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W. W. Wenzel^a; G. Wieshammer^a

^a Institute of Soil Science, University of Agriculture, Vienna, Austria

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SUCTION CUP MATERIALS AND THEIR POTENTIAL TO BIAS TRACE METAL ANALYSES OF SOIL SOLUTIONS: A REVIEW

W. W. WENZEL* and G. WIESHAMMER

*Institute of Soil Science, University of Agriculture, Gregor Mendel-Strasse 33, A-1180
Vienna, Austria*

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We reviewed the effects of physical and chemical characteristics of filter materials on trace metal concentrations in soil solutions to evaluate their suitability for porous sections of suction cups. Among the materials described in the literature, e.g. ceramics, Al_2O_3 , sintered Ni or glass, and various plastic filters, a great variation in bubbling pressure, pore size, permeability, chemical composition and stability, CEC, and trace metal dissolution/precipitation or adsorption/desorption processes was found. A low adsorption capacity suggests plastic materials are suitable, provided the bubbling pressure is high enough. All other materials have disadvantages in one or more properties, e.g. release of trace metal impurities into the soil solution, clogging of pores by precipitation of previously dissolved compounds, or sorption of trace metals.

Many reported experiments on sorption of trace metals by various materials are not relevant because of the unrealistic high metal concentrations of the test solutions. Our experiments with realistic concentrations revealed that sorption processes during the extraction may alter trace metal concentrations in soil solutions significantly.

Ceramic or Al_2O_3 cups are commonly used, but they adsorb appreciable amounts of trace metals. Therefore, we conclude that metal fluxes and budgets based on such data have to be interpreted with caution. To improve data comparability, detailed description of suction cup materials in the method sections of papers would be required. Moreover, more development and testing with plastic materials should be done, aimed at the optimization of both physical and chemical properties.

KEY WORDS: Trace metals, soil, filtration, suction cups, adsorption.

INTRODUCTION

Trace metals have been increasingly introduced into the biosphere by human activities during the last decades, often markedly exceeding natural fluxes. Systems analyses of pathways of trace metals in the environment indicate that soils are often major sinks.¹

Direct monitoring of trace metal accumulation in soils by repeated sampling at the same site and measurement of total metal concentrations is very limited by spatial variation.^{2,3} Given present atmospheric input rates, significant changes of trace element concentrations in the soil will be detectable only after several decades,² although these changes could be ecotoxicologically relevant. Therefore, input-output analysis is a more powerful tool for monitoring trace metal accumulation in soils.⁴ A method widely applied for monitoring solute transport towards the groundwater is the analysis of soil solution and seepage water.⁵

* Author to whom correspondence should be addressed

Published data on trace metal concentrations in soil solutions are relatively rare,⁶⁻⁸ but are urgently needed for monitoring trace metal fluxes and for calibrating existing models for the prediction of groundwater contamination by trace metals through the soil pathway.^{4,9}

Moreover, an evaluation of the reliability and comparability with respect to methodology in the construction, installation and operation of the suction-cups is required.¹⁰⁻¹²

In this review we discuss some characteristics of diverse suction-cup materials along with the relevance of published data on trace metal concentrations in soil solutions.

CONCENTRATIONS OF SOME TRACE METALS IN SOIL SOLUTIONS

Common ranges of trace elements in soil solutions are summarized in Table 1. As indicated, the data were obtained by suction cups and lysimeters varying in type of construction, tension applied and the materials used. In the following sections, the range of trace metal concentrations found in these soil solutions will be used for the evaluation of sorption tests as reported in the literature.

CHARACTERISTICS OF SUCTION-CUP MATERIALS

Essentially, modifications of at least nine different materials have been used for the construction of the hydrophilic section of suction cups (Table 2).²⁶ In the seventies and

Table 1 Trace metal concentrations ($\mu\text{g L}^{-1}$) in mineral soil solutions. The authors, the type of suction cup and the pH of the soil solutions are indicated.^{7,8,13-25}

Author	Method	pH	Cd	Cr	Cu	Ni	Pb	Zn
Heinrichs and Mayer (1980)	(a)	3.9-4.3	2.9-5.1	0.6-0.7	18-27	3.1-15	5.1-6.3	190-570
Peters (1990)	(b)	3.2-8.1	0.01-3.8		1.8-7.6		0.2-11.1	15.1-231
Schultz (1987)	(b)		3-4		1.9-9.6		2-33	195-546
Nicolson (1988)	(b)	4.4			41-52			
Zöttl (1985)	(c)						1.3	6
Lochmann (1983, 1985)	(c)	2.3-4.4						40-360
McColl (1981)	(b)	6.2-6.9			37-78			49.6-71.6
Feger (1986)							7-12	
Turner <i>et al.</i> (1985)	(d)	3.3-4.9					0-35	
Friedland and Johnson (1985)	(d)						1.0-3.7	
Bergkvist (1987c)	(e)	2.8-4.4	0.61-1.73	0.81-1.86	1.43-4.03	0.89-4.14	1.02-19.5	34.4-151
	(e)	2.8-4.3	0.39-0.86	1.2-2.31	0.71-4.07	1.8-3.6	0.95-17.1	38.4-75.2
Bergkvist (1987a)	(e)	2.9-4.5	0.32-1.88	0.44-2.67	1.14-5.85	1.08-6.03	0.5-32	16.7-150
	(e)	3.1-4.3	0.36-2.71	0.69-2.04	1.45-3.2	3.05-12.9	0.69-6.28	30.6-186
Bergkvist <i>et al.</i> (1988)	(e)	low	0.3-3.2		0.79-7.4		0.31-2.1	160-430
Rasmussen (1986)	(e)	2.7-3.6	5-7.4			2.3-12.1		9.6-295
Entire range		2.3-8.1	0.01-5.7	0.44-2.67	0.71-78	0.89-15	0.2-35	6-570

