Bull. Environ. Contam. Toxicol. (1998) 61:325-332

Bulletin of Environmental Contamination and Toxicology

Determination of Soil Water Phosphorus with a New Nylon Suction Cup

T. Tischner, G. Nützmann, R. Pöthig

Institute of Freshwater Ecology and Inland Fisheries, Rudower Chaussee 6a,
D-12484 Berlin, Germany

Received: 13 April 1998/Accepted: 21 July 1998

Phosphorus leaching from upper soil to near surface groundwater contributes significantly to eutrophication of surface waters (Lademann and Pöthig 1994). The process of vertical P movement and leaching with the percolating water is of great importance especially in highly fertilized sandy soils (Mansell et al. 1991; Tischner and Nützmann 1997).

Commonly ceramic suction cups are used for sampling of soil solution and quantifying solute transport in the unsaturated zone. Element concentrations in the extract, however, depend on the sampling method and on the type of suction cup (Grossmann et. al. 1990). Several studies were conducted to characterize the phosphorus sorption properties of ceramic cups. Zimmermann et. al. (1978) found that only 43% of phosphate were recovered after being passed through a ceramic cup. Similar results were obtained from Bottcher et. al. (1984) and Nagpal (1982). Therefore, it is recommended that water sampler made of ceramics should not be used for determining soil solution phosphorus (Hetsch et. al. 1979, DVWK 1990).

With regard to many trace substances including phosphorus no alterations of test solutions have been observed for PTFE suction cups (Rasmussen et al. 1986; Andersen 1994). But due to the low bubbling pressure their field use seems to be disadvantageous. Grossmann et al. (1990) and Wenzel and Wieshammer (1995) tested the properties of nylon suction cups. Their low adsorption capacity suggests that nylon sampler are suitable for determining a variety of trace elements. However, for the determination of phosphorus the sorption properties of nylon cups have not been analyzed yet.

In this report a new nylon suction cup (Fa. UGT Müncheberg, Germany) is presented. It is shown that for this sampler at typical P concentrations for soils no significant sorption of phosphorus occurs. Field experiences support this statement.

MATERIALS AND METHODS

The new soil water sampler consists of a PE (polyethylen) tube, a multilayer filter and a collector. The filter tube in the middle part of the cup is composed of three layers: the outer, hydrophilic PE cover, the nylon membrane with 0.45 µm pore width, and an inner porous PE body for stabilizing the filter. Chemical properties

---

Correspondence to: T. Tischner

and the bubbling pressure are mainly determined by the nylon membrane, whereas the thin outer PE cover serves for mechanical protection. Below the filter, at the lower end, a PE collector with 100ml volume is connected to the filter. The whole suction cup has a sample volume of 250ml. All three parts of the sampler are tightly held with thread joints and silicon O-rings.

Sorption experiments were carried out with distilled water and solutions containing phosphorus, calcium and iron in typical concentration ranges for soils. The solutions were sucked into the sampler by an underpressure of 10kPa and succeedingly analyzed. The sorption characteristics of this soil water sampler were laboratory examined as following:

1. Rinsing the suction cups with distilled water and analyzing of the percolate with respect to P.
2. Sorption tests with KH_2PO_4 (pH 5.3) solutions at two different concentrations.
3. Sorption tests with KH_2PO_4/aCl_2 (pH 6.5) solutions for stepwise increasing and following decreasing concentrations (0.1-1.0 mg/l P, 10-100mg/l Ca).
4. Sorption tests with $KH_2PO_4/FeCl_3$ (pH 3.5) solutions at two different P and Fe concentrations.

In section 3 and 4 the pH was adjusted by addition of NaOH and HCl respectively. All investigations were conducted with three suction cups. After each individual test the cups were allowed to drip out and no further cleaning was done. Thereby a pore volume of 22±3 ml (determined by weight measurements) remains in the sampler and could affect following solutions. However, after each complete test procedure (point 2-4, see above) the cups were repeatedly washed by drawing 250ml distilled water through the cup and succeedingly dried. The use of acids for cleaning was omitted, because acid wash could possibly enhance P sorption (Bottcher et. al. 1984).

