Sorption of Trace Metals by Standard and Micro Suction Cups in the Absence and Presence of Dissolved Organic Carbon

D. Rais, B. Nowack, R. Schulin, and J. Luster*

ABSTRACT

Both the bioavailability of a trace metal (TM) in a soil and the risk of leaching to the ground water are linked to the metals concentration in the soil solution. Sampling soil solution by tension lysimetry with suction cups is a simple and established technique that is increasingly used for monitoring dissolved TM in soils. Of major concern, however, is the sorption of TM by the walls of the samplers. Metal sorption by different materials used in suction cups can vary widely, depending also on the chemistry of the soil solution. We compared the sorption of Cu, Zn, Cd, and Pb by different standard-size and micro suction cups in the laboratory at two pH values (4.5 and 7.5 or 8.0) in absence and presence of dissolved organic carbon (DOC). In addition, we investigated the sorption of DOC from different origins by the cup materials. At both pH values, the weakest sorption of all four TMs was exhibited by standard-size suction cups based on nylon membranes and by hollow fibers made from polyvinyl alcohol (PVA). At alkaline pH, borosilicate glass, ceramic materials, and polytetrafluorethylene (PTFE) mixed with silicate were characterized by generally strong sorption of all investigated TMs. In addition, Cu and Pb were strongly sorbed at low pH by PTFE–silicate and a ceramic material used for the construction of standard-size suction cups. On the other hand, sorption of Cu, Zn, and Cd by ceramic capillaries produced from pure aluminum oxide was negligible at low pH. Micro suction cups made of an unknown polymerous tube sorbed Cu strongly, but were well suited to monitor Zn, Cd, and Pb at low pH, and, in the presence of DOC, also at high pH. Major cations (Na^+, Mg^{2+}, K^+, Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}) were not or very weakly sorbed by all cup materials, except for Mg^{2+}, K^+, and Ca^{2+} by borosilicate glass at pH 7.5. Trace metal sorption by suction cups was generally greatly reduced in the presence of DOC, especially at alkaline pH. The sorption of DOC itself depended on its source. Dissolved organic carbon from leaf litter extracts with a probably large hydrophobic fraction was sorbed more strongly than mainly hydrophilic DOC from a mineral soil solution.

The soil solution is the medium linking soil matrix, plant roots, and ground water. Its chemical composition mirrors important soil and rhizosphere processes such as nutrient cycling, organic matter turnover, or trace metal (TM) leaching. Tension lysimeters built from porous suction cups offer a convenient way to collect soil solution continuously at a given location, with minimum disturbance. Sorption of the analytes of interest to the walls of the cups, pore clogging, or release of components from the cup material may, however, interfere with the sampling process and alter the composition of the sampled solution as it is transferred from the soil into the sampler. Compared to major anions and cations, many TMs are generally strongly sorbed by mineral and organic surfaces.

Ceramic suction cups, which are most widely used, are characterized by a relatively large cation exchange capacity (CEC). As a consequence, they can sorb large amounts of TM cations (Grossmann et al., 1990). They can also sorb dissolved organic carbon (DOC) and inorganic anions such as phosphate (Grossmann et al., 1990; Wenzel and Wieshammer, 1995; Wenzel et al., 1997). In addition, ceramic cups have been found to release Na, Mg, Al, K, and Ca under acidic conditions (Grover and Lamborn, 1970; Hansen and Harris, 1975; Litaor, 1988; Raulund-Rasmussen, 1989; Wenzel and Wieshammer, 1995).

Suction cups made from borosilicate glass exhibit very little retention of DOC (Wessel-Bothe et al., 2000). Little is known, however, about the sorption of trace elements by glass cups. McGuire et al. (1992) noted significant sorption of Cr, Co, Cd, and Zn by fritted glass at pH 6.5. Koch and Grupe (1993) investigated the sorption of Mn, Ni, Cu, Zn, Cd, and Pb by borosilicate glass cups at pH 4 and reported weak sorption of Cu and strong sorption of Pb.

Suction cups made from plastic materials have received much attention because of their low CEC compared to ceramic and glass cups. The two most commonly used types are polytetrafluorethylene (PTFE) and nylon cups. Cups produced by Prenart Equipment ApS (Frederiksberg, Denmark) consist of a porous body made from PTFE mixed with a silicate to reduce hydrophobicity. Sorption of Cu, Zn, Cd, and Pb by these cups was found to be a problem at $pH > 4.5$ despite the rather low CEC (Andersen et al., 2002). However, this study was performed at an ionic strength which was far above what is normally found in soil solutions.

Nylon membranes had negligible effects on TM concentrations between pH 3 and 5, and only weak effects at pH 6 (Wenzel and Wieshammer, 1995; Wenzel et al., 1997). Under alkaline conditions, little sorption of Zn and Cd but strong sorption of Cu and Pb were reported (Grossmann et al., 1990; Grossmann and Udluft, 1991).

Standard-size suction cups with diameters of 2 to 3 cm and dead volumes in the mL range are of limited use when high spatial resolution is required (e.g., to distinguish between bulk and rhizosphere soil solution), or when the influence of the sampling on water fluxes or soil structure needs to be minimal. For such purposes,

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Abbreviations: CEC, cation exchange capacity; DOC, dissolved organic carbon; PTFE, polytetrafluorethylene; PVA, polyvinyl alcohol; TM, trace metal.

Table 1. Properties of the standard-size suction cups as given by the manufacturer, except pore volume, which was determined in this study. Average values are listed except for pore size.

	Cup material			
Property	**Ceramic**	**Borosilicate glass**	**PTFE†**	**Nylon**
Cup dimension (L × OD‡), cm	**5.5 × 2.1**	**6 × 3.2**	**9.5 × 2.1**	**9.5 × 3.2**
Porous area, cm^{2} (cm length)$^{-1}$	**6.60**	**10.05**	**6.60**	**10.05**
Pore volume, mL (cm length)$^{-1}$	**0.4**	**0.5**	**0.4**	**0.3**
Maximum pore size, μm	**2.5**	**1**	**2**	**0.45**
Bubble point, hPa	**1500**	**1500**	**450**	**2000**

† Polytetrafluorethylene.
‡ Outer diameter.

micro suction cups with diameters between 1 and 2.5 mm have been developed during the last decade. They include polymerous tubes, ceramic capillaries (Göttlein et al., 1996), and hollow fibers made from polyvinyl alcohol, polysulfone, or polyacrylonitrile (Yanai et al., 1993; Jones and Edwards, 1993; Menzies and Guppy, 2000). The influence of micro suction cup materials on soil solution samples has been studied by Jones and Edwards (1993), Yanai et al. (1993), Göttlein et al. (1996), Spangenberg et al. (1997), and Cabrera (1998). However, only Menzies and Guppy (2000) studied the influence on TM concentrations. They found that a polyacrylonitrile hollow fiber sorbed no inorganic analytes, including TM, in detectable quantities.

