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Dissolved Inorganic and Organic Phosphorus in Soil Water from an Acid Forest Soil Collected by Ceramic and PTFE Soil Water Samplers

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Being a major nutritional element phosphorus transfer within or between ecosystems can be of great importance. Phosphorus leaching from the rooted soil zone will not be available to plants any longer. Dissolved phosphorus leaching from one compartment or the entire ecosystem will inevitably be input to a neighbouring compartment or ecosystem where it in turn may either be beneficial serving as a fertilizer or contribute to eutrophication. In order to quantify such fluxes it is clearly necessary to account for all dissolved phosphorus irrespective of the chemical nature of compounds containing it. It is well known that at many places with acid soils relatively large amounts of organic molecules are percolating through the upper soil horizons (*e.g.* Petersen 1976). The phosphorus associated with such organic molecules must be accounted for. In this paper data suggesting that the organically bound phosphorus fraction can be quantitatively important is presented together with an indication of different sampling efficiencies between two soil water sampler designs.

MATERIALS AND METHODS

Analyses of phosphate and total phosphorus, respectively, was performed on soil water samples collected during 13 months from a 67 yr old Norway spruce (*Picea abies* [L.] Karst) field site in the Klosterhede Plantation in the western most part of Denmark (56°33'N, 8°24'E). Annual precipitation in the area averages c. 900 mm with the largest amounts in late summer and autumn. The topography is completely flat and there is no surface runoff. The area drains into the underlying aquifer, which is found at 6-8 m depth.

The soil is a nutrient poor and well drained podzol (USDA Soil Taxonomy: Typic Haplorthod) developed on sandy outwash material deposited at the end of the last glaciation period. The profile consists of: an O horizon c. 10 cm deep; c. 10 cm A and E horizons (sand); a B horizon (sand), with distinct Bh-Bhs-Bs subhorizons, merging into the C horizon (gravelly

Table 1. Selected properties of the Klosterhede soil. Carbon determined from dry combustion, P by 2-hour extraction with 0.1 M H_2SO_4. Depth measured from mineral soil surface. (Partly adapted from Raulund-Rasmussen 1993).

Horizon	cm	pH (H_2O)	C gkg^{-1}	P $mgkg^{-1}$
O	-8-0	3.8	420	77
A	0-7	3.9	29	7
E	7-11	3.9	18	12
Bh	11-15	4.1	46	13
Bhs	15-35	4.4	17	20
Bs	35-54	4.4	5.1	33
BC	54-100	4.4	1.5	66
C	100-	4.4	1.4	57

sand); the boundaries are clear and the spatial variation is relatively small.

A few selected soil properties including the carbon and phosphorus contents are given in Table 1. Further data on the soil is given elsewhere (Beier *et al.* 1992, Raulund-Rasmussen 1993). Soil water samples were obtained using two different porous cup tension soil water samplers: (1) a ceramic type (P80,Staatliche Porzellan-Manufaktur,Berlin, Germany) and (2) a poly(tetrafluoroethene) (PTFE) type (PRENART standard,Prenart Equipment ApS,Frederiksberg,Denmark), installed in the E (15cm) and the BC (55cm) horizon, respectively. Mean pore size for the ceramic type was c. 10 μm and somewhat less for the PTFE type, both with a cylindrical design of c. 20 mm outer diameter and a length of c. 50 mm. The cups were acid washed prior to installation. All cups had been installed and operated several months before the period discussed here.

The sampling was continuous with a partial vacuum of c. 10 kPa (0.1 bar) below soil tension maintained throughout each period by a battery driven pump triggered by a tensiometer controlled regulator (Rasmussen *et al.* 1986). Glass bottles placed in thermoboxes buried in the ground to avoid heating during summer and freezing during winter served both as partial vacuum reservoirs and sample collectors. Each glass bottle yielded a combined sample as it was connected by polyethylene tubes to three individual sampler cups installed in parallel; the inlet of the tubes in the samplers was at the bottom of the cups. Thus, water drawn into the cups was continuously transferred to the glass bottles avoiding a prolonged contact time between the cup material and the sample. At the end of a sampling period three of these combined samples from ceramic cups and one from PTFE cups were obtained from each depth.

Samples were brought to the laboratory at 3-5 week intervals and stored in a refrigerator (+4°C) without prior addition of preserving agents. Significant changes in measured parameters during storage have not been detected, not even at prolonged periods.