(a) Al_2O_3 tension plate lysimeter (b) Ceramic tension suction cup (c) Tension lysimeter unspecified
(d) Sand filled funnels (e) Plexiglass zero tension lysimeter (container)

Table 2 Overview on materials used for the construction of suction cups.^{26,30-32}

<i>Material</i>	<i>Type/producer</i>
(1) Ceramic	(a) P80, Staatliche Porzellanmanufaktur Berlin, FRG (b) Diapor 8 G, Schumachersche Fabrik Bietigheim, FRG (c) Soil Moisture Equipment Corp., Santa Barbara, California, USA
(2) Aluminumoxide	(a) Haldenwanger Berlin, FRG
(3) Sintered nickel	(a) Krebsöge
(4) Fritted glass	Various types, e.g. Corning ultrafine
(5) Teflon	Various types
(6) PVC	Various types
(7) Polypropylene	(a) Wolf Filter Technik, 7252 Weil der Stadt, FRG
(8) Nylon	(a) Millipore Filter G.m.b.H., 6078 Neu-Isenburg, FRG, e.g. type UHWP 293 oo (b) Pall, 6072 Dreieich, FRG (c) Gelman Sciences, Inc., 600 South Wagner Road, Ann Arbor, Michigan 48106
(9) Polyvinyl fluoride	(a) Millipore Filter G.m.b.H., 6078 Neu-Isenburg (FRG)

early eighties, mainly ceramics were used, while alternate materials such as aluminium oxides and Ni-sinter received less attention. Starting in the early eighties, various plastic materials low in specific surface were increasingly tested in the laboratory, but, with few exceptions, have not yet been tested extensively under field conditions.²⁷⁻²⁹

The materials used for the construction of suction cups (Table 2) differ enormously in physical, physico-chemical and chemical properties (Table 3-5). Depending on the producer and the type of modification, even for the same type of material, the characteristics such as chemical and mineralogical composition, pore diameter and air entrance value (bubbling pressure) are highly variable (Table 5).

Table 3 Chemical composition and structure of suction cup materials.³³⁻³⁶

<i>Material</i>	<i>Chemical composition and structure</i>
(1) Ceramics	(a) P80: 70-90% mullite (3 Al ₂ O ₃ , 2 SiO ₂ /2Al ₂ O ₃ , SiO ₂) + corundum (Al ₂ O ₃) (c) SM: 70% quartz (SiO ₂) + 10% MgO + 8% Al ₂ O ₃
(2) Aluminum oxide	Al ₂ O ₃
(3) Sintered nickel	Ni
(4) Fritted glass	SiO ₂
(5) Teflon	-CF ₂ -
(6) PVC	-CH ₂ -CH- Cl
(7) Polypropylene	-CH ₂ -CH-CH ₂ -CH- CH ₃ CH ₃
(8) Nylon	-OC-(CH ₂) ₄ -CO-NH-(CH ₂) ₆ -NH-CO-(CH ₂) ₄ -CO-NH-(CH ₂) ₆ -NH-
(9) Polyvinylfluoride	F -CH ₂ -C- F

Table 4 Elemental composition of various suction cup materials.³³⁻³⁵

Material	Si	Na	K	Ca	Mg	Fe	Al	Cd	Co	Cu	Mn	Ni	Pb	Zn
Type	g kg ⁻¹							mg kg ⁻¹						
Ceramic														
P80 ^a	88	1.1	2.5	0.6	0.43	0.8	176				<0.1			
P80 ^b	133	0.7	2.5	0.7	0.6	4.2	344							
Diapor 8 G ^c		2.3	3.7	1.2	0.65	2.8	>300	1.5	4	15	40	150	40	15
Soil moisture ^b	322	2.8	7.5	26	61	3.5	42							
Aluminumoxide														
Haldenwanger Berlin ^c		0.4	0.1	0.1	0.85	0.2	>100	0.1	<0.1	<10	<10	<10	8	40
Sintered nickel														
Strebel <i>et al.</i> (1975) ^c		0.1	0.3	0.2	0.01	0.01	<0.01	0.3	0.5	<10	<10	10 ⁶	6	<15

^aextracted by hydrofluoric acid (Raulund-Rasmussen, 1989).³³^bextracted by concentrated hydrochloric plus hydrofluoric acid (Raulund-Rasmussen, 1991).³⁴^cextracted by hydrofluoric plus perchloric acid (cited in Hädrich *et al.*, 1977).³⁵**Table 5** Physical and physico-chemical characteristics of various suction cup materials.