The aim of our work was to fill a number of knowledge gaps identified above. In particular, little data are available for alkaline conditions, on the influence of DOC, and, in general, for micro suction cups. We performed laboratory tests in which we compared several commercially available standard-size and micro suction cups. The tests were performed at weakly acidic and alkaline pH, at an ionic strength typical for soil solutions in forest soils, at TM concentrations found in polluted and nonpolluted soils, and in the absence or presence of DOC from different sources.

MATERIALS AND METHODS

Suction Cup Characteristics

Four types of commercially available standard-size suction cups were tested: a ceramic cup (Soilmoisture Equipment Corp., Santa Barbara, CA); a borosilicate glass cup (EcoTech GmbH, Bonn, Germany); a cup made from PTFE intimately mixed with a silicate to reduce its hydrophobicity (Prenart Equipment ApS); and a cup based on a nylon membrane supported by a polyethylene substructure and covered by a polyethylene shield (EcoTech).

Three different materials for the construction of micro suction cups were tested: a ceramic capillary produced from aluminum oxide with only little impurities (PI Ceramic, Lederhose, Germany); a hollow fiber made from polyvinyl alcohol (PVA; Yanai et al., 1993); and a tube made of an unknown polymer (Rhizon MOM; Eijkelkamp Equipment, Giesbeek, the Netherlands). Dimensions and selected properties of the different cups and materials are listed in Tables 1 and 2.

Table 2. Properties of the micro suction cup materials as given by the manufacturer or in the literature, except pore volume, which was determined in this study. Average values are listed except for the pore size of the ceramic and polyvinyl alcohol (PVA) materials.

	Cup material		
Property	**Ceramic**	**PVA**	**Polymer**
OD†, cm	**0.1**	**0.09**	**0.25**
Porous area, cm^{2} (cm length)$^{-1}$	**0.31**	**0.28**	**0.79**
Pore volume, μL (cm length)$^{-1}$	**2.8**	**1.8**	**10**
Maximum pore size, μm	**1**	**0.04**	**0.1 (average)**
Bubble point, hPa	**NS‡**	**NS‡**	**2000**

† Outer diameter.
‡ Not specified.

Percolation Experiments with Standard-Size Suction Cups

Before the experiments, the suction cups were cleaned. By means of a peristaltic pump, first 100 mL 1 *M* HCl, then 100 mL 1 *M* NaOH were pumped through the cups at a flow rate of 40 mL h^{-1}. Before and after the NaOH washing, the cups were rinsed with doubly deionized water (Millipore, Billerica, MA). The final rinsing was stopped when pH and conductivity had reached the values of doubly deionized water. Then synthetic soil solutions, that with respect to major anions and cations mimicked the composition of soil solutions from an acidic (pH 4.5) and a calcareous (pH 7.5) sandy soil, were pumped through the cups. The composition of these solutions is given in Table 3. The pH was adjusted by means of HCl or NaOH. All chemicals were reagent grade or better. A stepwise protocol with TM concentrations varying at three different levels (Table 3) was adapted from Grossmann et al. (1990):

Step 0: preconditioning phase; 2500 mL; TM at Level 1
Step 1: 250 mL; TM at Level 2
Step 2: 250 mL; TM at Level 3
Step 3: 250 mL; TM at Level 1
Step 4: 250 mL; TM at Level 3; plus 9 mg L^{-1} DOC

A flow rate of 20 mL h^{-1} was chosen. This corresponds to the maximum flow rate measured for nylon cups in loamy sands to loams at a constant vacuum of 500 hPa (data not shown). The DOC in Step 4 was added as an equimolar mixture of undiluted spruce (*Picea abies* L.), poplar (*Populus tremula* L.), birch (*Betula pendula* L.), and willow (*Salix viminalis* L.) litter extracts, which were prepared according to Luster et al. (1996). Briefly, 2.5 g dried (40°C) and ground litter were suspended in 100 mL water, purged with nitrogen, and mixed in a closed plastic bottle on an end-over-end shaker for 20 h. Then, the suspension was filtered (0.45 μm) immediately.

At different time steps, the chemical composition of the percolates was compared with the initial concentrations. The contribution of mixing to the retarded breakthrough of analytes was evaluated based on the percolation of a 1 mmol L^{-1} NaCl solution and the analysis of the Cl^{-} concentrations in the percolate. For nylon, PTFE, and ceramic cups, the influence of mixing was restricted to the first sample within one experimental step, where 85, 77, and 90%, respectively, of the initial Cl^{-} concentration were measured. Metal concentrations in the first sample of each experimental step were corrected for

Table 3. Composition of the solutions used in the laboratory tests of suction cup materials. For the standard-size suction cups, trace metal (TM) concentrations refer to the concentrations in Steps (0, 3)/1/(2, 4), and dissolved organic carbon (DOC) concentrations to the concentrations in Steps (1, 2, 3)/4. For the micro suction cups, TM concentrations refer to the concentrations in Steps (1, 3, 5)/2/4. The pH, DOC, and other ions refer to the concentrations in Steps (1, 2, 3, 5)/4.

	Standard-size suction cups		Micro suction cups	
	Acidic solution	Alkaline solution	Acidic solution	Alkaline solution
pH	4.5	7.5	4.5/4.5	8/8
DOC, mg L^{-1}	0/9†	0/9†	0/3‡	0/20‡
Ion, μmol L^{-1}				
Cu	0.083/0.153/1.41	0.018/0.061/1.05	0.168/1.37/1.70	0.052/0.73/1.76
Zn	0.43/0.82/7.01	0.36/0.69/6.08	0.51/6.65/6.99	0.49/6.55/5.98
Cd	0.011/0.027/0.26	0.013/0.028/0.25	0.012/0.28/0.26	0.014/0.20/0.24
Pb	0.003/0.006/0.045	0.001/0.004/0.024	0.010/0.047/0.047	0.002/0.020/0.031
Na	113	114	114/99	142/94
Mg	217	216	210/58	210/230
K	45	38	34/34	69/36
Ca	530	1933	529/<60	1640/2400
Cl	418	1031	443/137	1107/30
NO_3	161	1175	129/3	1189/20
SO_4	519	522	496/281	512/108
CO_3	0	835	0/130	1000/6000

† Leaf litter extract.
‡ Free soil percolation water.

mixing based on these factors. For glass cups, 42% of the initial Cl^- concentrations was measured in the first sample, and 89% in the second sample.

In an additional experiment, we investigated the sorption of DOC from a mineral soil solution by nylon cups. The percolation water collected at the bottom of a lysimeter was pumped through cleaned cups as described above. The lysimeter was filled with 15 cm of topsoil (weakly acid loam), 80 cm of subsoil (calcareous loamy sand), and a 50-cm quartz sand and gravel drainage packing. It was stocked with a young forest (mixed stand of spruce, poplar, willow, and birch).

