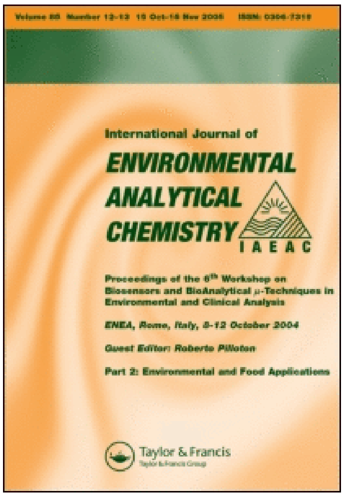

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Speciation of Aluminum, Cadmium, Copper, and Lead in Humic Soil Solutions-A Comparison of the Ion Exchange Column Procedure and Equilibrium Dialysis

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SPECIATION OF ALUMINUM, CADMIUM, COPPER, AND LEAD IN HUMIC SOIL SOLUTIONS—A COMPARISON OF THE ION EXCHANGE COLUMN PROCEDURE AND EQUILIBRIUM DIALYSIS

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Metal speciation of Al, Cd, Cu, and Pb was studied in soil solutions containing humic substances (HS). The ion exchange column procedure was optimized and compared with a modification of the equilibrium dialysis (ED). A soil solution, for which the metal speciation at equilibrium could be calculated, was obtained from the ED. The solution was processed through columns with pH-adjusted ($pH_{effluent} = pH_{influent}$) and Na^+ saturated strong cation exchange resins.

Using a pH-adjusted exchanger, there was only a slight dissociation of Al-humic complexes (AlHS) in the column ($\bar{x} = 7\%$). The dissociation was independent of pH (4.0–5.5) and ν_{Al} (μmol Al bound/g HS) in the range 51–500.

The kinetic lability of CdHS, CuHS, and PbHS in the pH-adjusted exchanger (Cd > Pb > Cu) was greater than for AlHS. Among the heavy metals, the ion exchange column procedure was most suitable for fractionating Cu into humic and non-humic forms. The CuHS concentration obtained with the Na^+ exchanger was 90–109% of the one obtained with ED, the variability being independent of ν_{Cu} (μmol Cu bound/g HS), though slightly dependent of sample pH.

KEY WORDS: Aluminum, heavy metals, speciation, humic substances, equilibrium dialysis, ion exchange fractionation.

INTRODUCTION

A knowledge of the chemical speciation is essential for understanding transport mechanisms and biological interactions of metals in soils and natural waters. The important role of soluble organics as ligands in soil solutions has recently been reviewed.[1] These organics are dominated by humic substances[2] (HS), which also complex metals most effectively.[3]

Among the methods available for speciation of trace metals in natural waters, anod stripping voltammetry (ASV) and ion exchange fractionation are probably the most widely used. Since surface-active compounds, like HS, may interfere in the ASV technique (see e.g. refs. 4–6), this method should not be used uncritically in speciation studies on soil solutions rich in HS.

Both Chelex-100[7–9] and strong cation exchange resins[10–14] have been used in trace metal speciation studies. The sample is passed through a column containing the resin. Free hydrated metals and labile complexes are retained. Hence, the metal fractions obtained are operationally defined. In several studies using strong cation exchange resins the contact time between the sample and the resin has not been reported.[11-13] This is unfortunate since the contact time probably affects the results to a great extent. Few studies have been published where the Chelex-100 or the ion exchange method is calibrated to equilibrium conditions in solutions containing HS. Experiments with Donnan dialysis[10] showed that the lability of Cu, Pb, and Zn-humic acid complexes increased in the order Cu < Pb < Zn. The lability in the Chelex-100 column was greater than in the ion exchange column.

The ion exchange column procedure was originally proposed for Al speciation studies[15,16] and has frequently been used for that purpose in environmental analyses.[17,18,19] Despite the rapid acceptance of the method, few investigations of the assumptions on which it is based have been reported. Recently, Backes and Tipping[20] compared the ion exchange procedure with equilibrium dialysis (ED). Their study showed that the lability of humic-complexed Al (AlHS) increased when ν_{Al} (μmol Al bound/g HS) increased. Up to $\nu_{Al} = 300$–400 there was almost no difference between the two methods. However, when ν_{Al} exceeded that level the discrepancy rapidly increased and was approximately 25% at $\nu_{Al} = 1000$. The results were explained by the presence of complexing sites having different strength.

ED has been used for speciation of trace metals[21,22] and Al[23] in freshwaters. One problem, however, is the permeation of low molecular weight organics[22-24], that affects the speciation in an unpredictable way. In the paper by Backes and Tipping,[20] this problem was overcome to a great extent by using a high molecular weight HS fraction.

