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# Inorganic and organic P in soil solutions from three upland soils

## *I. Effect of soil solution extraction conditions, soil type and season*

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## Abstract

Soil solutions from three P-deficient Cambisols were analyzed for inorganic orthophosphate ($P_i$), organically combined phosphorus ($P_o$), total phosphorus ($P_t$) and residual phosphorus ($P_r = P_t - (P_o + P_i)$). The solutions were obtained by centrifugation of soil samples wetted-up to 90% field capacity. Increasing the centrifugal force from 750 to 1400 × g (for 60 minutes) increased the volume of soil solution obtained by 17–35%. Increasing the centrifugation period from 30 to 90 minutes (at 1000 × *g*) increased the volume by 2–12%. The effect of the different centrifugation conditions on the P composition of soil solutions were not critical and had little effect on either $P_t$ concentration or on the distribution of P between $P_i$, $P_o$ and $P_r$ fractions. Soil solutions were also obtained on a seasonal basis over a 2-year period. The soils, fresh from the field, were wetted-up to 90% field capacity and centrifuged at 1000 × *g* for 60 minutes to isolate the soil solution. Although the soils were derived from contrasting parent rock, and had different Fe and Al sesquioxide contents, the $P_t$ concentrations of the soil solutions and the distribution between the fractions were similar. Annual average $P_t$ concentrations for the 3 soils ranged from 93 to 114 and 63 to 89 $\mu g\, dm^{-3}$ during the first and second year, respectively. Seasonal changes were of a similar order as those resulting from differences in soil type. During May, June, August and October soil solutions had average $P_t$ concentrations ranging from 82 to 111 and 51 to 119 $\mu g\ P\, dm^{-3}$ in 1989 and 1990, respectively. $P_o$ was a major P component in soil solution and exceeded the amount of $P_i$ by about 5–20 times.

## Introduction

The analysis of various organic and inorganic forms of particulate and dissolved phosphorus (Broberg and Persson, 1988; Broberg and Pettersson, 1988) and their significance as sources of bioavailable P (Boström et al., 1988; Jansson, 1988) are well documented for lakes and sediments. In soil, despite the large amount of work on the characterization of P, relatively little attention has focused on P in soil solution although the importance of the soil solution in nutrient supply and transport is recognised. This lack of attention has resulted from difficulties in sampling soil solution, limitations in the volumes of solution which can be obtained, and the relative difficulties in analysis of solutions containing low concentrations of P (generally $<0.3\ mg\, dm^{-3}$).

In some soil solutions, organically bound phosphorus ($P_0$) can be the dominant fraction (Dalal, 1977; Harrison, 1987) but little is known about the role of this component in the P nutrition of plants. In P-deficient upland soils such forms of

P may be an important source of P for plants, or a major form in loss of P into the aquatic environment. The composition of soil solution is controlled by several interactive processes. Clay minerals and sesquioxides can sequester P and have a large influence on soil solution composition (Stumm and Morgan, 1970). Biological processes resulting in mineralization or immobilization of P, combined with seasonal changes in the solubility of organic matter, also have influence (Magid and Nielsen, 1992).

Several methods of obtaining soil solution are known (see reviews by Richards, 1941; Litaor, 1988). The merits and application of some of these to different situations have been discussed (Campbell et al., 1989). Centrifugation of soil (Adams et al., 1980; Elkhatib et al., 1987; Gillman, 1976; Reynolds, 1984) is a simple method of obtaining soil solutions but no detailed information on the effect of conditions on the P composition of soil solution exists.

In our study soil solutions were obtained by centrifugation of field moist soils wetted-up to 90% field capacity and we provide information about the composition of soil solutions from three different soil types under upland conditions. Amounts of inorganic orthophosphate ($P_i$), $P_0$, total phosphorus ($P_t$) and residual phosphorus ($P_r = P_t - (P_o + P_i)$) were measured. The sensitivity of these measurements to different centrifugal forces has been determined and the composition of the soil solutions compared with the clay mineral and sesquioxide contents of the soils. By field sampling over a 2-year period seasonal variations in the P composition of soil solutions have also been measured.

More detailed discussion on the role of $P_o$ in plant nutrition, and the effect of defoliation and fertilizer treatments on soil solution composition, are reported in Part 2 (Shand et al., 1994).