Percolation Experiments with Micro Suction Cups

Ten-centimeter-long cups made of ceramic capillaries and PVA hollow fibers were cleaned with 6.5 mL 1 m*M* HNO_3 at a flow rate of 2 mL h^{-1}. Prefabricated cups, also 10 cm long, made of the polymerous tubes, were cleaned with 13 mL 1 m*M* HNO_3 at a flow rate of 4 mL h^{-1}. Then, the ceramic and PVA cups were rinsed with about 25 mL doubly deionized water and the polymer cups with about 50 mL until pH and conductivity of the percolates remained almost unchanged.

The sequence of test solutions, the composition of which is listed in Table 3, was slightly different from the one used for the standard-size suction cups:

Step 1: 12 mL (ceramic, PVA) or 25 mL (polymer) synthetic solution; TM at Level 1
Step 2: 12 mL (ceramic, PVA) or 25 mL (polymer) synthetic solution; TM at Level 3
Step 3: 12 mL (ceramic, PVA) or 25 mL (polymer) synthetic solution; TM at Level 1
Step 4: 12 mL (ceramic, PVA) or 25 mL (polymer) free percolation water from a lysimeter, filled either with a calcareous subsoil as described above or with an acidic subsoil (sandy loam), spiked with TM at Level 3.
Step 5: 12 mL (ceramic, PVA) or 25 mL (polymer) synthetic solution; TM at Level 1

The flow rate was 1.3 mL h^{-1} (ceramic, PVA) or 2.5 mL h^{-1} (polymer). The contribution of mixing to the retarded breakthrough of percolates, based on a test with Cl^- as described above, was negligible for all micro suction cups.

Analytical Methods

Solution concentrations of Cu, Zn, Cd, Pb, Na, Mg, K, Ca, and Mn were determined by inductively coupled plasma mass spectrometry (Elan 6000; PerkinElmer, Wellesley, MA), concentrations of Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} by ion chromatography (DX-120; Dionex, Sunnyvale, CA), DOC concentrations with a total organic C analyzer (TOC-V; Shimadzu, Kyoto, Japan), and pH potentiometrically (Glass Electrode C 4000-8; Radiometer Analytical SAS, Villeurbanne, France). Before analysis, the samples were filtered (0.45 μm; ME 25; Schleicher and Schuell, Dassel, Germany). The light absorption by DOC was measured at 254 nm (Cary 50; Varian, Palo Alto, CA). Except for light absorption, the accuracy of all analytical data was checked by analyzing certified standard reference materials with each series of analysis. With these measures, a laboratory precision of 0.15 units for pH, and less than 10% for all other parameters, was achieved. Metal speciation in synthetic soil solutions was calculated using the WHAM 6.0 model (Tipping, 1998).

RESULTS

Cleaning of Standard-Size Suction Cups

Percolation with HCl led to an initial release of Pb from nylon and ceramic cups. At the end of this cleaning step, Pb in the percolates was below the detection limit. Also Mg, Al, Ca, and Cl^- were released from the ceramic cups, while large amounts of Si and some Na were dissolved from the glass cups. In the beginning, the nylon cups released about 4 mg L^{-1} DOC. After cleaning with NaOH and rinsing with 4 L of water, the DOC release decreased to about 0.5 mg L^{-1} and remained constant as long as the cups were in use. The release of DOC was larger at alkaline (0.8 mg L^{-1}) than at acidic conditions (0.4 mg L^{-1}). Ceramic and PTFE cups released only about half as much DOC as the nylon cups.

Cleaning of Micro Suction Cups

During acid cleaning, Zn concentrations in the percolates from all three cups were between 0.4 and 0.5 μmol L^{-1}, and Cu concentrations between 0.04 and 0.08 μmol L^{-1}. Ceramic cups leached 4 μmol L^{-1} Pb

