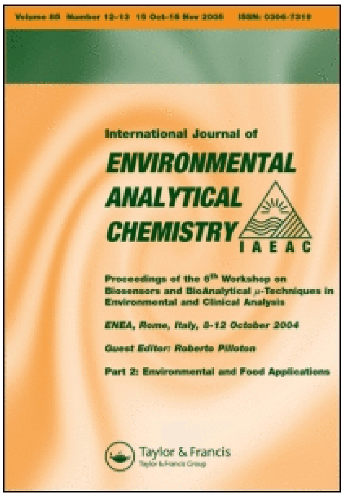

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FACTORS AFFECTING THE INVESTIGATION OF HEAVY METAL SPECIATION IN FOREST SOILS USING THIN-CHANNEL ULTRAFILTRATION

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In order to evaluate the usefulness of thin channel ultrafiltration for heavy metal speciation studies in litter extracts, the leaching and adsorption phenomena associated with this separation process were examined using different membranes.

After washing the ultrafiltration assembly successively with dilute HNO_3 and H_2O, no leaching was detectable. On the other hand, losses up to 100% of initial Pb- and Cu-content were detected on filtering an ionic standard solution. The retention of heavy metals decreased in the following order $Pb > Cu \gg Cd > Zn$. Membranes composed of regenerated cellulose had the highest retention potential for heavy metal ions and were therefore not suitable for speciation studies.

Using membranes with low heavy metal adsorption capacity (e.g. polycarbonate, polysulfone), thin-channel ultrafiltration was a reliable method for speciation studies based on size fractionation. However, changes in organic-metal association which occur in the separation step could be minimized using thin-channel ultrafiltration technique. This fact has to be taken into consideration when interpreting ultrafiltration data.

The size distributions in various water extracts obtained by using thin-channel ultrafiltration are compared and discussed.

INTRODUCTION

The accumulation of heavy metals in the upper part of the soil (organic layers, mineral horizons high in organic matter) is well known.[1] Nevertheless the role of a given element in this soil system cannot be determined only on the basis of its total content or its accumulation rate. In order to interpret the behavior of a particular element in terms of, for example, plant uptake, toxicity and mobility within this soil compartment, it is necessary to characterize the specific form in which it appears. Therefore methods are required which allow the speciation and analysis of the different forms—which can be present in very low concentrations —without perturbation of the media.

A wide range of techniques has been applied in speciation studies.[2] The forms of metals in soils have generally been investigated by sequential solvent extraction using different reagents. Owing to the lack of selectivity of these reagents, the results so obtained must be interpreted with care. Speciation in the solution phase has been investigated using different analytical methods such as electro ultrafiltration and ion exchange (charge separation), dialysis, gel chromatography, ultrafiltration (size distribution), voltammetry as well as computer modelling. It was the aim of this study to develop an approach for the speciation of heavy metals in the water extract of organic layers of forest soils, based on size fractionation as a preliminary stage of a multi-step speciation scheme. For this purpose the usefulness of thin channel-ultrafiltration in a cascade procedure was evaluated.

MATERIAL AND METHODS

All bottles and containers used for sampling, storage and analytical procedures were washed with 0.1 M HNO_3 and highly purified water to avoid contamination of the samples. Bottles in contact with litter extracts were soaked in 10^{-3} M NaOH prior to the cleaning procedure. All handling of the samples in the laboratory was done in clean benches.

1. Chemicals

All reagents were of analytical grade (Merck); the HNO_3 was distilled before being used to acidify the samples. All water used in this study was deionized water purified by ion-exchange and filtration through active charcoal and an 0.45 μm filter (Millipore Corp., Milli-Q).

2. Filtration

Filtrations were carried out by means of an ultrafiltration assembly based on an Amicon Model TCF10 coupled with a Masterflex pump using Tygon and polyethylene tubing. Two different ultrafiltration cells were constructed, one made of teflon (PTFE), and the other of plexiglas. As membrane support, a porous PTFE disk (thickness 2 mm, pore size 60 μm) was employed. The cell capacity was 500 ml with a membrane surface diameter of 90 mm. The filtration experiments were performed using Sartorius (0.45 μm, cellulose nitrate), Nuclepore (0.03 μm, polycarbonate), Spectra/Por (type C, MWCO: 10 K and 500) and Amicon membranes (PM10, YC05) under nitrogen pressure (700–2500 hPa, depending on the membrane).