In the present study on metal speciation in soil solutions containing humic substances, the ion exchange column procedure was compared with a modification of the ED. A soil solution for which the metal speciation at equilibrium could be calculated was obtained from the ED. The solution was processed through columns with pH-adjusted ($pH_{effluent} = pH_{influent}$) and Na^+ saturated strong cation exchange resins. The metals included in the study were Al, Cd, Cu, and Pb. The objectives were:

1) To evaluate the suitability of the modified ED technique as a reference method in metal speciation studies involving humic substances;
2) To study how Na^+ and pH-adjusted exchangers affect the recovery of metal-humic complexes at different sample pH and ν (μmol metal bound/g HS);
3) To optimize the contact time between sample and resin;
4) To test the reproducibility of the ion exchange column method.

MATERIALS AND METHODS

Experimental design and theory

In the ED experiments two or five tubings containing 100 ml soil solution (inner solution) were suspended in 9500 ml of a solution consisting of inorganic ions dissolved in aq. dest. (outer solution). All was arranged in an 11 litre polyethylene bucket with a protecting lid. The outer solution contained major anions and cations at the same concentrations as in the soil solution, plus trace concentrations of Al, Cd, Cu, and Pb. The outer solution was continuously stirred, using a magnetic stirrer, in order to minimize equilibration time.

When equilibrium was attained, the inner solution was transferred to a polyethylene bottle. Samples were taken from the inner and the outer solutions for analysis of total concentrations of Al, Cd, Cu, and Pb, major cations and anions, dissolved organic carbon (DOC), and absorbance. The molecular weight distribution of the humic substances (HS) in the inner solution was studied using gel filtration chromatography (GFC). The remaining inner solution was processed through two different ion exchange columns, using the procedure described in the ion exchange column procedure section.

A great advantage with the experimental design used was that the ratio between the volumes of the outer and inner solutions was 20 or 48. Low molecular weight organics (e.g. fulvic acids and aliphatic acids) that permeated into the outer solution, and thus affected the metal speciation were diluted 20 or 48 times, respectively. Since the penetration of a soil-derived fulvic acid could be as high as 30% for the tubings used in this study,[24] I decided to use pre-dialysis in order to further minimize the concentration of unwanted ligands in the outer solution.

At equilibrium, the concentrations of all inorganic metal species were the same in the outer and inner solutions. If the concentration of organic ligands in the outer solution could be neglected, the concentration of metal-humic complexes in the inner solution was obtained as the difference between the total metal concentrations in the inner and outer solutions. The speciation of inorganic Cd, Cu, and Pb was calculated using equilibrium constants from Lindsay.[25] A BASIC program was used to calculate the inorganic Al speciation. Species considered and their associated equilibrium constant were taken from LaZerte.[23] Activity coefficients were calculated using the extended Debye–Hückel equation.

If the non-mobile HS inside the dialysis tubings make up a substantial fraction of the total equivalents of anions, a Donnan dis-equilibrium will occur.[26] This was, however, corrected for according to LaZerte.[23] Complexation of Ca and Mg with HS in the inner solution was considered in the calculations.

Equilibrium dialysis

Spectra/Por 7 dialysis tubing with a molecular weight cutoff of 1,000 (24.2-mm-diameter) was used in all experiments. The tubing was cleaned by soaking in 1% conc. HNO_3 according to LaZerte[23] before use. Disposable polyethylene gloves were worn whenever handling the dialysis tubing.

The soil solution was collected from a brown forest soil in a birch (*Betula pendula* Roth) stand, using a 15-cm-deep percolation lysimeter.[27] Before use, it was filtered through 0.45 μm membrane filters, spiked with 26.3 or 52.6 μM total F^-, and adjusted to the desired pH.

Table 1 Concentrations (μM) of major ionic constituents in the birch soil solution

Cations:	$Ca^{2+} = 92$	Anions:	$Cl^- = 264$
	$Mg^{2+} = 40$		$NO_3^- = <5$
	$K^+ = 320$		$SO_4^{2-} = 316$
	$Na^+ = 312$		

The outer solution had the same composition of major cations and anions in all experiments. Concentrations were the same as in the soil solution (Table 1). It also contained Al, Cd, Cu, Pb, and F^-, in experiments 6–11 (refer to Tables 2 and 3), at the following total concentrations: 1.85, 1.78×10^{-2}, 1.57×10^{-1}, 4.83×10^{-2}, and 26.3 μM. In experiments 1–5, the total concentrations of Cu and Pb were varied, being $3.15 \times 10^{-3} - 6.29 \times 10^{-2}$ and $2.41 \times 10^{-3} - 1.93 \times 10^{-2}$ μM, respectively. The concentrations of the other elements were, however, the same. The desired concentrations of Cd, Cu, and Pb were achieved by diluting BDH SpectrosoL standard solutions. The following salts (Merck p.a. quality) were used to get the desired concentrations of the other ions: $Al(NO_3)_3 \cdot 9H_2O$, $CaCl_2 \cdot 2H_2O$, K_2SO_4, $MgCl_2 \cdot 6H_2O$, NaF, and Na_2SO_4. The pH was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH.