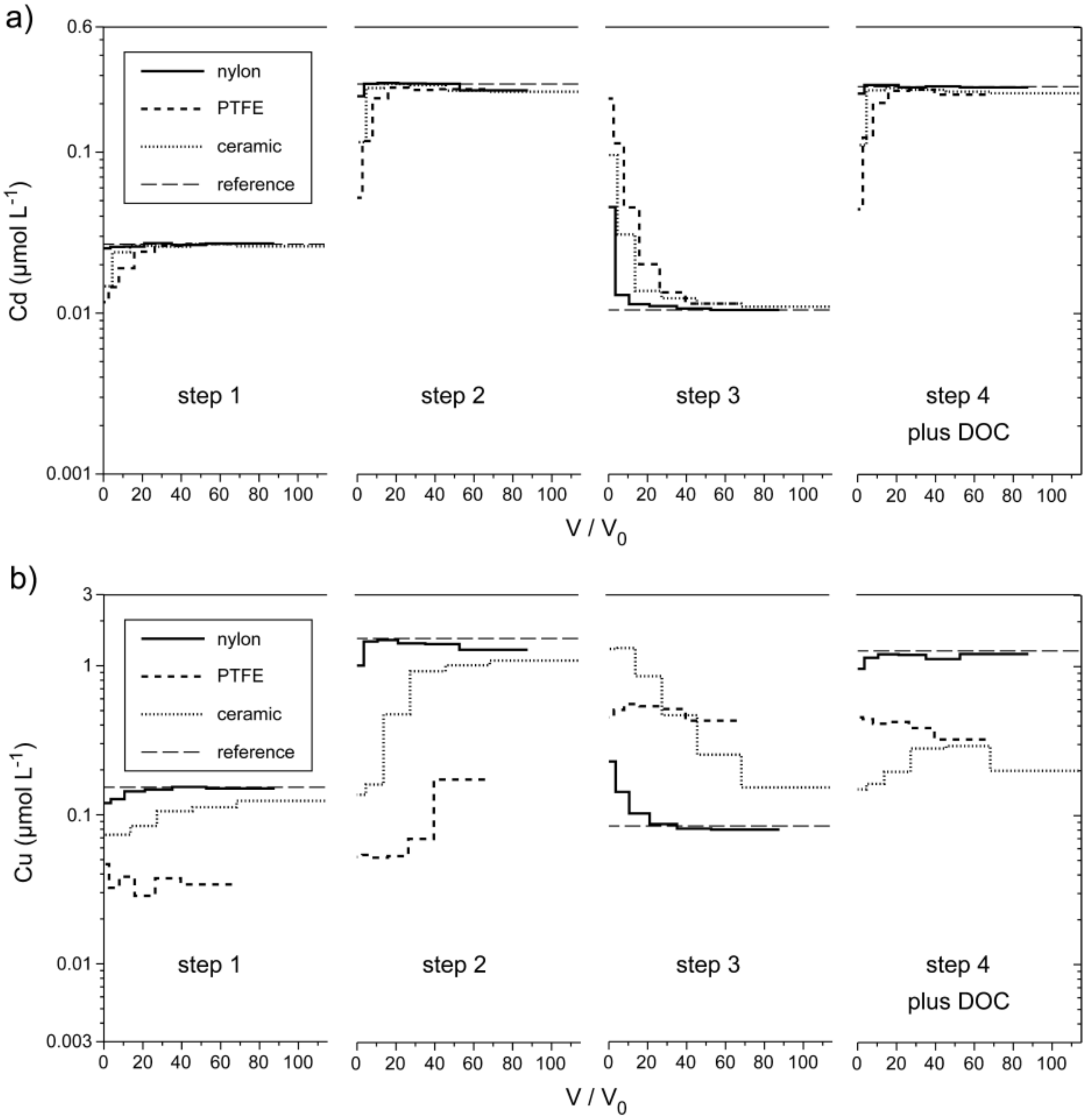

Fig. 1. Cadmium (a) and copper (b) concentrations, corrected for mixing, in the percolate collected from different standard-size suction cups at pH 4.5. For the conditions at Steps 1 to 4 of the experiment refer to the Materials and Methods section and Table 3. Volumes are given in multiples of the pore volume (V_0) of the respective cup. The reference lines show the expected metal concentrations if no interaction with the cup materials occurred (i.e., the concentration measured in the initial solution).

and 1.2 nmol L^{-1} Cd, polymer cups less than 0.6 nmol L^{-1} Cd and no Pb. The PVA cups did not release any Cd and about 0.09 µmol L^{-1} Pb. In addition, significant amounts of Al, K, and Mn were released by the ceramic cups. At the end of the rinsing with water, all cation concentrations were below the detection limit.

Sorption of Trace Metals, Major Cations, and Anions by Standard-Size Suction Cups at Acidic pH

The Cd concentrations in the percolate of all cups closely followed the initial concentrations under all tested conditions (Fig. 1a), and sorption was considered weak (Table 5). Zinc behaved similarly, but recovery of the large Zn concentrations in Step 2 was smaller than for Cd (Table 4), and overall sorption by the ceramic cup was considered moderate (Table 5). At lower concentrations, neither Cd nor Zn retention occurred. Copper concentrations in the percolate of the nylon cup closely followed the initial concentrations at the beginning of each percolation step (Fig. 1b). However, some Cu was sorbed after leaching of 35 pore volumes in Step 2. At the smaller TM concentrations (Step 1), no Cu sorption was observed. In the absence of DOC, the ceramic cup exhibited strong retardation of the Cu breakthrough (Step 2), and in the presence of DOC (Step 4) Cu was strongly sorbed without any indication of later release (Fig. 1b). Retardation and sorption of Cu by the PTFE

Table 4. Percentage of metal, anion, and dissolved organic carbon (DOC) recovery for standard-size suction cups in the absence or presence of DOC from a leaf litter extract (Steps 2 and 4 of the percolation experiment, respectively; for conditions refer to the Materials and Methods section and Table 3) after 88 pore volumes for nylon, 66 for polytetrafluorethylene (PTFE), 83 for glass, and 68 for ceramic cups; this corresponds to an approximate percolate of 250 mL for all cups except ceramic (150 mL).

	Recovery							
	Nylon		PTFE		Glass		Ceramic	
	pH							
	4.5	7.5	4.5	7.5	4.5	7.5	4.5	7.5
	%							
Cu	84/95	41/80	11/25	0/9	ND†	0/40	66/23	0/3
Zn	81/92	88/98	84/90	4/206	ND	0/0	84/86	0/1
Cd	91/99	84/88	93/89	22/77	ND	1/1	91/93	2/59
Pb	91/87	16/16	3/7	5/2	ND	4/3	1/2	4/2
Na	93/92	96/91	93/93	98/91	ND	205/174	95/92	90/92
Mg	90/93	95/93	91/94	96/94	ND	88/72	93/92	90/94
K	39/100	93/95	40/99	92/98	ND	0/0	40/97	90/97
Ca	92/96	78/57	94/96	78/59	ND	74/52	96/95	77/58
Cl	100/102	103/101	98/102	102/98	ND	99/100	100/104	101/99
NO_3	93/84	101/96	96/95	103/97	ND	99/97	96/94	100/95
SO_4	98/101	102/99	95/102	103/98	ND	100/100	95/105	101/97
DOC	NA‡/56	NA/66	NA/70	NA/62	ND	NA/86	NA/71	NA/74

† No experiment.
‡ Not applicable.

Table 5. Qualitative evaluation of the general sorption characteristics of the different standard-size suction cup materials. This evaluation is based on the laboratory tests with synthetic soil solution of pH 4.5 and 7.5 in the absence or presence of dissolved organic carbon (DOC) (Steps 2 and 4; for conditions refer to the Materials and Methods section and Table 3).†

	Cu	Zn	Cd	Pb
			pH 4.5	
Nylon	+/0	+/+	+/0	+/+
PTFE‡	+++/+++	+/+	+/+	+++/+++
Glass	ND	ND	ND	ND
Ceramic	++/+++	++/+	+/+	+++/+++
			pH 7.5	
Nylon	+++/+	+/0	+/+	+++/+++
PTFE	+++/+++	+++/d	+++/++	+++/+++
Glass	+++/+++	+++/+++	+++/+++	+++/+++
Ceramic	+++/+++	+++/d	+++/d	+++/+++

† 0, negligible sorption (<5%); +, weak sorption (5–20%); ++, moderate sorption (20–40%); +++, strong sorption (>40%); d, desorption; ND, no experiment.
‡ Polytetrafluorethylene.

cup was even stronger (Fig. 1b). Lead was almost completely sorbed by PTFE and ceramic cups, while Pb sorption by nylon cups was found to be weak (Table 5).

The major nutrient anions were only very weakly sorbed, except for some NO_3^- retention by the nylon cup (Table 4). All cups retained some Na, Mg, and Ca, and K was strongly sorbed in the absence of DOC.

Sorption of Trace Metals, Major Cations, and Anions by Standard-Size Suction Cups at Alkaline pH

The retention of Cd increased in the order nylon < PTFE << ceramic < glass (Fig. 2a). In the absence of DOC, glass and ceramic cups retained Cd added in Step 2 almost completely (Table 4). Overall, the Cd sorption by PTFE, ceramic, and glass cups was considered strong, while the sorption by nylon was weak (Table 5). Addition of DOC resulted in the desorption of previously sorbed Cd from the ceramic cup after about 75 pore volumes, and the sorption by PTFE cups was reduced to moderate. Zinc sorption by the tested cups was similar as the one of Cd in the absence of DOC (Table 4 and 5). The addition of DOC led to desorption of Zn from PTFE and ceramic cups, and Zn sorption by the nylon cup became negligible. In the absence of DOC, Cu was completely sorbed by all cup materials except nylon, for which a strong retardation of the breakthrough was observed (Fig. 2b). In the presence of DOC, Cu sorption by nylon was only weak (Fig. 2b, Tables 4 and 5). Also the Cu sorption by the other cup materials was reduced but still strong. Lead was almost completely sorbed under all conditions (Tables 4 and 5). Of the major ions, Ca, Mg, and Na were partly retained by all cups, and K was completely sorbed by glass (Table 4).