Material	Max. pore diameter [μm]	Bubbling pressure [hPa]	Permeability [mL MPa ⁻¹ s ⁻¹]	CEC [mmol _c cup ⁻¹]	Wall thickness [mm]
Ceramic					
P80 ^a	1.00	4000	4.2	0.40–0.65 ^b	
SM B5M3		140–460 ^d			4
SM B1MC		920–1100 ^d			4
SM 1910		1060–2000 ^d			2.4
SM B2M2		> 2000 ^d			4
SM unspecified ^e	0.9	1000			
Aluminumoxide					
Haldenwanger Berlin ^a	0.50	6000	6.7	0.39	
Unspecified alundum	5	80–150			2.4
Unspecified alundum	20	35–55			2.4
Nylon pall^a					
Millipore UHWP 293 oo ^c	0.5	700	290	0.1	
Gelman Sciences Versapor 200 ^f	0.20	200			0.19
Teflon					
		3–12 ^d			4
Fritted glass					
Unspecified		140–160 ^d			3
Corning ultrafine ^g	0.9–1.4	2500			

^aGrossmann *et al.* (1990).²⁸ ^bat pH = 8 ^cRaulund-Rasmussen (1991).³⁴ ^dBottcher *et al.* (1984).³⁷^eGermann (1972).³¹ ^fWenzel and Steffek (personal communication).³⁸ ^gSilkworth and Grigal (1981).³⁹

AIR ENTRANCE VALUES OF SUCTION CUP MATERIALS

Within the range of soil matric potential to be investigated, suction cups are designed to maintain the applied vacuum against penetration of air into the cup. Suction cups made of various materials have been tested by being placed into distilled water and applying

gradually increasing pressure on the inside of the tubes, and recording the pressure when the first bubble is observed (bubbling pressure or air entrance value).³⁷ Occasionally, a second record was made when 25% of the surface was bubbling, and the range of pressure between the first bubble and the latter was reported (Table 5).³⁷ Hydrophilic materials, e.g. ceramic and Al_2O_3 , show commonly higher bubbling pressures than more hydrophobic plastic (Table 5). For instance, the bubbling pressure of completely hydrophilic materials is theoretically 1000 hPa at a pore size of 3 μm , while for more hydrophobic materials a smaller pore size is required.⁴⁰ Therefore, within the same type of material, the bubbling pressure depends on the maximum pore diameter. The bubbling pressure decreases expectedly with increasing pore size of the Al_2O_3 cups, but conversely, increases with the pore size of nylon cups (Table 5). This apparent deviation from theory is presumably caused by variation in the properties of the nylon used, e.g. hydrophobic characteristics, deviation from circular pore shape, and wall thickness as affected by the production technology.

The use of materials with low bubbling pressures is greatly reduced in unsaturated soils, for water can be extracted from the soil only when the soil water tension is less than the bubbling pressure of the cup.³⁷ Accordingly, some materials listed in Table 5 are not suitable for extraction of water from a wide range of unsaturated soils.

INTERACTIONS BETWEEN SUCTION CUP MATERIALS AND SOIL SOLUTION

Various methodological problems may occur through interactions between suction cup materials and the soil solution. The most important are dissolution of the materials with release of major and trace elements, subsequent precipitation of metal species and clogging of pores, as well as adsorption/desorption reactions of trace elements with cup materials.

Chemical stability of the materials and release of metals from the suction-cup material

Under acidic conditions, ceramic cups are chemically unstable, presumably caused by proton-induced dissolution of the cup material.³⁴ The rate of dissolution depends on the mineralogical and chemical composition of the material (Tables 3 and 4). Ceramics with a high proportion of non-amorphous Al_2O_3 (mullite, corundum) and low in base cations (Mg, Ca, K) are more stable.³⁴ The release of elements is governed by the chemical composition of the cup and the pH of the soil solution (Figure 1). With decreasing pH, dissolution generally increases, and Al is favorably dissolved instead of Ca and Mg (Figure 1). According to Raulund-Rasmussen,³⁴ the extent of errors due to dissolution of ceramic cups depends on whether Al activity in the solution is undersaturated with respect to the Al compounds in the suction cup, and decreases with increasing solution intake rates and with efficiency of the rinsing procedures prior to sampling.

While plastics are commonly not contaminated with trace elements, other materials may contain certain amounts of Al, Cu, Zn, Ni or Cd (Table 4).²⁶ From ceramic and Al_2O_3 , these contaminants can be removed by washing the cups with about 100–1000 mL 0.1–1 M HCl.²⁶ Sintered nickel is chemically unstable under acidic conditions thus leading to continued dissolution of Ni and subsequent precipitation of $\text{Ni}(\text{OH})_2$. Consequently, the electrical conductivity of the percolated solution as well as the porosity of the cups changes significantly with time.^{35,41} Also, pH solutions sampled with cups of sintered Ni were reported to deviate from the actual values.⁵

