

# Landscape and Watershed Processes

## Phosphorus Export from an Agricultural Watershed: Linking Source and Transport Mechanisms

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### ABSTRACT

Many source and transport factors control P loss from agricultural landscapes; however, little information is available on how these factors are linked at a watershed scale. Thus, we investigated mechanisms controlling P release from soil and stream sediments in relation to storm and baseflow P concentrations at four flumes and in the channel of an agricultural watershed. Baseflow dissolved reactive phosphorus (DRP) concentrations were greater at the watershed outflow (Flume 1; 0.042 mg L<sup>-1</sup>) than uppermost flume (Flume 4; 0.028 mg L<sup>-1</sup>). Conversely, DRP concentrations were greater at Flume 4 (0.304 mg L<sup>-1</sup>) than Flume 1 (0.128 mg L<sup>-1</sup>) during stormflow. Similar trends in total phosphorus (TP) concentration were also observed. During stormflow, stream P concentrations are controlled by overland flow-generated erosion from areas of the watershed coincident with high soil P. In-channel decreases in P concentration during stormflow were attributed to sediment deposition, resorption of P, and dilution. The increase in baseflow P concentrations downstream was controlled by channel sediments. Phosphorus sorption maximum of Flume 4 sediment (532 mg kg<sup>-1</sup>) was greater than at the outlet Flume 1 (227 mg kg<sup>-1</sup>). Indeed, the decrease in P desorption between Flumes 1 and 4 sediment (0.046 to 0.025 mg L<sup>-1</sup>) was similar to the difference in baseflow DRP between Flumes 1 and 4 (0.042 to 0.028 mg L<sup>-1</sup>). This study shows that erosion, soil P concentration, and channel sediment P sorption properties influence streamflow DRP and TP. A better understanding of the spatial and temporal distribution of these processes and their connectivity over the landscape will aid targeting remedial practices.

INPUTS of phosphorus (P) into surface waters from diffuse agricultural pollution can increase the potential for eutrophication (Carpenter et al., 1998). Many factors have been identified in controlling P export from agricultural land to surface water (Gburek et al., 2000; Sharpley and Tunney, 2000). These factors can be categorized into those that influence the source of P and those that influence its transport.

Sources of P include P inputs such as manures and fertilizers and the soil itself, while transport of P is facilitated by topography and the movement of water over or through the soil profile. The mechanisms that link the sources and transport of P include P solubility and/or the detachment of P-containing particles into solution (i.e., erosion).

Much work has been done to demonstrate the influence of source factors such as the soil and its management on the loss of P from a watershed. For example,

Edwards and Daniel (1993) showed that dissolved reactive phosphorus (DRP) concentrations in surface runoff increased 60 fold (0.8 to 47.0 mg L<sup>-1</sup>) between plots amended with poultry litter at rates of 0 compared with 870 kg N ha<sup>-1</sup>. Similarly, for transport, Pionke et al. (1999) found that flow rate had a positive curvilinear relationship with dissolved reactive P concentration of a stream draining a 7.3-km<sup>2</sup> central Pennsylvania watershed of the Chesapeake Basin. However, little work has demonstrated a clear link between source and transport factors for P loss at a watershed scale. McDowell and Trudgill (2000) showed that 0.01 M CaCl<sub>2</sub>-soluble P in soil was related to P in streamflow from a watershed dominated by subsurface flow; however, this is only indirect evidence of connectivity between source and transport mechanisms.

We present here evidence for connectivity between source and transport factors, by detailing the mechanisms and kinetics of soil P release, erosion, and channel sediments, to explain trends in stream P concentrations from a 39.5-ha watershed in central Pennsylvania, USA.

### MATERIALS AND METHODS

#### Study Area and Sampling

The study was conducted in a 39.5-ha subwatershed of Mahantango Creek, a tributary to the Susquehanna River and ultimately the Chesapeake Bay (Fig. 1). The watershed is typical of upland agricultural watersheds within the nonglaciated, folded and faulted, Appalachian Valley and Ridge Physiographic Province. Soils are either Typic Dystrochrepts or Typic Fragiudults (channery silt loams) with slopes ranging from 1 to 20%. Climate is temperate and humid with an average rainfall of 1100 mm yr<sup>-1</sup> (measured at a rain gauge 2.5 km away) and streamflow of 450 mm yr<sup>-1</sup>.

Land use is predominantly in soybean [*Glycine max* (L.) Merr.], wheat (*Triticum aestivum* L.), or corn (*Zea mays* L.) (50 to 60% varying from year to year) with a small amount of pasture (10 to 20%). The remaining land (30%) is wooded. In the last 10 yr, cropped land north of the stream channel received about 60 m<sup>3</sup> ha<sup>-1</sup> yr<sup>-1</sup> pig slurry in spring (about 100 kg P ha<sup>-1</sup> yr<sup>-1</sup>, assuming a slurry P content of 1.6 g L<sup>-1</sup>; Gilbertson et al., 1979). South of the stream channel, approximately 5 Mg ha<sup>-1</sup> yr<sup>-1</sup> poultry manure was added each spring (about 85 kg P ha<sup>-1</sup> yr<sup>-1</sup>, assuming a manure P content of 16.9 g kg<sup>-1</sup>; Gilbertson et al., 1979).

The watershed is divided into four segments based on topography and drainage patterns derived from a detailed topographic survey and visual reconnaissance (Fig. 1). Beginning in May 1996, streamflow below each segment was continuously

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**Abbreviations:** DRP, dissolved reactive phosphorus; EPC, equilibrium phosphorus concentration; TP, total phosphorus.

