

# Dissolved Phosphorus from Undisturbed Soil Cores: Related to Adsorption Strength, Flow Rate, or Soil Structure?

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## ABSTRACT

While the rapid transport of nonadsorbed chemicals is relatively well understood, preferential transport of adsorbable chemicals including P requires further study. Our objective was to characterize subsurface P transport in glaciated soils of the northeastern USA. Large intact columns from five soils with differing structures were subjected in duplicate to both synthetic acid rainfall at a low rate simulating natural rainfall, and ponded water for observing saturated flow. The rain was enriched with inorganic and organic P after baseline conditions were established. Drainage water P concentrations were measured and adsorption isotherms were determined. Type of flow was characterized using Cl breakthrough curves and visualizations of blue dye patterns. Baseline P concentrations in drainage water were 0.02 to 0.04 mg L<sup>-1</sup>. At low flow rates, P appeared in the drainage water soon after application of either inorganic or organic P for the silt loam soil (firm, moderate coarse prismatic parting to moderate medium subangular blocky structure) in which preferential flow paths carried most of the water flow. In contrast, the soils in which matrix type flow dominated (weak fine granular or weak medium subangular blocky structures) had little or no increase in drainage water P. However, under ponded conditions all soils exhibited preferential flow and rapid P breakthrough. Elevated P concentration in the drainage water could not be explained by the P adsorption strength with the possible exception of the sandy loam soil, where the outflow P concentration was consistently low. Variation in flow rate in conjunction with soil structure satisfactorily explained elevated concentrations of dissolved inorganic and organic P in drainage water from surface applied P.

PHOSPHORUS in runoff and subsurface flow from agricultural land contributes to eutrophication of surface water bodies (Scott et al., 1998b; Sharpley et al., 1999). Public awareness of eutrophication and its link to agriculture has led to legislative measures encouraging agriculture to reduce its P contributions to streams (Sharpley et al., 2000). The traditional approach to decreasing P loadings has been by reducing P in runoff by controlling erosion and associated particulate P (Sharpley et al., 1994). Recent studies suggest that particulate P has a much smaller effect on lake or stream eutrophication than dissolved P because particulate P settles to the bottom while dissolved P is directly available for algal growth (Fozzard et al., 1999). Dissolved P can enter waterways via surface and subsurface flow paths, especially through agricultural tile lines (Sims et al., 1998; Stamm et al., 1998; Laubel et al., 1999), and can make up a substantial part of overall P loss during low flow conditions in the summer, when high temperatures

favor eutrophication (Chardon et al., 1997; Delgado and Torrent, 1999; Reddy et al., 1999). This study focused on the subsurface transport of P for soils in the Northeast, which are usually glaciated, with acid pH, and often have a restrictive layer within 1-m depth.

Phosphorus has a high affinity to soil and, therefore, generally moves slowly downward through the soil matrix (Eghball et al., 1990; Sims et al., 1998) or laterally with interflow. Small but significant quantities of P may move via preferential flow paths (Jensen et al., 1998; Ulén et al., 1998; Simard et al., 2000) with little adsorption to the soil matrix (Mansell et al., 1985; Jensen et al., 1998). High rainfall rates will cause water to bypass the soil matrix and flow preferentially through a small portion of the soil (Scott et al., 1998a; Armstrong et al., 1999). Little is known about when the shift from predominantly matrix flow to preferential flow occurs for different soils (Jensen et al., 2000).

Under preferential flow conditions, the greatest P concentrations appear in leachate shortly after P application (Scott et al., 1998a; Stamm et al., 1998; Laubel et al., 1999; Jensen et al., 2000; Simard et al., 2000) and concentrations vary spatially (Stagnitti et al., 1998). Because under udic moisture interpedal spaces, wormholes, and decayed root channels are more prevalent in fine-textured soils regimes, macropore preferential flow is generally considered more significant in these soils, in contrast to coarse-textured soils (Boll et al., 1997; Jensen et al., 1998; Ulén et al., 1998) where fingered and funnel flow may occur. Although the chemical and mineralogical composition of the soil determines P adsorption isotherms and kinetics (Mansell et al., 1977; Parfitt, 1978; Grant and Heaney, 1997), high pore-water velocities can override the kinetics (Armstrong et al., 1999; Simard et al., 2000) because the residence time can be too short for the solute to diffuse to reaction sites on the macropore wall (Jensen et al., 1998).

The various forms and phase transformation reactions of P complicate the prediction of transport (Grant and Heaney, 1997). Evidence of dissolved organic P loss in leachate is mixed. Transport studies on dissolved organic P in soil in pure glycerophosphate form (Castro and Rolston, 1977) indicated that the relative effluent glycerophosphate concentration ( $C/C_0$ ) reached 0.5 after 1.8 pore volumes, as opposed to Cl<sup>-</sup> reaching the same relative concentration after only 0.8 pore volumes. Similarly, limited movement of phytate P was reported by Bowman et al. (1967) who concluded that organic P tended to accumulate in the surface with little downward movement through the root zone. However, long-term field trials using manure application concluded that organic P actually traveled deeper in the profile than ortho P

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Abbreviations: DOC, dissolved organic C.

forms (Sims et al., 1998). Movement and loss of P have been correlated with redistribution of dissolved organic matter in forest soils (Donald et al., 1993), streams and wetlands (Reddy et al., 1999), and cropped and grassed lands (Ekholm et al., 1999).

As a consequence, despite many studies on the adsorption and movement of P in different soils, P transport can be accurately predicted only after breakthrough curves have been established for a range of flow rates, which is cumbersome and impractical for field conditions. In this study, we hypothesize that soil survey descriptions of soil structure with both rainfall rate and moisture status can provide an estimate for the potential of preferentially transported P. The objective is to test this hypothesis for a range of soils from the northeastern USA.

## MATERIALS AND METHODS

Phosphorus movement (both ortho and organic) was measured in five different soils with widely varying structural properties under low rainfall intensity and under ponded conditions. The soils were characterized for the extent of macropore flow using both  $\text{Cl}^-$  tracer breakthrough curves as well as dye staining of flow paths. Phosphorus adsorption isotherms were determined to compare the adsorption potential with transport/retention of solute P.

### Site Descriptions

Five soils from New York State ranging in texture from sandy loam to clay loam, with structures ranging from massive to moderate coarse, prismatic were examined. Taxonomic classification, texture, and structure of important pedological units in each soil are presented in Table 1. The soil series examined were: (i) Hudson silt loam/silty clay loam (firm, moderate coarse prismatic parting to medium, subangular blocky structure); (ii) Honeoye loam (weak, medium, subangular blocky); (iii) Lackawanna channery silt loam (weak medium subangular blocky parting to medium granular); (iv) Genesee silt loam (granular, friable); and (v) Arkport sandy loam (massive to friable, weak, medium subangular blocky). All soils were moderately to well-drained, and occur in udic moisture regimes.

The soils were derived from various parent materials (Soil Survey Division, USDA-NRCS, 2001). The Hudson series was

developed in clayey and silty lacustrine sediments, with moderate slow surface permeability and moderate subsurface permeability. The Honeoye series was formed in glacial till strongly influenced by limestone and calcareous shale. The Lackawanna series, formed in till derived from reddish colored sandstone, siltstone, and shale, has a dense fragipan starting at 43 to 90 cm below the soil surface. The Genesee soil series was formed in loamy alluvium on flood plains, moderately permeable in the solum and moderately or moderately rapid permeable in the substratum. The Arkport soil series, formed in glacio-fluvial deposits, has a high content of fine and very fine sand, with thin horizontal bands of loamy material in the subsoil at the 40-cm depth. Earlier experiments have shown a well-defined macropore network and preferential flow for Hudson and Arkport soils (Steenhuis et al., 1994; Ogawa et al., 1999).

### Excavation and Sampling

Intact columns with a diameter slightly smaller than 36 cm were excavated from an area between two parallel trenches that were dug 75 cm apart. After excavating, the soil columns were shaped by shaving the soil and a polyethylene drainage pipe (36 cm i.d.) was placed around each column. Expanding polyurethane foam was injected between the soil and the pipe and allowed to cure before columns were transported to the laboratory. Target lengths were 55 cm, but column lengths were limited by the unconsolidated platy rock fragments at the 40-cm depth for the Lackawanna soil and, in the Arkport, by clean coarse sand lenses at a slightly shallower depth.