By adding F^- to the inner and outer solutions precipitation of $Al(OH)_3$ and the formation of polynuclear Al-hydroxy-complexes were avoided. ν_{Al} was also decreased. In a preliminary study, the latter was shown to be important, since the permeation of HS into the outer solution increased when ν_{Al} increased. This was probably an effect of a decreased net negative charge and/or an increased coiled structure of the HS molecule.

In the pre-dialysis, soil solutions were dialyzed for 48 hours against the same outer solution that were used in the dialysis experiments, but with no addition of heavy metals and Al. The pH was 4.5 for experiments 1–9 and 5.0 for experiments 10–11. Pre-dialysis was, however, neither used in the dialysis experiments associated with the ion exchange experiments where the flow rate was optimized, nor in the dialysis experiment where equilibration time was studied.

Ion exchange column procedure

The column was 16 mm in diameter and contained 15 ml of the prepared resin (Doulite 225 SRC 9, 14–52 mesh). Before use, the resin was cleaned by soaking in three portions of 5 M HCl for 24 hours with continuous air stirring. The main portion of the resin was converted to the Na^+ form by soaking in 1 M NaOH for about one hour. The resins were then rinsed on a Büchner funnel with deionized water.

Two types of prepared exchangers were used, one pH-adjusted and one Na^+ exchanger. The pH-adjusted exchanger was prepared by adjusting the proportions of Na^+ and H^+ resin in such a way that the pH remained unchanged, when a $NaNO_3$ solution with the same pH and ionic strength (1.3 mM) as the sample was passed through the exchanger. The pH in the soil solution effluents was hence within ±0.1 pH units of that of the sample.

A constant sample application rate was obtained using a peristaltic pump.

The first 60 ml of the sample solutions were discarded. The sample was then collected in duplicate in 20 ml polyethylene bottles. All samples were processed with freshly prepared resins.

Chemical analyses

All vessels and bottles used for standard solutions, samples, etc. were soaked in 10% conc. HNO_3 for at least 48 hours. Samples were stored in the dark at 4 °C. Samples for metal analyses and DOC were acidified to pH 2 or 3 with HNO_3.

Total concentrations of Ca, K, Mg, and Na were determined by acetylene-air flame atomic absorption spectroscopy (AAS) (Varian AA6), K and Na with 7.5 mM Cs^+, and Ca and Mg with 72 mM La^{3+} in standard and sample solutions. Analyses of total concentrations of Al, Cd, Cu, and Pb were performed by flameless AAS (Varian AA-475 spectrophotometer and GTA-95 graphite tube atomizer). The graphite tubes were supplied with L'Vov's platform. Matrix modifiers[28] were used when analyzing Cd and Pb. Standards were made from BDH standard solutions. When analyzing outer solutions with Cu and Pb concentrations <16 and <7.2 nM the solutions were preconcentrated ten times. 250 ml of the samples were evaporated until dryness in an evaporation cabinet at 95 °C. The evaporation residue was dissolved in 2.5 ml hot conc. HNO_3 (BDH, ARISTAR) and then diluted to 25 ml.

Total concentrations of Ca, K, Mg, and Na were determined by acetylene-analyzed by ion chromatography. Since a negative peak interfered with the F^- peak, the added concentration of F^- was used when the speciation of Al in the outer solution was calculated.

DOC was determined by infrared technique using a Beckman 915B carbon analyzer, and the UV-absorbance was determined on a Perkin Elmer spectrophotometer model 124 ($\lambda = 260$ nm). Samples were chromatographed on a Toyo Soda TSK 2000 SW column using a Varian (model 5000) HPLC system. The mobile phase used was 0.15 M $NaNO_3$ adjusted to pH 6.0. The HS eluted was measured with a UV detector set at 260 nm. In order to obtain approximate molecular weights of the HS, the column was calibrated with polystyrene sulphonates having a narrow molecular weight distribution (Pressure Chemicals Co.).