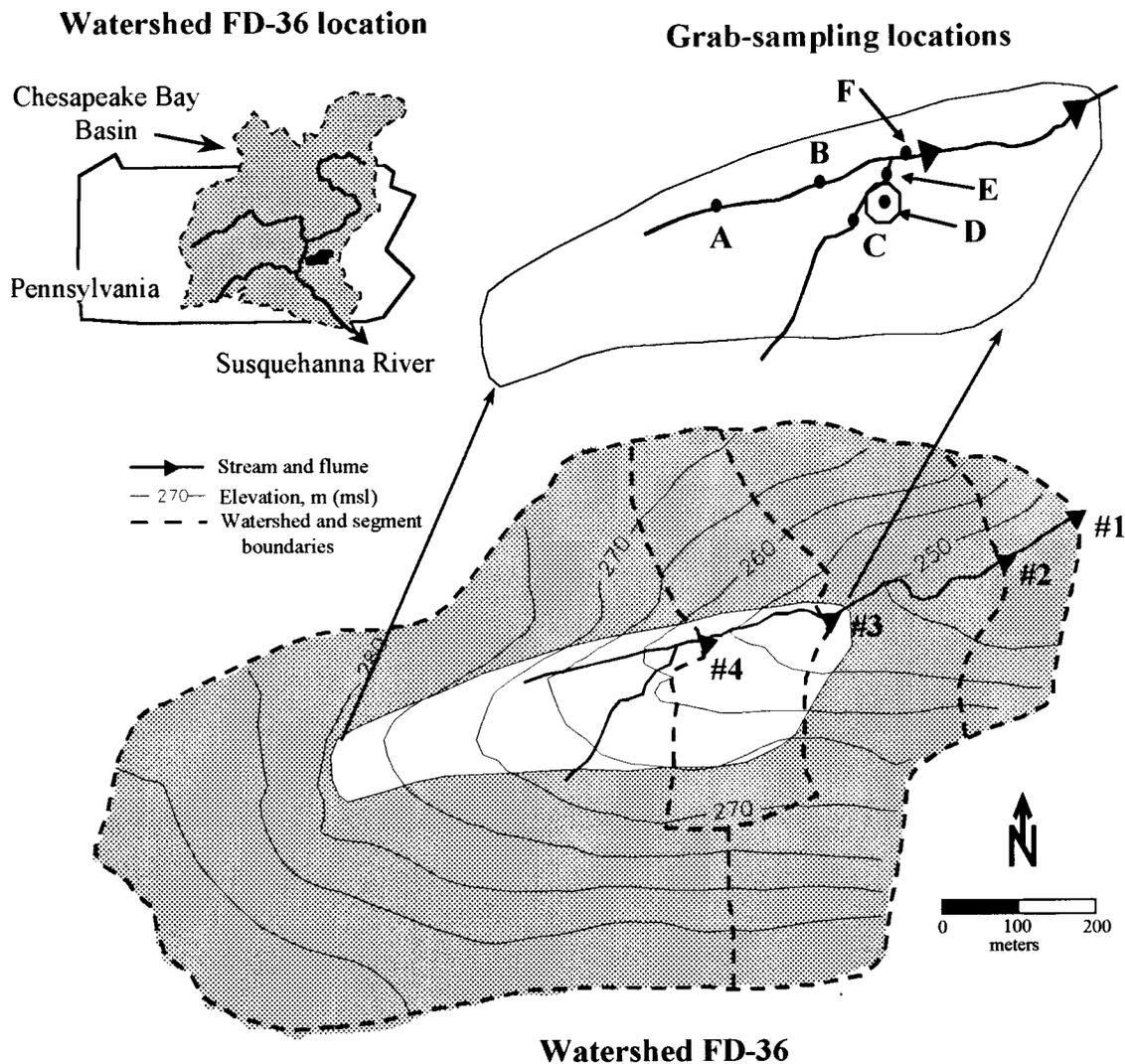


Fig. 1. Location, topography, soil types (grey = Typic Dystrochrept, white = Typic Fragiudult), and instrumentation of Watershed FD-36, Pennsylvania. Letters refer to grab samples taken in October 2000.

monitored using recording H-flumes, and water samples taken automatically during storm hydrographs at 5- to 120-min intervals using programmable stage-activated samplers. Baseflow samples were taken at each flume at weekly intervals. Additional “grab samples” were taken on three occasions in October 2000 at areas (including a small retention pond linked to the stream) beyond Flume 4 (noted by the letters A through F in Fig. 1).

In July 1996, soil samples (0–5 cm depth) were collected on a 30-m grid over the watershed (Table 1). The samples were air-dried and sieved (2 mm). In addition, immediately

in front of each flume, sediment samples were collected and air-dried, crushed, and sieved (<2 mm).

**Overland Flow**

One sample (0–5 cm depth) each of the two soil types (Typic Dystrochrept and Typic Fragiudult) was taken in July 1998 from cultivated fields within 10 m of the stream channel in the watershed. Mehlich-3 soil P concentration was 540 mg kg<sup>-1</sup> for the Typic Dystrochrept and 580 mg kg<sup>-1</sup> for the Typic Fragiudult. These soils had received swine manure at ca. 75

Table 1. Area of each watershed segment, the number of soil samples (0–5 cm) collected on a 30-m grid and Mehlich-3 P concentrations.

Segment	Area	Channel length	Number of samples	Mehlich-3 P			Percent of soils of a Mehlich-3 P concentration in each watershed segment			
				Mean	Min.	Max.	<30	30–100	100–200	>200
	ha	m		mg kg <sup>-1</sup>			%			
1	2.34	86	26	118	14	404	16	44	9	30
2	8.92	222	99	166	7	788	43	13	6	38
3	4.70	106	52	199	21	449	6	16	39	39
4	23.58	332	262	141	10	775	41	9	21	29
<b>Total</b>	<b>39.54</b>	<b>746</b>	<b>439</b>	<b>168</b>	<b>7</b>	<b>788</b>	<b>34</b>	<b>14</b>	<b>19</b>	<b>33</b>

kg P ha<sup>-1</sup> 2 wk prior to sampling. Soils were air-dried, sieved (<4 mm), and packed into impermeable boxes (18 cm wide, 15 cm deep, and 275 cm long) to a bulk density of 1.2 g cm<sup>-3</sup>. Surface runoff was generated by applying simulated rainfall (tap water, P less than the detection limit of 0.005 mg P L<sup>-1</sup>) at 50 mm h<sup>-1</sup> for 30 min to each boxed soil, which was set to have a 5% slope. All rainfall was produced with precalibrated nozzles 2.7 m above the soil surface, approximating size, velocity, and impact energies of natural rainfall (Shelton et al., 1985). Samples of overland flow were taken after runoff had initiated at 1-min intervals up to 6 min and at 5-min intervals thereafter (for a total of 40 min). A subsample of these was filtered (<0.45 μm) and stored at 4°C in the dark until analysis (<1 wk). An additional unfiltered subsample was then filtered (<0.45 μm) 24 h later for comparison.