### Column Preparation and Rainmaker

In the laboratory, the bottom 1 cm of soil was removed from the column base, which was fitted with a drainage system consisting of a 2-mm mesh nylon screen placed against the soil followed by 1-cm thick plastic grating and a double-ring plastic support plate with a center drainage hole. The plate had an outer perimeter ring (24 cm i.d.) that separated and excluded any flow along the boundary from the flow through the center of the column. Silicone sealant was used for making the drainage assembly watertight. The surface of the columns remained undisturbed except for the removal of surface organic residues and rock fragments.

For the unsaturated flow experiments, water and solutes were applied using a rainmaker 3 m above the soil surface,

**Table 1. Soil classification and description of selected horizons.**

Soil series and classification	Description of texture and structure
<b>Arkport:</b> coarse-loamy, mixed, active, mesic Lamellic Hapludalfs	A (0–23 cm): very fine sandy loam, weak fine granular structure, very friable; BE1 (23–38 cm): very fine sandy loam, weak fine granular structure, friable; BE2 (38–71 cm): loamy fine sand with very sandy loam lamellae, massive, very friable
<b>Hudson:</b> fine, illitic, mesic Glossaquic Hapludalfs	Ap (0–13 cm): silt loam, moderate, medium granular, friable; E (13–20 cm): silt loam, weak thick platy, friable; B/E (20–41 cm) silty clay, moderate very coarse prismatic structure parting to moderate medium subangular blocky, firm; Bt (41–71 cm): silty clay, moderate very coarse prismatic structure parting to moderate medium subangular blocky, firm
<b>Honeoye:</b> fine-loamy, mixed, active, mesic Glossic Hapludalfs	Ap (0–20 cm): loam, moderate medium and fine granular structure, friable; B/E (20–30 cm): loam, moderate medium subangular blocky structure, friable; Bt1 (30–46 cm): gravelly loam, moderate medium subangular blocky, friable
<b>Genesee:</b> fine-loamy, mixed, superactive, mesic Fluventic Eutrudepts	Ap (0–20 cm): silt loam, moderate fine and medium granular, friable; Bw1 (20–36 cm): silt loam, weak medium subangular blocky structure parting to weak medium granular, friable; Bw2 (26–60 cm): loam, weak medium subangular blocky structure parting to weak medium granular, friable
<b>Lackawanna:</b> coarse-loamy, mixed, active, mesic Typic Fragiudepts	Ap (0–20 cm): channery silt loam, weak fine granular structure, friable; Bw1 (20–33 cm): channery silt loam, weak thin platy structure parting to weak fine granular, friable; Bw2 (33–66 cm): channery loam, weak fine and medium subangular blocky, friable

Table 2. Outline of performed experiments.

Ongoing experiments	Experiment	Dates	Days to next stage	amount		rate	Rainfall			Measured	
				begin	end		cm h <sup>-1</sup>	ortho P	phytate P		Cl
1	baseline ortho P	January	12	begin	end	0.2	0	0	0	ortho P, C	5 soils
2	obtaining steady state flow	3/16-3/28	13	-58	0	0.2	0	0	0	ortho P, org P	5 soils
2	ortho P added	3/28-5/5	17	0	197	0.2	10	0	0	ortho P, org P	5 soils
2, 3	phytate added	4/10-4/27	3	62	144	0.2	10	25	0	ortho P, org P	5 soils
2, 3	cleanup surface	4/28-5/1	1	144	158	0.2	0	0	0	ortho P, org P	5 soils
2, 3	phytate high rate	5/1-5/2	4	158	178	0.8	10	25	0	ortho P, org P	5 soils
2, 3	leaching with ortho P	5/2-5/5	7	178	197	0.2	10	0	0	ortho P, org P	5 soils
2, 3	leaching acid rain	5/5-5/12	6	198	231	0.2	0	0	0	ortho P, org P	5 soils
2, 3, 4	chloride breakthrough	5/12-5/18	14	231	260	0.2	0	0	60	ortho P, org P, Cl	5 soils
4	leaching	5/18-6/10		260		0.2	0	0	0	Cl	5 soils
5	blue dye	6/10-6/13				0.2	0	0	0	none	5 soils
6	saturated P	summer				ponded	25	0	0	ortho P	3 soils
7	saturated Cl	September				ponded	0	0	60	Cl	2 soils

delivering drop sizes of approximately 3.2 mm. The rainmaker consisted of two dripper needles mounted on a X-Y computer-controlled tracking system, which caused the dripper to randomly distribute rainfall over a 110 by 120 cm rectangular area. Rainwater was pumped using a peristaltic pump to the drippers from a 120-L supply barrel, which was in turn fed from a larger 285-L barrel. The supply barrels had constant head devices and mechanical agitation was used to minimize the potential for concentration gradients. To mitigate raindrop impact and consequent surface sealing, the surface of the columns was covered with multiple layers of plastic mesh with 1-mm openings. Saturated flow experiments were performed by maintaining a constant head of 0.5 cm ponded on the soil surface by a Mariotte bottle-fed system.

The leachate was collected, immediately filtered (0.45- $\mu$ m nominal porosity), and stored in closed bottles at 4°C until analysis (usually within 48 h for ortho and organic P). Leachate was not filtered for the Cl<sup>-</sup> breakthrough tests.

### Leaching Experiments

Leaching experiments were performed with various solutes and rainfall rates with replicate soil columns for each of the five soil types. These 10 columns were used for five different leaching experiments (Table 2). The experiments were sequenced so that they would minimally interfere with each other. First, baseline P concentrations were assessed for 12 d. After establishing steady state, movement of ortho P through the columns was then examined. After 13 d, organic P in the form of phytic acid was applied twice to each column at two different flow rates. Chloride breakthrough curves were then determined for all the columns over the course of 12 d. Finally, a 1% (wt/wt) solution of brilliant blue dye (C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>3</sub>) (FD&C blue dye No. 1, Warner-Jenkinson, St. Louis, MO) was added to indicate flow paths (Steenhuis et al., 1990; Flury and Flühler, 1995; Forrer et al., 2000). Infiltration characteristics for these soils were determined under steady unsaturated conditions during the experimental period. In addition to five unsaturated flow experiments, two additional saturated flow experiments were performed on an additional set of six columns (two each from Hudson, Honeoye, and Genesee). Both P and Cl were applied by shallow ponding of water on the surface of the columns. The experiments are summarized in Table 2 and described below in chronological order.

#### Experiment 1—Baseline Ortho P and C

For Exp. 1, synthetic acid rain was applied at a constant 0.2 cm h<sup>-1</sup> rate to the moist field columns. The acid rain (pH 4) was similar to that occurring in the northeastern USA with a composition as reported in Richards et al. (2000). Unlike all subsequent experiments, the two replicates were conducted sequentially, the first running from 10 Jan. to 21 Jan. 2000 and the second replicate from 16 Feb. to 3 Mar. 2000. Leachate flowed in two containers and was collected twice daily. A subsample was taken and filtered through the 0.45- $\mu$ m filter. Ortho P and organic C were measured in the filtrate (referred to as “baseline P and C”).

#### Experiment 2—Transport of Ortho P

After a short break, acid rain was added on 16 Mar. 2000 at a rate of 0.2 cm h<sup>-1</sup>. Replicates for this and all subsequent experiments were run simultaneously. Once the leachate P concentration had stabilized, acid rainfall with 10 mg P L<sup>-1</sup> (as KH<sub>2</sub>PO<sub>4</sub>) was initiated on 28 Mar. 2000 at the same 0.2 cm h<sup>-1</sup> rate. This concentration was selected because it was near the greatest concentration in runoff from recently applied,

heavily manured fields observed over many years (Walter et al., 2001). The P application was stopped on 5 May 2000 after almost 240 cm of cumulative rain. Filtered leachates were analyzed for ortho and total P. Experiments 3 and 4 were superimposed on this treatment (e.g., other solutes in addition to the 10 mg ortho P L<sup>-1</sup>).