RESULTS AND DISCUSSION

Equilibrium dialysis

The equilibrium rate for a metal in the dialysis system was mainly a function of

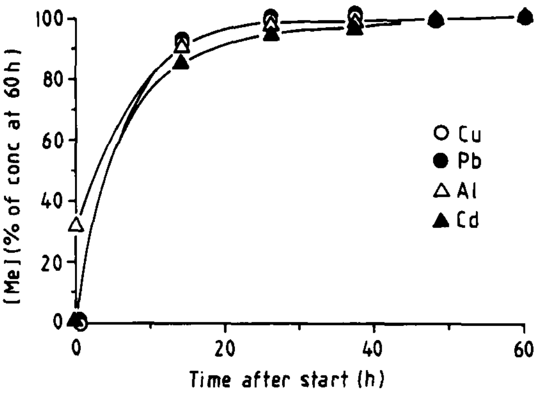

Figure 1 Equilibration rate for Al, Cd, Cu, and Pb in the equilibrium dialysis system. Each point represents the mean of two dialysis tubings. The total concentration of Al, Cd, Cu, and Pb, respectively, at equilibrium was 36.4, 2.24×10^{-2}, 1.16, and 4.65×10^{-1} μM. Major ions were as in Table 1. [HS] = 20.5 mg C/l, $[F^-]_{total} = 52.6$ μM, pH = 5.0.

the surface to volume ratio of the dialysis tubings, the stirring rate, and the temperature. The co-diffusing anion has also been shown to be of great importance, at least in systems with no stirring.[23] All these parameters were kept constant during and between the experiments. The rate at which the metals approached equilibrium inside the dialysis tubings was relatively similar for the different metals, despite large differences in concentrations (Figure 1). Equilibrium was attained after at least 48 hours. This equilibration time was chosen throughout the study.

Organic substances were determined by two independent methods, DOC and absorbance. No organic substances in the outer solutions could be detected with either methods except at pH 4.0, where the DOC concentration was 0.2 mg/l. These organic substances, probably low molecular weight HS, were assumed not to affect the metal speciation significantly. The approximate molecular weight distribution of the HS, before and after dialysis, is shown in Figure 2. The peak maxima occurred at an approximate molecular weight of 1100, which is close to previously reported number-average molecular weights for soil and water fulvic acids.[29,30]

The speciation of Al, Cd, Cu, and Pb in the inner solution is shown in Tables 2 and 3. The proportion of metals in complexes with HS generally increased when pH and the concentration of HS increased. At constant pH (4.5) and concentration of HS ($\bar{x} = 15.2$ mg/l, CV = 2.4%; CV = coefficient of variation), but varying total concentration of Cu (71.8–384 nM) and Pb (16.0–67.9 nM), the proportion of CuHS and PbHS increased as the total concentrations decreased (Table 3). CuHS increased from 87 to 96% and PbHS from 75 to 87%. An inverse relationship between complexing strength for metals by HS and ν is however well known (see e.g. ref. 31 for a detailed discussion).

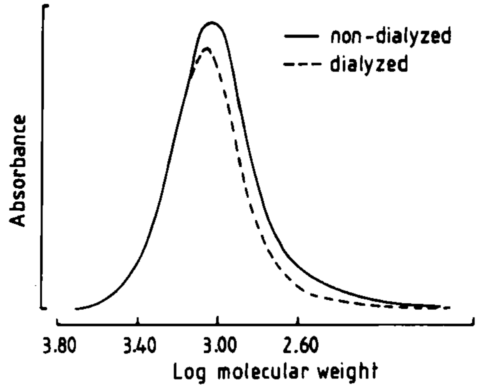

Figure 2 Approximate molecular weight distribution of the humic substances (HS) in the soil solution used. The effects of dialysis is also illustrated (expt. 11, Tables 2 and 3).

Table 2 Speciation of Al in the dialyzed soil solutions. Only species contributing to more than 1% of the total inorganic concentration (except for Al^{3+}) are reported. Concentration of HS was calculated from DOC data, assuming a carbon content of 50%.[1]

Expt.	*pH*	$[HS]$ (mg/l)	μM				
			$[Al^{3+}] \times 10^4$	$[AlF^{2+}] \times 10$	$[AlF_2^+]$	$[AlF_3^0] \times 10$	$[AlHS]$
1	4.5	15.3	5.9	1.1	1.24	5.0	1.96
2	4.5	15.7	5.9	1.1	1.24	5.0	1.93
3	4.5	14.7	6.0	1.2	1.26	5.1	1.86
4	4.5	15.3	5.8	1.1	1.23	4.9	1.91
5	4.5	15.1	6.0	1.1	1.25	5.0	1.88
6	4.0	17.4	8.3	1.4	1.43	5.2	0.886
7	4.5	19.6	6.3	1.2	1.30	5.2	2.25
8[a]	5.0	19.6	5.7	1.1	1.24	5.0	4.29
9[a]	5.5	19.6	5.0	1.0	1.13	4.7	6.75
10[a]	5.0	41.4	7.7	1.4	1.50	5.8	10.6
11[a]	5.0	79.2	9.9	1.7	1.74	6.4	18.6

[a] Correction made for Donnan dis-equilibrium.