### Soil and Water Analyses

All water samples from the watershed were filtered (<0.45 μm) and refrigerated at 4°C until analysis for DRP using the colorimetric molybdenum-blue method of Murphy and Riley (1962). Total phosphorus (TP) concentration of unfiltered stream and overland flow samples was also determined colorimetrically after Kjeldahl digestion (Bremner and Mulvaney, 1982). Mehlich-3 soil P concentration was determined by extraction of 1 g soil with 10 mL of 0.2 M CH<sub>3</sub>COOH, 0.25 M NH<sub>4</sub>NO<sub>3</sub>, 0.015 M NH<sub>4</sub>F, 0.013 M HNO<sub>3</sub>, and 0.001 M EDTA for 5 min (Mehlich, 1984). Percent clay, silt, and sand were determined by either hydrometer (for soils) or pipette (for sediments) methods without sample pretreatment to remove organic matter (Sheldrick and Wang, 1994). Suspended sediment concentration of unfiltered stream and overland flow samples was determined gravimetrically after evaporation to dryness at 105°C.

The kinetics of DRP desorption from sediments was studied in three replicates of soil to water ratios of 1 to 5, 10, 100 and 1000 after shaking times of 2, 10, 30, 120, 300 and 1440 min and filtration (<0.45 μm). Due to the low levels of P desorbed, a malachite green method was modified from Ohno and Zibil-ske (1991). The method was identical, except solutions were made up to 25 mL with distilled water after the initial reaction period of 10 min. The detection limit for P was 0.002 mg L<sup>-1</sup>. A preliminary analysis of the desorption data fitted to power (Sharpley and Ahuja, 1983), first-order (Chien and Clayton, 1980), second-order (Chien and Clayton, 1980), parabolic diffusion (Vig and Dev, 1979), and an expanded Elovich equation (Polyzopoulos et al., 1986) showed that while the best fits were obtained using the expanded Elovich equation, the use of extra parameters versus a simpler equation (e.g., power) was not justified (*F* test, *p* > 0.05). Among those equations with the least parameters (power, parabolic diffusion, and first order), the power equation best described P desorption:

$$Q = at^b \quad [1]$$

where *Q* = amount (mg kg<sup>-1</sup>) of released P at time *t* (min), and *a* and *b* are constants.

The sorption of P was assessed in each sediment sample by shaking, for 16 hours, 2 g of sample with 40 mL of deionized water containing 0, 1, 2, 5, 10, and 20 mg P (as KH<sub>2</sub>PO<sub>4</sub>) L<sup>-1</sup>. Each sample was centrifuged and filtered (<0.45 μm) before P was determined by the method of Murphy and Riley (1962). Curves of P sorbed against P in solution were fitted to the Langmuir equation and a sorption maximum was calculated.

### Statistical Analyses

All basic statistical procedures (mean, standard errors), analysis of variance, and curve fitting were performed using

**Table 2. Minimum, maximum, and mean dissolved reactive P, total P, and suspended sediment for each flume for weekly baseflow samples during 1996–1998.**

Flume	Minimum	Maximum	Mean
<b>Dissolved reactive P (mg L<sup>-1</sup>)</b>			
1	0.010	0.527	0.042
2	0.008	0.498	0.036
3	0.010	0.536	0.037
4	0.006	0.305	0.028
<b>Total P (mg L<sup>-1</sup>)</b>			
1	0.003	0.252	0.097
2	0.037	0.159	0.056
3	0.045	0.149	0.081
4	0.007	0.105	0.053
<b>Suspended sediment (g L<sup>-1</sup>)</b>			
1	0.100	0.184	0.142
2	0.082	0.228	0.155
3	0.077	0.213	0.145
4	0.153	0.202	0.177

SPSS v10.0 (SPSS, 1999). Geostatistics were performed using Surfer v7.0 (Golden Software, 1999).

## RESULTS AND DISCUSSION

### Trends in Stream Phosphorus Concentrations

Within the watershed, four flumes are located at intervals along the stream, with Flume 4 being furthest from the watershed outflow at Flume 1. Concentrations of DRP and TP in weekly samples of baseflow were consistently greater at Flume 1 than Flumes 2 or 3, with Flume 4 having, on average, the lowest DRP and TP concentration (Table 2). However, during stormflow, Sharpley et al. (1999) found that concentrations of DRP and TP were greatest at Flume 4 and decreased in a uniform manner to each flume downstream (Table 3). It was also noted that this paralleled a decrease in the percentage of near-stream soils (<60 m from the channel) in excess of 200 mg kg<sup>-1</sup> Mehlich-3 soil P. This Mehlich-3 soil P concentration coincides with a threshold, above which soils become “leaky”, losing proportionately more P in overland and subsurface flow than soils below this threshold (McDowell and Sharpley,

**Table 3. Minimum, maximum, and mean dissolved reactive P, total P, and suspended sediment for each flume during storms from August to November 1996 (data adapted from Sharpley et al., 1999).**

Flume	Minimum	Maximum	Mean
<b>Dissolved reactive P (mg L<sup>-1</sup>)</b>			
1	0.005	1.090	0.128
2	0.011	1.320	0.174
3	0.010	1.470	0.202
4	0.009	1.545	0.304
<b>Total P (mg L<sup>-1</sup>)</b>			
1	0.024	1.318	0.400
2	0.056	1.779	0.478
3	0.078	3.027	0.923
4	0.118	3.409	0.708
<b>Suspended sediment (g L<sup>-1</sup>)</b>			
1	0.014	0.896	0.247
2	0.090	1.059	0.331
3	0.118	3.229	0.772
4	0.045	7.927	0.554

2001). Clearly, within this watershed, processes that control stream P concentrations and that link P in the landscape to P in the stream channel differ with the hydrologic conditions of the watershed (i.e., soil moisture patterns).

The dichotomy between concentrations of both DRP and TP of base and stormflow may be indicative of the introduction of a source of P into the system above Flume 4. This could be conceived as a *point source*, because the uniform decrease in P concentration at each flume downstream is consistent with simple dilution. For example, the effect of dilution on storm and baseflow is evident when the concentration at Flumes 4, 3, and 2 is near or equal to the concentration at Flume 1, after accounting for any added volume (e.g., dilution factor = [volume at Flume 2/volume at Flume 1] × concentration at Flume 2). This was the case for the slope of a regression of stormflow concentrations for Flumes 2 or 3 against Flume 1 (Flume 1 = 1.09 × Flume 3,  $R^2 = 0.994$ ,  $p < 0.001$ ; Flume 1 = 0.970 × Flume 2,  $R^2 = 0.994$ ,  $p < 0.001$ ) and nearly the same between Flumes 4 and 1 (Flume 1 = 1.45 × Flume 4,  $R^2 = 0.988$ ,  $p < 0.001$ ). However, for baseflow, simple dilution from Flume 4 to Flume 1 was not evident, as DRP and TP concentrations increased downstream (Table 2).