### Experiment 3—Transport of Organic P

Since the P concentration in the drainage water for Exp. 2 was low for four of the five columns, input concentrations for organic P were increased. Consequently, phytate (phytic acid sodium salt, C<sub>6</sub>H<sub>6</sub>O<sub>24</sub>P<sub>6</sub>Na<sub>12</sub>) was added at a concentration of 25 mg L<sup>-1</sup> to the acid rain water (already containing 10 mg ortho P L<sup>-1</sup>) and was applied to the same columns at two rain intensities: 0.2 cm h<sup>-1</sup> in Phase I and 0.8 cm h<sup>-1</sup> in Phase II. Phase I began on 10 Apr. 2000 and continued until 27 Apr. 2000. At the end of Phase I, dispersion of clay at the soil surface was visible as well as a white precipitate, which formed from a phytic acid reaction with the soil Fe (Bowman et al., 1967). While P-free (ortho and phytate P) rain continued, the surface of all the columns was vacuum cleaned to remove the dispersed soil, which restored pore openings to the surface. To avoid further clay dispersion, 42 mg Ca L<sup>-1</sup> (P-free CaSO<sub>4</sub>) rain was added for 3 d (28, 29, and 30 Apr. 2000). Phase II leaching at 0.8 cm h<sup>-1</sup> rain intensity included the addition of Ca to avoid dispersion. On 1 May 2000, the same phytic acid and ortho P solution was adjusted to a Na adsorption ratio (SAR) of 7.5 by adding CaSO<sub>4</sub>. This was applied with 0.8 cm rain h<sup>-1</sup>. On 2 May 2000 and after a total application of 20 cm, the rain intensity was reduced back to 0.2 cm h<sup>-1</sup>. Phosphorus-free acid rain was started at a rate of 0.2 cm h<sup>-1</sup> on 5 May 2000. Over this period of time, both total P and ortho P were determined in the leachate, with organic P determined by difference (total minus ortho).

### Experiment 4—Unsaturated Cl<sup>-</sup> Breakthrough

On 12 May 2000, a Cl<sup>-</sup> solution (600 mg Cl<sup>-</sup> L<sup>-1</sup>, made from CaCl<sub>2</sub> in tap water originally containing <20 mg Cl<sup>-</sup> L<sup>-1</sup>) was added to all columns. On 18 May 2000 the outflow concentration equalled the inflow concentration in all columns, and the rain solution was switched back to tap water. Percolate sampling varied over the course of the experiment from several times a day (when rapid changes were expected to occur) to twice a day under more stable conditions.

### Experiment 5—Marking Unsaturated Flow Paths with Blue Dye

Experiments were performed only with unsaturated flow because previous studies in our laboratory had shown preferential flow under ponded conditions is common for soils in the northeastern USA (Boll et al., 1997). After Exp. 4 ended, the rain was continued for another 3 d, after which a 1% solution of FD&C blue dye No. 1 was applied at a rate of 0.2 cm h<sup>-1</sup>. The amount of blue dye solution added was determined by trial and error such that the ultimate dye penetration would be near the bottom of the column. For the Hudson soil, cumulative applications of 0.5 cm with the blue dye solution gave the best results. An application of 2.5 cm blue dye yielded the best outcome for the other soils. After drainage, the columns were first cut longitudinally into two halves. One half was cut sequentially in longitudinal (vertical) layers 2- to 3-cm thick. The other half was sliced into 2- to 3-cm thick horizontal layers. Each exposed face was photographed (Lackawanna not shown because of poor quality).

### Experiment 6—P Transport under Saturated Flow

Phosphorus movement under saturated flow was examined in a different set of undisturbed columns, two each of Hudson, Honeoye, and Genesee soils. A constant head of 0.5 cm was maintained by a Mariotte bottle-fed system. A 25 mg P L<sup>-1</sup> solution (KH<sub>2</sub>PO<sub>4</sub> in tap water) was applied at a constant flow rate. Leachate was collected several times during the first 2 h immediately after switching to the P solution and twice per hour thereafter. After percolate P had reached the inflow concentration, the solution was switched back to tap water. This occurred at widely varying cumulative percolate depths for different soils.

### Experiment 7—Saturated Cl<sup>-</sup> Breakthrough

Chloride breakthrough under saturated conditions was determined for the columns that had the fastest (Hudson) and the slowest (Genesee) breakthrough of Cl<sup>-</sup> under unsaturated conditions. Water containing 600 mg Cl<sup>-</sup> L<sup>-1</sup> (from CaCl<sub>2</sub>) was ponded with a head of 0.5 cm, resulting in flow rates of 17.6 and 6.8 cm h<sup>-1</sup> for the Hudson and Genesee soils, respectively.

### Experiment 8—Batch P Adsorption Isotherm

Phosphorus adsorption coefficients (*k<sub>d</sub>*) for the soils were determined from adsorption isotherms developed through batch experiments (Syers et al., 1973; Castro and Rolston, 1977). Soil from the upper two horizons of each series was passed through a 2-mm sieve. Next, 10 g of soil was equilibrated in triplicate with 10 mL aqueous solutions containing 0, 6, 12, 36, 60, 84, 105, 150, 300, 600, 1200, and 1800 mg P L<sup>-1</sup> (as KH<sub>2</sub>PO<sub>4</sub>). To better mimic what occurs in field soils, mechanical shaking was avoided and the suspension was gently hand mixed and left for 24 h to attain sorption equilibrium at room temperature (Chen et al., 1996) and then filtered (0.45-μm nominal porosity). The amount of P added but not recovered in solution was assumed to be adsorbed. Amount of P sorbed by the soil was calculated from the concentration change in solution phase. Phosphorus sorption was expressed on a dry-soil weight basis.

### Parameter Estimation

The adsorption isotherm was fitted to the Langmuir equation (Castro and Rolston, 1977), which has the form:

$$X = \frac{bKC_w}{1 + KC_w} \quad [1]$$

or rearranged in linear form:

$$\frac{C_w}{X} = \frac{1}{Kb} + \frac{C_w}{b} \quad [2]$$

where *X* equals P sorption by the soil (mg P kg<sup>-1</sup> soil), *C<sub>w</sub>* equals P concentration in solution at equilibrium (mg P L<sup>-1</sup>), *K* equals the constant related to binding strength (when *C* = 1/*K* then *X* = *b*/2 or half of the sites on the soil are filled with P) [L (mg P)<sup>-1</sup>], and *b* = maximum P sorption on the soil (mg P kg<sup>-1</sup> soil).

Plots of *C<sub>w</sub>/X* versus *C<sub>w</sub>* were linearly regressed; *b* was found by the reciprocal of the slope of the regression line. The Langmuir constant *K* was obtained by dividing the slope (1/*b*) by the intercept (1/*Kb*).

To investigate the degree of adsorption at the application concentration of 10 mg L<sup>-1</sup>, we determined the adsorption partition coefficient, *k<sub>d</sub>*, by finding the tangent to the Langmuir isotherm at this concentration. Differentiating Eq. [1] with respect to *C* gives:

$$\frac{dx}{dC_w} = \frac{bK}{1 + KC_w} - \frac{bK^2C_w}{(1 + KC_w)^2} \quad [3]$$

or:

$$k_d = \frac{1}{1 + KC_w} \left[ bK - \frac{bK^2C_w}{(1 + KC_w)} \right] \quad [4]$$

To obtain the parameters describing solute flow, the Cl<sup>-</sup> breakthrough concentrations were fitted to convective-dispersive models. We used the nonlinear program CXTFIT for the one-domain Cl<sup>-</sup> breakthrough (Toride et al., 1995). From the CXTFIT output, we calculated the average pore-water velocity, average retention time, and dispersivity for Cl<sup>-</sup>.

**Analytical Methods**

Phosphorus in solution was analyzed colorimetrically using the ascorbic acid Standard Method 424F (American Public Health Association, American Water Works Association, Water Pollution Control Federation [APHA/AWWA/WPCF], 1985). Total dissolved organic C (DOC) was determined with an OI Analytical Model 1010(OI Analytical, College Station, TX) wet oxidation analyzer which conforms to Standard Method 5310D (American Water Works Association, 1985). Total P was determined by an acidic persulfate digestion procedure (Standard Method 424C.III, American Water Works Association, 1985). Five milliliters of percolate was added to the digestion vessel followed by 2 mL of 2.5 M H<sub>2</sub>SO<sub>4</sub> and 400 mg ammonium persulfate. The digestion vessels, with un-tightened lids, were placed in an autoclave for 1 h at 120°C. When cool, the digested solution was transferred quantitatively to 25-mL volumetric flasks and diluted to 25 mL with 8 mL of coloring reagent and deionized water. Phosphorus was determined colorimetrically with the standards carried throughout the digestion process.

Chloride in the percolate was analyzed with a potentiometer (Orion ionmeter 720 A, Thermo Orion, Beverly, MA)

equipped with a Cl<sup>-</sup> selective electrode (Orion 94-17B) used in conjunction with a standard reference electrode (Orion 94-02), and temperature probe calibrated for the given range of Cl<sup>-</sup> concentration. The instrument was calibrated at least once a day with four standards made in tap water to account for background concentrations.