All membranes were discarded after each filtration except for the Spec/Por C10K, C500 and Amicon PM10 and YC05, which were used three times. Initial preparation of this second group of membranes involved a (minimum) 24 h soaking in 10% ethanol (to remove organic impurities). To remove organic residues after each filtration, the membranes were left to stand overnight in 10^{-3} M NaOH and washed subsequently with water *in situ* in the filtration apparatus.

3. Samples

Samples from the organic layer of a beech stand (*Fagus sylvatica*) were taken according to the definition given by Babel;[3] the resulting nomenclature is used throughout. A detailed description of the sampling site (Oberstammheim, a rural landscape) has been published previously.[4] The organic horizons were dried at 50 °C for 24 h. To ensure good homogeneity, the samples were ground in a ball mill consisting of a polyamide container with teflon grinding spheres. The samples were stored in the dark at −4 °C until analysis. Extracts were obtained by shaking 5 g of the organic layers with 200 ml water on a reciprocating shaker for two hours. The pH ($CaCl_2$) of these extracts ranged from 5.2–5.7. For heavy metal determination the extracts were acidified and analysed within a week.

4. *Metal Content and Dissolved Organic Carbon (DOC)*

In the preliminary adsorption tests, the determination of heavy metals was carried out electrochemically using differential pulse anodic stripping voltammetry (DPASV) at the dropping mercury drop electrode (Metrohm VA-Processor 646, VA-Stand 647). The Zn content of the acidified litter extracts (pH 1) was determined by flame atomic absorption spectrometry (AAS) on an IL Model 451. The metals Cd, Pb and Cu in the extract were measured by flameless AAS (GFAAS) on an IL 755 graphite furnace mounted on an IL 451 model using $Pd(NO_3)_2$ and $Mg(NO_3)_2$ as matrix modifiers for Cd and $(NH_4)H_2PO_4$ for Pb. For all AAS measurements a Deuterium background correction to compensate non-specific absorption was used.

The DOC values of the litter extracts were measured using a Dorman DC 80 analyzer after eliminating the inorganic carbon by acidifying (HNO_3) and degassing the samples with N_2 for 5 min. Because of the high DOC content of the extracts, the final pH was not allowed to fall below 4 in order to avoid coagulation of the organic matter. To prevent bacterial growth NaN_3 was added.

RESULTS AND DISCUSSION

1. *Filtration*

By using ultrafiltration techniques, the molecules in solution were separated on the basis of size. Molecules larger than the membrane pore size were retained on the surface of the membrane. The accumulation of retained molecules formed a concentrated gel layer (concentration polarization), which acted as a secondary membrane. The gel layer significantly altered the characteristics of the original membrane, leading to a decline in filtration flux rate, inconsistent fractions and irreversible alteration of the original metal-organic association. Concentration polarization could be reduced by cascade filtration and by using a stirred cell or a sample flow parallel to the membrane surface. The latter technique (known as a tangential flow system) was applied in this speciation study, using a thin channel flow over the membrane. This parallel flow causes fluid shear against the membrane, reducing concentration polarization and minimizing therefore the boundary gel layer thickness. Using this technique, changes in the metal-organic association were minimized and high flow rates could be achieved. Nevertheless,

Table 1 Tested membranes, cut off and composition

Type	*Cut off*	*Material of*	
		Membrane	*Support*
Sartorius 0.45 μm	0.45 μm	Cellulose nitrate	—
Nuclepore 0.03 μm	0.03 μm	Polycarbonate	—
Spec/Por C10K	10000 MW	Reg. cellulose	Reg. cellulose
Spec/Por C500	500 MW	Reg. cellulose	Reg. cellulose
Amicon PM10	10000 MW	Polysulfone	Polysulfone
Amicon YM2	1000 MW	Reg. cellulose	Reg. cellulose
Amicon YC05	500 MW	Reg. cellulose	Reg. cellulose

substances sensitive to shear forces might have been altered. In order to minimize the alteration of the sample solution, applied pressure and cross flow rate were carefully selected. Theoretical modelling of ultrafiltration processes has been reviewed by Cheryan.[5]

The first 30 ml of the filtrate was used to rinse the PE-bottles in which the filtrate was collected. To avoid large concentration gradients, 1/3 of the initial extract volume was left in the filtration cell. After filtration (0.45 μm), KNO_3 was added to produce a 0.01 M KNO_3 electrolyte concentration.