To study phosphorus leaching these nylon suction cups have been installed at a field test site for more than two years. The test site comprises an area of about $100m^2$ and is located ca. 20km to the east of Berlin. From four depth (30, 60, 120, 180cm) and in 3-5 repetitions soil solution was extracted. The applied suction (10 to 40kPa), generated by vacuum supplying system, depends on depth. For monitoring the near surface groundwater composition a groundwater well (2”) without gravel packing has been installed. Samples were taken from the uppermost groundwater horizon (200-250cm depth) by using a packer system. Before sampling the well was purged until no more changes (less than 3% in 5 minutes) of the electrical conductivity occur. The pumping rate was about 0.5 l/mm.

Phosphorus was determined photometrically (D11 EN 1189). The analytical uncertainty is about 2% and at least 0.005mg/l.

RESULTS AND DISCUSSION

At first the suction cups were rinsed with distilled water to test for phosphorus release. Commonly soil water sampler made of plastics are chemically pretreated for improving their hydrophilic behaviour. Thus, possibly chemicals containing

Table 1. Results of sorption tests with P solution for three suction cups at pH=5.3. (ext.: external solution)

Test	P [mg/l] ext.	P [mg/l] in the suction cup			
		cup 1	cup 2	cup 3	mean
1	1.02	0.98	0.97	0.95	0.97±0.02
2	1.02	0.96	0.99	0.97	0.97±0.02
3	1.02	1.01	1.01	0.99	1.00±0.01
4	0.100	0.165	0.170	0.180	0.170±0.015
5	0.100	0.105	0.105	0.100	0.105±0.010
6	0.100	0.095	0.100	0.100	0.100±0.010

phosphorus could get in contact with the membrane and be released during operation. However, after the treatment with distilled water in the percolate no phosphorus was detected (<0.003mg/l P). Advantageous to other types of samplers here no initial P release out of the membrane occurs.

The results of sorption tests with high and low external P concentrations are shown in Table 1. For the high P level (test 1-3) the concentration in the percolated solution is slightly smaller than in the external solution. However, the deviations are less than 5%. Including the variance between the suction cups and analytical uncertainty no significant sorption can be stated. As the external P level decreases initially (test 4) much higher concentrations in the suction cups were obtained. Especially for this test the influence of the residual solution has to be considered. Assuming no sorption or desorption the expected concentration in the suction cup can be calculated as following (c stands for concentration and V for fluid volume):

$$c = \frac{c_{\mathrm{new}} V_{new} + c_{old} V_{old}}{V_{tot}}$$

with: (1)

$$V_{tot} = V_{new} + V_{old} = 250ml \qquad \text{and:} \qquad V_{old} = 22 \pm 3ml$$

The indices „new“ and „old“ refer to the actually drawn solution and to the residual solution of the previous test. It can be seen that for strong concentration differences in consecutive test solutions the influence of the residual pore volume is important. Applying equation (1) to test 4 (Table 1) the expected concentration is 0.180±0.010mg/l. The observed mean concentration is in the range and even slightly smaller than the expected value and therefore the residual solution may account for higher concentrations in test 4. Assuming desorption of P deviations between external solution and solution in the suction cups should also be observed in subsequent tests 5 and 6. Hence from the tests in Table 1 no sorption or desorption of phosphorus can be stated.

In natural soil and groundwater systems calcium is one of the most abundant elements and an important reactant for phosphorus. It should be tested if sorption