**RESULTS**

The chronological order of experiments was planned to minimize interference between experiments by doing the baseline study first and the destructive sampling last. However, the results will be presented in the following conceptual order: (i) preferential flow path determinations using blue dye and Cl<sup>-</sup> (Exp. 4, 5, and 8); (ii) soil P adsorption characteristics (Exp. 8); and (iii) drainage water P concentrations following applications of acid rain, ortho P, and organic P (Exp. 1, 2, 3, and 6).

**Flow Path Marking**

Figure 1 shows the distribution pattern of blue dye under unsaturated flow conditions in the undisturbed soil columns after application of 0.5 cm (Hudson) or 2.5 cm (all other soils) dye solution at 0.2 cm h<sup>-1</sup> (Exp. 5). All soils had an uneven dye front and a distribution zone (Fig. 1), defined as the wetted region in the surface of the soil where the applied water moves laterally to the preferential flow paths. Visible in the Hudson is a thin distribution zone and preferential flow paths to a depth of 20 to 25 cm. There is also a preferential flow path at greater depth that originated in the distribution zone at a location different than the photographed cross-section. Preferential flow paths in the Hudson followed earthworm (annelid) channels, while in the Honeoye

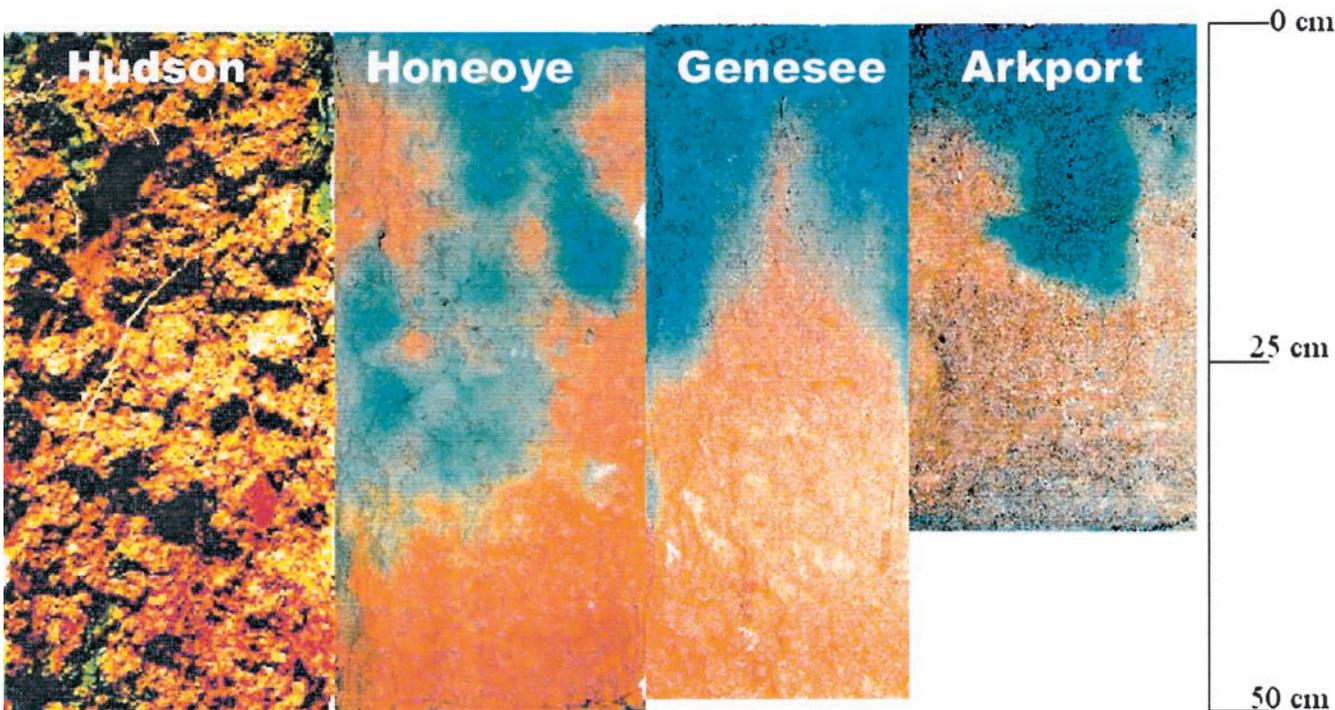


Fig. 1. Blue dye staining of four of the five soils examined. The rainfall/dye intensity was 0.2 cm h<sup>-1</sup>, stopped after a total accumulation of 0.5 cm for the Hudson soil and after 2.5 cm for other soils.

soil, the dye followed ped surfaces but diffused radially because the peds were not firm. The Arkport wetted uniformly in the distribution zone with a depth of 5 to 10 cm, comparable with but more uniformly than the Hudson. Below the distribution zone, a 10-cm wide finger formed that moved slightly upward after it reached a coarse lens (Fig. 1). Fingering flow is caused by instability at the wetting front and occurs in homogenous soils. The Lackawanna (not shown) and Genesee had diffuse flow with no signs of preferential dye movement through macropores, as both soils had a basically granular structure. For the Genesee soil, a wetting front with two finger-like features formed.

Horizontal cross-sections taken at 2.5-cm intervals (not shown because of poor contrast) give further insight into how water and dissolved constituents moved downward from the surface. For all soils, the upper 1 to 5 cm was homogeneously stained, but differences between soils appear below that depth. In the strongly structured Hudson soil, the dye is visible only as discrete spots associated with fractures and biopores; in the Honeoye soils, the dye appears as diffuse spots around biopores. In the Arkport, Genesee, and Lackawanna columns, the dye is distributed as diffuse spots not associated with structural features.

In summary, the main difference between the soils is the degree of preferential flow. In the Hudson soil, with its dense matrix ("firm" in Table 1), there is very little movement into the matrix from the preferentially moving water, which results in only a very small portion of the matrix being wetted. Thus, a small amount of water can move deeply. In the other soils, the conductivity of the matrix is greater and a larger portion of the matrix is wetted. Consequently, for a given amount of water applied, the dye front penetration is deeper for the Hudson than the other soils.

### Chloride Breakthrough

The relative  $\text{Cl}^-$  concentrations in the outflow water are plotted against cumulative rainfall in Fig. 2 for selected columns under both steady unsaturated (Exp. 4) and saturated (Exp. 7) conditions. As expected, there was a large variation in  $\text{Cl}^-$  breakthrough among the five soils and between the two flow conditions. In the Hudson soil, concentrations increased almost immediately after the tracer was applied for both the unsaturated and saturated columns. The ratio  $C/C_0$  reached a plateau after 15 cm of rainfall under unsaturated conditions (Fig. 2a) and 4 cm when the water was ponded (Fig. 2b). For the Genesee soil, the initial unsaturated flow  $\text{Cl}^-$  breakthrough took the longest of all soils tested and did not occur until 10 cm of outflow (Fig. 2a), but under saturated flow conditions, the initial delay was much shorter, similar to the Hudson soil. However, the concentration in the drainage water did not become equal to the input concentration until 30 cm of outflow (Fig. 2b). After switching back to acid rain, the recession concentration profiles in the percolate mirrored the rising concentration profiles. For the Hudson, a sharp decline in  $\text{Cl}^-$  concentration was noted compared with the