Orthophosphate, P_i ($H_2PO_4^-$ ions in the present pH-range), was determined without pretreatment of samples on an autoanalyzer using the molybdate-blue method given by Aspila *et al.* (1976) modified to obtain a lower concentration of sulphuric acid and using larger volumes of cleansing water between samples. Total phosphorus (P_{total}) was determined using the same procedure following an in-line oxidative digestion with potassium peroxysulphate in warm (90-95 °C) sulphuric acid solution. The digestion was assumed to be complete. The measured orthophosphate was assumed to include all inorganic P and hence the difference — P_{total} minus P_i — was assumed to be a valid estimate of organically bound phosphorus. Inorganic polyphosphates would be included in this estimate

Table 2. Total (P_{total}) and inorganic phosphate (P_i) phosphorus concentrations in samples from two soil depths using two soil water sampler types. Ceramic type: mean ± s.d. (n = 1-3); PTFE type: one combined sample. Unit: [µg/l]. n.a. indicates too little water available for analysis.

	E horizon (-15cm)				BC horizon (-55cm)			
	P_{total}		P_i		P_{total}		P_i	
week	ceramic	PTFE	ceramic	PTFE	ceramic	PTFE	ceramic	PTFE
2	103±14	n.a.	52±4	n.a.	97±16		32±4	
6	frost period				frost period			
11	frost period				frost period			
18	129±11	151	n.a.	83	n.a.	129	n.a.	74
24	89±6	205	75±23	98	90±4	195	27±14	n.a.
27	236±122	n.a.	250±134	n.a.	95±2	140	40±6	n.a.
32	96±38	583	85±39	n.a.	86±36	257	40±10	158
36	104±19	227	38±30	93	79±7	157	13±4	56
39	86±17	n.a.	63±12	n.a.	80±9	196	69±5	91
44	75±5	407	39± -	n.a.	125±68	248	107±-	164
50	73±22	180	62±38	n.a.	71±20	139	34±19	52

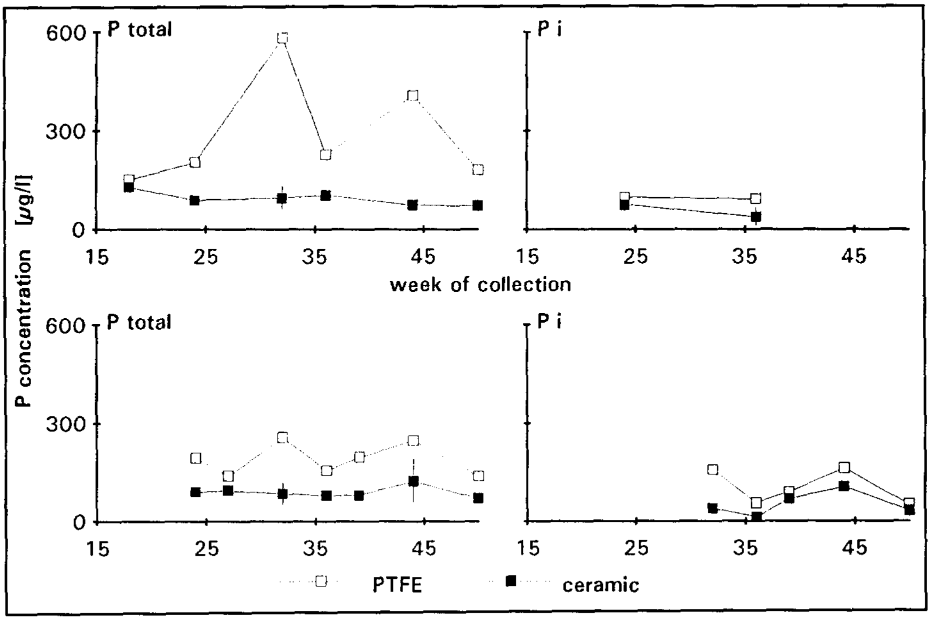

Figure 1. Soil water concentrations of P_{total} (left subplots) and P_i (right subplots) from the two soil depths plotted vs. time of collection. Only data from Table 2 with concurrent observations from the two sampler types are included. Error bars show ± one s.d. for the ceramic type.

of organic phosphorus content, but are generally believed to occur in negligible amounts (*e.g.* Lindsay 1979).

RESULTS AND DISCUSSION

During winter months (January to March) no soil water could be collected due to frost. During summer only small amounts of water could be collected but there were no periods with soil moisture levels too low to allow sampling. However, too little water was available for phosphorus analysis from a number of collection periods. The soil water content of P_{total} and P_i found in samples from the two soil depths and two sampler types is given in Table 2.

