Residual phosphorus in runoff from successional forest on abandoned agricultural land:

1. Biogeochemical and hydrological processes

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Abstract. Soluble reactive phosphorus (SRP) concentrations measured in runoff from abandoned agricultural land now in forest succession in the northeastern United States were significantly higher than expected from undisturbed forest land. This finding differs from P uptake in hardwood forest succession following natural disturbance. Field monitoring of a 16.6 ha old-field regrowth forest stand in the Catskills Mountains, New York, USA demonstrated runoff SRP trends including an early summer flush that could not be explained by simple dilution. An assay of outflow sediment and biomass, flowpath sediment and biomass, forest floor leaf litter and biomass, and Bh horizon mineral soil indicated that surface litter from the regrowth forest provided the most significant contribution to the elevated SRP in runoff. It is posited that microbial mineralization of residual organic P in surface litter coupled with the transient process of SRP mobilization at the soil surface resulting from a rising saturated layer followed by dissolution in surface runoff may elevate SRP to the range observed. Measured SRP concentrations remain lower than reported values for crop or pastureland. The results reported represent an important deviation from the prevailing view that forest land does not contribute to eutrophication (based on enhanced P uptake in forest succession); this is a consequence of residual P from land abandonment - a widespread practice throughout the northeastern US and other regions.

Introduction

The rate of agricultural land abandonment in the northeastern United States peaked late last century but the practice continues to occur across widespread areas (Stanton & Bills 1997). The potential eutrophication impacts on receiving waters of nutrient cycling in the resulting successional forest

are not adequately documented. Successional forest on abandoned agricultural land generates significant runoff volumes throughout this region (for example, 49% of annual runoff volume was generated on old-field regrowth forest in the 31.7 km² watershed in which this study site is located; Scott et al. 1998). As a result, it is imperative that nutrient export from abandoned land should be quantified.

Of particular concern is phosphorus (P) – the limiting nutrient for many fresh water systems that results in significant summer season eutrophication of reservoirs in the study area (NYCDEP 1995). Soluble reactive P (SRP) concentrations in excess of 0.010 mg L⁻¹ have been shown to cause accelerated algae growth (originally presented by Vollenweider & Kerekes 1980 and subsequently advanced by Sharpley & Smith 1989; Sharpley & Smith 1992). It is recognized that particulate-solution P partitioning during instream transport may occur. Further, algae in receiving waters may hydrolize organic P. This study does not address nitrogen, which is often the limiting nutrient in the ocean and coastal receiving waters.

The land application of manure, including pasturing of animals, can result in a net build-up of soil P (Beauchemin et al. 1996; Klausner & Bouldin 1983), much of which is bound in forms not immediately available for plant uptake, including non-labile P and soil organic matter. Based on these considerations, we hypothesize that increased residual P pools can lead to SRP concentrations in runoff that are higher than from unmanured land (although lower than prior to land abandonment when manure was still being applied). In the context of an abandoned field forest stand in the Catskills Mountains, New York, USA, the objectives of this paper are to: a) identify biogeochemical processes capable of releasing residual P and contributing to the eutrophication of receiving waters, b) link P sources with hydrological transport processes, and c) assess the coupled processes which result in the observed runoff SRP concentrations.

Phosphorus cycling during forest succession

Undisturbed, mature hardwood ecosystems in humid, eastern North America cycle nutrients conservatively, particularly P (Likens & Bormann 1995; Zhang & Mitchell 1995; Yanai 1992; Swank & Crossley 1988). However, P conservation may vary considerably in forest ecosystems, e.g., P cycling was shown to be leaky in old-growth boreal forests (Schoenau et al. 1989). Similarly, P dynamics in riparian forests were shown to have significant spatial and temporal variability (Lyons et al. 1998) and were linked to hydrologic P transport.

Early forest succession after land abandonment is dominated by competition for resources (De-Steven 1991; Zak et al. 1990; Abrams 1988). Nutrients

– P in particular – are sequestered in biomass (Vitousek & Reiners 1975). As a result of conservative nutrient cycling in the forest ecosystem, P largely remains bound in biomass (Díaz-Raviña et al. 1995; Joergensen et al. 1995; Yanai 1992). Although new leaves and shoots have the highest P concentrations by weight (Mou et al. 1993) early in succession, the largest P pool in a maturing forest is old (trunk) wood (Reiners 1992). With the build-up of organic matter on the floor of the maturing forest, the flux of organic P mineralized through microbial activity increases (Compton & Cole 1998; Christensen et al. 1996; Gressel et al. 1996; Tiessen et al. 1994; Antibus et al. 1992; Illmer & Schinner 1992; Pang & Kolenko 1986). The implications of enhanced microbial mineralization of residual organic P on abandoned agricultural land are crucial for the elevated SRP concentrations described in this study.