Ion exchange column procedure

In the ion exchange column procedure it is assumed that metals complexed to HS pass through the column while inorganic metal species are retained on the exchanger. Since the dissociation of natural alumino-organic complexes has been shown to depend on the contact time with the resin,[16] it was necessary to optimize the flow rate through the column for the resin type used.

The ion exchange results were compared with ED results, using the latter as a reference. In order to determine the leakage of inorganic Al species, also solutions without HS (composition of major ions as in Table 1) were processed.

Table 3 Speciation of Cu, Pb, and Cd in the dialyzed soil solutions. Only species contributing to more than 1% of the total inorganic concentration are reported. Concentration of HS was calculated from DOC data, assuming a carbon content of 50%.[1]

Expt.	*pH*	*[HS] (mg/l)*	*nM*									
			[Cd^{2+}]	*[$CdCl^{+}$] × 10*	*[$CdSO_4^0$]*	*[CdHS]*	*[Pb^{2+}]*	*[$PbSO_4^0$]*	*[PbHS]*	*[Cu^{2+}]*	*[$CuSO_4^0$]*	*[CuHS]*
1	4.5	15.3	16.4	3.5	1.06	3.33	1.94	0.18	13.9	2.54	0.13	69.1
2	4.5	15.7	16.4	3.5	1.06	3.02	3.09	0.30	21.5	5.83	0.31	110
3	4.5	14.7	16.5	3.6	1.07	2.85	7.22	0.69	32.4	11.5	0.60	165
4	4.5	15.3	16.3	3.5	1.05	2.49	11.5	1.1	42.9	23.2	1.2	239
5	4.5	15.1	16.5	3.5	1.06	2.85	15.7	1.5	50.7	46.9	2.5	335
6	4.0	17.4	16.2	2.4	1.03	1.78	37.3	3.5	60.8	102	5.3	348
7	4.5	19.6	15.9	3.0	1.02	2.67	41.8	4.0	125	108	5.7	655
8[a]	5.0	19.6	15.8	2.9	1.00	4.35	31.2	2.9	186	87.0	4.5	823
9[a]	5.5	19.6	16.6	3.0	1.06	6.68	35.0	3.3	301	94.9	4.9	1290
10[a]	5.0	41.4	16.8	3.0	0.95	6.76	32.4	2.7	298	67.4	3.1	1300
11[a]	5.0	79.2	17.9	3.3	1.00	14.3	28.9	2.4	431	53.4	2.4	1760

[a] Correction made for Donnan dis-equilibrium.

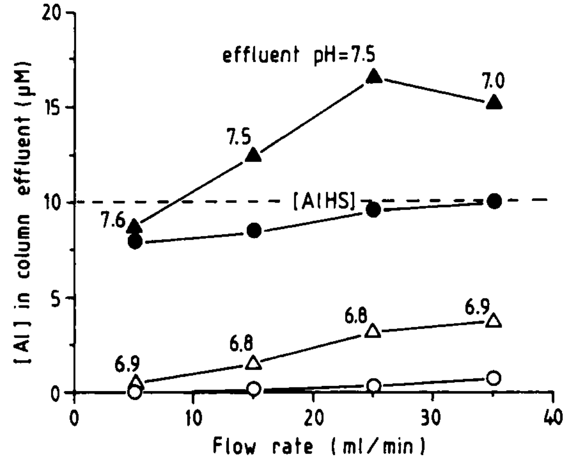

Figure 3 The concentration of Al in the ion exchange column effluent as a function of the flow rate through the column. Filled symbols represent a dialyzed soil solution ($[\mathrm{Al}]_{\mathrm{total}} = 27.9\,\mu\mathrm{M}$, [HS] = 10.2 mg C/l) and open symbols a solution without HS ($[\mathrm{Al}]_{\mathrm{total}} = 18.5\,\mu\mathrm{M}$). In both solutions, the total F^- concentration 52.6 μM, the pH 5.0, and the major ions was as in Table 1. Circles and triangles denote that a pH-adjusted and a Na^+ exchanger was used, respectively. The broken line is the concentration of AlHS determined by equilibrium dialysis.

The pH-adjusted exchanger and a flow rate of 25 ml/min was optimal for fractionating Al into humic-complexed and inorganic species (Figure 3). A flow rate of 35 ml/min only increased the leakage of inorganic species. When processing the solutions without HS at 25 ml/min, the adsorption of Al to the pH-adjusted exchanger was $\geq 98\%$ at total Al concentrations of 1.85–185 μM. The presence of 52.6 μM total F^- did not affect the adsorption of 18.5 μM Al. The influence of the relatively high F^- concentration on the results should thus be limited to lower the AlHS concentration, as F^- acts as a competing ligand to HS. A prerequisite is that the formation of ternary complexes between Al^{3+}, F^-, and HS can be neglected.

