means of ultrafiltration and of resin extraction can be compared to the finding by Belin et al. (1993) of a clear correspondence between DOM ultra-

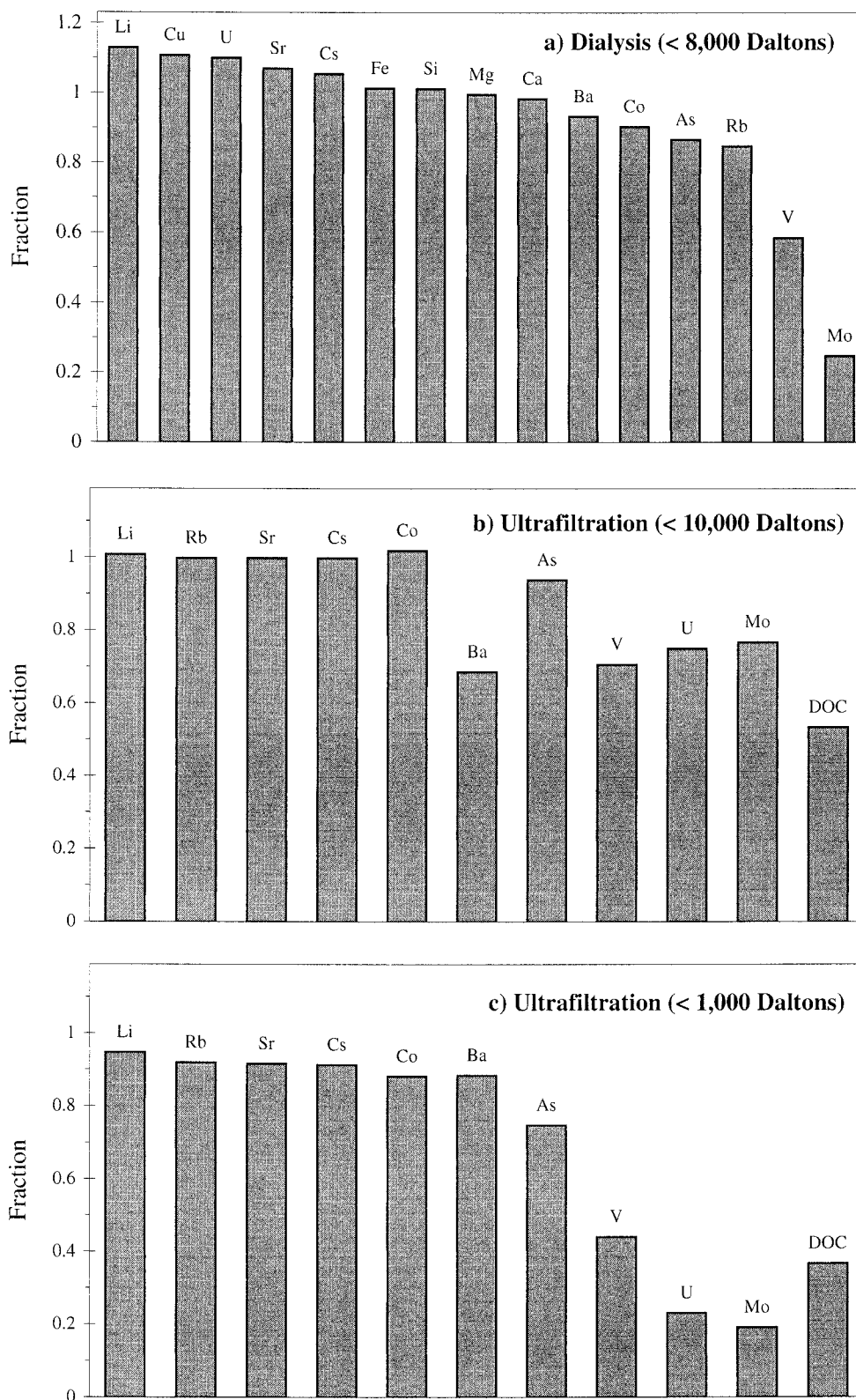


Fig. 4. Concentration ratio of ultrafiltered or dialyzed fractions to total "dissolved". (a) <8,000 dalton dialyzed fraction (80 m), (b) <10,000 dalton ultrafiltered fraction (85 m), (c) <1,000 dalton ultrafiltered fraction (85 m).

filtered fractions and resin extracts as regards to fluorescence characteristics. Indications of such general associations between U, Mo, V, and organic matter are widely reported in nature from field as well as from experimental studies (Disnar 1981; Helz et al. 1996; Zeh et al. 1997).

Fe, Mn, Zn, Pb, and other trace metals currently found associated with macro-molecular organic fractions or colloids (De Vitre et al. 1988; K uchler et al. 1994; Martin and Dai 1995, Yagi 1988) were found to be almost unextractable by XAD (at acid pH) and DEAE resins (at neutral pH) in the anoxic bottom water of Lake Pavin. In the anoxic hypolimnion of Lake Fukami-ike, Yagi (1988) found a large proportion of Mn to be extractable by XAD at neutral pH, but not at acid pH. Ultrafiltration data suggested the XAD-extractable Mn was in colloidal form. Unfortunately, Lake Pavin Fe and Mn ultrafiltration data are missing. Fe data from the in situ dialysis experiments revealed no colloidal iron fractions >8,000 daltons.

In Lake Pavin bottom layer, stable (nonacid-labile) trace metal organic associations, representing large amounts of some dissolved species (U, Mo) and minor amounts (1–20%) of a larger panel of elements were isolated on XAD. Moreover U, Mo, and V seem largely bound to colloidal matter. Conversely, elements like the alkalis, B, and Ba were not found significantly bound to organics relative to their concentrations in the water column. All elements with conservative behavior in the bottom layer (Li, Cs, Rb, B) were not found associated with organic matter. Those trace metals (U, MO, V, Sb) scavenged during upward dispersion were found bound to organic matter or colloids to a greater or lesser extent. Scavenging of trace metals may result from binding to adsorbed DOM (Davis 1984; Tessier et al. 1996). Barium, one of the most reactive elements in the monimolimnion, did not appear to be significantly bound to DOM. Therefore different mechanisms are involved in the removal of Ba and other traces (U, V, Mo, . . .) at the bottom of the lake. Organic matter may be of prime importance for the latter, although direct interaction with inorganic particles (e.g., iron phosphate) is probably responsible for the cycling of Ba. More generally, the finding of high percentages of XAD extractable and colloidal U and Mo in the anoxic waters of Lake Pavin is relevant to uranium speciation performed by ultrafiltration in anoxic groundwaters (Zeh et al. 1997).

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