A careful reading of the literature cited above indicates that there is a lack of studies that deal with nutrient cycling during forest succession on abandoned agricultural land. The fate and cycling of P inputs from historical farm practices are not well understood. For forest plantation establishment, research has been conducted on the effects on soil-water-nutrient dynamics of fertilization (Harding & Jokela 1994; Edwards et al. 1991) and site preparation including burning (Lebo & Herrmann 1998). Odum (1960) reported on residual fertilizer leaching from abandoned agricultural land.

It is generally accepted that long-term manuring can cause elevated soil P levels (Nair et al. 1998; Schaffner & Oglesby 1978). In central New York State where this study is based, for example, historical P application rates in manure were 5–75 kg ha⁻¹ yr⁻¹, estimated loss in crop or fodder harvest was 2–50 kg ha⁻¹ yr⁻¹, and loss in leaching and runoff was 1–5 kg ha⁻¹ yr⁻¹ (Scott et al. 1998). As a result, during the period of manuring, soil P build-up was in the range of 2–20 kg ha⁻¹ yr⁻¹. Much of this P was bound in forms not immediately available for plant uptake, including non-labile P and organic matter.

As a consequence of increased P pools and nutrient dynamics during forest succession, the release of residual P from earlier agricultural activity is deduced to take place as the stand matures when trunk wood begins to fall and decay (40–60 years in typical hardwood forests). Analogously, P removal with harvested timber has been shown to be significant (Mou et al. 1993; Reiners 1992; Yanai 1991). The subsequent release of SRP to runoff can only take place when two conditions are met: i) P mineralization is more rapid than uptake, and ii) hydrological mobilization and transport processes remove SRP in such a way as to prevent re-adsorption by mineral soil which is low in P.

The principal processes that could account for residual P release include weathering and mineralization. Weathering is unlikely given the very pronounced seasonality of observed SRP signals (see below). Because P mineralization in acid soils is mediated by aerobes, saturated conditions may inhibit net P release until ponded water dries from the forest floor (Joergensen et al. 1995). If this is the case, during periods of high microbial activity (spring and summer), SRP concentrations in runoff will rise significantly when the forest floor dries and mineralization outpaces uptake. SRP concentrations in the periods of low microbial activity (autumn and winter), which also correspond to increased soil saturation, are likely to be depressed as observed for the study site. As a result, the lack of hydrological evidence strongly suggests that biogeochemical processes are responsible for residual P release, and that microbial mineralization is likely linked to P release.

The effect on SRP concentrations of soil drainage after forest clear felling has been described by Adamson and Hornung (1990) who postulated that poor drainage explained the observed mobilization of Fe and P. The dynamics described in this study reflect a separate set of coupled processes, i.e, the release of P bound in decaying biomass, with seasonal trends corresponding to microbial mineralization cycles and SRP removal driven by transient water table rise and rapid surface runoff. Given that the 0.010 mg L^{-1} SRP threshold at which algae growth in receiving water becomes accelerated (Sharpley & Smith 1989) is only marginally higher than SRP concentrations measured for undisturbed hardwood forests (0.006 to 0.008 mg L⁻¹ as reported for the study area by P. Longabucco, New York State Dept. Environ. Conserv. 1997, pers. communication; and for eastern hardwood forests more generally by Haith et al. 1992; Swank & Crossley 1988; Omernik 1977), a slight increase in runoff SRP due to residual P may contribute to eutrophication. We have noted in the Introduction, however, that solution-particulate partitioning of P occurs during instream transport; as a result, caution must be exercised in interpreting SRP concentrations in runoff vs. those reaching receiving waters. The specific assays and hydrological analyses described in greater detail below for the Catskills study site indicate that residual P does elevate runoff SRP into the potential eutrophication range. Based on these processes, in part 2 of this paper we calculate hydrological and SRP mass balances and subsequently parameterize and run a physically based P transport model (Scott & Walter 2001).

Methods and materials

The study site is a 16.6 ha forest stand located at the headwaters of the Delaware River basin (42°21′ N, 74°52′ W) in the Catskills Mountains of New York State, USA (Figure 1). Climate is humid continental with average annual temperature of 8 °C. Average precipitation is 1123 mm yr⁻¹ with 381

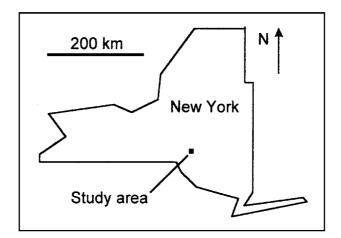


Figure 1. Location of the study area.

mm yr⁻¹ (34%) occurring as snow. Elevation varies from 662 m to 732 m (Figure 2). A 1938 air photo shows that the site was pasture. The present forest stand is dominated by 40–50 year old sugar maple (*Acer saccharum*), soft maple (*Acer rubrum*), aspen (*Populus grandidentata*), birch (*Betula papyrifera* Marsh.), yellow birch (*Betula alleghaniensis*), and thornapple (*Crataegus spp.*). A small stand of old-growth forest (1.3 ha), visible on the air photo, occupies the northern edge of the site and is comprised primarily of ironwood (*Carpinus caroliniana*) and white ash (*Fraxinus americana*), estimated to be 100 years or older.