The Na^+ exchanger overestimated the humic complexed fraction of Al to a great extent, due to leakage of anionic inorganic species formed when the pH was increased (e.g. at pH = 7.0, $\mathrm{Al(OH)}_4^-$ constitutes 93% of the total inorganic Al). Driscoll[16] also stressed the importance of using a pH-adjusted exchanger, but found no differences in the effluent concentration of Al when natural water samples were analyzed using pH 5 and pH 7 columns. The effluent pH was, however, not reported.

There was only a slight dissociation of AlHS in the ion exchange column (Figure 4). The dissociation was constant ($\bar{x} = 7\%$) and independent of pH (4.0–5.5) and ν_{Al} (51–500).

The results are in accordance with the results of Backes and Tipping,[20] obtained at $\nu_{\mathrm{Al}} < 300$–400. At $\nu_{\mathrm{Al}} = 500$, however, the discrepancy between the two methods did not increase in the way reported by Backes and Tipping.[20] In fact, HS from different sources was used in the two investigations, but in their study a high molecular weight HS fraction was used. In this study, however, the molecular weight distribution of the HS was moderately altered during the 96 hours of

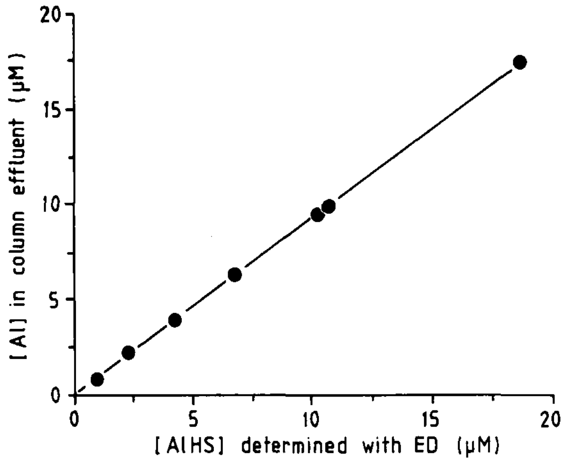

Figure 4 The concentration of Al in effluent from the pH-adjusted exchanger as a function of the concentration of AlHS determined by equilibrium dialysis (ED). Throughout, a flow rate of 25 ml/min was used. The same samples as in expt. 6–11 (Table 2). Also included is the sample of Figure 3 having a $[\mathrm{Al}]_{\mathrm{total}}$ of 27.9 µM and a [HS] of 10.2 mg C/l. $y=0.028+0.932x$, $r^2=1.00$, $n=7$.

dialysis (Figure 2). The total loss of HS, measured as absorbance, was in the range 12–29%. In another study, Backes and Tipping[32] report a lower carboxylic acid content for a high molecular weight HS fraction (3.5×10^{-3} eq./g HS) than for the sample as a whole (5.5×10^{-3} eq./g HS). If natural waters are processed, the ion exchange column method may therefore not, to the extent reported by Backes and Tipping,[20] underestimate AlHS at $\nu_{\mathrm{Al}}>300$–400.

The ion exchange column procedure has been used for speciation of Al in soil solutions from S. Sweden. ν_{Al} (calculated from DOC data) was normally in the range 200–800, dependent on soil depth, soil type, and tree species (D. Berggren, unpublished data). In soil solutions where AlHS made up the major fraction, like solutions from A-horizons of podzols, ν_{Al} was <400.

The flow rate was optimized for Cd, Cu, and Pb in the same way as for Al (Figure 5). There were large differences in the recovery of metal-humic substance complexes between the Na^+ and pH-adjusted exchangers. The effluent concentrations obtained with the Na^+ exchanger corresponded best to the results obtained with ED. A flow rate of 25 ml/min was chosen in the subsequent experiments, since no (Cu) or very small (Cd and Pb) differences in the recovery between 25 and 35 ml/min were obtained with the Na^+ exchanger. Traces of Cd (0.2–0.3 nM) and Cu (2–3 nM) were found in the effluent at 35 ml/min but not at 25 ml/min, when a solution without HS was passed through the exchangers (total concentrations of Cd, Cu, and Pb were 17.8, 157, and 48.3 nM, respectively, and the composition of major ions was as in Table 1).