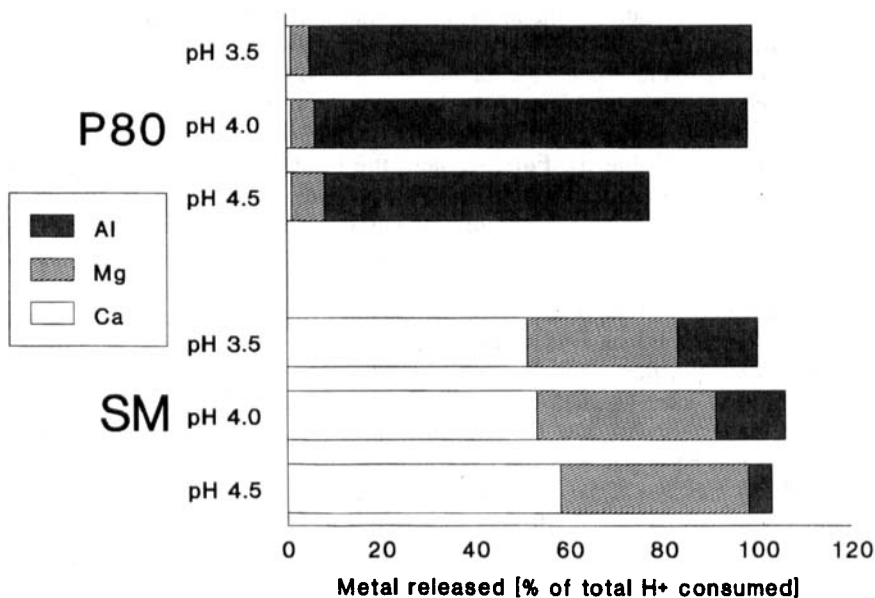


Figure 1 Relative amounts of Al, Ca and Mg released from two ceramics as affected by their chemical composition and solution pH. Ceramic 1 (P80 cup) is high in non-amorphous Al_2O_3 , ceramic 2 (Soil Moisture, SM) is high in Ca, Mg, and K (compare Table 4). Data obtained from Raulund-Rasmussen (1991).³⁴

Clogging of pores and filter effects

As mentioned, pores of sintered Ni materials may be clogged by precipitation of previously dissolved Ni as $\text{Ni}(\text{OH})_2$. Similarly, precipitation of $\text{Al}(\text{OH})_3$ and secondary Ca and Mg carbonates may clogg pores of ceramic and Al_2O_3 materials.³⁴

Independent of the cup material, clogging of pores may occur through precipitation of compounds from the soil solution supersaturated with respect to the solid phase. Accordingly, precipitation of phosphates and aluminium hydroxy sulphates was reported by several authors.^{35,42} Morrison reported substantial clogging of pores by biofilm growth that could be minimized by backfill with silica flour instead with soil material after installation of the cups.²⁷ Decreases of the intake rate were about 25, 18 and 6%, respectively, for the loam, sand and silica slurries used for backfill.²⁷

According to the pore size, colloids and macro-molecules are filtered by suction cup materials, but, since adsorption may occur simultaneously, it is difficult to distinguish between these processes.⁴⁰ Increasing elimination of Fe, Al, Si, phosphate and organic compounds with decreasing pore size of various materials was found by several authors.^{42,43} Significant reductions of the concentrations of Al, Fe, Si and organic C preferably occurred after filtration through materials with pore diameters less than $0.05 \mu\text{m}$.⁴³

Trace metal adsorption and desorption reactions with various suction-cup materials

A further process that may lead to erroneous results is adsorption of metals from the soil solution by suction-cup materials, and, subsequently, their partial desorption when the

metal concentration in the soil solution decreases again.^{5,26,40} The significance of sorption processes depends on the cation exchange capacity (CEC) of the material,⁴⁰ the reversibility of metal specific adsorption,²⁶ and the range of concentration and temporal variability of the respective metal in soil solution (Table 1).

Although the sorption reaction is considered as being reversible, the kinetics of adsorption and desorption may differ.^{35,42}

The CEC of suction-cup materials varies widely (Table 5). Due to their low specific surface and a low charge density, plastic materials are usually lower in CEC than ceramic and Al_2O_3 .⁴⁰ For instance, the CEC's of Al_2O_3 and ceramic cups were reported to exceed that of a nylon cup by 5–7 times (Table 5).⁴⁰ Accordingly, much greater volumes of test solutions are needed to percolate through Al_2O_3 suction cups than through cups made of nylon to reach the initial metal concentrations in the eluate (Figure 2)²⁸. The adsorption reaction was found to depend clearly on pH. At pH 4, after percolation of 300 cm^3 test solution about 100% of the initial metal concentrations were recovered in the eluate, independent of the material, e.g. nylon, Al_2O_3 and ceramic. At pH 8, less than 10% of the initial concentrations were found in the eluates after percolation of 300 cm^3 test solution through Al_2O_3 and ceramic cups, but, except for Pb (52%), more than 80% after percolation through nylon cups (Figure 2).⁴⁰