Sorption of Trace Metals, Major Cations, and Anions by Micro Suction Cups at Acidic pH

Cadmium and Zn concentrations were not much affected by any cup material (Fig. 3a; Table 6). Copper sorption by the ceramic capillaries was negligible, and weak by the PVA hollow fibers (Fig. 3b; Table 6). The strong sorption of Cu by the polymer cup in the absence of DOC was reduced on the addition of DOC. On the other hand, overall the polymer exhibited the weakest sorption of Pb (Table 6). Because some Pb was released from the ceramic material during the entire test, Pb sorption was not evaluated. Major cations and anions were not sorbed by any material (data not shown).

Sorption of Trace Metals, Major Cations, and Anions by Micro Suction Cups at Alkaline pH

Cups made of PVA hollow fibers retarded Cd and Zn breakthrough (Fig. 4a), but overall sorption was neglible to weak (Table 6). The small Cd concentrations in Step 1 were strongly sorbed by the ceramic capillaries, but the large concentrations in Step 2 were recovered completely after some delay (Fig. 4a). In the presence of DOC, Cd was strongly sorbed by the ceramic, but released again in Step 5. The addition of DOC reduced

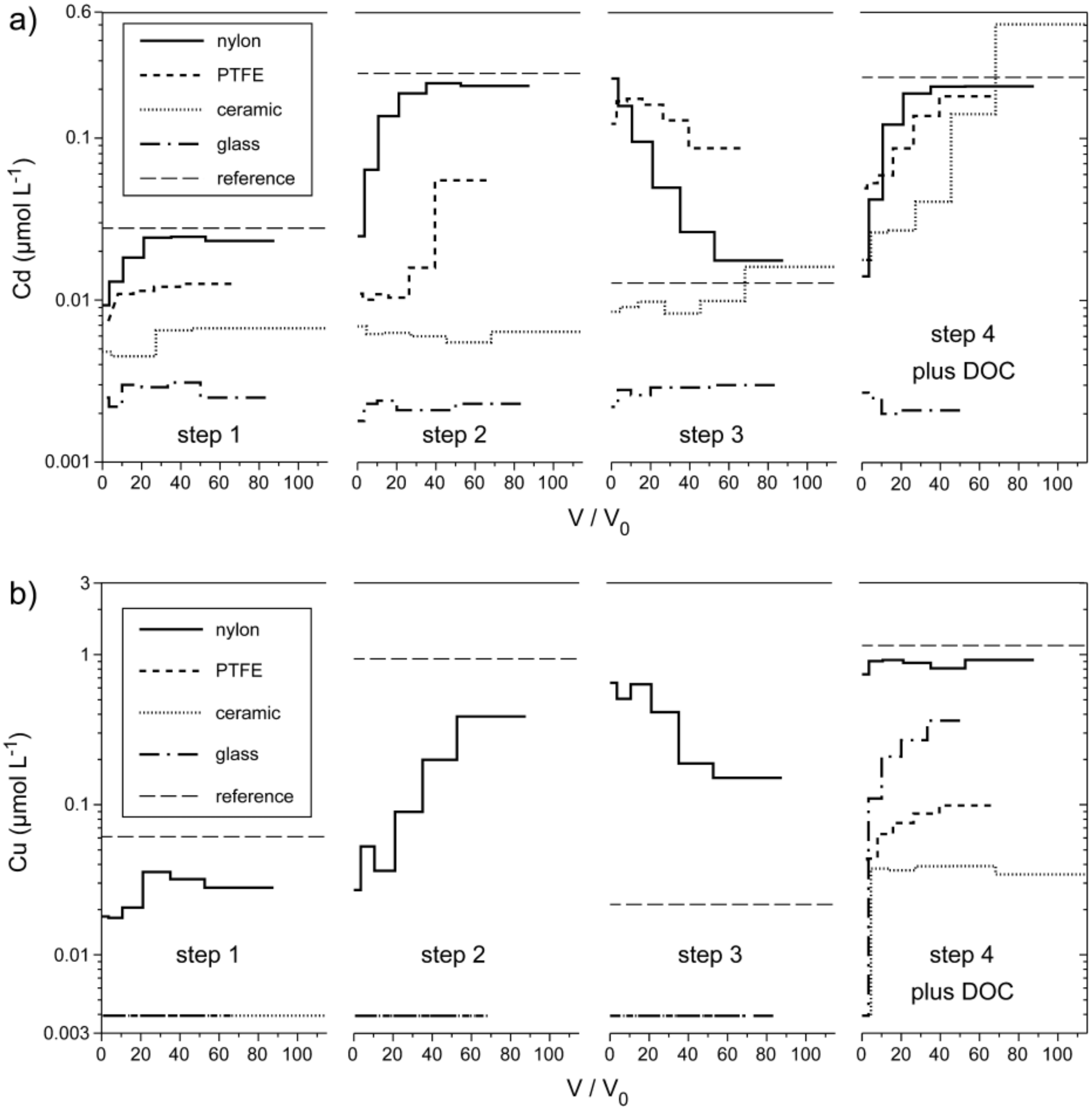

Fig. 2. Cadmium (a) and copper (b) concentrations, corrected for mixing, in the percolate collected from different standard-size suction cups at pH 7.5. For the conditions at Steps 1 to 4 of the experiment refer to the Materials and Methods section and Table 3. Volumes are given in multiples of the pore volume (V_0) of the respective cup. The reference lines show the expected metal concentrations if no interaction with the cup materials occurred (i.e., the concentration measured in the initial solution). Copper concentrations in the percolates from polytetrafluorethylene (PTFE), ceramic, and glass cups in Steps 1, 2, and 3 were all below the detection limit of 0.004 μmol L^{-1} and are plotted at this value.

Cd sorption by the polymer cups from moderate to weak (Fig. 4a; Table 6). Sorption of Zn by ceramic and polymer cups was similar to Cd (Table 6). Additional Cu and Pb in Step 2 was almost completely sorbed by all cup materials (Fig. 4b; Table 6). In the presence of DOC Cu was less sorbed or was desorbed from the cup materials, and Pb was desorbed from PVA and polymer cups, but completely retained by the ceramic capillaries. Major cations and anions were not sorbed by any material (data not shown).

Sorption of Dissolved Organic Carbon by Standard-Size Suction Cups

At alkaline conditions, the retention of DOC from litter extracts increased in the order glass < ceramic < nylon < PTFE (Table 4). At acidic conditions, DOC retention was larger for ceramic and nylon cups, but smaller for PTFE (Table 4). By contrast, based on light absorption at 254 nm, DOC from the alkaline lysimeter percolation water was not sorbed by nylon cups for more than 420 dead volumes (data not shown).