The relationship between sample pH and the effluent concentrations of Cu, Pb,

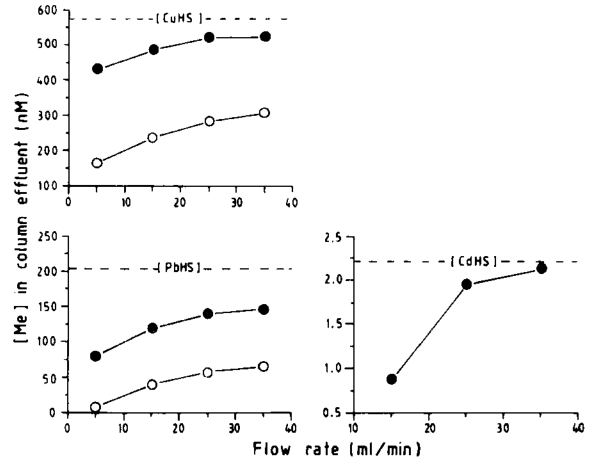

Figure 5 The concentration of Cd, Cu, and Pb in the ion exchange column effluent as a function of the flow rate through the column. Open and filled circles denote that a pH-adjusted and a Na$^+$ exchanger was used. The broken lines represent the concentrations of metal-humic complexes determined by equilibrium dialysis. The total concentration of Cd, Cu, and Pb, respectively, was 19.2, 661, and 251 nM. [HS] = 10.2 mg C/l, pH = 5.0, and the major ions was as in Table 1.

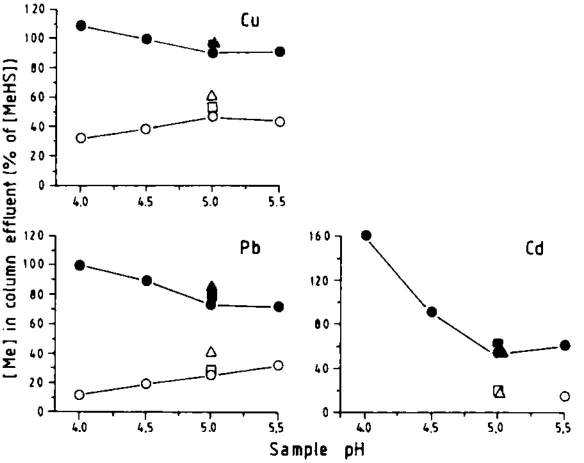

Figure 6 The concentrations of Cd, Cu, and Pb in the ion exchange column effluent as a function of the sample pH. The same samples as in expt. 6–11 (Table 3). Circles, quadrates, and triangles, respectively, refer to expt. 6–9, 10, and 11. Open and filled symbols denote that a pH-adjusted and a Na$^+$ exchanger was used.

and Cd is shown in Figure 6. The samples are the same as in expt. 6–11 (Table 3) and have relatively (compared with natural waters) high values of ν_{Cu} and ν_{Pb}. The effluent concentration of the Na$^+$ exchanger corresponded best to the metal-humic concentration found in the ED experiments. The following equilibrium reaction may be used to explain the behaviour of the heavy metal ions in the different exchangers. It assumes complexation to sites of salicylic acid type.[33,34]

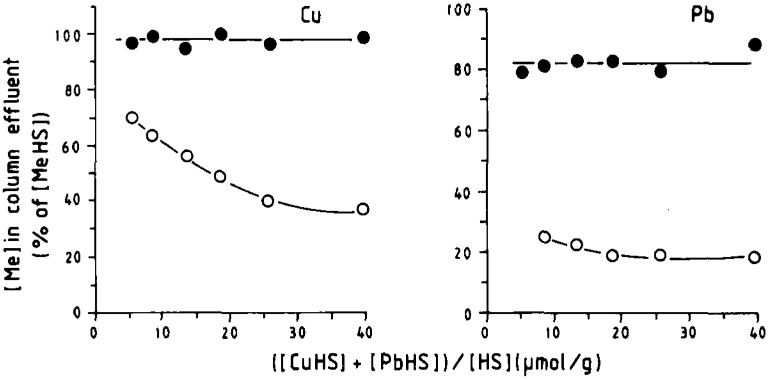

Figure 7 Effect of different ν_{Cu} and ν_{Pb} ($\nu = \mu$mol metal bound/g HS) on the recovery of CuHS and PbHS from columns with Na^+ (filled circles) and pH-adjusted (open circles) resins. The same samples as in expt. 1–5 and 7 (Table 3). ν_{Al} and ν_{Cd} was approximately constant in all experiments ($\bar{x} = 124\,\mu$mol Al/g HS, CV = 4%, $\bar{x} = 0.18\,\mu$mol Cd/g HS, CV = 16%).

$$Me^{n+} + HL^- \rightleftharpoons MeL^{(n-2)} + H^+$$

Me^{n+}, $MeL^{(n-2)}$, and HL^- are, respectively, the free hydrated metal, metal complexed to HS, and free ligand site. The adsorption of H^+ to the Na^+ exchanger ($pH_{effluent} = 6.6$–7.4) tended to shift the metal-humic equilibrium "to the right" and, thus, counteracted the dissociation of the metal-humic complexes. Slow kinetics of the metal-humic equilibrium (e.g. Cu) resulted in a relatively small dissociation in the pH-adjusted exchanger and little response to sample pH in the Na^+ exchanger (Figure 6). At fast kinetics, as for Cd, there was a considerable dissociation in the pH-adjusted exchanger as well as in the Na^+ exchanger at high sample pH (5.0 and 5.5). At low sample pH (4.0), on the other hand, the fraction of Cd-humic complexes was strongly overestimated using the Na^+ exchanger, due to an increased complexation when pH in the column was increased.

