

# Vadose Zone Processes and Chemical Transport

## Phosphorus Exchangeability and Leaching Losses from Two Grassland Soils

S. Sinaj,\* C. Stamm, G. S. Toor, L. M. Condrón, T. Hendry, H. J. Di, K. C. Cameron, and E. Frossard

### ABSTRACT

Although phosphate phosphorus (P) is strongly sorbed in many soils, it may be quickly transported through the soil by preferential flow. Under flood irrigation, preferential flow is especially pronounced and associated solute losses may be important. Phosphorus losses induced by flood irrigation were investigated in a lysimeter study. Detailed soil chemical analyses revealed that P was very mobile in the topsoil, but the higher P-fixing capacity of the subsoil appeared to restrict P mobility. Application of a dye tracer enabled preferential flow pathways to be identified. Soil sampling according to dye staining patterns revealed that exchangeable P was significantly greater in preferential flow areas as compared with the unstained soil matrix. This could be partly attributed to the accumulation of organic carbon and P, together with enhanced leaching of Al- and Fe-oxides in the preferential flow areas, which resulted in reduced P sorption. The irrigation water caused a rapid hydrologic response by displacement of resident water from the subsoil. Despite the occurrence of preferential flow, most of the outflowing water was resident soil water and very low in P. In these soils the occurrence of preferential flow per se is not sufficient to cause large P losses even if the topsoil is rich in P. It appears that the P was retained in lower parts of the soil profile characterized by a very high P-fixing capacity. This study demonstrates the risks associated with assessing potential P losses on the basis of P mobility in the topsoil alone.

**I**N NATURAL ECOSYSTEMS, phosphorus is commonly a limiting nutrient for plant growth and is generally recycled and retained efficiently. In agricultural systems P inputs in the form of mineral and/or organic fertilizers are necessary to increase the production and replace P removed in plant and/or animal products. An imbalance between P inputs and outputs over time may result in excessive P accumulation in the soil and increase the likelihood of P transfer from the soil to ground and surface water (Sharpley and Rekolainen, 1997; Haygarth et al., 1998). Improved understanding of soil P dynamics and associated transport is central to better agronomic and environmental management of P. Mobilization of P from the soil to ground and surface water is principally determined by the amount of P in the soil and the physico-chemical as well as the biological processes determining the fraction of the P pool that is in equilibrium with soil solution. The proportion of soil

solution P transferred to ground or surface water depends primarily on the interplay with the flowing water and its associated energy (Haygarth and Jarvis, 1999).

Soil available P is commonly estimated using a variety of methods that includes extraction with water (van der Pauw, 1971), dilute acids and bases (Kamprath and Watson, 1980), anion exchange resin (Sibbesen, 1978), and iron oxide-impregnated paper (van der Zee et al., 1987; Pote et al., 1996; Chardon et al., 1996), as well as isotopic exchange (Fardeau, 1996; Di et al., 1997). These methods are used to estimate the amount of soil P that is available for plant uptake. Recently, attempts have been made to use these measurements to define the potential for transfer of P from soil to water by overland flow (runoff) and/or subsurface flow (leaching) (Heckrath et al., 1995; Sharpley, 1995; Pote et al., 1996; Sibbesen and Sharpley, 1997; McDowell and Trudgill, 2000; Hesketh and Brookes, 2000; McDowell and Condrón, 2000). For example, Heckrath et al. (1995) used Olsen-P concentrations in the topsoil as an index of potential P loss by leaching from soil and suggested a critical value of 60 mg kg<sup>-1</sup> in arable soils at Rothamsted (UK), above which there is an increased risk of significant P loss in subsurface drains. In addition, the findings of Heathwaite and Dils (2000) highlighted the importance of preferential flow pathways in P loss from grassland soils. However, it is important to note that the precise nature of the relationship between topsoil P status and P loss by overland or subsurface flow in different environments remains to be determined and is likely to be influenced by a combination of physical, chemical, biological, and environmental factors.

Research over the last 25 years has shown that infiltrating water is in many cases restricted to a small part of the soil volume (Jury and Flühler, 1992; Flury et al., 1994; Steenhuis et al., 1996). Such behavior is often called preferential flow, which may result in fast transport of even strongly sorbing substances into deep soil layers and ground water. The increasing understanding of preferential flow has also changed the view of how P may be lost from soils into waters. Traditionally, it was assumed that leaching of P was negligible in most soils since P is generally strongly sorbed by the soil

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**Abbreviations:**  $C_p$ , concentration of phosphorus in a soil water extract; DPS, degree of phosphorus saturation;  $E_{1min}$ , phosphorus isotopically exchangeable within one minute; L1 and L2, Lismore lysimeters;  $P_i$ , inorganic phosphorus;  $P_o$ , organic phosphorus;  $P_t$ , total phosphorus;  $R/r1$ , the ratio of total introduced radioactivity ( $R$ ) to the radioactivity remaining in solution after one minute of isotopic exchange ( $r1$ ); T1 and T2, Templeton lysimeters;  $T_m$ , the mean residence time of phosphate ions in soil solution.

**Table 1. Selected chemical properties of undeveloped (natural) Templeton and Lismore soils (New Zealand Soil Bureau, 1968).**

Depth cm	pH in H <sub>2</sub> O (1:2.5)	Organic C	Total N	Total P	CEC†	Base saturation
			g kg <sup>-1</sup> soil		cmol <sub>c</sub> kg <sup>-1</sup>	%
			<b>Templeton</b>			
0–7.5	5.1	44	2.9	0.750	15.8	42
7.5–20	5.4	30	2.1	0.650	13.3	39
20–30	5.4	20	1.9	–	11.9	36
30–40	6.0	10	0.8	0.390	8.5	54
40–50	6.3	5	0.4	0.340	8.9	76
			<b>Lismore</b>			
0–7.5	4.9	38	2.7	0.740	13.6	38
7.5–15	5.3	28	2.2	0.690	12.0	31
15–25	5.6	18	1.6	–	11.3	28
25–37.5	5.7	10	1.0	0.490	8.7	32
37.5–50	6.0	6	0.7	0.680	9.8	28

† Cation exchange capacity.

matrix. Hence, losses via erosion and surface runoff were considered the main processes. Over the last 10 years, an increasing number of studies (Addiscott et al., 2000; Heckrath et al., 1995; Sims et al., 1998; Stamm et al., 1998) have demonstrated P losses by preferential flow into the subsoil and especially into subsurface drainage systems. The relationship between preferred flow paths in soil and the associated chemical and biological processes are not well understood, although it has been shown that the soil matrix can differ markedly from the regions of preferential solute and water transport (Pierret et al., 1999; Bundt et al., 2000). In order to understand the process of P loss from a given soil it is necessary to examine the size and availability of soil P pools, the flow regime operating within the soil, and the spatial and temporal variability of P availability in the soil.

Significant P loss from agricultural land is likely to be associated with intensive animal production systems such as dairy farming. In recent years, dairy farming has been expanding in New Zealand, and between 1985 and 1995 dairy cow numbers increased by 40% from 2.9 to 4.1 million. This increase in dairy farming has the potential to affect environmental quality via enhanced P loss from soil (Cameron et al., 2001). The main objective of this study was to examine the relationship between the spatial variability of P availability in the flow field of the soil and the effect it has on P loss by leaching from undisturbed monoliths of two grassland soils under irrigation.