## Materials and methods

### *Sites and treatments*

Two Dystric and a Eutric Cambisol (brown forest soils) from proximate locations in the NE of Scotland were studied (Table 1). The soils were classified under the Soil Survey of Scotland (1969) as belonging to the Foudland, Insch and Tarves Associations. They were from upland areas 400 m above sea level. All had been used for grazing and had an established grass/clover sward. The soils had pH values in 0.1 *M* $CaCl_2$ of about 5, moderate organic matter contents

*Table 1.* Soil characteristics and locations

| Association[a] | Parent material | National Grid Ref | pH ($CaCl_2$) | Particle size[b] (%) | | | Oxalate extractable (%) | | LOI[c] (%) | Bulk density (g cm$^{-3}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Sand | Silt | Clay | Fe | Al | | |
| Foudland | Fine-grained schists and derived drifts | NJ341195 | 4.8 | 61 | 29 | 10 | 1.01 | 0.51 | 11.4 | 0.90 |
| Insch | Basic rocks and derived drifts | NJ346195 | 5.3 | 71 | 21 | 8 | 2.08 | 0.99 | 13.4 | 0.92 |
| Tarves | Intermediate and basic gneiss and derived drifts, mixed drifts from acid and basic rocks | NJ348184 | 5.2 | 67 | 25 | 8 | 1.02 | 0.64 | 11.4 | 0.97 |

[a] Soil Survey of Scotland (1969).

[b] Sand 2000–20, silt 20–2 and clay <2 μm.

[c] Loss on ignition.

(11–13%) and similar texture. Under the criterion applied for advisory purposes (MISR/SAC, 1985) these soils had very low ($< 10$ mg P kg$^{-1}$) or low (10–25 mg P kg$^{-1}$) acetic acid extractable P (Table 2).

At each site, twenty eight 1 m × 1 m plots were arranged in a 7 × 4 block within a 10 m × 10 m fenced enclosure erected during 1988. Treatments were allocated using a completely randomised design to 20 of the plots within the enclosure. In 1989 the treatments, replicated 4 times, were: (a) cutting to 2 cm every 2–4 weeks between May and October; (b) no cutting until October and (c) bare soil. Bare soil plots were obtained by herbicide application (Monsanto 'Roundup', 2 cm$^3$ m$^{-2}$) in autumn 1988 and were maintained by careful hand weeding. Eight plots were maintained for use in 1990 by cutting to about 10 cm every 2–4 weeks. In 1990, the treatments, replicated 4 times, were: (a) NPK fertilizer (25:5:5) and (b) NPK fertilizer (20:10:10). Both treatments were applied by hand at 25 g m$^{-2}$ during mid-April and were to the plots maintained in the previous year by cutting to about 10 cm. Herbage was cut to a height of 2 cm every 2–4 weeks, as in 1989, and removed. The bare soil plots, established in 1988, were used during 1989 and 1990.

Rainfall at each site was measured with a funnel gauge fitted with a trip device (0.5 mm) and data logger.

### Soil and soil solutions

Bulk samples of the 3 soils were taken during March 1992 from areas within the enclosure but outside the 7 × 4 m$^2$ blocks. The soils were screened ($< 6$ mm) and stored in sealed plastic sacks in a cool place and these were used to assess the effects of centrifugation conditions on the volume and P composition of soil solution.

Soil samples from the 1 m × 1 m plots were taken in 1989 and 1990 during May, June, August and October immediately following herbage cutting. Four separate cores (5 cm diameter and 18 cm deep) were removed and combined from each 1 m × 1 m plot. These samples were stored overnight at 4 °C, screened ($< 6$ mm) and immediately processed to obtain soil as follows.

Soil moisture contents were determined by drying sub-samples at 105 °C for 16 hours. Sufficient high purity water was added to 300 g samples of the soils to raise the moisture content to 90% of field capacity (about 32% w/w in all cases). The water was added to duplicate subsamples of soil in polythene bags which were then sealed and the contents mixed. After 48 hours at 4 °C, the bags of soil were equilibrated to room temperature (20 °C) overnight, and unless otherwise stated centrifuged for 1 hour at 1000 × $g$ to extract soil solution. The centrifuge cells held 300 g of soil and were fitted with polypropylene filter supports, Whatman No 42 papers and polythene liners (Linehan et al., 1985). Duplicate samples of soil solution (from a total of 600 g soil) were combined and centrifuged for 1 hour at 25000 × $g$ to remove traces of suspended material. The supernatant was decanted off for analysis. The samples were analyzed without filtration. A comparison between filtered (0.45 $\mu$m), and unfiltered soil solutions obtained in this way, showed there to be no significant differences between the soluble P fractions.