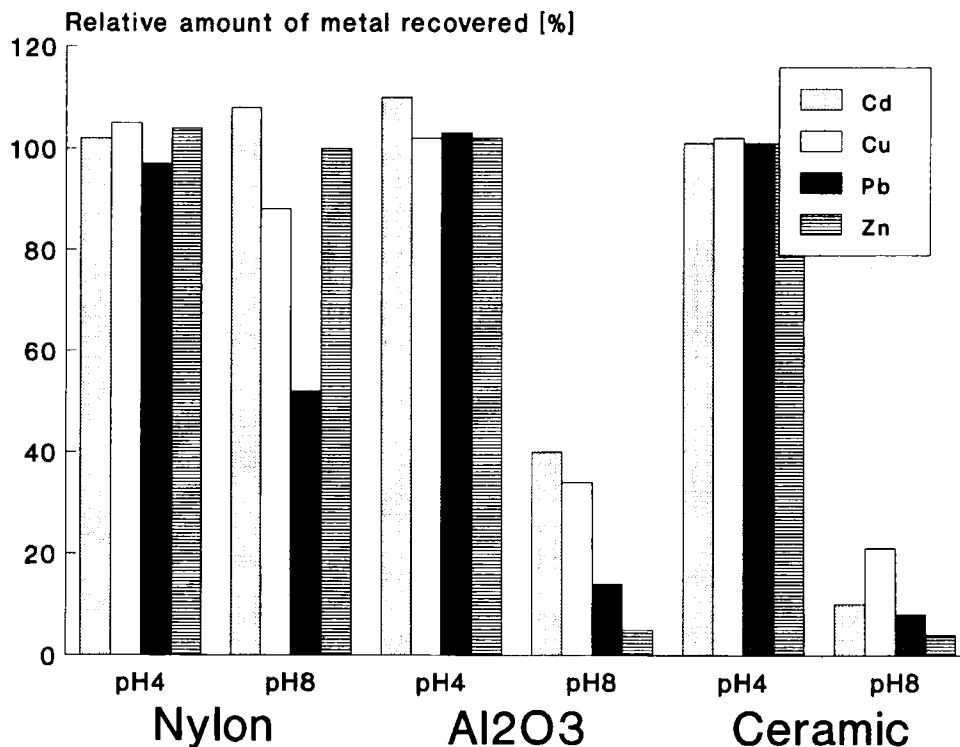


Figure 2 Relative amounts of metals recovered after percolation of 300 mL test solutions at pH 4 and 8, respectively, containing 25 mg L^{-1} Cd and each 30 mg L^{-1} Cu, Pb and Zn (compare Table 6). Data obtained from Großmann and Udluft (1991).⁴⁰

Similarly, Hädrich *et al.*³⁵ tested suction cups made of Al₂O₃ (type: Haldenwanger, Berlin) and sintered nickel with test solutions of pH 4 on the adsorption of Al, Cd, Co, Mn, Ni, Zn, Cu and Pb. From the results it was concluded that after three months conditioning, Al₂O₃ cups adsorbed only negligible amounts of those elements. Only non-organically bound Pb was adsorbed significantly. Short-term variations of metal concentrations in the test solutions were reproduced well for most trace metals except for Cu and Pb. Initially, suction cups of sintered Ni yielded similar results but released great amounts of Ni into the soil solution and were chemically unstable under acidic conditions in addition to other disadvantages.³⁵

Testing porous teflon (3 µm) by percolation with monoionic standards (1000 µg L⁻¹) of Mn, Pb and Zn, Morrison²⁷ found no detectable adsorption of these metals.

The trace metal concentrations of the test solutions used by Hädrich *et al.*³⁵ and Morrison²⁷ exceeded the concentrations found in soil solutions (Table 1) by a factor of about 10 and 1000, respectively (Table 6). The low adsorption of trace metals onto nylon as reported by Grossmann and Udluft⁴⁰ seemed to indicate that this material would be appropriate for the construction of suction cups, independent of the pH of the soil solution,^{5,40} but again, the metal concentrations of the test solutions exceeded those found in soil solutions up by a factor of about 10 (Table 6).

Consequently, the experiments conducted with unrealistic high metal concentrations in the test solution show only qualitative differences between suction cup materials, but are not suitable for the evaluation of those materials for realistic conditions. In this context it should be noted that in the experiment of Grossmann and Udluft⁴⁰ just Pb, that was tested at the lowest molar concentration (0.14 µmol_c Pb L⁻¹ vs. 0.23 µmol_c Cd L⁻¹ and > 0.44 µmol_c Co, Cu, Mn, Ni, and Zn L⁻¹, respectively), showed by far the lowest proportion recovered in the eluate after percolation of 300 cm³ test solution (52% at pH 8).⁴⁰

We conducted experiments to investigate adsorption of Cd, Cu and Pb on ceramic (P80) and nylon cups at more realistic conditions.³⁸ The cups were constructed of a porous (pore diameter 200 µm) polyethylene tube (length 100 mm, effective diameter 17 mm), mantled by a nylon membrane (0.2 µm pore diameter, Versapor 200, Gelman Sciences). All other parts were made of acrylic glass or polyethylene, respectively. The compositions of the test solutions correspond with those found in soil solutions (compare Table 1) and are indicated in Table 6. The suction cups were rinsed with 1 L 0.05 M

Table 6 Concentrations of Al and trace metals in test solutions used in various adsorption experiments (µg L⁻¹).^{27,35,38,40}

Source	Al	Cd	Co	Cu	Mn	Ni	Pb	Zn
Morrison ²⁷					1000		1000	1000
Grossmann and Udluft ^{40,a}		25	25	30	25	25	30	30
Hädrich <i>et al.</i> ^{35,b}	2000	2	4	5	25	25	30	30
Wenzel and Steffek ^{38,c}		0.8/3.5		5/25			5/25	

^a Recalculated from molar concentrations

^b Estimated by multiplication of soil solution concentrations presented in the article by a factor ten as indicated by the authors.