## MATERIALS AND METHODS

### Soil and Lysimeters

The experiment was carried out using lysimeters (50 cm in diameter, 70 cm deep) installed in a field lysimeter facility at Lincoln University, Canterbury, New Zealand. Duplicate lysimeters containing two free draining grassland soils (Templeton: T1 and T2 and Lismore: L1 and L2) from the Canterbury Plains were used in this study. The Templeton soil is a fine sandy loam (Immature Pallic Soil [New Zealand], Udic Ustochrept [USA]) formed from weakly weathered greywacke alluvium that was under a predominantly ryegrass (*Lolium perenne* L.)–white clover (*Trifolium repens* L.) pasture for 9 yr (Silva et al., 2000). The Lismore soil is a stony silt loam (Orthic

Brown Soil [New Zealand], Udic Ustochrept [USA]) formed from moderately weathered greywacke loess and had been under border-dyke (flood) irrigation with ryegrass–white clover pasture for 45 yr. Selected chemical properties of undeveloped (natural) Templeton and Lismore soils are shown in Table 1 (New Zealand Soil Bureau, 1968).

A detailed description of the methodology used to collect the lysimeters is given elsewhere (Cameron et al., 1992). In brief, the lysimeter consisted of a steel cylindrical casing that was pushed into the soil to collect an intact soil monolith. A cutting ring at the base of cylinder created a 5-mm annular gap between the soil and the casing. This gap was filled with liquefied petroleum jelly, which solidified and formed a seal to prevent edge flow. The bottom 40 mm of soil was removed from the cylinder and replaced with a mixture of washed sand and gravel. The lysimeters were installed in the field with the surface at ground level, thus ensuring normal growing conditions. Leachate was collected via a free draining outlet at the base of each lysimeter.

The Templeton lysimeters (T1, T2) used for the present study were taken in May 1996 and received 30 kg P ha<sup>-1</sup> yr<sup>-1</sup> as single superphosphate and dairy shed effluent (400 kg N ha<sup>-1</sup> yr<sup>-1</sup>; 40–60 kg P ha<sup>-1</sup> yr<sup>-1</sup>) over a 2-yr period (to April 1998). Thereafter, the Templeton lysimeters were maintained without P addition until November 1999. The Lismore lysimeters (L1, L2) were taken in April 1998 and were also maintained without P addition until November 1999. Phosphorus fertilizer as single superphosphate (45 kg P ha<sup>-1</sup>) was applied to the lysimeters on 22 Nov. 1999. In accordance with normal farm practice, the lysimeters were irrigated (100 mm) on 7 and 21 December 1999 prior to the detailed experiments described below.

### Irrigation Experiments

The experimental treatment started on 11 Jan. 2000. In the upper 11 cm we measured a volumetric water content of about 0.26 m<sup>3</sup> m<sup>-3</sup> in the Lismore soil (TDR measurement, measured by a 15-cm rod inserted at an angle to a depth of 11 cm) before the start of the first irrigation. An equivalent of 40.8 mm of potassium bromide solution (KBr: 50 mg Br<sup>-</sup> L<sup>-1</sup>) was applied as tracer with flood irrigation to the lysimeters to assess the movement of the irrigated water through the soil profile. This volume corresponds to about 0.12 pore volumes. The cumulative outflow was monitored with a balance and the samples were taken for leachate analysis at the same times as discharge was measured (see below). Of all samples an aliquot was filtered immediately (0.20-µm cellulose membrane

filters) and stored at 4°C. Phosphorus analyses were performed within 48 h after sampling.

The lysimeters were allowed to drain for 48 h, by which time drainage had completely ceased from all lysimeters. Thereafter, the same irrigation procedure was repeated on the same lysimeters with KBr and Brilliant Blue dye (C.I. 42 090, 4 g L<sup>-1</sup>) in order to stain the flow paths in the soil. The outflow was monitored as in the first experiment. Again, the drainage was followed for 48 h until the outflow had stopped.

### Flow Rate Analysis

Flow rates were measured at temporal resolutions of 3 to 5 min after the onset of outflow when the discharge changed rapidly. Later on the intervals were prolonged up to 12 h at the very end of the experiment. For each lysimeter and each irrigation 16 to 20 measurements and leachate samples were taken during the experiment. In order to compare the flow rates we fitted an analytical function  $Q[t]$  with the measured cumulative discharge values for each lysimeter and in each trial. The function  $Q[t]$  corresponds to the behavior of two mixing cells arranged in series. Conceptually, they represent a saturated zone in the topsoil due to the ponded infiltration as well as saturated areas above the lower boundary due to the capillary barrier effect of the sand-gravel mixture. Part of the water from the first cell was allowed to discharge, directly bypassing the second cell. Therefore, it was necessary to estimate three parameters: two effective hydraulic constants of the mixing cells describing the relationship between the height of the water table and discharge, and the ratio of the water being discharged directly from the first cell. These parameters were obtained by the Levenberg-Marquard routine as implemented in Mathematica 4.0 (Wolfram Research, 1999). The flow rates  $q[t]$  were obtained as the time derivative of  $Q[t]$ .

### Load Estimation

The cumulative solute loads were calculated as the sum of the load of two parts. The first part was the load from the samples collected for chemical analysis. Sampling consisted of sampling the outflow for defined periods of time. Hence, for these periods, the load was directly calculated from the measured volume and concentration. For the periods between sampling the solute concentrations were assumed to change linearly in time. Based on this assumption the average concentration for the time between sampling was estimated and the load was calculated as the product of the measured discharge volume and the estimated concentration.

### Soil Sampling

At the end of the irrigation experiment, before removing the lysimeters, small soil cores (20 mm in diameter, 75 mm long) were taken for conventional P testing. Thereafter, the lysimeters were lifted from the field by a tractor. The lysimeters were fixed in a horizontal position and the steel cylinder was cut open so that the soil remained undisturbed in the lower half of the cylinder.

For each lysimeter two to three vertical (from the soil surface to the bottom) profiles were prepared. After having defined the pedological horizons, soil samples were taken within each horizon according to stained patterns. In the surface horizon (about 0–7.5 cm), the dye solution had infiltrated in a homogeneous manner in all four lysimeters. Based on visual observation it was not possible to distinguish between matrix (nonstained) and preferred (stained) flow paths in this part of the soil. Accordingly, stained and unstained areas were distinguished only below 7.5 cm. In the lower part of the soils,

the preferential areas were clearly separated from the matrix zones. For each depth and lysimeter, three to four vertical individual samples (20–30 g each) were taken separately according to stained patterns to form a composite sample of stained and a composite sample of unstained soil. After sampling, plant residues were removed from the samples, and the soil was air-dried and sieved to <2 mm.

### Soil Analyses

Total carbon (C) and nitrogen (N) were measured with an elemental analyzer (NA 1500; Carlo Erba, Rodano-Milan, Italy). Total phosphorus (P<sub>t</sub>) and total inorganic phosphorus (P<sub>i</sub>) were determined using malachite green colorimetry (Ohno and Zibilski, 1991) following soil digestion according to Saunders and Williams (1955). Total organic phosphorus (P<sub>o</sub>) was calculated as the difference between total P and total inorganic P. Orthophosphate concentration in the soil solution was determined using ion chromatography (Sinaj et al., 1998). Soil pH was measured in a suspension of 1 g of dry soil in 2.5 mL deionized water. The amounts of the active iron (Fe) and aluminum (Al) forms (crystalline oxides, poorly crystalline oxides, and organo-mineral complexes) were determined after a dithionite-citrate-bicarbonate extraction (Mehra and Jackson, 1960) using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Phosphorus, Fe, and Al concentrations in the acid ammonium oxalate extracts (McKeague and Day, 1966) were also determined using ICP-AES. Specific surface area (BET, m<sup>2</sup> g<sup>-1</sup>) was determined according to Weidler et al. (1998). The degree of phosphorus saturation (DPS) was computed using the P, Fe, and Al contents (mmol kg<sup>-1</sup>) extracted with acid ammonium oxalate (P<sub>ox</sub>, Fe<sub>ox</sub>, and Al<sub>ox</sub>, respectively):

$$\text{DPS} = [\text{P}_{\text{ox}}/\alpha(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})] \times 100 \quad [1]$$

Values reported for  $\alpha$  have ranged from 0.34 to 0.61, and a value of 0.5 was used in this study (Breeuwsma and Silva, 1992).