In addition to dilution, processes controlling P concentrations at each flume include in-channel processes such as P spiraling of stream sediments by the deposition or resuspension and sorption-desorption processes of particulate and dissolved P (Fox, 1989); and landscape processes such as transport of eroded soil and dissolved P in overland and subsurface flow subject to inherent differences in variable source area hydrology within the landscape and soil P concentrations (Sharpley et al., 1999).

### Linking Phosphorus in the Landscape to the Stream

#### Overland Flow

The connectivity of landscape processes to the stream is dependent upon a source of P and water flowing from that source to the stream. It is well known that the majority of TP within overland flow from cultivated fields is in particulate forms (Sharpley et al., 1995). Most of the watershed is cultivated, and Sharpley et al. (1999) noted that up to 90% of TP leaving the watershed was as particulate or organic P forms (defined as TP – DRP) from overland flow events. Pionke et al. (1999) also noted in an adjacent watershed that more than two-thirds of TP in stream flow was from overland flow during a 12-yr period. Consequently, most of the P that reaches the stream channel in this area is likely to be from the erosion of P-containing soil particles, within the saturated distance from the stream channel.

During stormflow from August to November 1996, sediment concentrations within the watershed were as great as 7.9 g L<sup>-1</sup> (Table 3). As mentioned above, this is most likely from sediment derived during overland flow. Data for the saturated distance from the stream channel presented by Sharpley et al. (1999) show that these distances, and hence where overland flow can

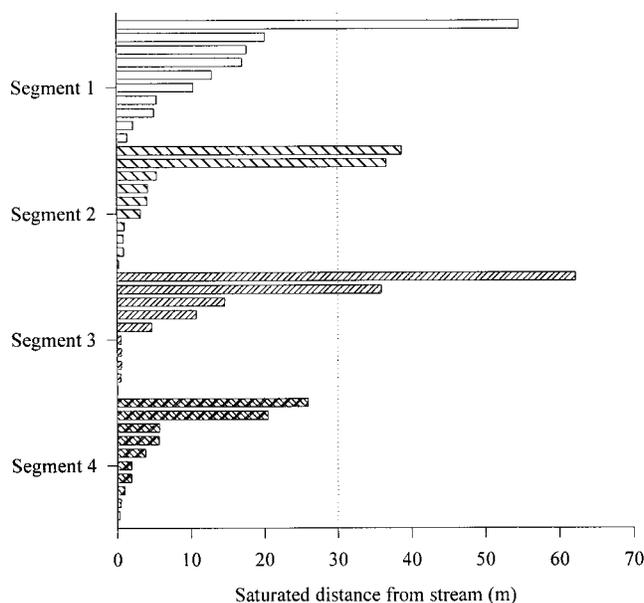
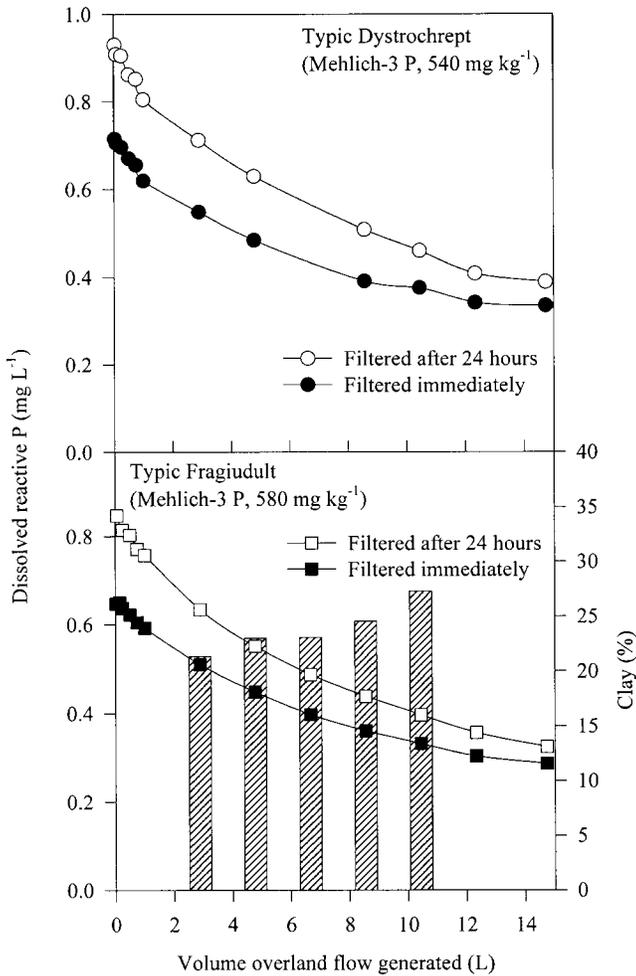


Fig. 2. Saturated distance from the stream for each segment for storms that occurred from August to November 1996 (data from Sharpley et al., 1999). The dashed line shows the saturated distance within which 90% of the storms influenced.

originate from, were as far as 62 m away from the channel (Fig. 2). However, 90% of the overland flow occurs from within 30 m of the stream channel (Fig. 2). This coincides with some areas where Mehlich-3 extractable P concentrations are in excess of 200 mg kg<sup>-1</sup>, although there is no guarantee that P will be transported from these sites.

#### Erosional Controls

Erosion rates differ due to many factors; two of the most important are soil type and topography. The effect of soil erosion in overland flow can be seen in Fig. 3 for the Typic Fragiudult and Typic Dystrachrept soil types. These soils were collected from within 10 m of the stream channel and are thus likely to contribute to stream P. The concentration of DRP in overland flow decreases with time during a 30-min rainfall on soils packed in boxes (Fig. 3). This can be described by a simple power function, indicative of those employed in erosion studies to define the Revised Universal Soil Loss Equation (RUSLE). This decrease of DRP in overland flow has been mentioned elsewhere. For example, Sharpley (1980a,b, 1985) noted that overland flow was initially enriched with DRP relative to latter events from the same soil and over the course of the event. Sharpley (1980a) attributed this decrease during flow to a dilution of the available pool of water-soluble P; however, the author also noted that the distribution of particle sizes changed during the event. Maguire et al. (1998) showed that the proportion of water-soluble P to TP was greater in coarse sediments than fine sediments. Indeed, particle size data for the Typic Fragiudult soil shows that the proportion of coarse sediments in overland flow is greater at the start of overland flow (when kinetic en-



**Fig. 3.** Dissolved reactive P lost in overland flow during a 30-min event for a Typic Fragiudult and Typic Dystrochrept soil. Bars represent percent clay in overland flow collected for the Typic Fragiudult soil.

ergy is greatest) and decreases as the event proceeds (and the erosion caused by the kinetic energy of rainfall impact and overland flow equilibrates).