^c Test solutions: (1) Pretreatment: Cd 0.2, Pb 2.5, Cu 2.5 µg L⁻¹
Al 1, Ca 1 mg L⁻¹
(2) Solution 1: Cd 0.8, Pb 5, Cu 5 µg L⁻¹
Al 2, Ca 2 mg L⁻¹
(3) Solution 2: Cd 3.5, Pb 25, Cu 25 µg L⁻¹
Al 20, Ca 10 mg L⁻¹

EDTA solution, washed twice with 1 L 1M HCl and finally with 5 L deionised water. After the cups were conditioned by percolation of 5 L solution containing very low trace metal concentrations (Table 6, pretreatment), the test solutions were percolated, starting with 250 mL solution 1, followed by the same amount of solution 2, and 120 mL of solution 1 (Table 6), aimed at simulating temporal variation in trace metal concentrations in soil solutions. The percolates of each three cups were combined prior to analysis. The experiments were conducted at pH 3 and 5 to evaluate the effect of pH on trace metal sorption by the suction cups. Cadmium, Cu and Pb concentrations in the eluates attained those of the test solution more rapidly in contact with the nylon than with the ceramic cups (Figures 3–8). The differences between the materials were more pronounced at higher pH. For instance, after percolation of 120 mL test solution of pH 5 only about

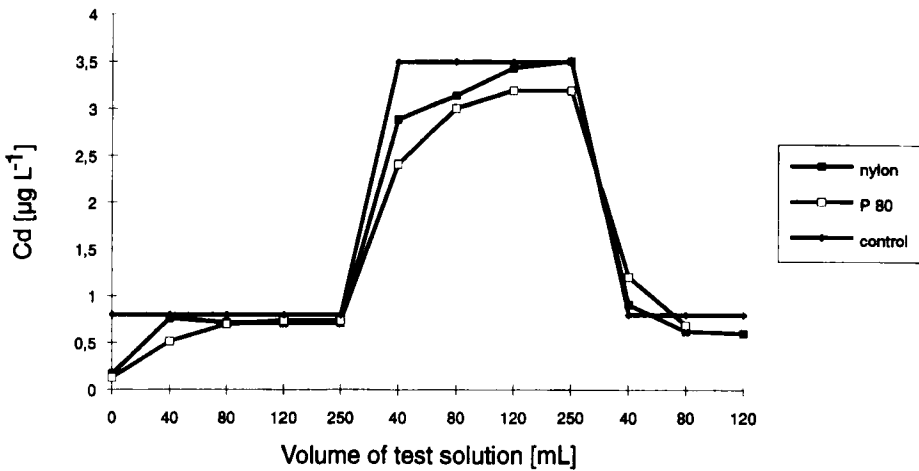


Figure 3 Adsorption and desorption of Cd by ceramic (P80, 0.1 µm) and nylon (Versapor 200, 0.2µm) alternately percolated with test solutions containing 0.8 and 3.5 µg L⁻¹, respectively, at pH 3 (average of 3 cups).³⁸

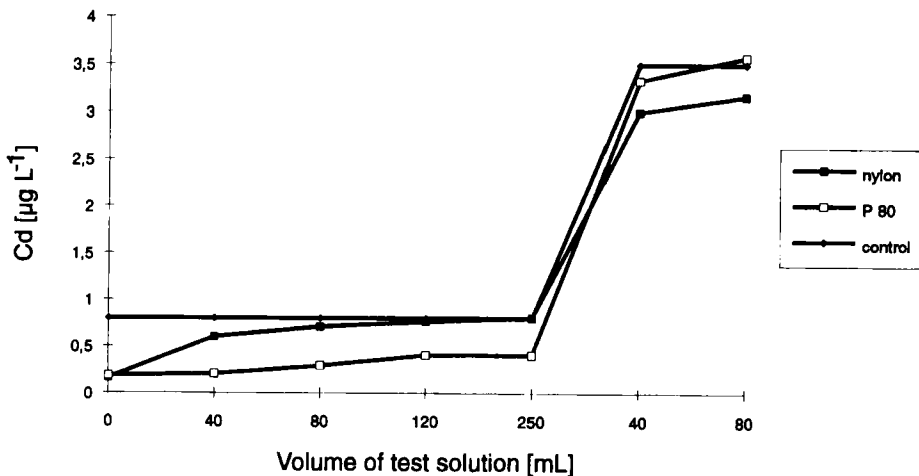


Figure 4 Adsorption of Cd by ceramic (P80, 0.1 µm) and nylon (Versapor 200, 0.2µm) alternately percolated with test solutions containing 0.8 and 3.5 µg L⁻¹, respectively, at pH 5 (average of 3 cups).³⁸

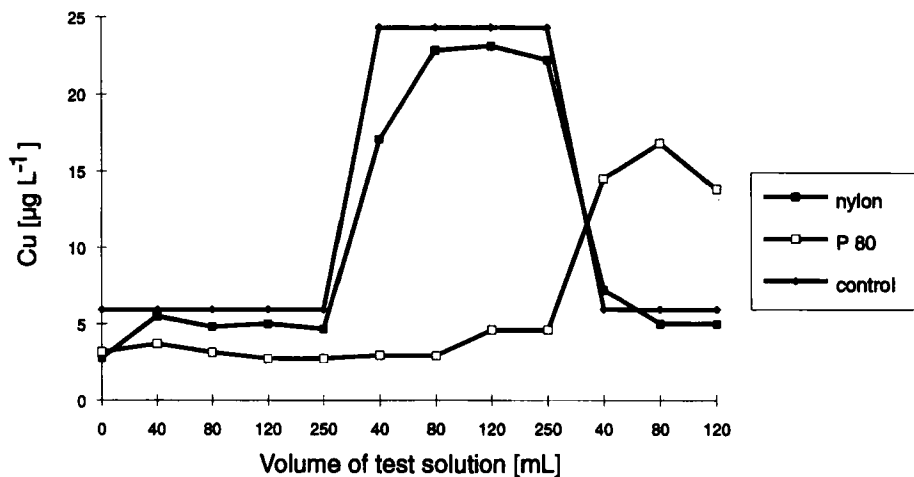


Figure 5 Adsorption and desorption of Cu by ceramic (P80, 0.1 μm) and nylon (Versapor 200, 0.2 μm) alternately percolated with test solution containing 5 and 25 $\mu\text{g L}^{-1}$, respectively, at pH 3 (average of 3 cups).³⁸