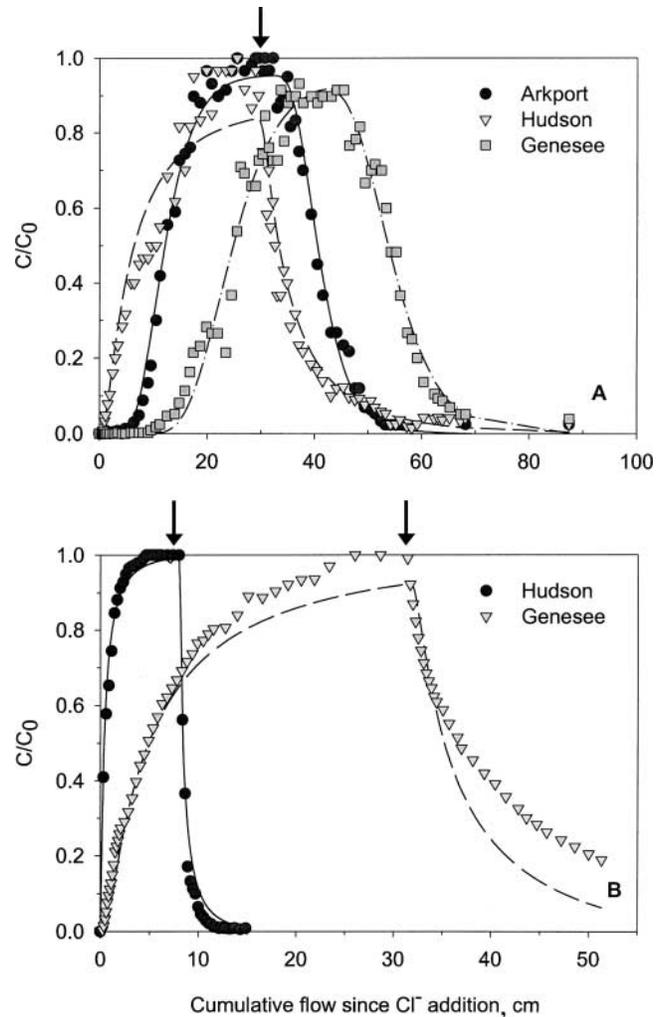


Fig. 2. Chloride concentration in drainage water in response to a  $\text{Cl}^-$  pulse. The arrow indicates  $\text{Cl}^-$  discontinued in rainfall: (a) unsaturated flow ( $0.2 \text{ cm h}^{-1}$  application rate, one replicate each of Hudson, Arkport, and Genesee soils); and (b) saturated flow (water applied under ponded conditions resulting in flow rates of  $17.6$  and  $6.8 \text{ cm h}^{-1}$  for Hudson and Genesee soils, respectively). Symbols are observed values. Lines are convective-dispersive equation best fits; parameter values are given in Table 3.

other soils, particularly the Genesee (Fig. 2a). The rapid movement of water and solutes through preferential flow paths for the Hudson under unsaturated conditions was corroborated by the blue dye experiments in Fig. 1.

For both flow rates, the solute velocity and the dispersion coefficient were obtained by fitting the convective-dispersive equation to the observed  $\text{Cl}^-$  concentration in the leachate using CXTFIT. The velocity, the dispersivity (i.e., quotient of the dispersion coefficient and the velocity), and the goodness of fit ( $R^2$ ) for all saturated and unsaturated experimental runs are shown in Table 3. Unsaturated  $\text{Cl}^-$  breakthrough curves for the Arkport, Honeoye, Genesee, and Lackawanna columns in which the matrix flow dominated (as indicated by the blue dye experiments) fitted the convective-dispersive equation well with  $R^2$  between 0.94 and 0.99. Dispersivity values were between 1 and 7 which are in the range observed (Roth et al., 1991). Solute velocities were, as

**Table 3. CXTFIT fitted parameters for the chloride breakthrough curves under saturated and unsaturated conditions.**

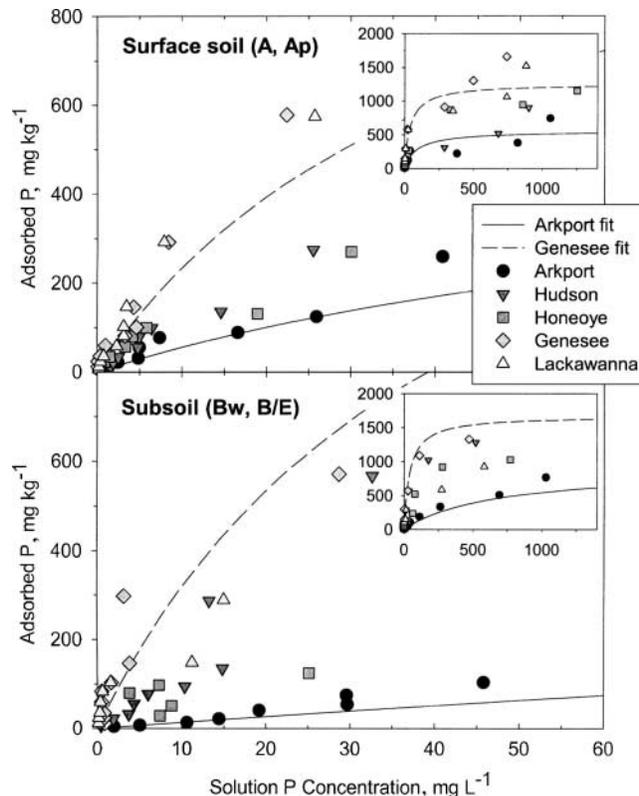
Soil	Flow rate/ replicate	CXTFIT parameters		
		Velocity	Dispersivity	R <sup>2</sup>
		cm h <sup>-1</sup>	cm	
Arkport	unsaturated 1	0.6	2.6	0.99
	unsaturated 2	0.44	1.1	0.96
Hudson	unsaturated 1	0.67	27.4	0.95
	unsaturated 2	0.66	208.2	0.86
Honeoye	saturated	9.7	56.5	0.99
	unsaturated 1	0.59	6.9	0.98
Genesee	unsaturated 2	0.52	2.7	0.99
	unsaturated 1	0.42	2.1	0.98
Lackawanna	unsaturated 2	0.42	4	0.97
	saturated	0.88	67.4	0.94
Lackawanna	unsaturated 1	0.46	2	0.98
	unsaturated 2	0.67	3.9	0.97

expected, 2 to 4 times greater than the application rate. For the Hudson columns, under both saturated and unsaturated flow regimes (which experienced preferential flow as indicated by blue dye), the CXTFIT algorithm attempted to fit the outflow data by greatly increasing the dispersivity, resulting in parameters without physical meaning. The same was true for the Genesee soil under saturated flow conditions.

**Phosphorus Adsorption Isotherms**

The fitted Langmuir isotherm (Eq. [1]) adsorption data for surface (A, Ap) and subsurface (Bw, B/E) soil horizons are listed in Table 4 (Exp. 8). In general, the Langmuir isotherm fitted the data well with an R<sup>2</sup> of 0.90 or better except for the Arkport soil where the R<sup>2</sup> was approximately 0.80 (Fig. 3). The figure depicts the range of concentrations of interest (<60 mg P L<sup>-1</sup>). To avoid clutter in the figure, only the boundary isotherms (i.e., the weakest and strongest P adsorbers) were given trend lines. Arkport adsorbed the least P for both A and B horizons. Genesee and Lackawanna had the greatest affinity for P, with Lackawanna showing slightly greater affinities at low concentrations (not shown).

The adsorption partition coefficients shown in Table 4 were calculated with Eq. [4] by using the fitted Langmuir isotherm parameters (Table 4) at C = 10 mg L<sup>-1</sup>. The adsorption partition coefficient is the quotient of the concentration of P adsorbed to the soil and the soil solution concentration. It is assumed to be constant over the range of concentration that occurs in the soil. The surface horizons from both the Arkport and Hudson soils had the smallest adsorption partition coefficient for the A horizon (Table 4). The Honeoye surface soil had slightly less P adsorption potential than both the



**Fig. 3. Soil P adsorption isotherms: (a) surface soil layer (A, Ap) and (b) subsoil (Bw, B/E) horizon. Inserted figures depict the whole range of values. Symbols represent the average of three replicates. Lines are fitted Langmuir isotherms for Arkport (lower) and Genesee (upper); fitted lines for other soils fell between those shown.**

Genesee and Lackawanna but greater than the Hudson and Arkport. With a coarse loamy sand texture, the Arkport sorbed the lowest amount of P in the subsurface B horizon. The Genesee and Lackawanna soils, in contrast, sorbed the most P.