Sorption of Dissolved Organic Carbon by Micro Suction Cups

Light absorption at 254 nm of the TM-spiked acid lysimeter drainage water was reduced by about 10% in the percolate of all cups (Fig. 5). By contrast, the light absorption of the alkaline drainage water was not reduced by any of the cup materials. At both pH values,

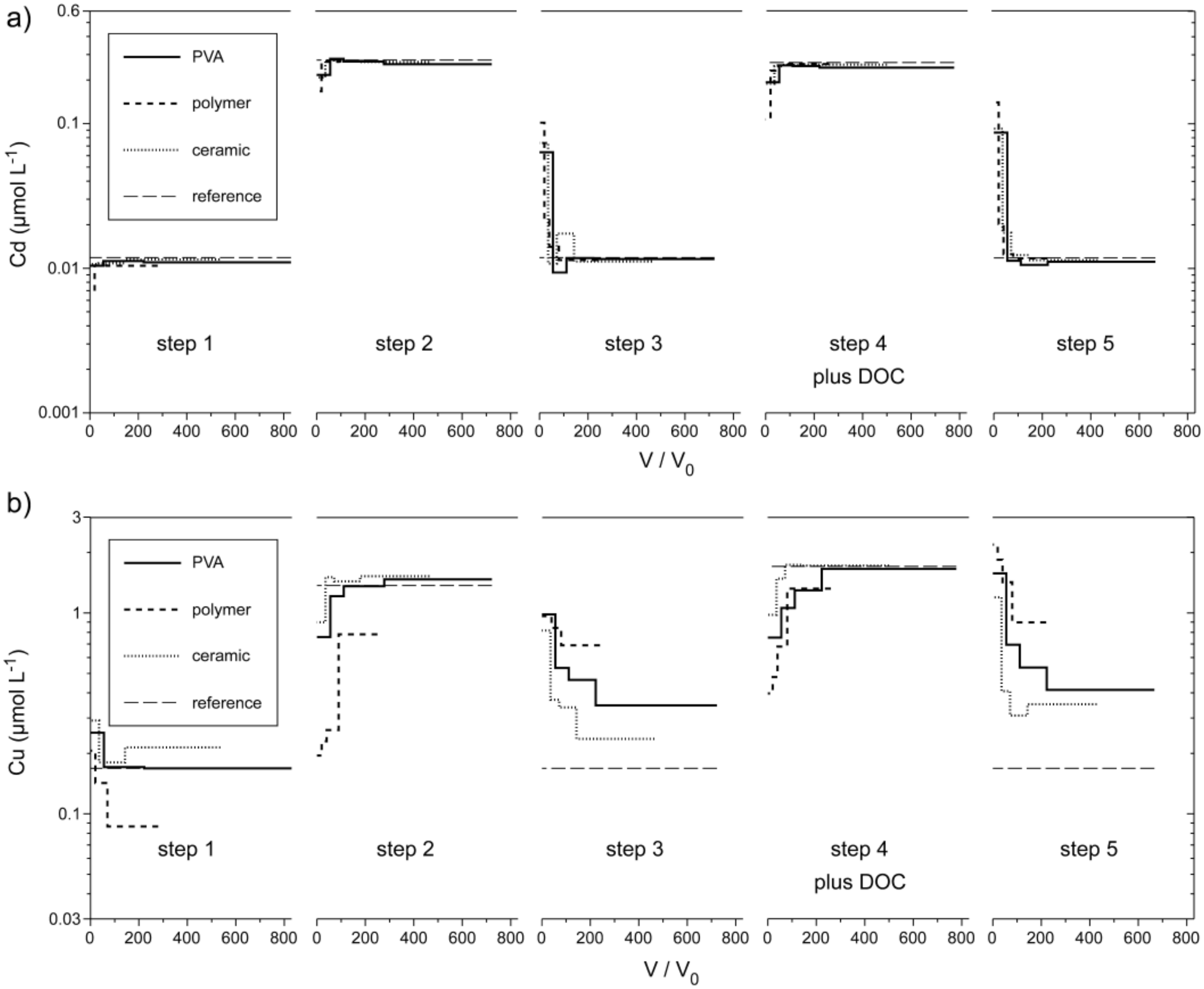

Fig. 3. Cadmium (a) and copper (b) concentrations in the percolate collected from different micro suction cups at pH 4.5. For the conditions at Steps 1 to 5 of the experiment refer to the Materials and Methods section and Table 3. Volumes are given in multiples of the pore volume (V_0) of the respective cup. The reference lines show the expected metal concentrations if no interaction with the cup materials occurred (i.e., the concentration measured in the initial solution). The reference line for Cu in Step 1 is at the same value as in Steps 3 and 5.

Table 6. Qualitative evaluation of the general sorption characteristics of the different micro suction cup materials. This evaluation is based on the laboratory tests with synthetic soil solution of pH 4.5 and 8.0 in the absence or presence of dissolved organic carbon (DOC) (Steps 2 and 4; for conditions refer to the Materials and Methods section and Table 3).†

	Cu	Zn	Cd	Pb
			pH 4.5	
Polymer	+++/++	0/0	0/0	+/+
PVA‡	+/+	0/0	0/0	0/+++
Ceramic	0/0	0/0	0/0	ND/ND
			pH 8.0	
Polymer	+++/++	++/0	++/+	+++/d
PVA	+++/d	0/0	0/+	+++/d
Ceramic	+++/0	++/+++	0/+++	+++/+++

† 0, negligible sorption (<5%); +, weak sorption (5–20%); ++, moderate sorption (20–40%); +++, strong sorption (>40%); d, desorption; ND, no evaluation possible.

‡ Polyvinyl alcohol.

the breakthrough of DOC from the PVA and ceramic cups occurred later than from the polymerous cup.

DISCUSSION

Trace Metal Sorption in the Absence of Dissolved Organic Carbon

The generally weaker sorption of TM under acidic than alkaline conditions confirms previous findings (Grossmann et al., 1990; Wenzel and Wieshammer, 1995; Wenzel et al., 1997; Andersen et al., 2002), and can be explained by competition of protons for the binding sites at the cup materials. In addition, the overall increase of sorption in the order Cd < Zn << Cu < Pb is in good agreement with the conclusions of Wenzel and Wieshammer (1995), that Zn and Cd are generally less strongly sorbed than Pb and Cu. This sorption behavior of suction cups is also similar to the one of clay minerals and oxides (McBride, 1989). Furthermore, our data con-