In order to select the optimal experimental conditions for the speciation studies in the litter extracts, the following factors were evaluated:

a) contamination of the samples due to the ultrafiltration assembly and the membrane of choice.

b) losses of heavy metals due to the ultrafiltration assembly system or the membranes.

2. *Contamination*

The following procedure was adopted to clean the ultrafiltration assembly: filtering c. 200 ml water (2×), 200 ml HNO_3, 200 ml water, 250 ml 0.01 M KNO_3. Using this cleaning procedure, no leaching of heavy metals either from the ultrafiltration cell or from the different membranes was detected.

3. *Losses of Heavy Metals*

The membranes under consideration are given in Table 1.

3.1 *Passage of heavy metal ions*

A solution containing 2 ppb each of Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} (all as nitrates) in 0.01 M KNO_3, pH 4 (HNO_3) was filtered through the different membranes. The resulting retention factors R_x are shown in Table 2. R_x was calculated as:

$$R_x = \frac{[X]_t - [X]_f}{[X]_t}$$

Table 2 Retention factors of the different membranes, 2 ppb Cd, Pb, Cu, Zn; electrolyte 0.01 M KNO_3; pH 4 (HNO_3) n = number of tests

Membrane	$R_{Cd}\%$	$R_{Pb}\%$	$R_{Cu}\%$	$R_{Zn}\%$	
Sartorius 0.45 μm	($n=5$)	−2	8	0	−10
Nuclepore 0.03 μm	($n=4$)	3	32	10	−1
PM10	($n=4$)	0	27	8	−2
C10K	($n=3$)	21	100	100	5
YM2	($n=3$)	28	100	100	0
YC05	($n=3$)	73	94	90	53
C05	($n=3$)	63	100	100	20

Table 3 Successive filtrations of litter extracts (pH 5.2) through an identical membrane

Membrane	*Filtration Nr*	*Cd [ppb]*	*Pb [ppb]*	*Cu [ppb]*	*Zn [ppb]*
0.45 μm	1	0.39	3.2	29.6	175
	2	0.38	3.5	30.1	164
	3	0.35	3.4	27.7	170
0.03 μm	1	0.28	2.3	21.2	148
	2	0.27	1.8	18.6	132
PM10	1	0.26	1.3[a]	13.6	121
	2	0.24	0.9[a]	13.2	110
YC05	1	<0.02	<0.4	<0.6	<10
	2	<0.02	<0.4	<0.6	<10

[a] Near detection limit of GFAAS.

where the subscripts t and f refer to the total concentration before filtration (2 ppb) and the concentration in the filtrate respectively. The errors incurred in R_x due to analytical measurements were estimated to be ±5%.

The retention of heavy metals tended to decrease in the following sequence: Pb > Cu ≫ Cd > Zn. Membranes composed of regenerated cellulose (C10K, YM2, YC05, C05) had a high retention potential, a fact which could not be explained by the low pore size of the membrane itself. Amicon PM10 (polysulfone) and Spec/Por C10K (reg. cellulose) yielded different results although the cut off of both membranes was c. 10 000 MW.

For the following experiments, only membranes with low retention factors were employed. Amicon YC05 was also chosen to evaluate the behavior of a low cut off membrane.

3.2 Losses of heavy metals in the litter extract

In order to evaluate losses of heavy metals during filtration of the extract, a litter extract was filtered twice or three times successively through an identical membrane. Between each filtration, a new membrane was used or as in the case of PM10 and YC05, they were washed according to the procedure described above.

The results in Table 3 indicate no reproducible losses for Sartorius 0.45 μm, whereas Nuclepore 0.03 μm and Amicon PM10 tended to retain heavy metals, but

Table 4 Percentage recovery of heavy metals upon filtering a litter extract (pH 5.1; number of tests: $n = 2$)

Membrane	*Cd%*	*Pb%*	*Cu%*	*Zn%*
0.03 μm	110	94	102	101
PM10	98	92	104	98

to a lesser extent than in the 0.01 M KNO_3 electrolyte. Concentrations in the filtrate of YC05 were in all cases below the detection limits of GFAAS, and therefore no prediction about the behavior of this membrane could be made. Since the expected heavy metal concentrations in the other litter extracts were of the same order of magnitude, the use of YC05 gave no reliable results for speciation studies. For that reason YC05 was excluded from further experiments.