The soils, derived from glacial till and acid sandstone and shale parent material, are coarse, loamy, mixed, frigid, lithic dystrochrepts of the Halcott-Mongaup-Vly, Elka-Vly complex, and Lewbeach series with the characteristics presented in Table 1. Physical properties are as reported in the STATSGO database. Available moisture content, $\theta_{\rm available}$, is defined as $\theta_{\rm saturation}$ - $\theta_{\rm fieldcapacity}$. Available nutrients and minerals (P, Fe, Al) were determined using standard New York State methods – Morgans's solution extraction (10% sodium acetate in 3% acetic acid buffered to pH 4.8, using a 1:5 w/v soil:solution ratio; Morgan 1941). Available P was measured colorimetrically by stannous chloride reduction; Fe_{available} and Al_{available} were measured by atomic absorption.

An assay was performed using biomass, sediment and mineral soil samples collected at the site on 29 April 1997. Four replicates were tested for total P (TP) and equilibrium SRP for each of the following types of P source material:

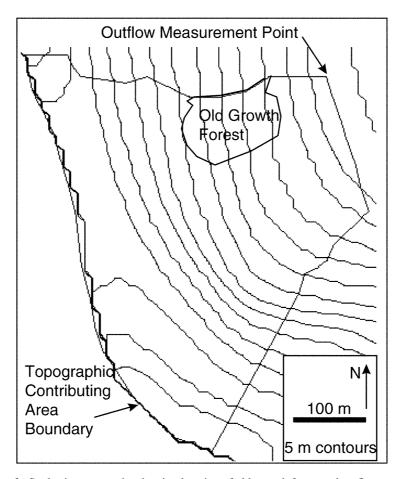


Figure 2. Study site topography showing location of old growth forest and outflow measurement point.

- 1. *outflow sediment and biomass* accumulated in the ditch at the entrance to the flume (see description of discharge gauging below, represents composite signal from the entire catchment),
- 2. *flowpath sediment and biomass* accumulated in the bed of an ephemeral flowpath not flowing when sampled which drains the regrowth forest area (represents transportable material from the largest runoff-contributing area),
- 3. *regrowth forest biomass*, especially leaf litter under maple (represents source material from the largest runoff-contributing area, approximately 92% of the topographic contributing area, see Figure 2),

Table 1. Physical and chemical properties of field site soils

		Series		
		Halcott-Mongaup-Vly	Elka-Vly complex	Lewbeach
Texture	Units	Channery silt loam,	Channery	Channery loam,
		very rocky	loam	very strong
Area	ha	2.3	7.9	6.4
Depth to bedrock	cm	38	150	38
Slope	%	0-22	9–35	0-33
$\theta_{ m saturation}$		0.22	0.46	0.26
$\theta_{ m field capacity}$		0.18	0.22	0.21
$\theta_{ m available}$		0.04	0.24	0.05
Rock content		0.58	0.20	0.55
Pavailable	${ m mg~kg^{-1}}$	1.774	1.342	1.841
pН		4.88	4.84	5.36
Organic matter	%	6.5	5.1	5.9
Fe _{available}	${\rm mg~kg^{-1}}$	42.2	39.9	14.9
Al _{available}	mg kg ⁻¹	181.2	151.6	122.4

- 4. *old growth forest biomass* for comparison with regrowth forest biomass (represents source material from approximately 8% of the topographic contributing area),
- 5. *Bh mineral soil* from under the regrowth forest area (represents source material for the groundwater concentration).

Assay sample material was oven-dried at 37 °C and ground in a crucible, combined with distilled-deionized water at ratios representative of the suspended solids concentrations measured in runoff (0.007–0.032 g L^{-1}) and mixed for 72 hr in a completely stirred reactor such that solid-solute equilibrium was achieved. Total P was extracted with ammonium persulfate and was determined by measuring ascorbic acid-reduced phosphomolybdate using a Turner Instruments $^{\circledR}$ 690 spectrophotometer at 880 nm following Standard Methods (1985). The SRP fraction was measured colorimetrically after filtration at 0.45 μm , as indicated below for water samples.

Water samples were filtered through Supor® 0.45 μ m filters under a vacuum of 70 kPa or less to separate the SRP fraction. Phosphorus concentration of the filtrate was determined colorimetrically at 880 nm as described above. All lab ware used was only for P analysis and, along with field sample bottles, was washed in concentrated acid for 24 hours, soaked in distilled-deionized water and dried at 37 °C prior to use.