*Table 2.* Acetic acid extractable P content of air dried soils (mg kg$^{-1}$) during 1989

| Soil | May<br>n = 12 | June<br>n = 12 | Aug<br>n = 12 | Oct<br>n = 12 | Mean[a] | Sem[b] |
|---|---|---|---|---|---|---|
| Foudland | 5.47 | 5.41 | 11.4 | 11.8 | 8.54 c | 1.33 (c) |
| Insch | 21.6 | 19.3 | 26.8 | 29.3 | 24.2 a | 0.87 (r) |
| Tarves | 13.6 | 16.5 | 24.4 | 23.8 | 19.6 b | |
| Mean[a] | 13.6 b | 13.7 b | 20.9 a | 21.6 a | 17.4 | |

[a] Means within the same row or column followed by a common letter are not significantly different ($p < 0.05$).
[b] Standard error of mean for comparison of seasonal values in the body of the table (c, r within column or row, respectively).
n = Number of replicates.

Soil samples for the determination of pH and acetic acid extractable P were air-dried and ground to pass a 2-mm screen.

### *P analysis*

Orthophosphate ($P_i$): The inorganic orthophosphate content of the soil solutions was measured colorimetrically by the phosphomolybdenum blue method (Murphy and Riley, 1962). The concentration of the ascorbic acid reducing solution was increased from 10 m*M* to 0.5 *M* because in the determination of organically bound P (see later), hydrogen peroxide residues consume the reducing agent (Ron Vaz et al., 1992). This concentration of reducing agent was used throughout the work. Optical densities (4 cm path) was measured at 882 nm after 30 minutes using a Cecil 393 spectrophotometer (Cecil Instruments Ltd., Cambridge, UK).

Organically bound P($P_o$): Soil solution (6 $cm^3$) was treated with 30% w/v hydrogen peroxide (30 $\mu$L) and pumped at 2 $cm^3 \, min^{-1}$ through a silica coil (50 turns) under ultra-violet illumination (15 watts). The residence time in the reactor was 12 minutes. The coil was flushed with water between samples. Orthophosphate in the eluent was determined by the procedure outlined earlier. $P_o$ was calculated by difference; $P_o = P_i$ (treated) $- P_i$ (untreated) (Henriksen, 1970).

Total P ($P_t$): Soil solution (5 $cm^3$) was acidified with 5.6 *M* $H_2SO_4$ (0.1 $cm^3$) and treated with $K_2S_2O_8$ (50 mg) to convert all P to orthophosphate. The solution was boiled for 30 minutes to reduce the volume by half. The cooled solution was neutralized with 1 *M* sodium hydroxide using 0.1% phenolphthalein as indicator (10 $\mu$L) and the volume adjusted to 5 $cm^3$ in a volumetric flask. Orthophosphate was determined by the procedure outlined earlier using appropriate phosphate standards (Greenberg et al., 1980).

Extractable phosphorus: Air dried soil (2.5 g) was shaken with 0.43 *M* acetic acid (100 $cm^3$) for 2 hours (MISR/SAC, 1985). The extracts were filtered (Whatman No 1) and the P content determined by ICP (inductively coupled plasma) optical emission spectrometry. Analysis was performed by ICP optical emission spectrometry as the facility was routinely available for samples in a matrix of 0.43 *M* acetic acid.

### *Clay analysis*

Particle size distribution in the soils was determined hydrometrically following dispersion in 2.3 m*M* sodium hexametaphosphate containing 3.0 m*M* sodium carbonate (Day, 1965). Clay fractions ($<2$ $\mu$m) for X-ray diffraction (XRD) and infra-red (IR) study were obtained from the soil by sedimentation following sonication and shaking in water at pH 8.5 (adjusted using ammonium hydroxide). XRD was performed with Co K$\alpha$ radiation. IR spectra were obtained using KBr discs.