### Isotopic Exchange Kinetics

The isotope exchange kinetics technique was described in detail by Fardeau (1996) and Frossard and Sinaj (1997). The following section gives only a rapid outline of the method.

When <sup>33</sup>PO<sub>4</sub> is added carrier-free to a soil solution system at a steady state, an exchange occurs between the added <sup>33</sup>PO<sub>4</sub> and exchangeable <sup>31</sup>PO<sub>4</sub> ions located on the solid phase of soil. The radioactivity in solution decreases with time  $t$  (expressed in minutes) according to the following equation:

$$r(t)/R = r(1)/R \times t^{-n} \quad [2]$$

where  $R$  is the total introduced radioactivity (MBq);  $r(1)$  and  $r(t)$  are the radioactivity (MBq) remaining in the solution after 1 min and  $t$  minutes, respectively; and  $n$  describes the rate of disappearance of the tracer from the solution after 1 min of isotopic exchange.

The quantity,  $E_{(t)}$  (mg P kg<sup>-1</sup> soil) of isotopically exchangeable P at time ( $t$ ) was calculated from Eq. [3], assuming that <sup>31</sup>PO<sub>4</sub> and <sup>33</sup>PO<sub>4</sub> had the same fate in the system, and that at a given time the specific activity of the phosphate in the soil solution was identical to that of the soil isotopically exchangeable phosphate:

$$E_{(t)} = 10C_p \times R/r(t) \quad [3]$$

For  $t = 1$  min,

$$E_{1\text{min}} = 10C_p \times R/r(1) \quad [4]$$

where  $C_p$  is the water-soluble phosphorus ( $\text{mg P L}^{-1}$ ). The factor of 10 arises from the soil to solution ratio of 1 g of soil in 10 mL of water so that  $10C_p$  is equivalent to the water-soluble P content of the soil, expressed in  $\text{mg kg}^{-1}$ . Additionally, the mean residence time of phosphate ions in soil solution ( $T_m$ , min) is calculated from the experimental data according to Fardeau et al. (1991):

$$T_m = [r(1)/R]^{1/n}/n \quad [5]$$

The isotopic exchange method gives information on the three factors characterizing soil P availability (Fardeau, 1996). The first factor is the phosphate concentration in the soil solution ( $C_p$ ), which represents the *intensity factor*. The second factor is the quantity of isotopically exchangeable P ( $E_{(t)}$ ), which gives information on the *quantity factor*. The quantity  $E_{1\text{min}}$  represents the pool of P ions that is exchanged during the first minute of the batch experiment. This homogenous pool, which contains ions in the soil solution plus ions located on the solid phase with the same mobility as the ions in the solution (Fardeau et al., 1985; Tran et al., 1988; Salcedo et al., 1991), is immediately available to crops without chemical transformation (Fardeau, 1996). The parameter  $R/r(1)$ , which is a ratio of total introduced radioactivity ( $R$ ) to the radioactivity remaining in solution after 1 min of isotopic exchange ( $r1$ ) is well correlated with the third factor, *soil P fixing capacity* (Tran et al., 1988; Salcedo et al., 1991; Frossard et al., 1993). It is considered to be very high for values  $>10$ , medium between 2.5 and 5, and low if  $<2.5$  (Fardeau et al., 1991).

### Leachate Analysis

For each leachate sample, dissolved reactive phosphorus (DRP) was determined on a  $<0.20\text{-}\mu\text{m}$  cellulose membrane-filtered subsample within 48 h using the malachite green colorimetry method (Ohno and Zibilski, 1991). In addition, total P was determined on an unfiltered aliquot of each leachate sample following sodium hydroxide-persulfate digestion (Ebina et al., 1983). Bromide was measured by ion chromatography using a Tecator FIAstar 5010 flow injector analyzer (Foss Tecator A/S, Hoganas, Sweden). Brilliant Blue was analyzed photometrically at 630 nm (UV-1601 spectrometer; Shimadzu Corporation, Kyoto, Japan).

## RESULTS

### Infiltration

In all lysimeters, the applied water infiltrated rapidly during both experiments (11 and 13 January). The soil surface was free of water after 1 to 6 min, although some local ponding persisted for a few minutes. In one of the Lismore lysimeters (L2), ponding was observed for up to 14 min in the second experiment. The water content in the soil increased very rapidly. In the Lismore lysimeter (L1), for example, the volumetric water content in the top 11 cm increased from 26.3 to 46.0% within only 2 min of irrigation and decreased rapidly to 33.4% after 107 min.

### Discharge

There was no discharge from the lysimeters at the beginning of the experiment. However, after irrigation, all four lysimeters responded very quickly, with the first

**Table 2. Water balance of the irrigation events. L1 and L2 = Lismore lysimeters, T1 and T2 = Templeton lysimeters.**

Irrigation date	Irrigation volume	Discharge ratio†			
		L1	L2	T1	T2
	mm				
7 Dec. 1999	100.0	0.55	0.47	0.09	0.49
21 Dec. 1999	100.0	0.70	0.33	0.24	0.53
11 Jan. 2000	40.8	0.73	0.75	0.98	0.72
13 Jan. 2000	40.8	0.86	0.85	0.88	0.80

† Discharge ratio = outflow volume/inflow volume.

outflow observed after 2.5 to 5.0 min. This behavior was consistent in both experiments. The flow rate increased rapidly in all the lysimeters and reached maximum values after only 8 (Templeton lysimeter, T1) to 16 min (Lismore lysimeter, L2), followed by a decreasing trend. The discharge had completely ceased in all the lysimeters after 24 h.

During the first experiment (11 Jan. 2000), the discharge ratio (outflow volume to irrigation volume) in L1, L2, and T2 lysimeters ranged from 72 to 75% (Table 2). However, T1 exhibited a different behavior, having a discharge ratio of 98%. In the second experiment, on 13 Jan. 2000, all discharge ratios were higher, and the variability within the lysimeters ranged from 80 to 86%. Apart from the extreme discharge ratio in T1 in the first experiment, no significant differences between the two soil types were observed. It should be noted that the discharge ratios were only 9 and 24% during the initial irrigation events in T1 (Table 2). The higher discharge in the later experiments seems to be due to the fact that a majority of the water was retained in the soil profile during the first irrigation event.

In comparing the outflow behavior of the lysimeters, the mean squared differences between the fitted flow rates between the two experiments of the lysimeters were calculated (excluding data for T1 in the first irrigation) (see above, Fig. 1). The hydrological responses between the two experiments of the same lysimeter were consistent in that the differences between the two irrigations of the same lysimeter were substantially smaller (with an average difference in flow rate of  $2.3 \pm 0.3 \text{ mL s}^{-1}$ ) than those between different lysimeters. Furthermore, the average differences between flow rates from lysimeters of different soil types were smaller ( $3.9 \pm 1.6 \text{ mL s}^{-1}$ ) than those of lysimeters of the same soil ( $4.9 \pm 2.0 \text{ mL s}^{-1}$ ). Hence, the within-soil-type variability was about the same as the between-soil-type variability.