Ceramic cup samples from both soil depths showed no seasonal variation pattern for neither P_{total} nor P_i (Table 2). No significant differences between the ceramic cup P_{total} content in samples from the two soil horizons were observed. The P_i content was significantly lower in BC-horizon samples during most of the time indicating either an immobilization of P_i in the upper part of the B-horizon or a poorer sampling efficiency.

In the E-horizon, ceramic cup samples had rather similar P_{total} and P_i contents in four periods indicating a non-significant fraction of organically bound phosphorus, while the opposite was true in three periods; P_{total} and

P_i contents were significantly different in the BC-horizon samples during most periods. The spatial variability as indicated in the standard deviation figures may obscure smaller differences.

Samples from the PTFE cups exhibited apparently large differences between P_{total} and P_i content in the E-horizon as well as between P_{total} content in the two horizons. In every sampling period with concurrent observations both P_{total} and P_i content was consistently higher in PTFE cup samples as shown in Figure 1. However, the lack of replicate samples from PTFE cups prevents assessment of the significance of these differences but the trend seems to be quite clear; further, if a standard deviation proportional to that found for ceramic cup samples is assumed the difference would be significant in most periods.

The apparent difference between the P_i content in concurrent samples from the two cup types in both horizons is in accordance with earlier indications of adsorption of phosphate ions onto ceramic cups (Bottcher *et al.* 1984, Grossmann 1988, Hansen and Harris 1975, Hetch *et al.* 1979, Morrison 1982, Talsma 1979). The design of the sampling system used in this study minimizing the contact time between the ceramic material and the sample may in part have prevented adsorption.

The lower P_{total} content in the BC-horizon samples compared to the E-horizon samples is readily explained by immobilization of dissolved organic molecules in the top of the B-horizon. The apparent difference between the P_{total} content in concurrent samples from the two cup types in both horizons may warrant greater attention. Guggenberger and Zech (1992) found the ceramic P80 cups to be unusable in the upper horizons of acid forest soils because of sorption of dissolved organic carbon, while they found no influence in B- and C-horizons. The results from the E-horizon in the present study showing the ceramic cups to be unable to allow the passage of a large fraction of the organically bound phosphorus support their finding. In this study the ceramic cups apparently also sampled less organically bound phosphorus in the BC-horizon. The organic carbon content was not measured in the samples reported on here, but measurements on samples collected more recently confirmed a higher content in samples from PTFE cups compared to ceramic cups, notably in the E-horizon but also in the BC-horizon (Beier *et al.* 1992).

A hydrological model (Villholdt 1988) showed the sampling periods ending in the weeks 2, 18, 44, and 50 to be the only periods with water percolating from the BC-horizon. The latter two periods had concurrent observations of the BC-horizon soil water P_{total} content from both sampler types allowing a calculation of the P_{total} efflux from the rooted parts of the soil. The calculated fluxes are given in Table 3. The efflux from the BC-horizon in these periods seems to be roughly twice as large using the P_{total} content in soil water samples from the PTFE type. However, this comparison can only be based on the mean flux values due to the lack

Table 3. Estimates of P_{total} effluxes from the BC-horizon in the two later sampling periods in dependence of sampler type. Water flux data from Villholdt (1988).

sampling period (week no.)	water efflux (mm)	P_{total} efflux (mg/m^2)	
		ceramic	PTFE
39-44	64	8.0	15.9
44-50	70	4.9	9.7

of replicate samples from the PTFE type, which prevents an estimation of the error associated with the calculated fluxes (thus, there is no need to discuss the errors associated with the hydrological model in this paper). If it is assumed that the apparently persistent (Figure 1) difference between the BC-horizon soil water P_{total} content from the two sampler types is significant, the site under study might actually have had a net loss of phosphorus. Thus, a calculation of the annual input-output budget based on the ceramic type samplers (not to be detailed here) showed only a slight net phosphorus accumulation (c. 20 mg P per m^2 and year). A net phosphorus loss would contradict the generally accepted fact that most forested ecosystems are not loosing phosphorus (*e.g.* Likens *et al.* 1977).

To obtain a complete quantification of the phosphorus content in soil water samples from acid forest soils the analysis of organically bound phosphorus cannot be omitted. Further, it is evident that the two porous cup sampler types performed differently and that the ceramic type apparently is less suited to sample soil water if phosphorus analysis is planned. I hope this paper may encourage researchers to acknowledge that the organically bound fraction of elements in solution can be significant and that the choice of soil water sampling equipment may greatly influence the composition of soil water samples obtained. This in turn has implications for the assessment of losses from or loads onto ecosystems and/or receptors (underlying aquifers, surface waters *etc.*) linked through hydrologic pathways.

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