In our current simulated rainfall-packed soil box study, sediment to solution ratios differed little during the 30-min event for both Typic Dystrochrept and Typic Fragiudult soils (Table 4). This indicates that while the total amount of sediment changes little, the proportion of fine particles in overland flow increases with time. Coarser particles, which may also contain some manure, were transported first. This is supported by the different desorption properties of the Typic Dystrochrept and Typic Fragiudult soils as represented by the DRP concentration of overland flow immediately and after 24 h (Fig. 3). The effect of increasing time between sample collection and filtration on the desorption of P from both Typic Dystrochrept and Typic Fragiudult soils to overland flow was greater at the beginning than end of the event and reflects the loss of coarse particles (with enhanced aggregate stability from previous manure additions) that contain more water-soluble P (Fig. 3).

From Table 4 it can be seen that the two soils behave

**Table 4.** Suspended sediment with time during a 30-min. overland flow event on a Typic Fragiudult and Typic Dystrochrept soil.

Soil	Sampling time	Suspended sediment
	min	g L <sup>-1</sup>
Typic Fragiudult	5	9.18
	10	14.85
	15	6.29
	20	5.64
	25	9.74
	30	7.45
		(8.91)†
Typic Dystrochrept	5	2.36
	10	4.32
	15	3.58
	20	4.12
	25	4.62
	30	3.37
		(3.72)

† Mean suspended sediment.

very differently. The Typic Fragiudult erodes at a rate nearly three times that of the Typic Dystrochrept soil. Consequently, one area of the watershed near Flumes 3 and 4 is dominated by a soil type that is much more likely to erode than the soil nearer to Flumes 1 and 2. To investigate the likely effect of soil type distribution, topography, and its potential loss, we multiplied clay content (as a crude measure of differentiating between the two soil types) by erosion potential (calculated by RUSLE, normalized relative to the highest value; McDowell et al., 2001) using the 30-m grid sampling (Fig. 4). Soils with clay content greater than 39% are predominantly Typic Fragiudults (mean sand, silt, clay content = 18 ± 0.7%, 43 ± 0.9%, 39 ± 0.7%; n = 40) and erosion was, therefore, weighted three times more than for Typic Dystrochrept soils with a clay content less than 39% (mean sand, silt, clay content = 21 ± 0.8%, 47 ± 0.8%, 33 ± 0.4%; n = 46).

Relative to the potential for soil loss close to the stream channel (e.g., 30 m, from which 90% of overland flow occurred during measured stormflow in 1996; Fig. 2), much more soil loss is likely from soils closer to Flumes 3 and 4 than at Flumes 1 and 2. Two of these areas (A and B, Fig. 1) coincide with high soil P concentrations and parallel the trends in stream P concentrations measured at Flumes 1 and 4. However, the relative contribution of these sites compared with other highly eroded sites of low P content is uncertain without direct analysis of source (soil) and sink (stream sediments) factors.

**In-Channel Controls**

To investigate source and sink factors controlling in-channel processes, stream flow samples were taken at various sites along the channel system (Fig. 1, Sites A to F and Flumes 1 to 4). At this sampling, DRP concentrations mirrored the trend in the mean concentrations for baseflow throughout 1996–1998 (Tables 2 and 5). At the confluence of the western and southern tributaries (Site F), streamflow DRP concentration was greater than at Flume 4, inferring that resorption by sediments or dilution by subsurface flow had occurred. By far, the

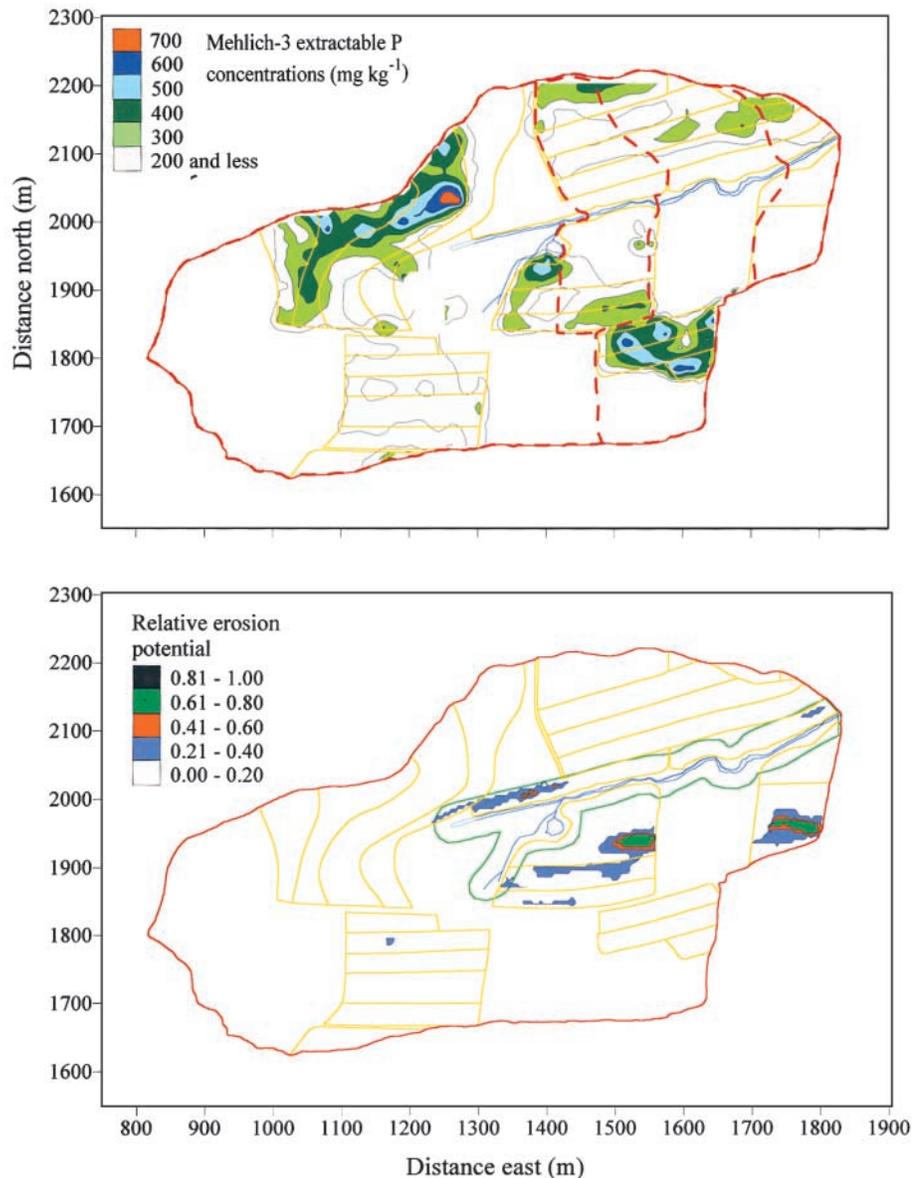


Fig. 4. The distribution of Mehlich-3 extractable P and the relative erosion potential within the watershed. Yellow lines refers to field boundaries, red to watershed segments, blue to stream channel and green to 30 m from stream channel.