In order to quantify the heavy metal losses due to filtration through 0.03 μm and PM10 membranes, a mass balance approach was applied. Only mass balance can give detailed information about adsorption losses. In the technique used above, the ultrafiltration itself or the storage of the filtrate between successive filtrations could cause some alteration of the extract solution (coagulation of organo-metallic complexes and/or fragmentation of these substances), leading to decrease or increase in the heavy metal content of the filtrate, unrelated to adsorption phenomena.

For the evaluation of mass balance, the extracts were filtered successively through 0.45 μm/0.03 μm/PM10 membranes. Each filtrate (2/3 of each initial volume) and the retained solution (1/3 of initial volume) from the 0.03 μm and PM10 filtrations were analyzed separately for heavy metal concentration, weighted with the corresponding volume, summed up and compared to the heavy metal content in the extract prior to filtration.

The results indicate that losses in the litter extract due to adsorption only occur for Pb, whereas, in inorganic model solutions, Cu and Pb are retained to a great extent (Table 2). This difference is most probably a result of the high complexing capacity of organic components in litter extracts[6,7] leading to the formation of organo-metallic complexes which could prevent the adsorption of the metals on the membranes. After successive filtrations of the litter extract through 0.03 μm and PM10 membranes, 86% of Pb was recovered. The same experiment was used to determinate the losses of DOC leading to a recovery of 93%.

3.3 Adsorption at the ultrafiltration assembly

Repeated filtration of organic rich extracts (DOC ~1000 mg/l) led to adsorption of organic material on the teflon UF-assembly. The same was true for the plexiglas assemblies. Soaking the assembly in NaOH and washing with detergents could not completely remove the adsorbed organic material. Filtering solutions low in organic material through this contaminated UF-assemblies might have led to losses of heavy metals due to adsorption at the "organic film" of the UF system as shown in Table 5.

The adsorption was selective for Pb and Cu, the two metals which form strong

Table 5 Retention factors for filtration of heavy metal standard solutions (2 ppb) through "contaminated" UF-assemblies

Electrolyte	*pH*	R_{Cd}%	R_{Pb}%	R_{Pb}	R_{Zn}%
0.01 M KNO_3	5.6	0	48	59	0
0.01 M KNO_3	2	0	13	6	0

complexes with organic material. The losses of Pb and Cu could not be prevented by filtering a divalent cation (e.g., 0.01 M $Mg(NO_3)_2$) prior to the analyte. The pH dependence of the adsorption losses (Table 5) supports the adsorption/complexation theory.

Subsequent filtering of solutions differing widely in their DOC content may therefore lead to adsorption problems. The removal of the "organic film" on the UF system by using strong oxidizing agents (e.g., H_2O_2) will be examined in further studies.

Despite these problems, thin-channel ultrafiltration seems to be a reliable method for speciation studies based on size fractionation, providing the litter extracts have comparably high DOC values and membranes with a low retention factor for heavy metals are used.

4. *Size Distribution in Litter Extracts*

As shown in Figure 1, the relative amount of water-extractable heavy metals and DOC decreases with increasing decomposition of the litter.

This is especially evident for the micronutrients Cu and Zn. Up to 20% of the total content of these metals were extractable with water.

In the L- and F-horizons, the heavy metals were less water soluble. This can be explained by the fact that water soluble heavy metals will have been washed out of the fallen leaves and transferred to lower soil compartments. In addition, the formation of water insoluble humic substances during litter decomposition may lead to a lower extractable content due to the high adsorption and complexation properties of these substances.

The size distributions of the heavy metals in the water extracts within the different organic horizons are shown in Figure 2.

Cd and Zn exhibit similar behavior. A high content of these elements in the water soluble extracts is smaller than 10000 MW, indicating a high mobility within these soil compartments. A decrease in the fraction smaller than 10000 MW along with an increase of the 0.45 μm–0.03 μm fraction during decomposition was observed. Adsorption by suspended particles was therefore more pronounced in the litter horizons than in the fallen leaves. A different pattern was shown for Cu and Pb. During decomposition, the fraction <10000 MW tended to increase, probably due to a larger complexing capacity of the organic material in this fraction. The 10000 MW–0.03 μm fraction was lower in the organic layers compared to the fallen leaves, indicating that this size of molecule was not primarily responsible for the water solubility of Pb and Cu in these layers.