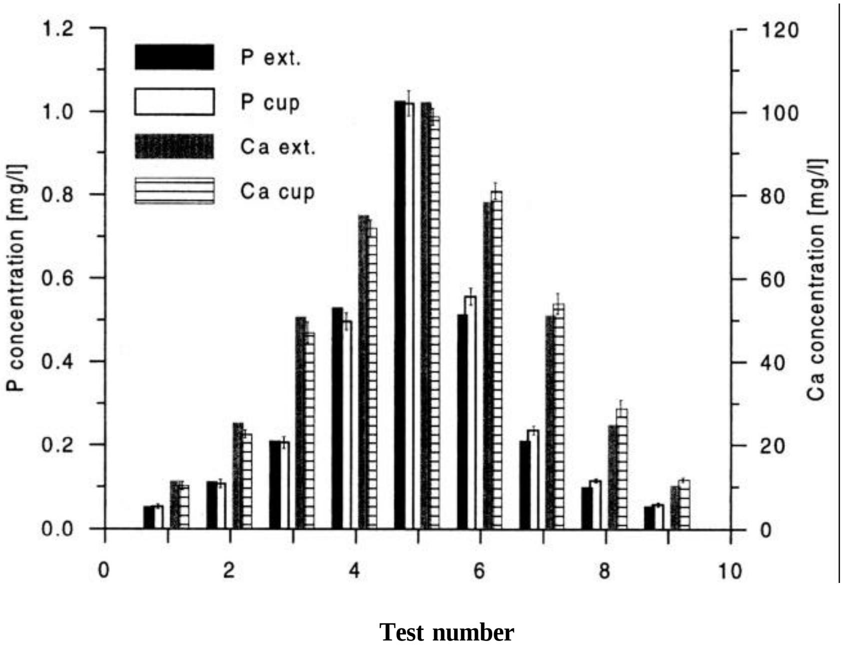

Figure 1. Concentration in the external solution (ext.) and in the sampler (cup) for tests with stepwise changing phosphorus and calcium concentration. The error bars show the data range for the three suction cups used.

occurs from solutions containing Ca. Several authors (Hansen and Harris 1975, Wenzel and Wieshammer 1995) have reported the precipitation of phosphates at the cup material. Caused by its microstructure nucleation should occur preferentially at the membrane whereas no precipitation in the bulk solution arises. The used test solutions are partly oversaturated with respect to several Ca phosphates, especially hydroxylapatite. For the solution with the highest concentration (Ca=100mg/l, $P[H_2PO_4 + HPO_4^{2-}]$=1mg/l, pH=6.5) this can be shown using the following reactions (Lindsay 1979):

$$Ca_5(PO_4)_3OH + 7H^+ \leftrightarrow 5Ca^{2+} + 3H_2PO_4^- + H_2O \qquad \lg k = 14.46$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \qquad \lg k = -7.20$$

The saturation is:

SI = 4.3 *with:* SI = lg(ion activity product / solubility product),

Hence, the solution is significantly oversaturated with respect to hydroxylapatite and precipitation can not be excluded. The test results are shown in Figure 1. For increasing external concentrations in the sampler slightly smaller mean values were found, whereas decreasing levels lead to slightly higher concentrations. For Ca as well as P the deviations are less than 12% and are more important for decreasing external concentrations. However, as it is shown in Table 2 for phosphorus the differences can be well explained with alterations due to the resi-

Table 2. P concentration in the external solution (ext.), in the suction cups (cup) and expected P concentration (exp.) corrected for the residual solution (concentrations in mg/l).

	Test								
	1	2	3	4	5	6	7	8	9
ext.	0.055	0.115	0.210	0.53	1.03	0.51	0.210	0.100	0.055
cup	0.055 *±0.005*	0.105 *±0.010*	0.205 *±0.015*	0.50 *±0.02*	1.02 *±0.03*	0.56 *±0.02*	0.240 *±0.010*	0.115 *±0.005*	0.060 *±0.005*
exp.	0.050	0.100	0.200	0.50	0.98	0.55	0.240	0.110	0.060

dual solution. Correcting for residual solution observed differences are in the range of uncertainty of the analytical determination method. Further, assuming sorption of phosphorus and calcium the similar behaviour of both elements would not be expected. Thus, the results suggest no sorption of Ca and P.

Under field conditions the extraction of soil water using suction cups is a slow process. To prove if the sampling time affects preceding findings, the same experiment series as depicted in Fig. 1 was carried out, but now the solution remained in the sampler and hence in contact with the filter material for about 20h. As before, even for longer times no sorption of Ca or P could be detected (results not shown).

From phosphate it is known that it is strongly sorbed by Fe(III) hydroxides (e.g. Goldberg and Sposito 1985). In soils under oxic conditions the total concentration of dissolved Fe(III) species is in the range of 10^{-3} - 10^{-4} mg/l at pH = 5 (Lindsay 1979) and often below the detection limit. Low redox however, leads to increased iron content in solution.

Soil solution under anoxic conditions that is passed through a suction cup will be oxidized. Caused by this redox change the formation of Fe(III) Colloids may occur possibly accompanied by sorption of P.