greatest DRP concentration was evident in the pond (Site D); however, little DRP was evident in the outflow from the pond (Site E), indicating that much DRP may be derived from the pond if it is disturbed (e.g., turbulence, mixing, and overland flow during a storm event). From land owner surveys, the origin and purpose of the P in the pond was to retain overland flow and sediment from surrounding manured fields during heavy rainfalls. Thus, the pond represents a periodic *point source* of DRP, from which P-enriched sediments may settle but be transported during stormflow, resulting in the dilution pattern seen from Flume 1 to Flume 4 (Tables 3 and 5 and Fig. 3).

**Baseflow**

Due to the undisturbed nature of stream sediments during baseflow, in-channel processes controlled by

these sediments are relatively small compared with stormflow. In order to assess the importance of the erosion of soil sediments and its connectivity with the

Table 5. Mean dissolved reactive phosphorus (DRP) in grab samples of stream water at each flume and additional sites within Segment 4 (n = 3).

Site	DRP concentration mg L <sup>-1</sup>
A (extreme westerly branch)	0.015
B (west branch near Flume 4)	0.016
C (pond inflow)	0.024
D (pond)	0.162
E (pond outflow)	0.021
F (confluence of west and southern branches)	0.023
Flume 1	0.015
Flume 2	0.012
Flume 3	0.012
Flume 4	0.011

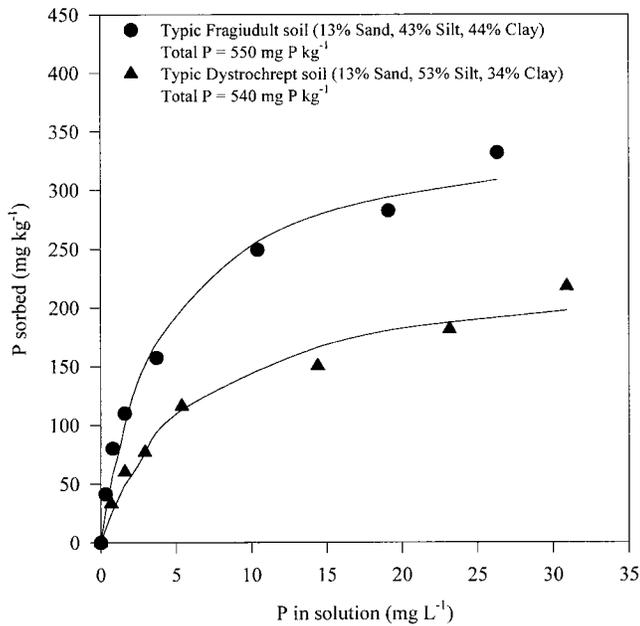


Fig. 5. Sorption isotherms for a Typic Fragiudult and Typic Dystrochrept soil of similar total P concentrations.

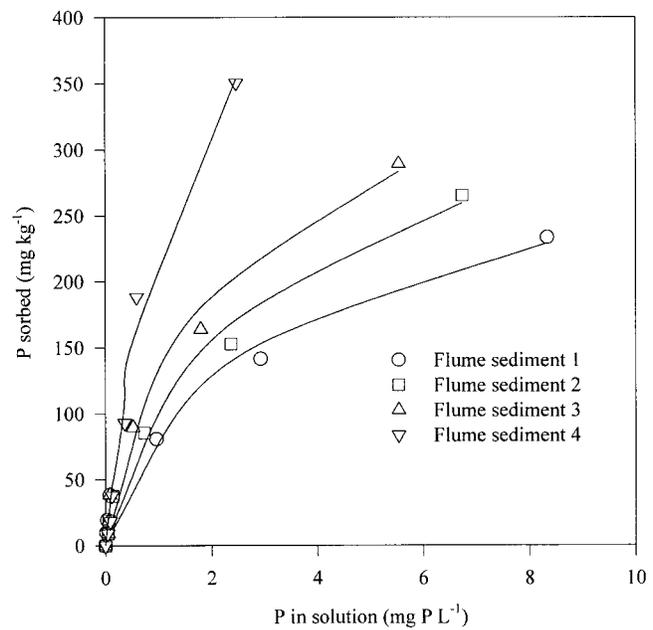


Fig. 6. Sorption isotherms for each flume sediment sample fitted to the Langmuir equation.

stream, sediment samples were collected from the channel immediately upstream from each flume. The P sorption-desorption characteristics of stream sediment were determined. Sediment at Flume 4 contained a greater proportion of clay than sediments from the other flumes. This coincides with the greater proportion of clay and likelihood of erosion near Flume 4 than the other flumes and provides evidence for the erosion of nearby soils to the stream (Table 6).

Soils with a greater clay concentration are known to exhibit a greater P sorption capacity (Syers et al., 1973). This is demonstrated in Fig. 5 for a Typic Fragiudult and Typic Dystrochrept soil collected from within 30 m of the stream channel during the watershed-grid sampling. These soils had similar TP concentrations (550 and 540 mg kg<sup>-1</sup>) and history of manure applications. In addition to the soil data, sediments at each of the flumes also show a difference in particle size characteristics and especially P sorption maximum (Fig. 6). Sediments at Flume 4 were able to sorb the most P while sediments at Flume 1 were the most saturated (Fig. 6, Table 6). Hence, while soils nearer to Flume 4 may erode much more than those near Flume 1, sediments deposited indicate that these probably originate from a relatively P-unsaturated source (Fig. 4 and 6). In addition,

P desorption data for each of the four sediments shows that sediments at Flume 1 desorb the greatest concentration of P, while those at Flume 4 desorb less than half the P (Fig. 7). This P desorption trend parallels the distribution of soil P saturation near the stream, and the concentration of P in baseflow at each flume. This provides further evidence of the connectivity between soil and stream.