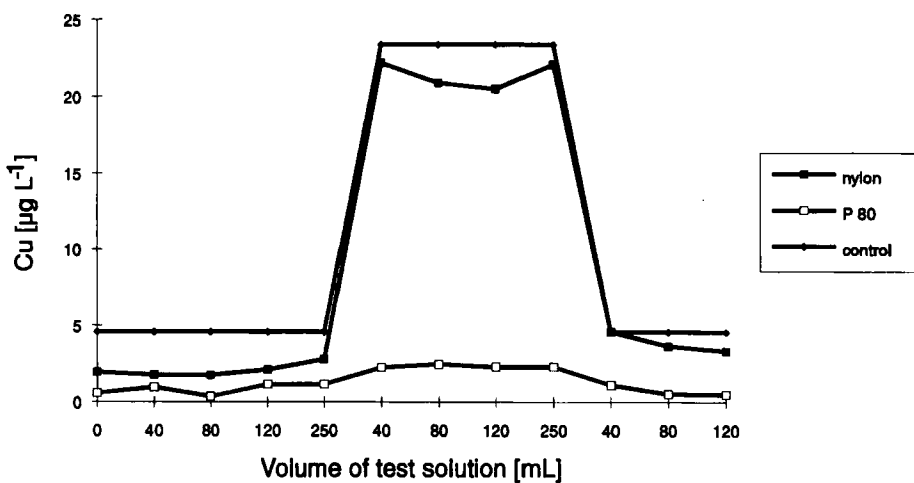


Figure 6 Adsorption of Cu by ceramic (P80, 0.1 μm) and nylon (Versapor 200, 0.2 μm) alternately percolated with test solutions containing 5 and 25 $\mu\text{g L}^{-1}$, respectively, at pH 5 (average of 3 cups).³⁸

50% of the initial Cd concentration was recovered in the eluate from the ceramic cups, while with the nylon cups equilibrium was almost attained after percolation of 40 mL. For Pb and Cu, the differences between the materials were even more pronounced. While the nylon cups reproduced the actual courses of trace metal concentrations in the test solutions reasonably well, this was not the case with the ceramic cups. The retardation during adsorption as well as desorption, i.e. for Pb and Cu, was much greater with ceramic cups, indicating that monitoring of the inherent temporal variation in trace metal concentrations would be impossible with the latter.

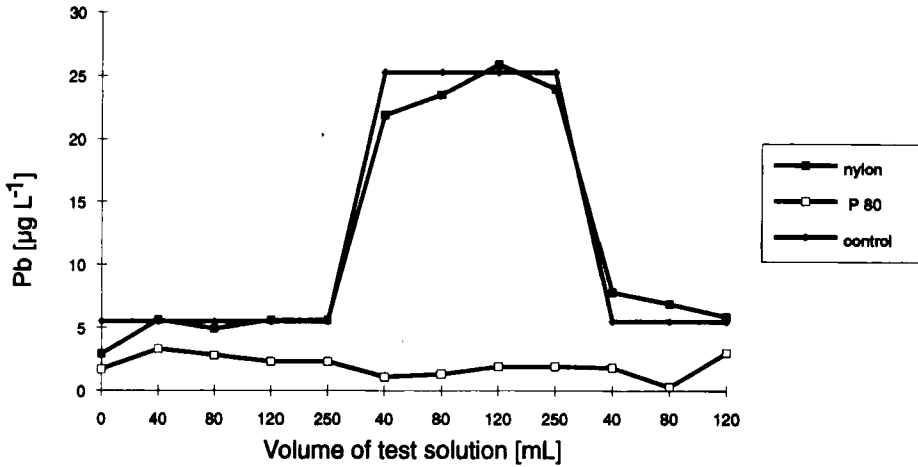


Figure 7 Adsorption and desorption of Pb by ceramic (P80, 0.1 µm) and nylon (Versapor 200, 0.2µm) alternately percolated with test solutions containing 5 and 25 µg L⁻¹, respectively, at pH 3 (average of 3 cups).³⁸

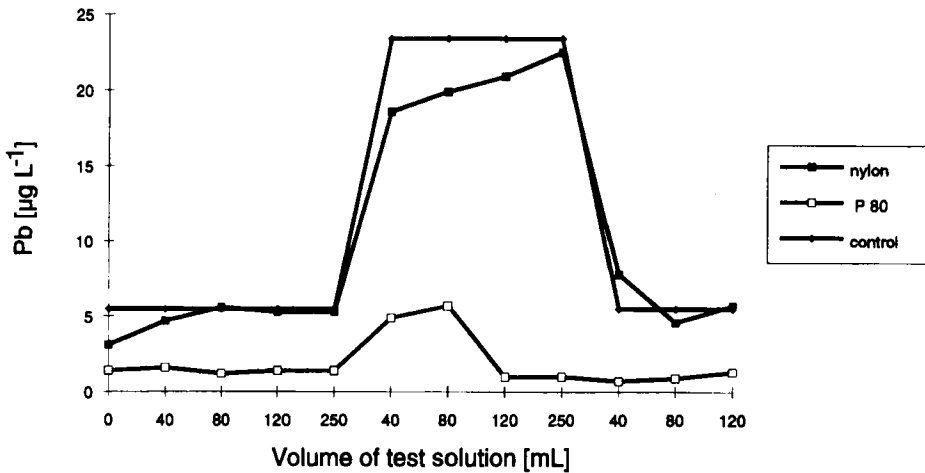


Figure 8 Adsorption of Pb by ceramic (P80, 0.1 µm) and nylon (Versapor 200, 0.2µm) alternately percolated with test solutions containing 5 and 25 µg L⁻¹, respectively, at pH 5 (average of 3 cups).³⁸