**Baseline Ortho Phosphorus and Dissolved Organic Carbon in Leachate**

Mean baseline leachate P concentrations (Exp. 1) were 0.08 mg L<sup>-1</sup> for all columns with 60 cm simulated acid rainfall spread over 12 d (Table 5). The greatest average concentrations were in the Arkport. Average baseline P concentrations in the Honeoye, Genesee, and Lackawanna were 0.05 mg L<sup>-1</sup> (Table 5). There was a surprisingly large short-term variation in concentrations for all columns. An example of the variation is given for Replicate 1 in Fig. 4. In one Arkport column, initial

**Table 4. Langmuir adsorption parameters and linear adsorption isotherm. K is defined by Eq. [1] (L mg<sup>-1</sup>), b is the maximum amount of P adsorbed (mg kg<sup>-1</sup> soil), R<sup>2</sup> is the regression coefficient, and k is the adsorption partition coefficient (L kg<sup>-1</sup>) tangent to isotherm at a P concentration in water of 10 mg L<sup>-1</sup>.**

	Surface horizon A(p)				Subsurface horizons (Bw, B/E)			
	K	b	R <sup>2</sup>	k	K	b	R <sup>2</sup>	k
Arkport	0.011	556	0.78	4.8	0	910	0.8	1.4
Hudson	0.017	526	0.94	6.5	0	1670	0.89	10.7
Honeoye	0.013	1250	0.99	12.4	0	1430	0.91	4.6
Genesee	0.025	1430	0.94	22.6	0.02	1670	0.98	24.7
Lackawanna	0.023	1250	0.94	19.5	0.04	1250	0.97	26.1

**Table 5. Average concentration and standard deviation for the baseline study (Exp. 1), ortho P addition (Exp. 2), and the first pulse of the phytate-P addition (Exp. 3) for the unsaturated flow experiments.**

Soil	Baseline		Ortho P addition		Organic P addition first pulse	
	average	stdev	average	stdev	average	stdev
	$\text{mg L}^{-1}$					
Arkport	0.14	0.11	0.29	0.16	0.11	0.17
Hudson	0.1	0.08	3.17	1.54	2.46	1.83
Honeoye	0.05	0.08	0.08	0.19	0.15	0.27
Genesee	0.05	0.09	0.03	0.06	0.34	0.5
Lackawanna	0.05	0.08	0.07	0.17	0.21	0.32

leachate P was as high as  $0.6 \text{ mg L}^{-1}$  (Fig. 4). In both the Arkport and Hudson columns, elevated concentrations were found shortly after acid rain application began. Leachate P was consistently less in the Lackawanna, Honeoye, and Genesee soils except for the fact that leachate P from all columns peaked once at about 30 cm of rain application for Replicate 1 (Fig. 4) and at 40 cm for Replicate 2 (not shown).

Dissolved organic C (data not shown) in the leachate also varied with the soil type: Arkport columns had the greatest initial DOC ( $25\text{--}30 \text{ mg L}^{-1}$ ), while Genesee had the least ( $7\text{--}12 \text{ mg L}^{-1}$ ). Unlike P, DOC levels steadily decreased, stabilizing between 3 to  $10 \text{ mg L}^{-1}$  for all soils.

### Phosphorus Transport

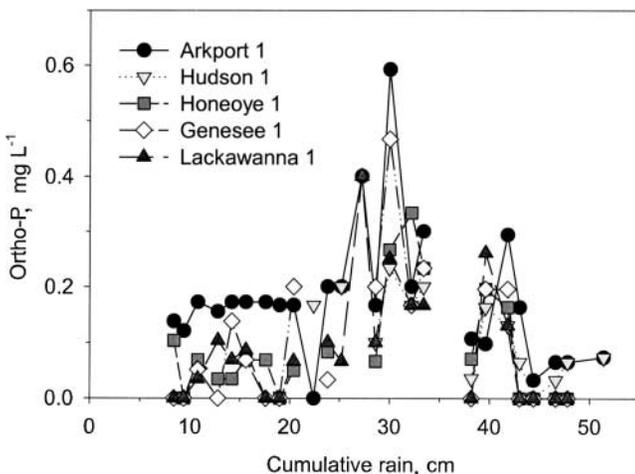
Ortho P breakthrough at steady unsaturated flow ( $0.2 \text{ cm h}^{-1}$  rain intensity) and saturated flow are presented first, followed by organic P breakthrough under unsaturated conditions.

**Ortho P breakthrough at steady unsaturated flow (Exp. 2).** At the  $0.2 \text{ cm h}^{-1}$  rain intensity, significant ortho P breakthrough occurred only in those Hudson columns in which P appeared in the leachate shortly after application, i.e.,  $<1 \text{ cm}$  percolate depth (Fig. 5). Percolate P then steadily increased to a relative concentration of 0.5 to 0.65 after 60 cm of rain application (Fig. 5). This P breakthrough was as fast or faster than  $\text{Cl}^{-}$ , indicating no retardation in the arrival time. After phytate P was added at 62 cm of rain, the Hudson leachate ortho P concentration initially decreased, followed

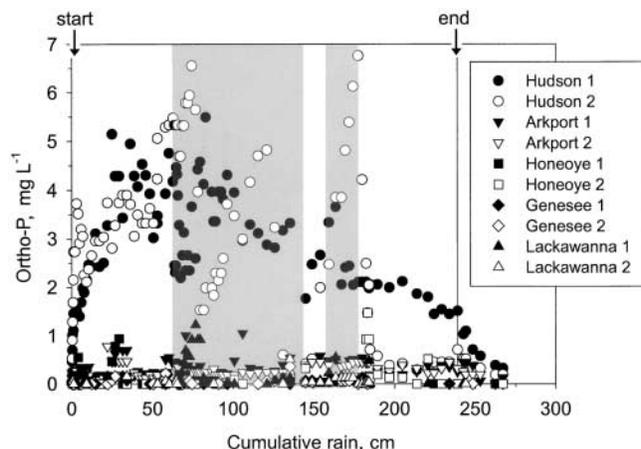
by an increase (quickly for Hudson Column1 [Hud1] and gradually for Column Hud2). The ortho P in the Hud2 increased sharply after the second phytate P addition at 158 cm of rain whereas the other columns showed minor breakthroughs (Table 5, Fig. 5). The Arkport had an elevated (relative to the baseline) ortho P concentration throughout the experiment while both the Honeoye and Lackawanna occasionally had elevated concentrations at 30 and 60 cm of rain.

**Ortho P breakthrough with saturated flow (Exp. 6).** Under saturated conditions, ortho P appeared immediately in the first few centimeters of the Hudson, Genesee, and Honeoye drainage water (Fig. 6). The maximum relative P concentration ( $C/C_0$ ) attained in the runoff water differed between soils. In the Honeoye and Genesee soil series, the relative effluent concentrations were between 0.5 and 0.75 even after an effluent depth of 250 cm. One Genesee column was close to 0.5 indicating, as discussed later, a greater portion of matrix flow compared with the other soils. After the influent P was halted, the effluent P concentration dropped more rapidly in the Hudson (Fig. 6a) columns than in the Genesee (Fig. 6b) and Honeoye Replicate 2 (Fig. 6c) columns.

**Organic P breakthrough (Exp. 3).** Phytate P ( $25 \text{ mg L}^{-1}$ ) was added after 62 cm of rain in Exp. 3 to a solution that already contained  $10 \text{ mg L}^{-1}$  ortho P. The average organic P in the leachate before the application of phytic acid was 1 to  $2 \text{ mg L}^{-1}$  in Hud2, 0.5 to  $1 \text{ mg L}^{-1}$  in Hud1, and  $<0.5 \text{ mg L}^{-1}$  in all other columns (Fig. 7). Phytate P appeared rapidly in the percolate from both Hudson columns, while the other soil columns showed



**Fig. 4. Baseline ortho-P concentrations in the outflow water under an application rate of  $0.2 \text{ cm h}^{-1}$  for one replicate of each soil.**



**Fig. 5. Ortho-P concentrations in outflow water under unsaturated flow ( $0.2 \text{ cm h}^{-1}$  flow rate). Shaded areas indicate periods when phytate P was added.**

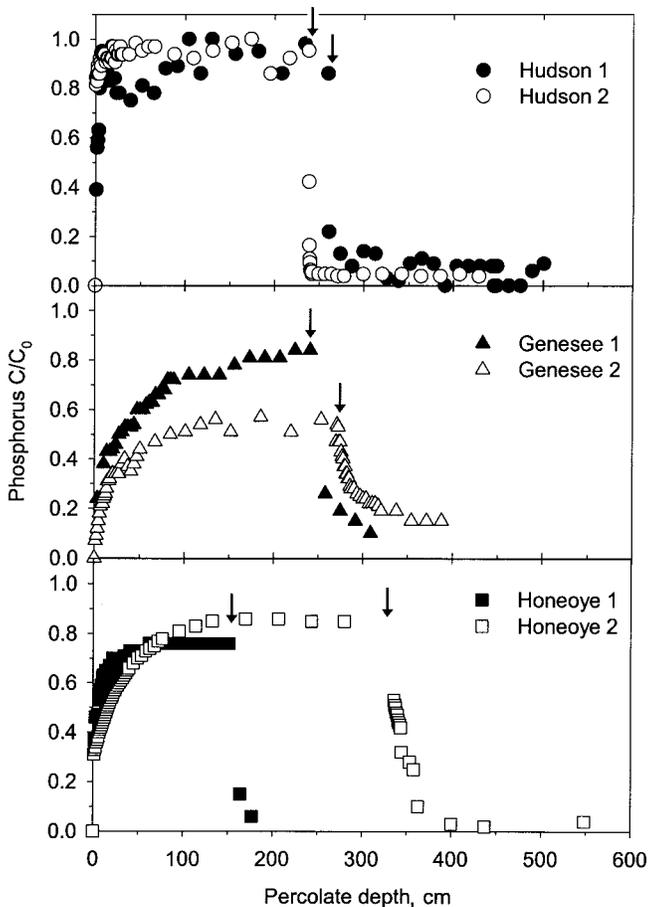


Fig. 6. Ortho-P concentrations in outflow water under ponded conditions: (a) Hudson, (b) Genesee, and (c) Honeoye. Arrows indicate when the applied solutions were switched back to water.

a limited leaching of organic P (Fig. 7 and 8). In the Hudson columns, effluent organic P increased to 9 mg L<sup>-1</sup> for Hud2 shortly after application and to 6 mg L<sup>-1</sup> after a brief delay in Hud1. After termination of phytate containing rain, organic P decreased steadily in the Hudson columns. The second time phytate was added (after 158 cm of rain), the Hud2 organic P increased slightly.