The relative importance of the controlling hydrologic and chemical processes will vary down the stream channel. Desorption of P from stream sediments at each flume differs with extraction time (Fig. 7), but follows standard desorption kinetics in the form of a simple power equation (Table 7; Sharpley and Ahuja, 1983). This data and sediment equilibrium phosphorus concentration (EPC) suggests that at least some of the P in

Table 6. Langmuir sorption parameters and particle size analysis for sediment at each flume.

Sediment at flume	P <sub>max</sub> mg kg <sup>-1</sup>	Affinity constant L g <sup>-1</sup>	EPC† mg L <sup>-1</sup>	Particle size analysis (%)		
				Clay	Silt	Sand
1	227	0.69	0.034	38	32	30
2	295	1.14	0.013	37	31	31
3	330	1.24	0.004	38	32	30
4	532	1.74	0.004	44	30	26

† Equilibrium phosphorus concentration.

Table 7. Kinetic parameters and the coefficient of determination for the fit of a power equation ( $Q = at^b$ ) to the desorption data.

Sediment and sediment to solution ratio	Power equation parameters		Coefficient of determination†
	a	b	
1, 1:5	0.021	0.109	0.968
	0.020	0.097	0.949
	0.0075	0.119	0.997
	0.0013	0.229	0.985
2, 1:5	0.017	0.077	0.996
	0.014	0.090	0.977
	0.0074	0.042	0.969
	0.0015	0.164	0.973
3, 1:5	0.014	0.035	0.968
	0.013	0.034	0.981
	0.0056	0.074	0.981
	0.0010	0.211	0.942
4, 1:5	0.014	0.081	0.976
	0.015	0.032	0.980
	0.0053	0.144	0.993
	0.0008	0.262	0.941

† Significant at the  $P < 0.05$  level.

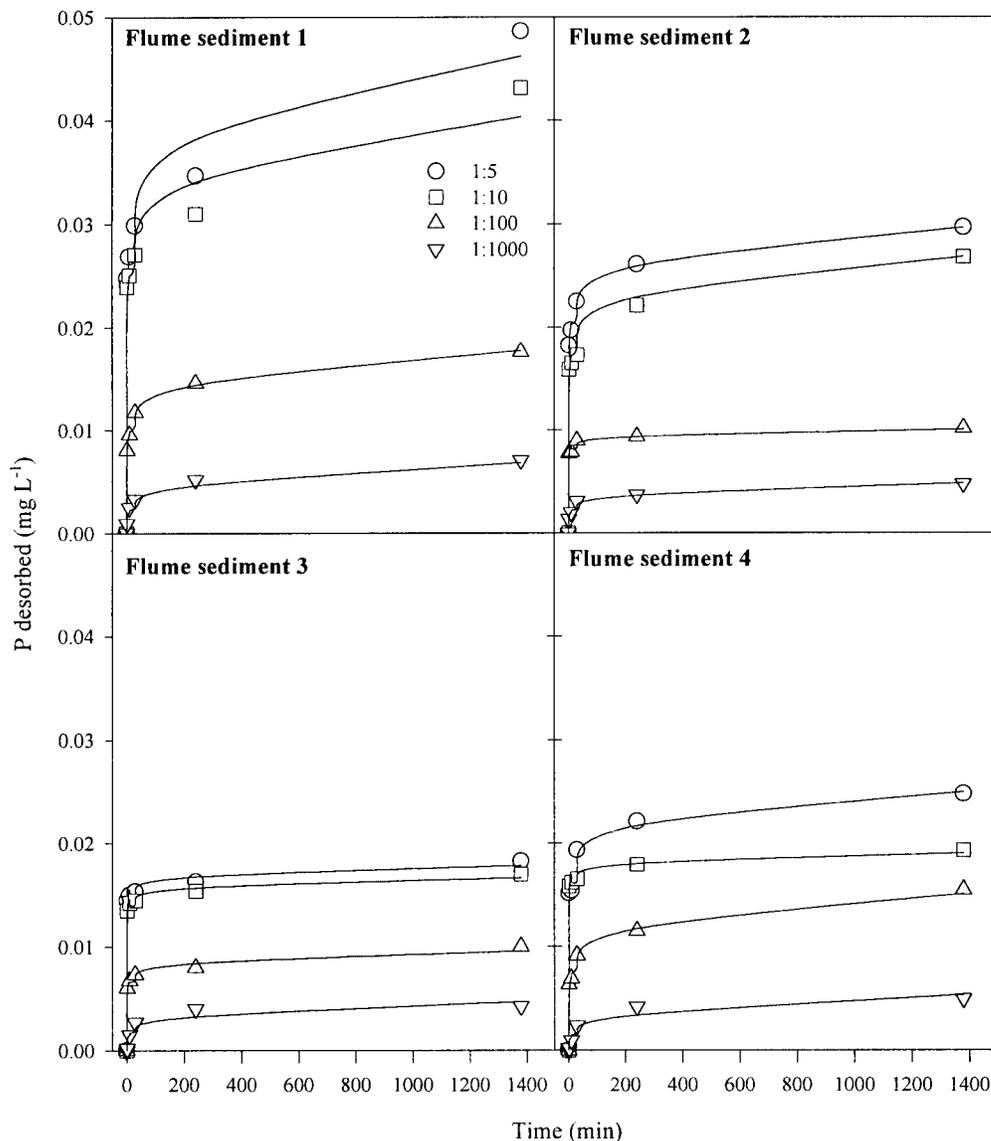


Fig. 7. Desorption of P at different sediment to water ratios with time for each flume sediment.

baseflow measured at each flume can be accounted for by desorption from deposited sediments. As an approximate indicator, desorption of P from sediment at Flume 1 occurred at nearly twice the rate as desorption from sediments at Flume 4. Consequently, sediment samples would desorb P into the stream if streamflow DRP concentration drops below the sediment EPC, and this effect would be greatest at Flume 1, which responds the fastest (Table 7). The decrease in P desorption between Flumes 1 and 4 (0.046 to 0.025 mg L<sup>-1</sup>; Fig. 7) is similar to the difference in mean DRP concentration of baseflow between Flumes 1 and 4 (0.042 to 0.028 mg L<sup>-1</sup>; Table 2). However, it must be mentioned that any estimate as to the quantitative contribution of sediments to baseflow remains unclear and subject to confounding errors caused by dilution or concentration from P in subsurface flow.