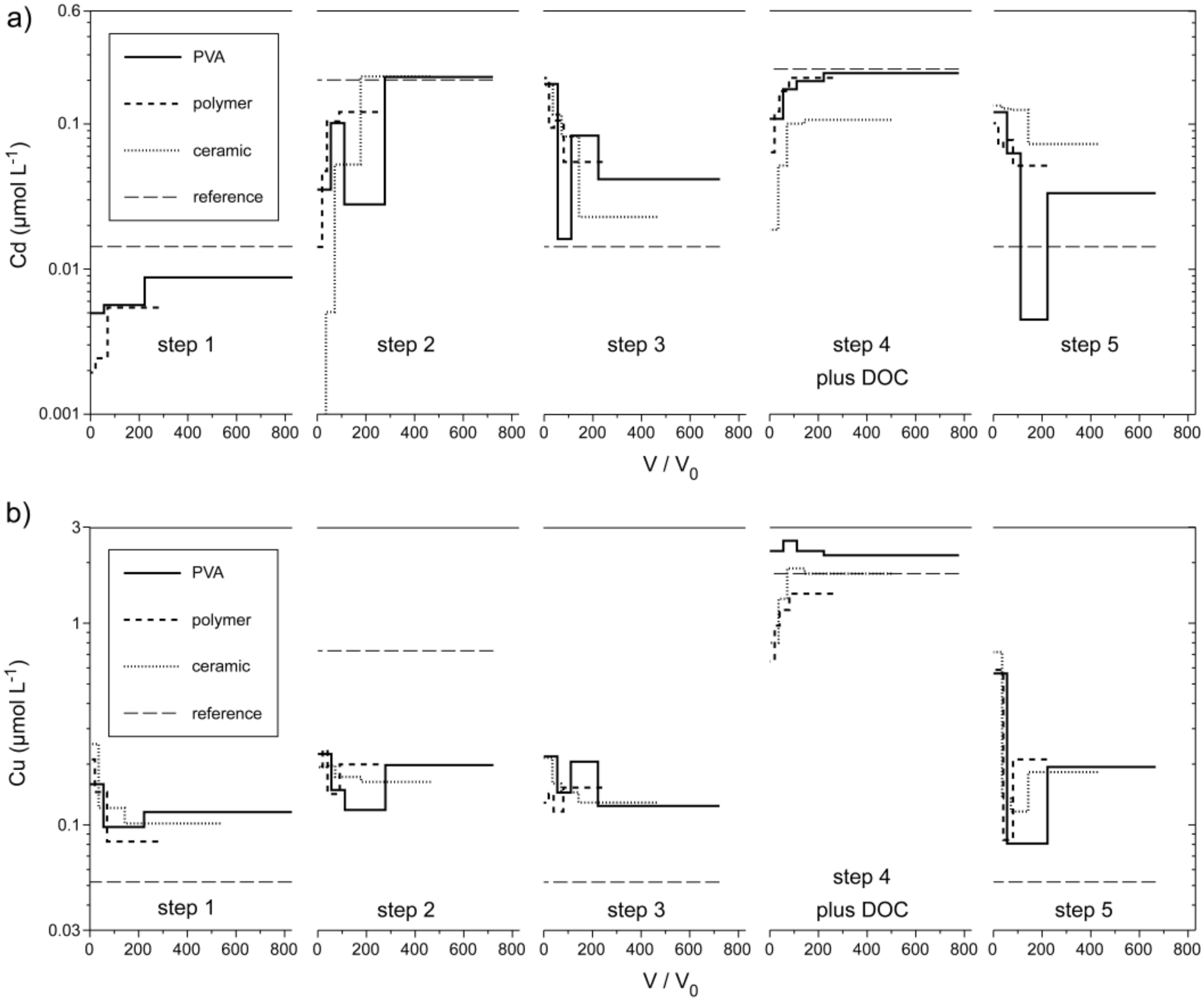

Fig. 4. Cadmium (a) and copper (b) concentrations in the percolate collected from different micro suction cups at pH 8.0. For the conditions at Steps 1 to 5 of the experiment refer to the Materials and Methods section and Table 3. Volumes are given in multiples of the pore volume (*V_0*) of the respective cup. The reference lines show the expected metal concentrations if no interaction with the cup materials occurred (i.e., the concentration measured in the initial solution). The Cd concentrations in the percolate from the ceramic cup in Step 1 were at 0.0001 μmol L^{-1}.

firm the results of previous studies that reported virtually no effect of nylon on the concentrations of most TM with the exception of Pb (Grossmann et al., 1990; Grossmann and Udluft, 1991; Wenzel and Wieshammer, 1995; Wenzel et al., 1997). The influence of PTFE cups on TM concentrations under realistic conditions has not been evaluated systematically yet. The strong sorption of all TM at alkaline conditions, and of Cu and Pb at acidic conditions is not expected from plastic materials because of their low CEC. The behavior can, however, be explained by the silicate material mixed into the PTFE to decrease hydrophobicity (Maitre et al., 1991). The strong TM sorption by both ceramic and borosilicate glass cups was expected because of their high CEC and pH-dependent specific metal binding sites (Grossmann et al., 1990).

The pure aluminium oxide ceramic used for the construction of micro suction cups sorbed TM much less than the ceramic material used for the construction of the standard suction cups, in particular at acidic pH. The polymerous cups performed satisfactorily only for Zn, Cd, and Pb at acidic conditions, while Cu was sorbed strongly at both pH values. By contrast, the hollow fibers made from PVA proved to be suitable for the monitoring of all investigated TM at acidic conditions and of Zn and Cd at alkaline conditions.

Sorption of Dissolved Organic Carbon

The larger sorption of DOC from leaf litter extracts on nylon cups than of DOC in the lysimeter drainage water can be related to differences in hydrophobicity. While DOC from a leaf litter extract is similar to DOC in leachates of the litter layer before entering the min-