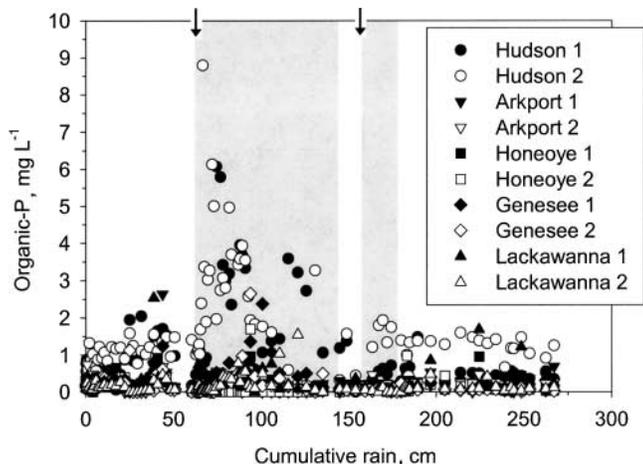


Fig. 7. Organic P concentrations in outflow water under unsaturated flow (0.2 cm h<sup>-1</sup> flow rate). Shaded areas indicate periods when phytate P was added.

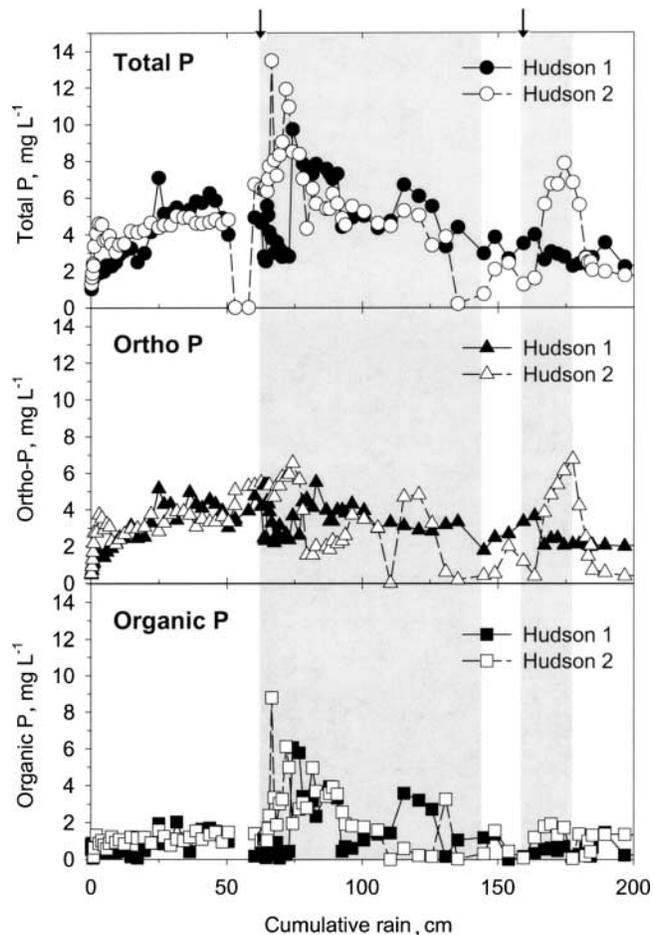


Fig. 8. Phosphorus concentration in outflow water for Hudson columns under unsaturated flow (0.2 cm h<sup>-1</sup> flow rate): (a) Total P, (b) Ortho P, and (c) Organic P. Shaded areas indicate periods when phytate P was added.

Only a few samples from the Genesee columns had an elevated (0.5 mg L<sup>-1</sup>) concentration around 100 cm of rain (Fig. 6). For all other times and soils, the organic P concentration remained near 0.5 mg L<sup>-1</sup>.

## DISCUSSION

As is typical for undisturbed soil columns with preferential flow paths present, there was a large variation in breakthrough curve results among treatment replicates. In contrast, conventional repacked soil columns generally show smaller variability between replications, but yield results that are far less realistic or applicable to field conditions.

### Ortho Phosphorus

Under unsaturated conditions (when ortho P rain was added at the low flow rate), some Hudson soil leachates had concentrations that were half of the input concentration, greatly increased above the baseline concentration. The Arkport soil had small effluent P concentrations that were, nevertheless, consistently greater than the baseline value. For the remaining soils (Genesee, Honeoye, and Lackawanna), the leachate P concentra-

tions were lower than the baseline conditions in all but a few samples (Table 5, Fig. 5).

Most studies use the convective-dispersive equation (Mansell et al., 1985; Notodarmojo et al., 1991) to explain differences in inorganic P leaching, such as the trends evident in Fig. 5. With this approach, the solution P concentration is thought to be inversely related to the strength of P adsorption to the soil (Shah et al., 1975), with greater water volumes required to leach P as the adsorption strength increases. Furthermore, convective flow assumes that the time of arrival for different flow rates is solely dependent on the amount of water leached. In our experiment, the results for the Genesee, Honeoye, and Lackawanna soils under low flow (Fig. 5) are consistent with this model: these soils had the greatest adsorption partition coefficients (Table 4) and a slower breakthrough, in contrast to the Hudson and Arkport soils with a small partition coefficient for P. However, our other results contradict the convective-dispersive approach: the Hudson soil exhibited a greater adsorption partition coefficient but an almost immediate P breakthrough, while the Arkport, despite a smaller adsorption partition coefficient, had no clear breakthrough. Another contrast with the convective-dispersive approach is the fact that the flow rate (not simply the cumulative flow) affected the breakthrough of P: breakthrough occurred within the first few centimeters of outflow for the saturated Genesee and Honeoye soils, while Arkport, despite a still lower coefficient, had no clear unsaturated breakthrough until at least 200 cm of rainfall. The limitation in the convective-dispersive approach for the prediction of P transport is therefore not because of unrealistic determination of the adsorption partition coefficients (as suggested by Ho and Notodarmojo, 1995; Chen et al., 1996) because our adsorption isotherms were determined at soil/solution ratios similar to those exhibited in the soil columns. The failure is instead caused by the rapid movement of the applied P in the preferential flow path, which violates the convective-dispersive equation assumption that all water flows with one average velocity with only minor variations around the mean because of dispersion. Furthermore, the travel time in the preferential flow path is too short for equilibration to occur between the solution P and the soil; the nonadsorbed portion of P thus moves at the same rate as  $\text{Cl}^-$ . The failure to attain equilibrium in P sorption can explain both why the first arrival of P is not retarded compared with  $\text{Cl}^-$  and why, at the same time, the concentration (relative to inflow) of P is smaller than  $\text{Cl}^-$ .