### *Oxalate extractable Fe and Al content of soil*

Air dried soil was shaken with acid ammonium oxalate (McKeague and Day, 1966). The extracts were filtered (Whatman No 1) and the Fe and Al contents determined by ICP optical emission spectrometry.

### *Statistical analysis*

Analysis of variance (ANOVA) was performed using 'Genstat 5' (1990). Results from the experiments testing the effects of centrifugal force on the composition of soil solutions were analyzed using 2-way ANOVA (soil type × centrifugation treatment). Seasonal data derived for the soils and soil solutions were analyzed using 3-way ANOVA (soil type × season × treatment); data from 1989 and 1990 were analyzed separately. Where the main effect of any factor was significant, individual treatment means were compared by the Student-Newman-Keuls' test using 'CoStat' (1986). Unless otherwise stated levels of significance were for $p < 0.05$.

## Results

### *Influence of centrifugation parameters on volume and composition of soil solution*

The volume of soil solution extracted increased with the centrifugal force and the duration of centrifugation and there were significant differences in these effects between soils. Increasing the centrifugal force from 750 to 1400 × $g$, increased the volume of soil solution from each of the soils by between 17 and 35%. Increasing the duration of centrifugation from 30 to 90 minutes significantly increased the volume of soil solution from the Foudland and Tarves soils by 19 and 30%, respectively, but there was no significant increase for the Insch soil (Table 3). When soil bulk densities (Table 1) were considered the volumes of soil solution obtained at 1000 × $g$ for 60 minutes were 79.2, 71.2 and 73.7 $\mathrm{cm^3\,dm^{-3}}$ from the Foudland, Insch and Tarves soils, respectively, changing the pattern of significance.

The P composition of soil solutions were dependent on the centrifugation conditions and the effects were not consistent between the different soil types (Table 3). Over the five different centrifugation conditions, there were no significant differences in $P_t$ concentrations in soil solutions from both the Foudland and Tarves soils. $P_t$ concentrations in the Insch soil solution increased above the other treatments to a value of 93 $\mu$g P $\mathrm{dm^{-3}}$ following centrifugation using 1000 × $g$ and the longest period (90 minutes). Differences in $P_i$ concentrations were also apparent in some instances. For example, in solutions from the Tarves soil there were differences with factors of about 2. However, the concentrations of $P_i$ in soil solutions from all the soils were low ($< 10$ $\mu$g P $\mathrm{dm^{-3}}$). Similarly the $P_o$ and $P_r$ fractions changed little except for the Tarves soil centrifuged at 1000 × $g$ for 90 minutes when there was a marked decline in $P_o$ and an increase in $P_r$ concentration.

## *Rainfall and air temperature*

Rainfall measurements (Table 4) on site, showed 1989 to be drier than 1990, with the main differences occurring during the winter period from October to January. There was a particularly dry period during July 1989 when monthly rainfall was 28 mm. Air temperatures were not measured on site. Average daily air temperatures from the Meteorological Office (1990 and 1991), relating to Glenlivet (about 9 km to the north west), indicate an earlier spring, a cooler July and warmer August in 1990 compared to 1989.

*Table 3.* Volume and P composition of soil solution isolated under different centrifugation conditions from bulk soil sample collected during 1992