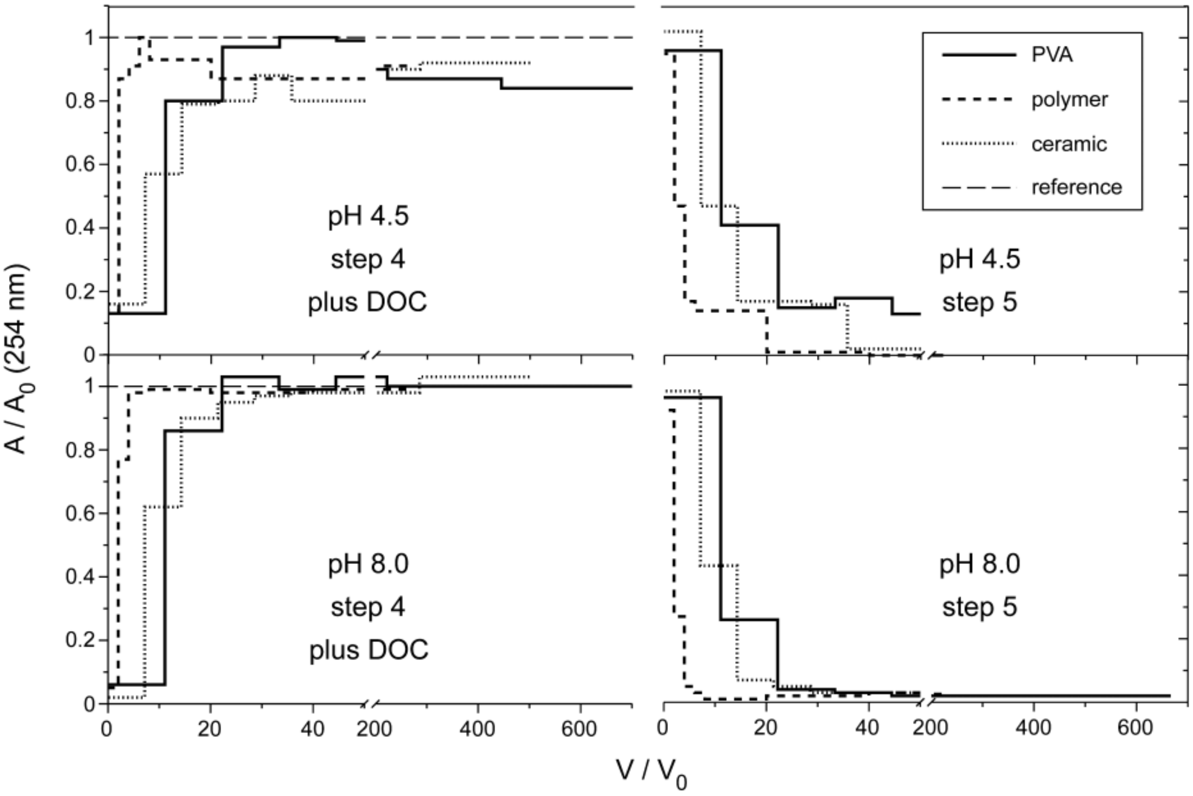

Fig. 5. Light absorption at 254 nm in the percolate collected from different micro suction cups at pH 4.5 and 8.0 in Steps 4 and 5 of the percolation experiment (for conditions refer to the Materials and Methods section and Table 3). Absorption is plotted relative to the absorption of the initial solution of Step 4 containing dissolved organic carbon (DOC) (A_0). Volumes are given in multiples of the pore volume (V_0) of the respective cup.

eral soil, DOC in the drainage water represents DOC in mineral soil horizons, the source of which is mainly old carbon from humified soil organic matter (Hagedorn et al., 2004). Guggenberger et al. (1998) found that the functional group content, carboxyl C, and aromatic C of DOC decreased with soil depth. Thus, the DOC in the drainage water can be considered chemically similar to the hydrophilic fraction of the litter extracts, with weaker sorption properties, a higher degree of oxidation, a larger proportion of saccharides, and lower molecular weight than the hydrophobic fraction (Guggenberger et al., 1998; Huang et al., 1998). These considerations suggest that the DOC sorbed on the cup materials was primarily the hydrophobic fraction. This is supported by the observation of Guggenberger and Zech (1992) that the hydrophobic fraction of DOC had decreased after percolating soil solution through ceramic P80 suction cups. Selective sorption of hydrophobic fractions can also explain the greater extent of litter DOC sorption on the more hydrophobic cup materials nylon and PTFE than on the hydrophilic ceramic and glass cups (Table 4). The stronger sorption of DOC at low pH than at high pH is in good agreement with the sorption behavior of DOC on mineral surfaces (Tipping and Hurley, 1988).

Trace Metal Sorption in the Presence of Dissolved Organic Carbon

Dissolved organic carbon can influence TM retention by cup materials in two ways. First, DOC can complex the metals. If the complexes are not sorbed, this can prevent metal retention by the cups, or lead to desorption of previously sorbed metals. Speciation calculations for the acidic synthetic soil solutions with DOC predicted 67% of Cu, 4% of Zn and Cd, and 52% of Pb to be present as complexes with fulvic acids. At pH 7.5, 85% of Cu, 7% of Zn, 10% of Cd, and 94% of Pb were calculated to be organically bound. Second, DOC sorption by the suction cups can increase their CEC, and, thus, the sorption of TM (Grossmann et al., 1990). In most cases, in particular at alkaline pH, we observed that addition of DOC reduced TM sorption or led to the release of previously sorbed metals. The opposite effect was observed in some cases for the ceramic materials and for the PVA hollow fibers.

Borosilicate glass was included in this study because of its low affinity to organic substances, which was confirmed by our results on DOC sorption. The hypothesis, however, that this would also lead to weaker TM retention in presence of DOC due to the formation of stable organo–metallic complexes was not confirmed. All TMs were sorbed completely by the glass cup also in presence of DOC. This suggests that either the adsorptive forces between TM and binding sites on the glass were stronger than the bonds between TM and DOC, or the metal–DOC complexes were sorbed to the binding sites of the glass by the formation of ternary complexes.

Our results on the sorption of Cu and Pb by standard-size ceramic suction cups in the presence of DOC confirm observations of Guggenberger and Zech (1992) for field-equilibrated and new acid-washed ceramic suction cups. Furthermore, Grossmann et al. (1990) studied the influence of DOC extracted from a Rendzina on TM sorption by nylon and observed similar effects as in our study.

CONCLUSIONS

Our tests demonstrate the importance of taking the effects of DOC on the sorption of TM on suction cups used in tension lysimetry into account. Metal retention was mostly reduced in the presence of DOC due to the formation of soluble complexes. The opposing effect of increased CEC due to sorption of DOC itself can be expected to be larger for DOC from fresh carbon sources like leaf litter containing large hydrophobic fractions than for mainly hydrophilic DOC originating from degradation of humified soil organic matter. Thus, the accuracy of monitoring TM in soil solution can be assumed to be better in deeper mineral soil horizons than just below the litter layer.

This study confirms the good properties of nylon membranes as construction material for suction cups if TMs have to be analyzed. Only Cu concentrations in the absence of DOC and Pb concentrations both in the absence and presence of DOC are expected to be strongly affected at high pH. According to Wenzel et al. (1997), the constant release of little amounts of carbon from the nylon cups themselves is not expected to affect metal speciation. Based on this, the construction of micro suction cups based on nylon membranes as proposed by Puschenreiter et al. (2005) is highly desirable. Overall, hollow fibers made from PVA are a well-suited construction material for micro suction cups. Only Pb at low pH in the presence of DOC, and Cu and Pb under alkaline conditions in the absence of DOC were strongly sorbed by PVA. Ceramic capillaries produced from pure aluminum oxide are also a good choice for monitoring Cu, Zn, and Cd concentrations at low pH, while the constant release of Pb restricts their use for this TM. At high pH, they may also be used for Cu and Cd depending on the concentration and type of DOC present. Cups made of polymerous tubes turned out to be well suited to observe Zn, Cd, and Pb concentrations at low pH and, in the presence of DOC, also at alkaline pH. On the other hand, Cu concentrations are expected to be biased at all conditions when using polymerous cups.

The results of this study for standard-size suction cups are valid for rather new cups that have been used for about 3 mo at constant vacuum (based on average flow rates for nylon cups observed in a lysimeter study). For micro suction cups, the length of our experiments corresponds to a use of about 6 mo [based on average flow rates observed for ceramic capillaries by Göttlein et al. (1996)]. With longer use, the sorption properties of suction cup materials may change.

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