The sorption effect is not only controlled by the material, but also depends on the pore size (Figure 9),⁴³ the solution pH,⁴³ and the sampling rate as affected by the suction applied.²⁸

Generally, adsorption and desorption are most important in unsaturated soils for the limited amount of water being extracted,³⁷ and in soils with high pH.

CONCLUSIONS

Based on the information available, no porous materials for suction cups has been tested yet sufficiently that would meet all characteristics required for the in-situ extraction of

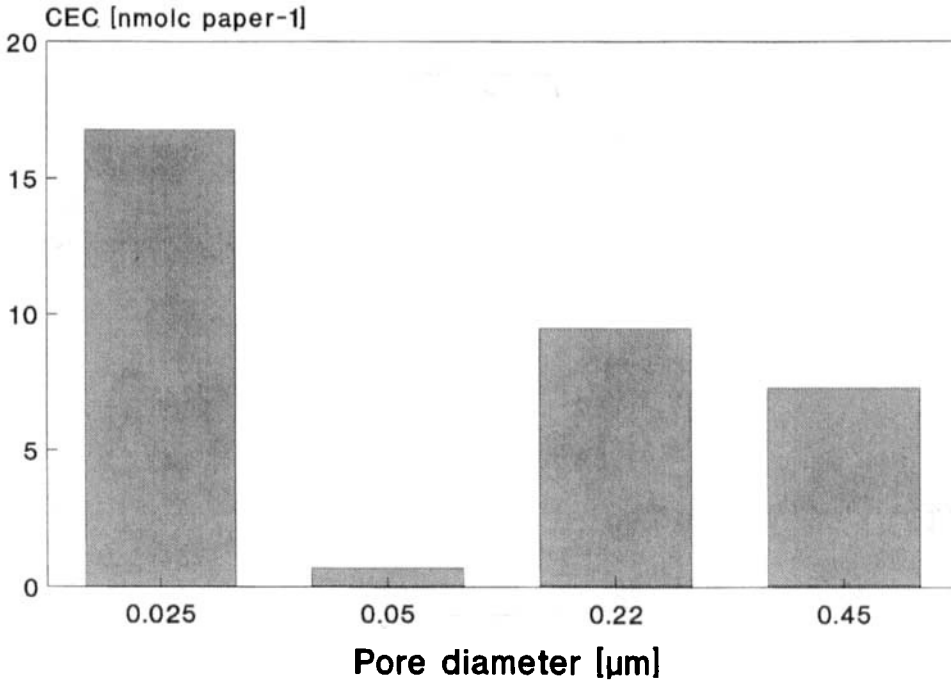


Figure 9 CEC of filter materials as affected by pore size. Data obtained from Menzies *et al.*⁴⁴

soil solutions to be analysed for trace metals. Cups of sintered Ni are not suitable for they are chemically unstable, continuously releasing considerable amounts of Ni into the soil solution, subsequently precipitated as $\text{Ni}(\text{OH})_2$. For their high bubbling pressure, some of the ceramic and Al_2O_3 materials are suitable to extract soil solutions contained in medium sized pores up to a suction of about $10^{4.2}$ (permanent wilting point), but are chemically not stable under highly acidic conditions. Moreover, cups made of such materials are known to adsorb significant amounts of trace metals, e.g. Pb and Cu, even from test solutions with unrealistic high concentrations. Our tests with realistic concentrations revealed that at pH 5 even Cd was adsorbed significantly by ceramic cups, followed by desorption when the concentration of Cd was decreased. Sorption processes are favoured by low intake rates as are common under dry conditions, and may lead to significant errors in the calculation of metal fluxes through the soil. Therefore, alternate materials, e.g. teflon, nylon, PVC, polypropylene, and polyvinylfluoride were proposed by several authors, but yet have not been tested sufficiently in the field. Laboratory tests reveal that such materials have low CEC and therefore low trace metal adsorption, they are chemically stable, and they lack of trace metal impurities. Unfortunately, comprehensive information on sorption of trace metals under realistic conditions as well as on bubbling pressures are scarce. Since this review indicates that the properties may differ widely according to the production technology, such materials should be tested extensively in order to optimize adsorption/desorption versus bubbling pressure characteristics.

Detailed description of suction cup materials in the method sections of papers would help to solve the methodological problems. With respect to adsorption processes, most

reported tests are irrelevant because of unrealistic high trace metal concentrations of the test solutions. Since in the past, trace metal concentrations in soil solutions were mainly obtained with ceramic or Al_2O_3 cups, we conclude that many trace metal budget calculations might significantly deviate from reality. Moreover, since suction-cup materials even of the same type may vary widely in physical and chemical properties, be cautious when comparing data.

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