| Soil | Analyte | Centrifugal force ( × $g$)/Time (minutes) | | | | | Sem | |
|---|---|---|---|---|---|---|---|---|
| | | 750/60<br>n = 4 | 1000/60<br>n = 8 | 1400/60<br>n = 4 | 1000/30<br>n = 4 | 1000/90<br>n = 4 | n = 4 | n = 8 |
| Foudland | Volume ($\mathrm{cm^3\,kg^{-1}}$ soil) | 83.0 b | 88.0 b | 104 a | 82.3 b | 98.2 a | 1.94 | 1.37 |
| Insch | | 77.1 b | 77.4 b | 90.1 a | 73.9 b | 78.8 b | | |
| Tarves | | 66.9 d | 75.9 c | 90.5 a | 62.5 d | 81.0 b | | |
| Foudland | $P_i$($\mu$g $\mathrm{dm^{-3}}$) | 5.9 c | 6.9 bc | 5.8 c | 9.3 a | 8.1 ab | 0.53 | 0.37 |
| Insch | | 5.2 b | 7.1 ab | 6.4 b | 7.2 ab | 8.6 a | | |
| Tarves | | 6.1 b | 8.3 a | 5.5 b | 9.6 a | 9.8 a | | |
| Foudland | $P_o$($\mu$g $\mathrm{dm^{-3}}$) | 10.9 ab | 10.9 ab | 12.9 a | 9.2 ab | 11.6 ab | 0.80 | 0.56 |
| Insch | | 11.3 a | 13.3 a | 14.3 a | 12.2 a | 12.5 a | | |
| Tarves | | 10.4 b | 9.3 b | 13.0 a | 8.7 b | 4.0 c | | |
| Foudland | $P_r$($\mu$g $\mathrm{dm^{-3}}$) | 32.0 a | 39.9 a | 35.1 a | 37.9 a | 34.8 a | 4.31 | 3.05 |
| Insch | | 44.2 b | 55.4 b | 56.2 b | 47.7 b | 70.8 a | | |
| Tarves | | 38.2 b | 41.0 b | 33.0 b | 35.3 b | 54.1 a | | |
| Foudland | $P_t$($\mu$g $\mathrm{dm^{-3}}$) | 48.9 a | 57.7 a | 53.8 a | 56.4 a | 54.8 a | 4.46 | 3.16 |
| Insch | | 60.7 b | 75.9 b | 76.9 b | 67.0 b | 93.2 a | | |
| Tarves | | 54.7 a | 58.5 a | 51.4 a | 53.6 a | 67.8 a | | |

Sem = Standard error of mean.
n = Number of replicates.
Means within the same row followed by a common letter are not significantly different ($p < 0.05$).

*Table 4.* Rainfall (mm) in years 1989 and 1990

| Year | Month | | | | | | | Annual total[a] |
|---|---|---|---|---|---|---|---|---|
| | April | May | June | July | Aug | Sept | Oct | |
| 1989 | 51 | 78 | 67 | 28 | 55 | 47 | 73 | 660 |
| 1990 | 43 | 54 | 74 | 75 | 71 | 96 | 130[b] | 1014 |

[a] Data from nearby weather station at Glenlivet (The Meteorological Office, 1990 and 1991).

[b] Measured only until 21 October; monthly value given is from the nearby weather station at Glenlivet (The Meteorological Office, 1991).

Data quoted from the Meteorological Office monthly weather reports is by permission of the Controller, HMSO, Norwich.

### *Influence of soil type and season on P composition of soil solution*

There were significant differences in the P composition of soil solution due to soil type and season, and the effects were not consistent over the 3 different soils (Table 5).

#### *(1) Soil*

During 1989, $P_i$, $P_o$, $P_r$ and $P_t$ concentrations in soil solution from each soil averaged over the year ranged from 4–6, 54–76, 32–37 and 93–114 $\mu$g P dm$^{-3}$, respectively (Table 6). There were no significant differences between the annual means for Insch and Tarves soils. $P_o$ in soil solutions from the Foudland site was about 25% lower than those from the other sites.

During 1990, $P_i$, $P_o$, $P_r$ and $P_t$ ranged from 7–9, 33–48, 23–31 and 63–89 $\mu$g P dm$^{-3}$, respectively. Although $P_i$ and $P_o$ were not significantly different in soil solutions from the Insch and Tarves soils, there were differences in their $P_r$ and $P_t$ concentrations.

The soils, as taken from the field, had significantly different moisture contents (Table 7) and the Foudland soil was wetter with an average annual moisture content 2–3% higher than the others. After wetting-up, the soils yielded significantly different amounts of soil solution. Yields of soil solution, averaged over the year, ranged between 67 (Foudland, 1990) and 84 cm$^3$ kg$^{-1}$ (Insch, 1990) (Table 7).

#### *(2) Season*

In 1989 the maximum seasonal concentrations of $P_i$, $P_o$ and $P_t$ were in solutions from soil sampled in August (Table 6). $P_r$ concentrations varied in a different manner and the seasonal average was at a maximum in solutions from soil sampled early in the year during May. Season also had a highly significant effect on acetic acid extractable P which reached maximum levels in August and October, but the effect was not consistent between soils (Table 2).