Experiments with solutions containing dissolved Fe(III) and P were conducted. At first the solution was oversaturated with respect to several Fe(III) hydroxides. This way the formation of Fe(III) Colloids, as it may occur at changing redox, can be achieved. In the second step P and Fe concentrations were reduced to test for desorption. The results are shown in Table 3. Caused by the oversaturation during the first test the concentration of dissolved Fe in the external solution decreases from 0.65 to 0.44mg/l. In test 1 and 2 in the percolate much lower Fe than in the

Table 3. Results of sorption tests with solutions containing P and Fe. (ext.: external solution; cup: solution in the suction cups.)

Test	P[mg/l] ext.	P[mg/l] cup 1	cup 2	cup 3	Fe[mg/l] ext.	Fe[mg/l] cup 1	cup 2	cup 3
1	0.99	0.73	0.72	0.75	0.65-0.44	0.27	0.29	0.31
2	0.98	0.84	0.85	0.81	0.43	0.29	0.29	0.33
3	0.100	0.135	0.135	0.130	0.06	0.12	0.13	0.13
4	0.095	0.090	0.100	0.100	0.05	0.05	0.04	0.06

external solution was found. Thereby retention of Fe at the nylon membrane is indicated. Also the P concentration decreases by 15-25%. In subsequent desorption tests close agreement between concentrations in the percolate and in the external solution is obtained with the exception of an initially slight Fe and P release.

The results show that preferentially on the membrane iron ions precipitate as colloidal Fe(III) hydroxide followed by the sorption of phosphorus. This assumption is additionally supported by the brown color of the cup surface after the tests. Some studies (Grossmann and Udluft 1991, Wenzel and Wieshammer 1995) show that according to the pore size colloids and macromolecules such as Fe(III) hydroxide are filtered by cup materials. This effect, known as “filter effect“ (Grossmann and Udluft 1991) occurs independently on the type of suction cup. Thus, the data in Table 3 suggest that the sorption of phosphorus results from previous precipitation and mechanical retention of Fe. The use of these soil water sampler for determining P in anoxic soils is therefore not advantageous. But this is a general problem of suction cups and does not limit the applicability of the new sampler in particular.

At the field test site solution from the uppermost horizon of the near surface groundwater (200-250cm depth) and from the bottom soil horizon (capillary fringe in 180cm depth) have been sampled. Soil water in the capillary fringe has been extracted by three new water sampler at lateral distances of 2, 4, and 6m from the groundwater well. Compared to temporal changes the composition of capillary fringe water does not significantly change with lateral distance from the borehole. From Table 4 the similar composition of ground- and capillary fringe water can be seen. Through comparison of P concentrations in groundwater and in the capillary fringe the feasibility of the soil water samplers may be tested. The P concentration in the capillary fringe is higher than in the groundwater (Figure 2). In wintertime almost no differences arise, whereas in summertime the solution concentration in the capillary fringe increases significantly. Lower groundwater levels in summer and dilution processes during groundwater recharge in winter can explain this time course. Supposing adsorption of phosphorus the similar concentrations would not be expected for such low concentrations. Further, the high temporal dynamicscontradicts phosphorus sorption at the suction cups.

The chemical properties of the new soil water sampler are advantageous. However, this does not apply to the hydraulic characteristics. Probably due to the relative large pore width of the outer PE cover, the application of the water sampler is limited to pressure heads <100mbar. To overcome this problem the manufacturer has offered an improved suction cup, where the outer PE cover was replaced by a PE grid. In this version the nylon membrane is in direct hydraulic

Table 4. Selected chemical parameters of capillary fringe water and of the near surface groundwater (concentrations in mg/l).

	NO_3-N	DOC	Ca	Fe	pH
capillary fringe	41±25	25±14	48±22	<0.03	5.5±1.0
groundwater	27±10	8.3±4.4	45±13	<0.03	4.9±0.8