Contrary to sample pH, different values of ν_{Cu} and ν_{Pb} did not affect the recovery of CuHS and PbHS from the Na^+ exchanger (Figure 7). In the pH-adjusted exchanger, however, the lability of especially Cu increased as ν_{Cu} increased. This is in accordance with the results of a kinetical study of the dissociation of CuHS.[35] The complexation of Cu to HS was described as a complexation to sites having a continuous distribution of lability (first-order rate constants in the range 0.001–40 s^{-1}). From Figure 7 it appears that the less labile sites are used at low ν_{Cu} and when more Cu is complexed it will couple to more labile sites. Data of DOC and total concentration of Cu indicate that the less labile sites are more than sufficient for complexing the Cu in soil solutions from Swedish podzols.[27] Since the difference between the Na^+ and pH-adjusted exchangers decreases with decreasing ν_{Cu}, only small differences between the two exchangers can be expected when processing such soil solutions.

When comparisons are possible, the data are in relatively good agreement with those of a previous report,[10] where the ion exchange column method was compared with Donnan dialysis. A Na^+ exchanger and a somewhat shorter

Table 4 The reproducibility of the cation exchange procedure. A birch soil solution ($<0.45\,\mu m$) was used (pH 4.50, DOC = 24.8 mg C/l). CV = coefficient of variation.

Metal (*Me*)	*Resin*	[*Me*] *after cation exchange* (μM)	*CV* (*n* = *3*) (%)	[*Me*] *before cation exchange* (μM)
Al	pH-adj.	19.9	2.2	24.8
Cd	Na^+	3.0×10^{-3}	1.7	1.97×10^{-2}
Cu	Na^+	1.34×10^{-1}	1.4	1.57×10^{-1}
Pb	Na^+	4.57×10^{-2}	2.5	6.71×10^{-2}

contact time (10 s) was used. When a solution containing humic acids (HA) ($\nu_{Cu} = 1{,}400$; $\nu_{Pb} = 1{,}100$; pH 6.0) was passed through the exchanger, the estimate of Cu and Pb in complexes with HA was 95 and 85%, respectively, of that obtained by Donnan dialysis.

The reproducibility of the ion exchange column procedure was good. When aliquots of soil solution were passed through three columns with a freshly prepared resin, the coefficients of variation were 1.4–2.5% for four metals (Table 4).

CONCLUSIONS

Using the equilibrium dialysis (ED) procedure reported, ideal (pH 4.5 to 5.5) or near ideal (pH 4.0) conditions were obtained: on one side of the dialysis membrane only inorganic metal species were present and on the other side both inorganic metal species and metals in complexes with humic substances (HS). Using flameless AAS, humic substance complexation at trace levels could be studied. It was also possible to obtain relatively large volumes of dialyzed solution (c. 500 ml). The ED procedure is suitable as a reference method in speciation studies of metals in natural waters containing HS.

The ion exchange procedure is a useful method for determining the concentration of AlHS, at least in solutions having $\nu_{Al} < 500$. The dissociation was 7% independent of pH (4.0–5.5) and ν_{Al} (51–500).

The ion exchange procedure is also a useful tool in estimating the concentration of CuHS in natural solutions where analytical methods like ASV and ion-selective electrode are not applicable. The CuHS concentration obtained with the Na^+ exchanger was 90–109% of the one obtained with ED, the variability being independent of ν_{Cu}, though slightly dependent of sample pH.

For fractionation of Pb and Cd into humic and non-humic forms, the ion exchange procedure cannot be recommended. The recovery of PbHS and CdHS from the Na^+ exchanger was strongly dependent on sample pH and from the pH-adjusted exchanger the recovery was poor (for $Pb \leqslant 41\%$ and for $Cd \leqslant 20\%$).

There are several advantages with the ion exchange procedure. It is rapid and sensitive (using flameless AAS, Varian AA-475 and GTA 95, and pre-concentration ten times, the lower limit of the analytical range is 8.9×10^{-2}, 1.6, and 7.2 ×

10^{-1} nM for Cd, Cu, and Pb, respectively). It is also insensitive to interference of high concentrations of electrochemically active compounds like HS.

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