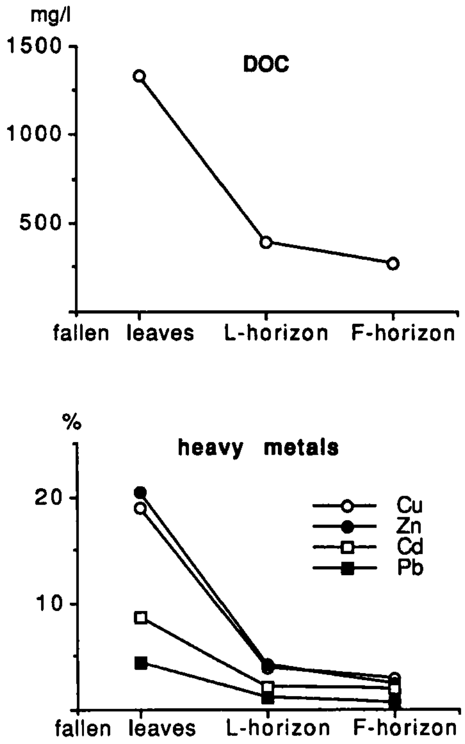

Figure 1 Water extractable DOC and heavy metal content in different organic horizons (heavy metal values as percent of the total content).

Between 26–38% of the extractable Pb was smaller than 10000 MW. This small amount was again an indicator for the low mobility of Pb within the organic layers. Pb tended to be strongly associated with suspended particles (>0.03 μm).

The size distribution of DOC was uniform over the different decomposition stages, i.e., c. 74% < 10000 MW, 13% between 100000 MW and 0.03 μm and 13% > 0.03 μm. This was in accordance with the distribution of DOC within different soils found by Buffle *et al.*[8]

It must be borne in mind that these litter extracts differ widely from soil solutions of lysimeter experiments.[9] Thus the size distribution may not be directly compatible.

CONCLUSION

The results indicate that Sartorius 0.45 μm, Nuclepore 0.03 μm and Amicon PM10 are the most useful membranes for size fractionation in litter extracts with regard to contamination and adsorption problems. Nevertheless the separation step may cause a modification of the chemical forms of the heavy metals. This change in organic-metal association can be minimized (e.g., by successive filtration and

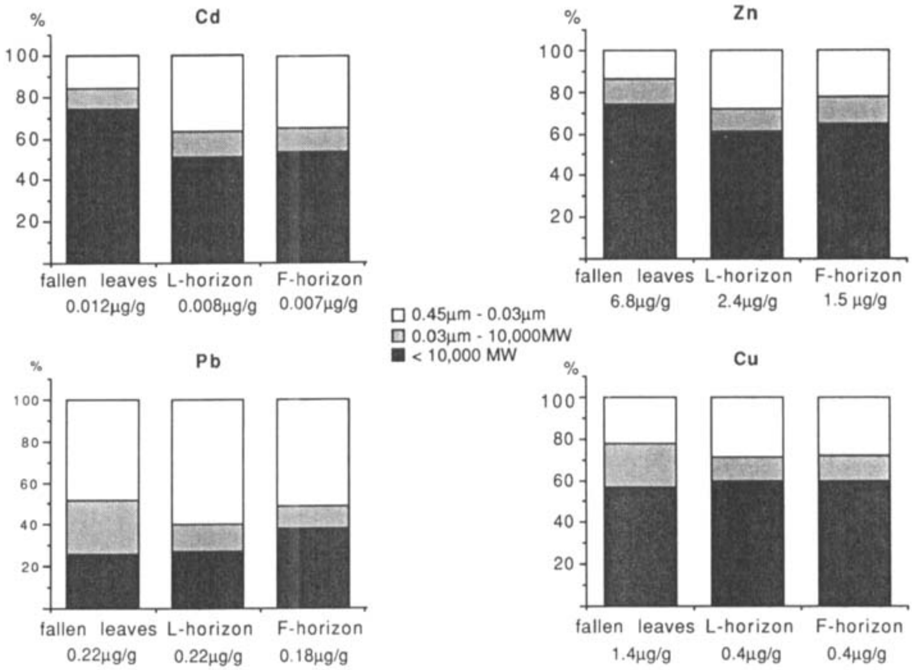

Figure 2 Size distribution of heavy metals in the water extractable content of different organic layers. Results in µg/g refer to the total water extractable content (shown as 100% in the y-axis) of the heavy metals in the horizons.

tangential flow systems) and has therefore to be taken into consideration when interpreting the data obtained by ultrafiltration.

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