In 1990 the maximum soil solution concen-

*Table 5.* Analysis of variance for soil solution and soil data

| | Analysis | Year | Soil | Season | Soil and season |
|---|---|---|---|---|---|
| Soil solution | $P_i$ | 1989 | ns | *** | *** |
| | | 1990 | ns | *** | ns |
| | $P_o$ | 1989 | *** | *** | *** |
| | | 1990 | ** | *** | *** |
| | $P_r$ | 1989 | ns | *** | *** |
| | | 1990 | * | *** | ** |
| | $P_t$ | 1989 | *** | *** | *** |
| | | 1990 | ** | *** | *** |
| Soil | Moisture | 1989 | *** | *** | *** |
| | | 1990 | *** | *** | ns |
| | Yield of soil solution | 1989 | *** | *** | *** |
| | | 1990 | *** | ns | * |

***, **, * Significant at $p = 0.001$, 0.01 and 0.05, respectively. ns = Not significant ($p > 0.05$).

Table 6. Effect of soil and season on P composition of soil solution ($\mu$g P dm$^{-3}$)

| Analyte | Soil[a] | Year 1989[b] May n = 12 | June n = 12 | Aug n = 12 | Oct n = 12 | Mean | Sem[c] | Year 1990[b] May n = 12 | June n = 12 | Aug n = 12 | Oct n = 12 | Mean | Sem[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_i$ | F | 2.7 | 2.0 | 12.1 | 5.6 | 5.6 a | 0.88 (c) | 5.5 | 7.2 | 7.5 | 8.9 | 7.3 a | 1.80 (c) |
| | I | 9.9 | 3.6 | 3.2 | 3.2 | 5.0 a | 0.86 (r) | 5.2 | 7.7 | 7.7 | 17.6 | 9.5 a | 1.79 (r) |
| | T | 3.9 | 2.6 | 7.2 | 3.8 | 4.4 a | | 6.7 | 6.9 | 8.7 | 9.8 | 8.0 a | |
| | Mean | 5.5 b | 2.7 a | 7.5 a | 4.2 b | 5.0 | | 5.8 b | 7.3 b | 7.9 b | 12.1 a | 8.3 | |
| $P_o$ | F | 39.0 | 30.7 | 91.9 | 55.1 | 54.2 b | 5.41 (c) | 25.8 | 23.8 | 30.9 | 49.8 | 32.6 b | 5.48 (c) |
| | I | 73.5 | 59.1 | 64.9 | 89.8 | 71.8 a | 5.20 (r) | 21.3 | 30.8 | 40.5 | 100 | 48.2 a | 5.27 (r) |
| | T | 54.1 | 39.7 | 132 | 79.0 | 76.2 a | | 49.2 | 40.0 | 45.8 | 48.9 | 46.0 a | |
| | Mean | 55.5 c | 43.2 d | 96.2 a | 74.6 b | 67.4 | | 32.1 b | 31.6 b | 39.1 b | 66.3 a | 42.3 | |
| $P_r$ | F | 41.0 | 33.3 | 36.5 | 25.5 | 34.1 a | 4.89 (c) | 11.7 | 21.7 | 26.9 | 30.6 | 22.7 b | 5.04 (c) |
| | I | 62.9 | 45.1 | 32.0 | 10.7 | 37.7 a | 4.64 (r) | 17.3 | 24.8 | 24.1 | 59.7 | 31.5 a | 5.06 (r) |
| | T | 42.1 | 29.0 | 25.5 | 32.4 | 32.2 a | | 10.0 | 16.0 | 35.9 | 32.3 | 23.5 b | |
| | Mean | 48.6 a | 35.8 b | 31.3 b | 22.9 c | 34.7 | | 13.0 c | 20.9 bc | 29.0 b | 40.8 a | 25.9 | |
| $P_t$ | F | 82.7 | 66.0 | 137 | 86.2 | 92.9 b | 7.38 (c) | 43.0 | 52.8 | 65.3 | 89.2 | 62.6 c | 9.30 (c) |
| | I | 150 | 108 | 100 | 104 | 114 a | 7.04 (r) | 43.9 | 63.3 | 72.2 | 177 | 89.2 a | 9.13 (r) |
| | T | 99.7 | 71.3 | 164 | 115 | 112 a | | 65.9 | 62.9 | 90.4 | 91.0 | 77.6 b | |
| | Mean | 111 b | 81.7 c | 134 a | 102 b | 107 | | 50.9 c | 59.7 c | 76.0 b | 119 a | 76.5 | |

[a] F = Foudland, I = Insch and T = Tarves Association soil; see Table 1.