### Solute Transport

In L1, L2, and T1 lysimeters, we observed an early concentration peak after only 480 to 1800 s (8 to 30 min) (Fig. 2), which corresponds to 2.3 to 10.5 mm of cumulative discharge. In contrast to these three lysimeters, a pronounced lag was observed in T2 with the tracer concentrations slowly increasing during the entire discharge period. Taken together, the results clearly demonstrated preferential tracer transport through the lysimeters.

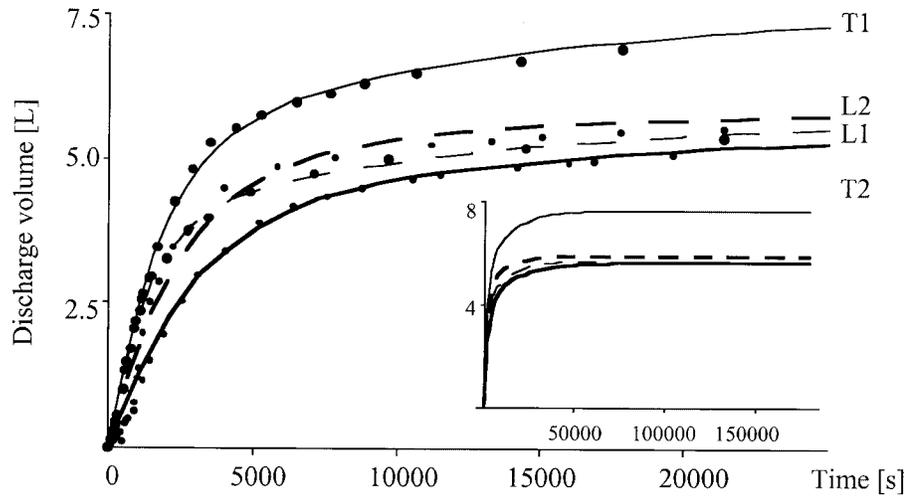


Fig. 1. Cumulative discharge of the four lysimeters in the first experiment (black points = observed data, lines = modeled data). L1 and L2 = Lismore lysimeters, T1 and T2 = Templeton lysimeters.

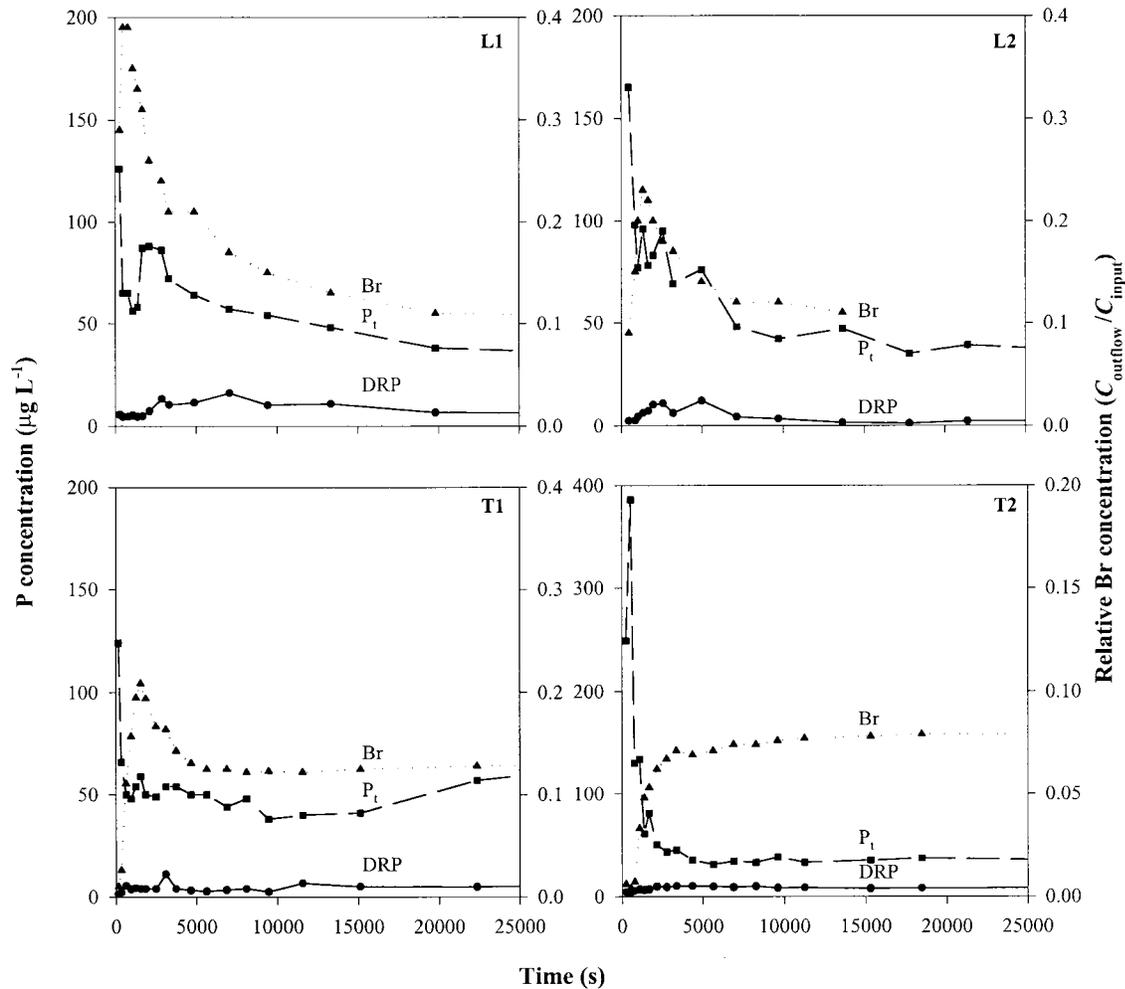


Fig. 2. Concentrations of total phosphorus ( $P_t$ ), dissolved reactive phosphorus (DRP), and Br in the first experiment (11 Jan. 2000). L1 and L2 = Lismore lysimeters, T1 and T2 = Templeton lysimeters. Note different scales for T2 compared with the other lysimeters.

In contrast to the early Br breakthrough and the fast hydrological response, the percentage of the new water that was collected in the drainage was low, ranging from only 4 to 20% (Table 3) in the first experiment. The

proportion of the new water was similar in the second experiment, as indicated by the breakthrough of the Brilliant Blue dye, where it ranged from 5.5 to 26%. It is evident from these numbers that the majority of the

**Table 3. Mass balances of the applied tracers Br and Brilliant Blue (BB). L1 and L2 = Lismore lysimeters, T1 and T2 = Templeton lysimeters.**

Irrigation date	Tracer export			
	L1	L2	T1	T2
	-% of input -			
Br, 11 Jan. 2000	19.9	11.3	14.0	4.3
Br, 13 Jan. 2000†	16.6	11.9	11.1	5.8
BB, 13 Jan. 2000	26.0	11.8	11.8	5.5

† Export is related to the total Br input of both irrigations.

drainage water was old or pre-event that was pushed out quickly from the soil.