### CONCLUSIONS

Controlling processes and trends in DRP and TP concentrations in the stream channel show a clear difference between storm and baseflow conditions. Processes that cause this difference may vary between the two conditions, but share a common origin in the connectivity between soil and water. It would appear that landscape processes, which include the movement of soil to the stream, are involved in the distribution of sediments within the stream channel. However, it appears unlikely that these are involved in determining P concentrations during stormflow. The identification and dilution pattern of a potential *point source* of P upstream of Flume 4, and the absence of its influence during baseflow indicates that this may account for a significant amount of P lost during stormflow. During baseflow, concentrations tend to increase as we move to the watershed outflow.

This can be explained by differences in soil and stream sediment particle sizes, sorption capacities, EPC, and desorption rates, which gives us an indication as to their relative influence in determining P in baseflow. However, this also yields an insight into the connectivity between stormflow, which may erode soil (and therefore carry its inherent physiochemical characteristics) from the landscape, and eventual effects upon baseflow via the sediments this transport deposits in the stream channel.

## REFERENCES

- Bremner, J.M., and C.S. Mulvaney. 1982. Nitrogen—Total. p. 595–624. *In* A.L. Page et al. (ed.) *Methods of soil analysis*. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Applic.* 8:559–568.
- Chien, S.H., and W.R. Clayton. 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci. Soc. Am. J.* 44:265–268.
- Edwards, D.R., and T.C. Daniel. 1993. Effects of litter application rate and rainfall intensity on quality of runoff from Fescuegrass plots. *J. Environ. Qual.* 22:361–365.
- Fox, L.E. 1989. A model for inorganic control of phosphate concentrations in river waters. *Geochim. Cosmochim. Acta* 53:417–428.
- Gburek, W.J., A.N. Sharpley, L. Heathwaite, and G.J. Folmar. 2000. Phosphorus management at the watershed scale: A modification of the phosphorus index. *J. Environ. Qual.* 29:130–144.
- Gilbertson, C.B., F.A. Norstadt, A.C. Mathers, R.F. Holt, A.P. Barnett, T.M. McCalla, C.A. Onstad, and R.A. Young. 1979. Animal waste utilization on cropland and pastureland—A manual for evaluating agronomic and environmental effects. USEPA Rep. EPA 600/2-79-059 and USDA Rep. URR 6. U.S. Gov. Print. Office., Washington, DC.
- Golden Software. 1999. *Surfer user's guide*. Release 7.0. Golden Software, Golden, CO.
- Maguire, R.O., A.C. Edwards, and M.J. Wilson. 1998. Influence of cultivation on the distribution of phosphorus in three soils from NE Scotland and their aggregate size fractions. *Soil Use Manage.* 14:147–153.
- McDowell, R.W., and A.N. Sharpley. 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. *J. Environ. Qual.* 30:508–520.
- McDowell, R.W., A.N. Sharpley, and P.J.A. Kleinman. 2001. Integrating phosphorus and nitrogen decision management at watershed scales. *In* *Integrated Decision-Making for Watershed Management*. Symp., Chevy Chase, MD. 7–9 Jan. 2001. Virginia Polytechnic Inst. and State Univ., Blacksburg, VA.
- McDowell, R.W., and S.T. Trudgill. 2000. Variation of phosphorus loss from a small catchment in south Devon, U.K. *Agric. Ecosyst. Environ.* 79:143–157.
- Mehlich, A. 1984. Mehlich-3 soil test extractant: A modification of Mehlich-2 extractant. *Commun. Soil Sci. Plant. Anal.* 15:1409–1416.
- Murphy, J., and J.R. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31–36.
- Ohno, T., and L.M. Zibilske. 1991. Determination of low concentrations of phosphorus in soil extracts using malachite green. *Soil Sci. Soc. Am. J.* 55:892–895.
- Pionke, H.B., W.J. Gburek, R.R. Schnabel, A.N. Sharpley, and G.F. Elwinger. 1999. Seasonal flow, nutrient concentrations, and loading patterns in stream flow draining an agricultural hill-land watershed. *J. Hydrol.* 220:62–73.
- Polyzopoulos, N.A., V.Z. Keramidas, and A. Pavatou. 1986. On the limitations of the simplified Elovich equation in describing the kinetics of phosphate sorption and release from soils. *J. Soil Sci.* 37:81–87.
- Sharpley, A.N. 1980a. The effect of storm interval on the transport of soluble phosphorus in runoff. *J. Environ. Qual.* 9:575–578.
- Sharpley, A.N. 1980b. The enrichment of soil phosphorus in runoff sediments. *J. Environ. Qual.* 9:521–526.
- Sharpley, A.N. 1985. The selective erosion of plant nutrients in runoff. *Soil Sci. Soc. Am. J.* 49:1527–1534.
- Sharpley, A.N., and L.R. Ahuja. 1983. A diffusion interpretation of soil phosphorus desorption. *Soil Sci.* 135:322–326.
- Sharpley, A.N., W.J. Gburek, G. Folmar, and H.B. Pionke. 1999. Sources of phosphorus exported from an agricultural watershed in Pennsylvania. *Agric. Water Manage.* 41:77–89.
- Sharpley, A.N., M.J. Hedley, E. Sibbesen, A. Hillbricht-Ilkowska, W.A. House, and L. Ryszkowski. 1995. Phosphorus transfers from terrestrial to aquatic ecosystems. p. 171–200. *In* H. Tiessen (ed.) *Phosphorus in the global environment: Transfers, cycles, and management*. John Wiley & Sons, New York.
- Sharpley, A.N., and H. Tunney. 2000. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st century. *J. Environ. Qual.* 29:176–181.
- Sheldrick, B.H., and C. Wang. 1994. Particle size distribution. p. 499–512. *In* M.R. Carter (ed.) *Soil science: Methods and analysis*. Lewis Publ., Boca Raton, FL.
- Shelton, C.H., R.D. von Bernuth, and S.P. Rajbhandari. 1985. A continuous-application rainfall simulator. *Trans. ASAE* 28:1115–1119.
- SPSS. 1999. *SPSS user's manual*. Release 10.0. SPSS, Chicago, IL.
- Syers, J.K., R.F. Harris, and D.E. Armstrong. 1973. Phosphate chemistry in lake sediments. *J. Environ. Qual.* 2:1–14.
- Vig, A.C., and G. Dev. 1979. Kinetics of phosphate desorption in soils. *J. Nucl. Agric. Biol.* 8:62–66.