[b] Means within the same row or column followed by a common letter are not significantly different ($p < 0.05$).

[c] Standard error of mean for comparison of seasonal values in the body of the table (c, r within column or row, respectively).

Table 7. Effect of soil type and season on soil moisture content and yield of soil solution

| Analyte | Soil[a] | Year 1989[b] May n = 12 | June n = 12 | Aug n = 12 | Oct n = 12 | Mean | Sem[c] | Year 1990[b] May n = 12 | June n = 12 | Aug n = 12 | Oct n = 12 | Mean | Sem[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Moisture (% w/w) | F | 32.5 | 25.1 | 22.2 | 29.4 | 27.3 a | 0.551 (c) | 31.9 | 33.6 | 29.8 | 33.2 | 32.1 a | 0.451 (c) |
| | I | 31.7 | 24.1 | 18.3 | 23.2 | 24.3 b | 0.498 (r) | 30.5 | 32.5 | 27.0 | 31.4 | 30.4 b | 0.435 (r) |
| | T | 31.7 | 24.1 | 19.2 | 22.4 | 24.3 b | | 29.0 | 30.9 | 26.3 | 29.8 | 29.0 c | |
| | Mean | 32.0 a | 24.4 b | 19.9 c | 25.0 b | 25.3 | | 30.5 c | 32.3 a | 27.7 d | 31.5 b | 30.5 | |
| Volume (cm$^3$ kg$^{-1}$) | F | 74.7 | 65.9 | 67.6 | 67.3 | 68.8 c | 2.74 (c) | 61.6 | 71.8 | 61.0 | 73.3 | 66.9 c | 2.69 (c) |
| | I | 68.4 | 84.4 | 94.1 | 84.5 | 82.9 a | 2.77 (r) | 85.7 | 85.6 | 86.1 | 80.4 | 84.4 a | 2.79 (r) |
| | T | 63.2 | 78.1 | 80.2 | 79.3 | 75.2 b | | 72.0 | 73.1 | 75.9 | 71.4 | 73.1 b | |
| | Mean | 68.8 b | 76.1 a | 80.7 a | 77.0 a | 75.7 | | 73.1 a | 76.8 a | 74.3 a | 75.0 a | 74.8 | |

[a] F = Foudland, I = Insch and T = Tarves Association soil; see Table 1.

[b] Means within the same row or column followed by a common letter are not significantly different ($p < 0.05$).

[c] Standard error of mean for comparison of seasonal values in the body of the table (c, r within column or row, respectively).

trations of $P_i$, $P_o$, $P_r$ and $P_t$ occurred later than in 1989 and maximum concentrations of these P species in soil solution were observed during October. Also in contrast with 1989, when the mean monthly $P_r$ concentration was maximum in May, the mean monthly $P_r$ concentration was minimum in May (Table 6).

### *Clay mineral and oxalate extractable Fe and Al content of the soils*

The soils contained similar amounts (8–10%) of clay material (Table 1) dominated by halloysite. The clay fractions also contained vermiculite, illite and quartz and IR analysis showed them to contain organic material with carboxylate and secondary amide functional groups characteristic of humic and fulvic substances.

The Insch soil contained about 2 and 1% by weight (air dry basis) oxalate extractable Fe and Al, respectively, double the amounts found in the Foudland and Tarves soils.

## Discussion

### *Centrifugation and wetting-up of soils*

To obtain soil solution by centrifugation the soil must be moist. Re-wetting air- and oven-dried soils is known to stimulate microbial activity, resulting in mineralization of organic N (Larsen and Widdowson, 1968). The effect on P is less clear and P concomitantly released does not follow the same path as N (Kuo and Jellum, 1987). Phosphorus may be taken up by micro-organisms and released later (Birch, 1964). Air drying soils may increase the amount of water soluble P (Ende, 1989).