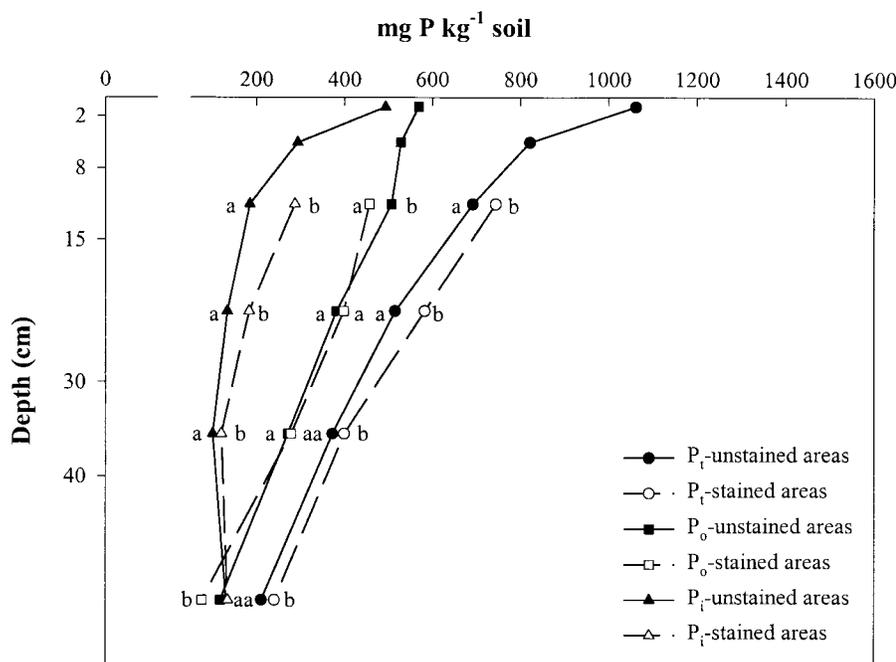
**Soil Phosphorus**

The total ( $P_t$ ), inorganic ( $P_i$ ), and organic ( $P_o$ ) P contents in the soil profiles of Templeton and Lismore (means of two lysimeters) are presented in the Fig. 3 and 4, respectively. Lismore soils contained higher concentrations of P than the Templeton soils at all depths. Within each lysimeter and for each of the P forms, there was a strong dependency of the concentrations on the depth; the highest values were measured in the topsoil and a general decrease was observed thereafter with depth. In the Templeton and Lismore soils, the  $P_i$  concentrations in the 0- to 2-cm depth were 1062 and 1340 mg P kg<sup>-1</sup> and decreased to about 250 and 600 mg P kg<sup>-1</sup> at 40 to 60 cm, respectively (Fig. 3 and 4). However, the lowest part of the soil profile (35–60 cm) in the Lismore soil had higher amounts of inorganic P and this increase was greater for the stained areas. This increase may be attributed to P transfer from the upper soil horizons. Apart from soil type and depth,  $P_t$  and  $P_i$  were

also affected by the position relative to the stained flow paths. The stained (preferential) and nonstained (matrix) areas were separated at all the depths. Higher concentrations of inorganic and total P were observed in the stained areas (Fig. 3 and 4). Total P was 7 to 15% and 4 to 16% higher in the preferential than in the matrix sites for the Templeton and Lismore soils, respectively. The differences for inorganic P were much higher in stained compared with unstained matrix areas and varied according to depth from 3 to 55% (Templeton) and from 9 to 42% (Lismore). Similar trends of higher P levels in the preferential flow areas compared with matrix were also seen for oxalate-extractable P (Tables 4 and 5), which is a general indicator of total sorbed P in acid soils (van der Zee and van Riemsdijk, 1988; Pautler and Sims, 2000). However, no consistent differences were observed for organic P, although there is a consistent decrease in the organic P with increasing depth and this trend is more conspicuous in the Templeton than the Lismore soils (Fig. 3 and 4).

**Isotopic Exchange Kinetics**

The concentration of  $P_i$  in the soil solution ( $C_p$ ) and the quantity of P in the  $E_{1min}$  pool in the surface horizons (0–2 and 2–7.5 cm) were very high (Tables 6 and 7). They were clearly above the optimum range (0.2 mg P L<sup>-1</sup> and 5 mg P kg<sup>-1</sup> soil, respectively, for  $C_p$  and  $E_{1min}$ ) for agricultural crops (Tran et al., 1988; Fox et al., 1990; Morel et al., 1992). As expected, the levels of  $C_p$  and  $E_{1min}$  decreased with depth in both soils. In contrast to the content of different P forms, the inorganic P in solution was higher in the Templeton as compared with the Lismore soil. The values of  $C_p$  and  $E_{1min}$  differed



**Fig. 3. Total ( $P_t$ ), organic ( $P_o$ ), and inorganic phosphorus ( $P_i$ ) (mg P kg<sup>-1</sup>) in stained and unstained areas of Templeton soil. For the letter pair a and b, the difference between stained and unstained areas is statistically significant at the 0.05 probability level, based on paired  $t$  tests. For the letter pair a and a, the difference between stained and unstained areas is not statistically significant at the 0.05 probability level, based on paired  $t$  tests.**

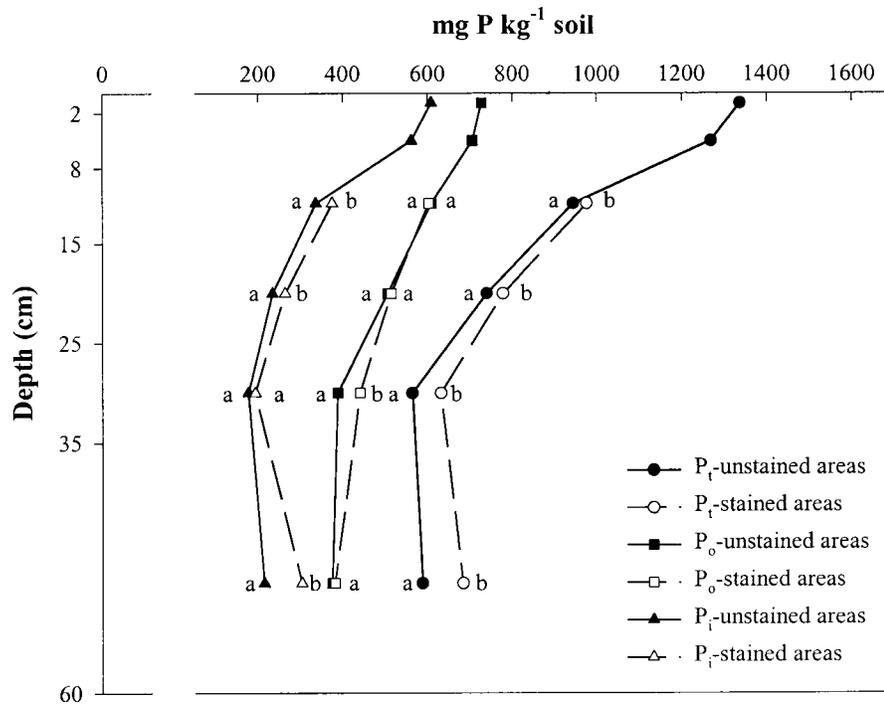


Fig. 4. Total ( $P_t$ ), organic ( $P_o$ ), and inorganic phosphorus ( $P_i$ ) ( $\text{mg P kg}^{-1}$ ) in stained and unstained areas of Lismore soil. For the letter pair a and b, the difference between stained and unstained areas is statistically significant at the 0.05 probability level, based on paired  $t$  tests. For the letter pair a and a, the difference between stained and unstained areas is not statistically significant at the 0.05 probability level, based on paired  $t$  tests.

with depth, according to the sampling in preferential and matrix areas. Both quantities were significantly higher in the preferential flow sites as compared with the matrix ( $p < 0.01$ ). In the 7.5- to 15-, 15- to 30-, and 40- to 65-cm depths, the concentrations of  $C_P$  and  $E_{1\text{min}}$  in preferential flow paths exceeded those of the adjacent matrix soil by a factor of more than two in both soils. These differences have to be attributed to the soil properties because in batch experiments we confirmed that the dye does not influence the P exchangeability.