To find a better theoretical basis for the observed P breakthrough, it is helpful to divide the flow paths into matrix and preferential flow components, as do many other researchers (Armstrong et al., 1999). The matrix flow region is defined as the portion of the soil where the water flows slowly, allowing intimate contact between the solute and the matrix. The preferential flow region consists of the flow paths where the water flows rapidly and the solute concentration is minimally affected by the soil conditions; consequently the input and output concentration can be nearly identical. Hergert et al. (1981) described how these two flow regions inter-

acted in a tile drainage study conducted with a Genesee soil at the same farm where the Genesee columns used in this experiment were extracted. As with our experiments under saturated flow conditions, an immediate increase in concentration in the tile water was noted (Hergert et al., 1981). Paraphrasing, they hypothesized that based on the equilibrium adsorption strength of P to the soil, the P in the surface soil could not have influenced the subsurface P near the tile line 90 cm below the surface during the rainfall event. They claimed, therefore, that the increases of P concentration in drainage water were the result of a portion of the water flowing directly from the surface to the outflow point. Under ponded flow conditions, the leachate P concentrations were, thus, greater because more water was derived from the surface layer with a high P content, in contrast to low flow conditions when there was a greater representation of low P subsurface water. Hergert et al. (1981) did not posit a mechanism for how surface water could flow through the subsoil, perhaps because the preferential flow theory was generally not accepted at that time. It is reasonable to assume that the wormholes and structural cracks form this macropore pathway. This is confirmed in our experiment by both the  $\text{Cl}^-$  breakthrough curves (Fig. 2) and by the blue dye additions (Fig. 1): whenever the  $\text{Cl}^-$  breakthrough data and blue dye indicated preferential flow was occurring (i.e., under ponded conditions for all soils, and at the low flow rate for the Hudson soil), the leachate P exceeded 50% of the input concentration (Fig. 5 for the first 60 cm of rain for the Hudson and Fig. 6 for all three soils). Therefore, the preferential transport of P depends on both soil characteristics and flow rate.

More difficult to explain is the low but consistent increase of ortho P in the drainage water of the unsaturated Arkport soil columns (Table 5, Fig. 5). The blue dye (Fig. 1) and the  $\text{Cl}^-$  breakthrough experiments (Table 3) indicated that matrix flow occurred. The convective-dispersive equation thus applies, indicating that adsorption properties should affect the P breakthrough. Given the low partition coefficient for the Arkport subsoil (Table 4), it is therefore likely that P passing through the plow layer did not adsorb into the coarse subsoil. However, it remains unclear why the P concentrations of all soils briefly increased at around 30 cm of rainfall (Fig. 5).

### Organic Phosphorus

The baseline organic P levels were relatively elevated during the first part of the experiment (0–62 cm of rain) before the phytate was added, especially for the second replicate of the Hudson soil (Fig. 6 and 7). There is no obvious explanation for this because both Hudson columns were taken in close proximity.

After phytate application at 62 cm of rain (Fig. 7), the leachate organic P did not increase from the soil columns that exhibited primarily matrix flow (e.g., Arkport, Honeoye, Genesee, and Lackawanna) (Fig. 7, Table 5). The only significant breakthrough of organic P occurred in the Hudson soil, where the preferential

flow facilitated transport (Fig. 7, Table 5), where the leachate organic P peaked shortly after the first phytate application (62 cm rain) and then decreased steadily. During the second phytate application (157–177 cm of rain with an application rate of  $0.8 \text{ cm h}^{-1}$ ), the organic P did not increase above the background levels. The leachate ortho P for the Hudson was affected by the phytate applications during the first pulse. The Hud1 ortho P decreased initially, while for the Hud2 it increased slightly. At 75 cm cumulative rain, the pattern reversed and the Hud1 had a greater ortho P concentration than the Hud2. From 90 to 110 cm, the ortho P concentration was the same for the two columns. During the second phytate pulse, the Hud2 ortho P concentration increased sharply. The ortho P concentrations following the phytate applications varied more than when only ortho P was added (Fig. 8b). Total P (the sum of organic and ortho P) is plotted for the two Hudson columns in Fig. 8a. Note that at 75 cm of cumulative rain, the leachate total P concentrations became remarkably similar for the two columns, continuing for the remainder of the first phytate application. The delay in organic P breakthrough in the Hud1 after phytate was applied (Fig. 8) is similar to the delay in ortho P after it was first applied (Fig. 5). The organic P loss pattern (elevated initial concentration decreasing in time with the same input concentration) is similar to that observed for *p*-nitrophenol degradation in macropore columns and to the degradation of 2-4 D in an undisturbed Hudson soil where microbial action within the macropores caused this pattern (Pivetz and Steenhuis, 1995; Pivetz et al., 1996). Since phytate mineralization can be performed by microbes such as *Aspergillus niger* (Bowman et al., 1967) and transport of phytate occurs through the macropores, we consider it likely that differences in microbial action among the soils determined the relative ratio of ortho P and organic P in the leachate water. We are currently conducting additional experiments to study the microbial degradation of phytate P in undisturbed laboratory columns.

Long-term studies have shown a positive correlation between the additions of organic matter in cropped and grassed lands with greater movement of P, in contrast to situations where there is little organic matter (Ekholm et al., 1999). In this regard, our study provides an interesting insight into the potential mechanisms—our results suggest that a critical element in the movement of organic P is the presence of macropores. Thus, introducing organic matter at the surface promotes the activity of worms feeding on the organic matter (Munyankusi et al., 1994; Gupta et al., 2001). These worms provide and maintain the paths in which the water with dissolved organic matter containing P can flow down and move to deeper depths than would occur in the absence of macropores.

### Predicting Phosphorus Leaching

We have shown that the adsorption partition coefficient can, at best, only partially explain the movement of P through the soil. We also have demonstrated that

P leaching depended on both soil structure and moisture content: under saturated conditions, P was transported by preferential flow paths in all soils tested but was transported preferentially only in the more strongly structured Hudson soil under unsaturated conditions. This suggests that the soil structure could be the dominant predictor of preferential P transport in upland soils where saturation rarely occurs, whereas the extent of saturation is a better indicator of P leaching potential in bottomlands where saturation is more common.

Saturation often occurs in the landscape when the ground water is near the surface, or when there is a perched water table near the surface. Soil surveys record evidence of saturation as evidenced by subsoil mottling or gleying. When saturation-prone areas are drained by agricultural tile lines, elevated P concentrations are observed in the drainage water during rainfall events shortly after manure applications (Jensen et al., 2000; Simard et al., 2000; Geohring et al., 2001). This is in agreement with our experimental findings.

In contrast to saturation observations, soil surveys do not contain explicit assessments of the likelihood of occurrence of preferential flow. Because direct collection of these data is impractical, it is important to find a surrogate that could indicate the potential occurrence of macropore flow under different soil moisture contents. It appears that soil structure could fulfill this role as the surrogate for indicating subsoil preferential flow, since classical descriptions of soil structure include degree of development or distinction, shape of pedes, relative size, and firmness of the structural units.

The structures of the soils tested in this experiment were, as is typically the case, more strongly developed in the subsurface (Bw2, Bt, BC) horizons than the surface (A, Ap) horizons (Table 1). At one extreme, the Arkport subsoil is a friable, weak, fine granular structure or massive and, at the other extreme, the Hudson subsoil is a firm, moderately developed very coarse prismatic structure parting to firm, moderate, medium subangular blocky structure. The description of the Hudson subsoil as “firm” indicates that the matrix in the subsoil is dense and may not conduct water even at low flow rates, thus water flow can occur only between the structural units. The Honeoye, Genesee, and Lackawanna subsoils are intermediate between these two extremes, with friable, weak to moderately developed medium sized subangular blocky structure parting to a weak, fine to medium friable granular structure. The observed pattern of unsaturated preferential P transport correlates well with the range of subsoil structure. Hence, the survey description of structure (in terms of degree of development, size, shape, and stability) can be used for indicating soils that, at prevailing rainfall rates, are likely to experience preferential flow and therefore be more likely to manifest preferential P transport. A subject for further inquiry is whether there are additional observations (such as simple penetration tests with blue dye applied at prevailing rainfall rates) that could be made during soil pit characterization that would contribute to predictions of preferential flow.

## CONCLUSIONS

Phosphorus movement was investigated in the laboratory under two flow regimes to examine if rainfall rate and moisture status can provide an estimate for the potential of preferentially transported P. Undisturbed soil columns with five different soils were used for five unsaturated flow leaching experiments and two saturated flow experiments. The experiments showed that when the applied P solution flowed through the soil matrix, very little applied P was leached through the columns. Under preferential flow conditions, an immediate breakthrough of P occurred. The adsorption partition coefficient was not a good predictor of the occurrence of early breakthrough. The soil survey description of soil structure seemed to be a good indicator of the rate at which preferential flow may occur and when preferential P leaching could occur. Our results suggest that the soil structure could be a dominant factor for predicting preferential transport of P in sloping upland soils where saturation rarely occurs. Conversely, the extent of saturation is likely a predominant factor for predicting P leaching in bottomlands where saturation is more common.

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