Increasing the moisture contents of field moist soils (wetting-up), and extracting soil solutions within a few days of collection can be expected to have a minimal perturbing effect on soil solution chemistry (Qian and Wolt, 1990) and was the approach adopted here. Jones and Edwards (1993) have reported that statistically significant changes occurred in soil solution composition during wetting-up of a soil developed on granitic parent material. Edmeades et al., (1985) observed that the concentrations of Na, K, Ca and Mg in soil solutions from re-wetted soils increased with soil moisture content. Wetting-up to fixed capacity will minimise variations due to these effects. The average moisture content of the samples in the current study was 25.3 and 30.5% w/w during 1989 and 1990, respectively. The driest soil samples were obtained during August when average moisture levels were 19.9 and 27.7% w/w during 1989 and 1990, respectively (Table 7).

The data obtained in the investigation of the effects of centrifugal force showed that the conditions of centrifugation were not critical with respect to the P composition of the soil solutions. Importantly for this type of study there appears to be very little release of P from intact plant or microbial cells (Zabowski, 1989).

### *Composition of soil solutions*

#### *Analytical methodology*

The analytical methods used in this study allow distinction between different chemical forms of P to be made. The phosphomolybdenum blue method measures inorganic orthophosphate ($P_i$). Under the conditions of analysis, where the pH falls below 1, hydrolysis of esters such as inositol hexaphosphate does not occur but phosphate weakly bound to soluble organic matter may be released resulting in over estimation of free orthophosphate (Gerke and Jungk, 1991). Acidic reagents may also release $P_i$ from colloids (De Haan and De Boer, 1986; De Haan et al., 1990) not removed during centrifugation or 0.45 $\mu$m filtration. Organically bound phosphate ($P_o$) was measured by difference after photochemical oxidation. In this assay polyphosphate sub-units released from molecules such as ATP are not measured (Ron Vaz et al., 1992). $P_r$, the difference between $P_t$ and the amount measured by the phosphomolybdenum blue method after photochemical oxidation ($P_i + P_o$) is a measure of polyphosphates and/or other unidentified species.

#### *Effect of soil type and season*

The moisture contents of the soils in the field, the volume of soil solution isolated after wetting-up, and the soil solution concentrations of $P_o$, $P_r$ and $P_t$ were influenced by soil type and season.

In the case of $P_i$, there was no significant effect due to soil in either 1989 or 1990, but season had a highly significant effect in both years. The soils did not behave in the same way and highly significant interactions between soil and season were noted for all the P species in 1989 and 1990, except $P_i$ during 1990.

In both years of the field study the main fraction in soil solution was $P_o$. On average $P_o$ accounted for 63% and 55% of the $P_t$ in soil solution during 1989 and 1990, respectively. Conversely $P_i$ was the smallest fraction and represented 5% and 11% of the $P_t$ during 1989 and 1990 respectively. $P_r$ was about 33% of the $P_t$ in both years. Comparison of effects between years was confounded by the addition of NPK fertilizer during 1990 and by differences in weather conditions. Season had more influence than soil type on the P composition of soil solution. Soil solution from the bulk soil samples used to test the effect of centrifugation had a $P_r$ content in excess of the amount of $P_o$. This may be due to the effects of storage of the soils for 9 months in sacks before use. During 1989 the Insch and Tarves soils had higher levels of acetic acid extractable P than the Foudland soil. It is notable that soil solution from Insch and Tarves soils did not have average annual $P_i$ contents significantly different from the Foudland soil.

### *Effect of clay minerals and sesquioxides*

The soils had similar clay contents and clay compositions. More importantly for P fixation, the Insch soil contained most oxalate extractable Fe and Al. These sesquioxide phases have a high capacity to retain P compounds. However the greater amounts of these phases in the Insch soil did not appear to influence the amounts of $P_i$, $P_o$ or $P_r$ in soil solutions from this soil compared to the others, either during 1989 or 1990.

## Conclusion

Centrifugation conditions were not critical with respect to the composition of soil solutions obtained from 3 Cambisols. Both soil type and season influenced the total amount of P in soil solution. The distribution of P between different forms in soil solutions from 3 contrasting soils was not large despite differences in parent rock and sesquioxide contents. Organically bound P was a major component of soil solution and exceeded the concentration of inorganic orthophosphate by up to 20 times.

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