The data presented in Tables 6 and 7 show that the

$R/r(1)$  is low in the surface horizons (0–2 and 2–7.5 cm) of both soils. The values of  $R/r(1)$  were much higher in the Lismore soil, indicating that the P fixing capacity of this soil is greater than the Templeton. This higher P fixing capacity in Lismore might be due to the greater amounts of dithionite- and oxalate-extractable Fe and Al in this soil (Tables 4 and 5). It is also reflected in the significant relationships observed between  $R/r(1)$  and dithionite extractable Al ( $r^2 = 0.91$ ,  $p < 0.01$ ) and Fe ( $r^2 = 0.85$ ,  $p < 0.01$ ). This is consistent with the results from other studies (Tran et al., 1988; Sinaj et al.,

Table 4. Selected properties of unstained matrix and stained flow path Templeton soils.

Depth cm	pH in $\text{H}_2\text{O}$	C	N	$\text{Fe}_{d\ddagger}$	$\text{Fe}_{ox\ddagger}$	$\text{Al}_{d\ddagger}$	$\text{Al}_{ox\ddagger}$	$\text{P}_{ox\ddagger}$	BET§	
										g $\text{kg}^{-1}$
Topsoil										
0–2	5.64	43.4	3.36	4.4	2.6	1.9	1.9	0.620	nd¶	
2–7.5	5.54	37.6	3.12	5.3	3.0	2.1	1.8	0.462	nd	
Unstained areas (matrix)										
7.5–15	5.38	28.3	2.02	4.9	2.7	2.1	1.7	0.364	nd	
15–30	5.12	21.1	1.51	5.3	3.4	2.3	2.2	0.343	10.8	
30–40	5.14	9.0	0.80	5.1	3.3	1.8	1.4	0.228	nd	
40–65	5.76	LD#	LD	3.7	2.4	1.0	1.1	0.147	7.1	
Stained areas (preferential flow areas)										
7.5–15	5.57*	29.7	2.21	5.2	2.8	2.0	1.8	0.395**	nd	
15–30	5.34**	23.6	1.62	5.3	3.1	2.3	1.9	0.382*	7.6**	
30–40	5.36*	16.2*	1.01	5.3	3.2	1.9	2.0	0.262*	nd	
40–65	5.81	LD	LD	3.4	2.0	0.7	0.9	0.177	5.9**	

\* Significant at the 0.05 probability level.

\*\* Significant at the 0.01 probability level.

† Dithionite–citrate–bicarbonate extractable iron and aluminum.

‡ Oxalate-extractable iron, aluminum, and phosphorus.

§ Specific surface area.

¶ Not determined.

# Limit of detection.

**Table 5. Selected properties of unstained matrix and stained flow path Lismore soils.**

Depth	pH	C	N	Fe <sub>d</sub> <sup>†</sup>	Fe <sub>ox</sub> <sup>‡</sup>	Al <sub>d</sub> <sup>†</sup>	Al <sub>ox</sub> <sup>‡</sup>	P <sub>ox</sub> <sup>‡</sup>	BET <sup>§</sup>
cm	g kg <sup>-1</sup>								m <sup>2</sup> g <sup>-1</sup>
Topsoil									
0-2	5.45	47.2	3.59	7.0	3.3	2.7	2.6	0.685	nd <sup>¶</sup>
2-7.5	5.42	38.5	3.23	7.5	2.8	3.1	2.5	0.556	nd
Unstained areas (matrix)									
7.5-15	5.39	34.1	2.85	8.1	2.9	3.4	2.6	0.420	nd
15-25	5.46	25.7	2.12	8.2	2.9	3.4	2.6	0.339	7.6
25-35	5.27	13.4	0.91	8.8	3.0	3.9	2.7	0.274	nd
35-60	5.15	10.2	0.84	10.1	4.1	5.6	5.1	0.345	20.7
Stained areas (preferential flow areas)									
7.5-15	5.51	35.3	2.88	7.3	2.7**	3.1*	2.4	0.451*	nd
15-25	5.52	26.8	2.29	8.1	2.5*	3.1*	2.5	0.352	6.5**
25-35	5.35	19.6*	1.52	8.7	2.7	3.7	2.7	0.316*	nd
35-60	5.22	15.1*	0.95	10.1	3.8	5.9	4.0*	0.449*	16.9**

\* Significant at the 0.05 probability level.  
 \*\* Significant at the 0.01 probability level.  
 † Dithionite-citrate-bicarbonate extractable iron and aluminum.  
 ‡ Oxalate-extractable iron, aluminum, and phosphorus.  
 § Specific surface area.  
 ¶ Not determined.

1992; Frossard et al., 1993) confirming that the Fe and Al oxides represent the major active fixing sites in the soil. Highly significant correlation was also found between *R/r*(1) and total C in both soils ( $r^2 = 0.92, p < 0.01$ ).

A significant increase in *R/r*(1) was observed not only with the increasing depth in both the soils but also with respect to the sampling position relevant to the stained and unstained areas. For all analyzed depths (except 35-60 cm in the Lismore soil), the *R/r*(1) values were significantly lower in stained than the corresponding values in unstained areas (Tables 6 and 7). This indicates that the P availability (determined by *C<sub>p</sub>*, *E<sub>1min</sub>*) is higher in the stained areas.

The mean residence time (*T<sub>m</sub>*) is the average time required to renew the phosphate ions present in the soil solution by an equal quantity derived from the solid phase. Reported *T<sub>m</sub>* values for tropical and temperate soils ranged from  $8 \times 10^{-6}$  to 0.4 min (Fardeau et al., 1991; Oberson et al., 1993; Frossard et al., 1995; Sinaj

et al., 1995). Data presented in Tables 6 and 7 for the surface horizons (0-2 and 2-7.5 cm) showed that the mean residence time of phosphate ions in the soil solution was very high compared with reported data. An important difference also existed between the two soils. The *T<sub>m</sub>* values of the surface horizons (0-2 and 2-7.5 cm) in Templeton soil were two to three times higher than the *T<sub>m</sub>* values of Lismore soil for the same horizons. The distribution of the *T<sub>m</sub>* values between preferential flow (stained) paths and the matrix is almost the same as in the case of *C<sub>p</sub>* and *E<sub>1min</sub>*. In the 7.5- to 15- and 15- to 30-cm depths of the Templeton soil, the mean residence time of phosphate ions in the soil solution in preferential flow paths exceeded that of the matrix by factors of 2.6 and 1.6, respectively. The differences between matrix and preferential flow paths in the Lismore soil were smaller compared with those in the Templeton soil but were statistically significant (except for the lowest part of the Lismore profile).