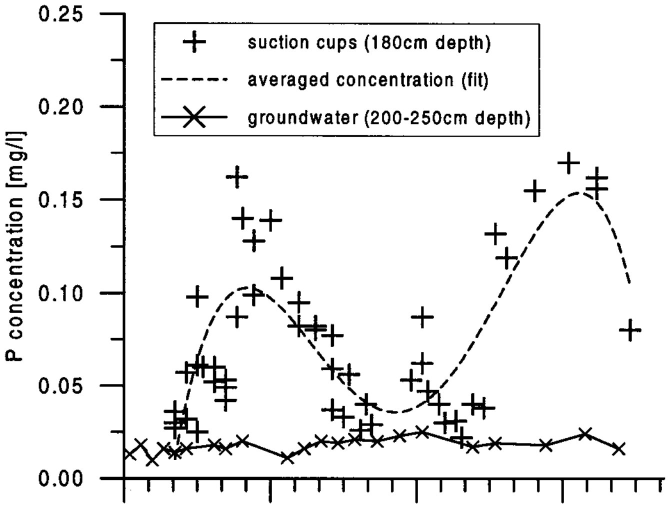

Figure 2. Observed P concentrations versus time in the near surface groundwater and in the capillary fringe at the field test site.

contact with the surrounding soil. Therefore better hydraulic properties can be expected, whereas the chemical properties should be still unchanged.

Acknowledgments. We are grateful to Dr. Seyfarth from UGT Müncheberg, Germany and his collegues for initiating the development of the new nylon suction cup and for their cooperation. This study was in part financed by the "Deutsche Bundesstiftung Umwelt", supporting the project "Experimental investigations and model calculations on phosphorus leaching from soil and groundwater in an agriculturally used catchment area of the river Spree".

REFERENCES

Andersen BR, (1994) Dissolved inorganic and organic phosphorus in soil water from an acid forest soil collected by ceramic and PTFE soil water samplers. Bull Environ Contam Toxicol 53:361-367

Bottcher AB, Miller LW, Campell KL (1984) Phosphorus adsorption in various soil-water extraction cup materials: effect of acid wash. Soil Sci 13:239-244

D11 EN1189 (1996) Bestimmung von Phosphor. Photometrisches Verfahren mittels Ammoniummolybdat.

DVWK (1990) Gewinnung von Bodenwasserproben mit Hilfe der Saugkerzen-Methode. Merkblatt Nr. 217

Goldberg S, Sposito G (1985) On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: A review. Commun Soil Sci Plant Anal 16:801-821

Grossmann J, Bredemeier M, Udluft P (1990) Sorption of trace metals by suction cups of aluminium oxide, ceramic and plastics. Z Pflanzenemähr Bodenk 153:359-364

Grossmann, J, Udluft P (1991) The extraction of soil water by the suction-cup method: A review. J Soil Sci 42:83-93

Hansen, EA, Harris AR (1975) Validity of soil-water samples collected with porous ceramic cups. Soil Sci Soc Am Proc 39:528-536

Hetsch W, Beese F, Ulrich B (1979) Die Beeinflussung der Bodenlösung durch Saugkerzen aus Ni-Sintermetall und Keramik. Z Pflanzenermähr Bodenkunde 142:29-38

Lademann H, Pöthig R (1994) Untersuchungen zur Phosphorbelastung, Phosphorverlagerung und Phosphorsorptionsfägkeit drainierter Agrarflächen als Beitrag zum Gewässerschutz. Vom Wasser 82:323-334

Lindsay WL (1979) Chemical equilibria in soils. Wiley Interscience, New York

Mansell RS, Bloom SA, Buroga B (1991) Phosphorous transport with water flow in acid, sandy soils. In: Bear J, Corapcioglu MJ (ed) Transport processes in porous media, 254-314, Washington

Nagpal, NK (1982) Comparison among and evaluation of ceramic porous cup soil water samplers for nutrient transport studies. Can J Soil Sci 62:685-694

Rasmussen L, Jorgensen P, Kruse S (1986) Soil water samplers in ion belance studies on acidic forest soils. Bull Environ Contam Toxicol 36:563-570

Tischner T, Nützmann G (1997) Untersuchungen zur Phosphorverlagerung im Boden und Grundwasser einer landwirtschaftlich genutzten Fläche. Mittlg Dtsch Bodenkundl Ges 85:373-376

Wenzel WW, Wieshammer G (1995) Suction cup materials and their potential to bias trace metal analyses of soil solutions: A review. Intern J Environ Anal Chem 59:277-290

Zimmermann CF, Price MT, Montgomery JR (1978) A comparison of ceramic and teflon in situ samplers for nutrient pore water detreminations. Estuar Coast Mar Sci 7:93-97