**Table 6. Kinetic parameters (*C<sub>p</sub>* and *R/r*1), isotopically exchangeable phosphorus within 1 minute (*E<sub>1min</sub>*), the mean residence time of phosphate ions in soil solution (*T<sub>m</sub>*), and the degree of phosphorus saturation (DPS) for unstained matrix and stained flow path Templeton soils.**

Depth	<i>C<sub>p</sub></i>	<i>R/r</i> 1	<i>E<sub>1min</sub></i>	<i>T<sub>m</sub></i>	DPS
cm	mg P L <sup>-1</sup>	mg P kg <sup>-1</sup> soil		min	%
Topsoil					
0-2	1.730	1.3	22.0	20.4	34.8
2-7.5	0.457	1.5	6.6	8.3	24.9
Unstained areas (matrix)					
7.5-15	0.044	2.5	1.1	2.7	20.8
15-30	0.016	4.2	0.7	1.1	15.6
30-40	0.006	10.5	0.6	0.6	12.2
40-65	0.001	9.3	0.1	0.9	13.6
Stained areas (preferential flow areas)					
7.5-15	0.097**	1.7**	1.7**	7.1**	22.1
15-30	0.045**	3.0**	1.4**	1.8*	19.2**
30-40	0.010*	6.9*	0.7	0.8*	13.1
40-65	0.090**	4.8**	4.1**	1.5**	13.5

\* Significant at the 0.05 probability level.  
 \*\* Significant at the 0.01 probability level.

**Table 7. Kinetic parameters (*C<sub>p</sub>* and *R/r*1), isotopically exchangeable phosphorus within 1 minute (*E<sub>1min</sub>*), the mean residence time of phosphate ions in soil solution (*T<sub>m</sub>*), and the degree of phosphorus saturation (DPS) for unstained matrix and stained flow path Lismore soils.**

Depth	<i>C<sub>p</sub></i>	<i>R/r</i> 1	<i>E<sub>1min</sub></i>	<i>T<sub>m</sub></i>	DPS
cm	mg P L <sup>-1</sup>	mg P kg <sup>-1</sup> soil		min	%
Topsoil					
0-2	0.931	1.9	17.7	6.7	28.9
2-7.5	0.508	2.5	12.5	4.3	25.5
Unstained areas (matrix)					
7.5-15	0.061	5.7	3.7	1.1	18.7
15-25	0.015	12.4	1.8	0.4	15.0
25-35	0.005	36.8	1.8	0.2	11.6
35-60	0.001	75.3	0.8	0.1	8.4
Stained areas (preferential flow areas)					
7.5-15	0.188**	3.8*	7.3**	2.1**	21.3**
15-25	0.033**	10.7*	3.6**	0.5*	16.3**
25-35	0.008*	27.1**	2.0	0.3**	13.8
35-60	0.003	65.7	1.5*	0.1	13.6**

\* Significant at the 0.05 probability level.  
 \*\* Significant at the 0.01 probability level.

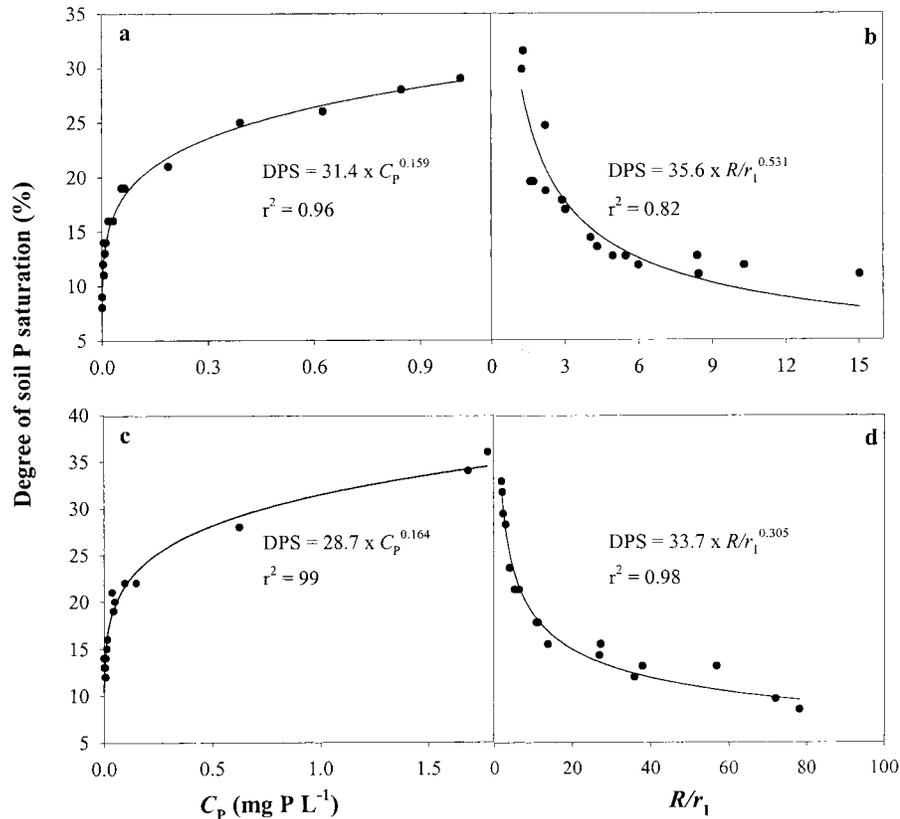


Fig. 5. Degree of phosphorus saturation (DPS, %) versus the concentration of P in soil solution ( $C_p$ ) and soil-P fixing capacity ( $R/r_1$ ) in Templeton (a and b) and Lismore (c and d) soils.

### Soil Phosphorus Saturation

A high degree of soil phosphorus saturation (DPS) may lead to significant P loss to shallow ground water and surface waters. Values for DPS of above 25% are commonly associated with the strongly increased risk of P loss in leaching or runoff and thus nonpoint-source pollution (Breeuwsma et al., 1995; Lookman et al., 1996). With regard to the soil profiles of Templeton and Lismore the DPS values ranged from 12.2 to 34.8% and 8.5 to 28.4%, respectively (Tables 6 and 7). Hence, only the uppermost layers (0–7.5 cm) of both soils could be considered as a risk of P loss in leaching. The significant relationships observed between the kinetic parameters  $C_p$  and  $R/r_1$  and DPS (Fig. 5) show that in these soils any of these parameters could be very good estimates of soil-P saturation.

### Phosphorus Loss

The concentration of P in leachates was determined following the two irrigation events in December 1999 as well as for the first experiment in January 2000 (Table 8; Fig. 2). During the first irrigation after P fertilizer was applied, the concentrations of all measured P forms (Table 8) were substantially higher than those measured afterward.

Phosphorus losses varied between 190 and 265 g  $P_t$   $ha^{-1}$  and 14 to 16 g  $DRP$   $ha^{-1}$  for L1, L2, and T2. The losses from T1 were much less, being 54 g  $ha^{-1}$  for  $P_t$  and only 2.5 g  $ha^{-1}$  for  $DRP$ . These small losses may be attributed to very little discharge from this lysimeter during the first irrigation (1.7 L versus 9.9 L as the average for the others). Other data from related studies have shown that annual  $P_t$  losses from Lismore soil

Table 8. Dissolved reactive phosphorus (DRP) and total phosphorus ( $P_t$ ) in lysimeter discharge. L1 and L2 = Lismore lysimeters, T1 and T2 = Templeton lysimeters.

Irrigation date	Flow-weighted concentrations							
	Lysimeters							
	L1		L2		T1		T2	
	DRP	$P_t$	DRP	$P_t$	DRP	$P_t$	DRP	$P_t$
	$\mu g L^{-1}$							
7 Dec. 1999	22.0	358.5	21.8	370.6	3.1	264.4	12.4	289.5
21 Dec. 1999	2.6	47.9	6.0	44.9	1.5	36.5	10.4	48.6
11 Jan. 2000	3.1	65.1	5.9	78.1	4.7	56.1	8.1	71.9

under flood irrigation were 850 to 2300 g ha<sup>-1</sup> compared with DRP losses of only 22 to 112 g ha<sup>-1</sup> (Condrón et al., 2000).

The differences between the two soils were small. The only significant difference observed was for the decrease of the DRP concentration from the first to the second irrigation. Whereas the concentrations in L1 and L2 decreased by 86 and 74%, the corresponding numbers for T1 and T2 were only 33 and 17%. This was in agreement with the higher P-fixing capacity of the Lismore soil (Tables 6 and 7).

The experiments in January 2000 offered some insights into the dynamics of the P export. The relationship between discharge and the concentration of P varied substantially for the different P forms (Fig. 2). There was a general trend of decreasing P<sub>i</sub> concentrations with time or cumulative discharge, with the highest concentration measured in the first sample. Only for T2 did we observe an increase from Sample 1 to 2. For L1, an increase was observed after the flow peak. The DRP concentration behaved differently. The peak concentrations were always measured after the discharge peak. No clear differences between the two soil types were detected.

Since P loss by leaching is believed to occur mainly by preferential flow, we expected some relationship between the P and Br concentrations. However, no obvious pattern could be detected for the temporal evolution of P and Br in the leachate. Furthermore, the P losses were not related to the amount of Br leached (i.e., the

proportion of irrigation water lost immediately from the lysimeter following irrigation) (Table 3).

### DISCUSSION AND CONCLUSIONS

Soil P forms and availability were influenced by sampling position relative to stained flow paths. With the exception of organic P all other P forms and measures of availability were influenced by the sampling location. The results indicate that P is more mobile and available in preferential flow areas. This may be partly due to the import of P via the preferred flow paths from the topsoil, which is rich in available P. The growth and decay of successive generations of roots and microorganisms could be an explanation for higher values of C in preferential regions (Tables 4 and 5). Pierret et al. (1999) and Bundt et al. (2000) have clearly demonstrated that the root and microbial biomass were significantly higher in preferential flow paths than in the matrix. The P availability may have been enhanced by possible reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> by organic C in these preferential sites, thereby releasing P. This is evident from the higher concentrations of oxalate-extractable P observed in the preferential flow areas (Tables 4 and 5). Bloom and Nater (1991) and Liang et al. (2000) reported that microorganisms and higher plants may enhance the dissolution and afterward the release of colloidal iron and aluminium oxides by secreting low molecular weight organic ligands (e.g., oxalate or citrate).

Several studies have shown that P loss via leaching may be much more important than predicted by the classical convection-dispersion equation (Stamm et al., 1998). Preferential flow bypassing the sorbing soil matrix was given as an explanation for these results. In this study the flood irrigation regime caused significant preferential flow. Soil analysis showed that the topsoil was very rich in available P. Furthermore, the P content and availability in the preferred flow paths in the subsoil were significantly greater than in the surrounding matrix. Hence, given the fast transport regime induced by the ponded irrigation, the observed preferential transport of solutes through the lysimeters and the large pool of available P would suggest that large P loss should have been observed. However, DRP and P<sub>i</sub> concentrations determined in leachate were very low. We have to explain therefore how a soil can retain P very strongly despite containing significant amounts of available P and the occurrence of preferential flow.

In order to understand the results obtained from this study it is necessary to consider the origin of the drainage water (leachate) generated. The Br and dye tracer showed that most of the discharge was pre-event water. The dye distribution in the profile indicates that a large proportion of the infiltrating water moved into the topsoil, suggesting that the topsoil might be the origin of the pre-event water in the leachate. However, a comparison of the soil-P analysis and the DRP concentrations in the outflow appears to contradict this idea. Figure 6 shows the C<sub>p</sub> values measured from the soil samples in comparison with the range of observed DRP values in the outflow. Obviously, the leachate is close to the qual-

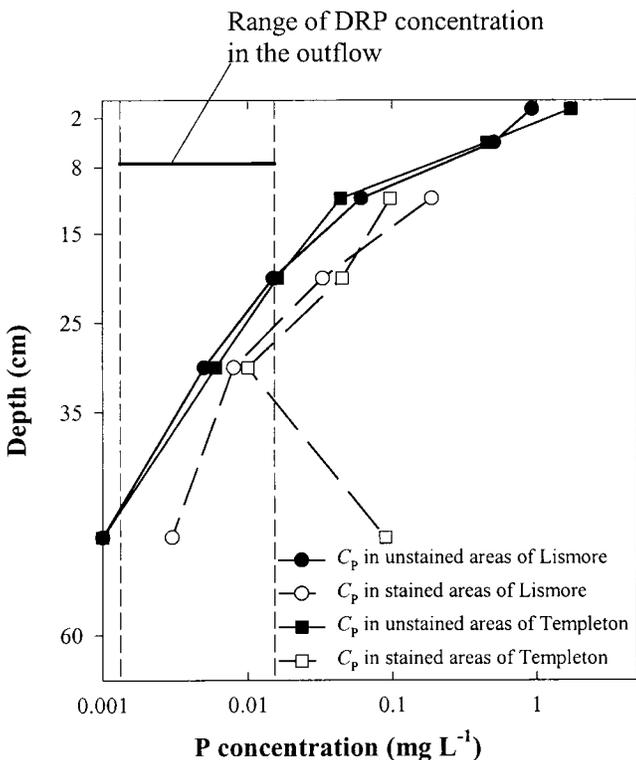


Fig. 6. Comparison of water-soluble phosphorus (C<sub>p</sub>) as a function of depths for both Lismore and Templeton soils and the range of measured DRP values in the leachate.

ity of the water-extractable P of the subsoil matrix. This indicates that the leachate was actually water present in the subsoil that was pushed out very quickly following water application. Since the stained irrigation water did not bypass the P-rich topsoil but stained the subsoil to a much lesser extent, we conclude that the infiltrating water saturated the topsoil first. This caused the outflow of a mixture of new and pre-event water from the topsoil into the subsoil. In the lower parts of the profile the influx from above caused the fast outflow of P-depleted water from the subsoil.

This fast hydrological response may be partly due to a high water content of pre-event water above the capillary barrier of the lower boundary. Although it is known that the boundary conditions of lysimeters may change the flow and transport behavior of water and solutes (e.g., Flury et al., 1999), the experiments demonstrate that there may be preferential flow occurring without large solute losses from the subsoil. Because of the very high P-fixing capacities of both subsoils, almost all P was retained very efficiently. The main conclusion to be drawn is that preferential transport of P-rich water from the topsoil into the subsoil does not necessarily mean large P losses if the preferential flow paths end in the matrix. In such cases the physico-chemical properties of the matrix are very important for determining fate of the solute.

The results of this study also have implications for soil-testing concepts for the assessment of the risk of water pollution due to diffuse losses from agricultural soils (Hesketh and Brookes, 2000; Sims et al., 2000). Based on the P mobility in the topsoil, the soil in the lysimeters might be considered "high-risk." However, the losses were small. Our case study demonstrates the inherent difficulty of such an approach: it only considers the P mobility in (part of) the topsoil and neglects the fate of the mobilized P along its flow path until it enters the water body of interest. This is not an argument for not using such tests, but it demonstrates the crucial role of understanding the entire flow path of a solute and the chemical interactions taking place along this path. The results of this study also indicate that these chemical interactions may differ for different flow paths.

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