Available Fe and Al were extracted with Morgan's solution and determined by atomic absorption. Organic matter (OM) was determined by loss

on ignition (LOI) at 550 °C for 2 hr following 110 °C for 2 to 4 hr, and is reported in Table 1 as 0.7*LOI - 0.23 (Northeast Coordinating Committee on Soil Testing 1995).

Surface runoff and shallow lateral flow (collectively treated as runoff throughout this paper) were collected at the site in a surface diversion ditch excavated (in 1993) approximately 1.5 m deep down to the impermeable layer. Runoff at the site was gauged using an H-flume installed in a propaneheated, insulated box (for instrumentation details, see Scott 1998a; Scott 1998b). Ice buildup during the winter was freed on a regular basis. Eight calibrations at different discharges using a stopwatch and graduated cylinder matched gauged flow within 11%. Loss under the flume headwalls (installed 30 cm into the fragipan and grouted with hydraulic cement and bentonite) was estimated to be less than 1 L s⁻¹ when head increases during peak discharge (<5% of Q). Runoff from the old growth forest could not be isolated, as upslope water flowed through this area.

Multiple runoff samples were collected at variable intervals during runoff events using an ISCO® automatic sampler. During periods of relatively constant discharge, single grab samples were collected. 'Events' were defined operationally on the basis of weather forecasts when flow was anticipated to rise significantly. Runoff discharge rate, precipitation, and solar radiation were logged on a 15 min interval. Air temperature, soil temperature (at 10 cm and 20 cm depth) were recorded at a separate location 960 m from the forest site, also on a 15 min interval. Snow depth and density and soil freezing were recorded at seven locations within the forest stand on 21 separate occasions during the winter of 1996–1997.

Results and discussion

SRP concentration in runoff

The SRP concentration analyses presented here were based on runoff samples (n = 156) collected between 1 February 1996 and 3 June 1997. Figure 3 shows the SRP time series – subsequently written as SRP(t) – which exhibits pronounced seasonality. The causes for this trend will be explored below.

Runoff discharge (Q) was continuously monitored for the 10 April 1996–26 March 1997 period, with the Q(t) hydrograph of recorded average daily runoff shown in Figure 4. Daily SRP mass export time series were generated with runoff event volumes assigned a mean SRP value interpolated from Figure 3; total mass SRP for the 351-day period of continuous discharge record was divided by the total runoff volume to calculate the flow-weighted SRP_{mean} of 0.0127 mg L^{-1} . Strictly, this result is not a true annual value

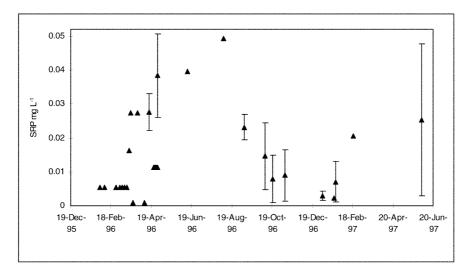


Figure 3. Soluble reactive phosphorus concentration series showing spring-summer flush (error bars \pm 1 standard error of event samples about flow-weighted mean; data points without error bars are single grab samples).

(351 instead of 365 days); however, it is within \pm 9% of annual SRP_{mean} as calculated using simulated flows for the additional 14 days (27 March–9 April 1996 or 27 March–9 April 1997) on either end of the period of record to a complete a full year (Scott 1998a).

The $0.0127~\text{mg}~\text{L}^{-1}~\text{SRP}_{\text{mean}}$ considerably exceeds the concentration expected in runoff from forest land, which in the northeastern US is typically less than $0.008~\text{mg}~\text{L}^{-1}$. An extensive literature review did not turn up any reference on SRP concentrations from successional forest on previously manured land. In Yanai (1992), and Swank and Crossley (1988), regrowth forest refers to logged or experimentally deforested land. Based on the following data and analyses, we suggest that the most plausible cause for the elevated SRP_{mean} of $0.0127~\text{mg}~\text{L}^{-1}$ is residual agricultural P.

While the April 1996–March 1997 period had precipitation 29% higher than the 42 yr average for Walton, NY (approximately 32 km from the study site), there is no reason to suggest that SRP concentrations in precipitation would vary as a result. The difference that can be attributed to increased precipitation is greater runoff volumes. SRP concentrations vary considerably during events, bolstering the hypothesis that a combination of biogeochemical and hydrological processes generated the SRP concentrations observed.

SRP concentrations in runoff from pasture are variable, with reported values ranging from 0.02-0.37 mg L⁻¹ for alfalfa, 0.01-0.03 mg L⁻¹ for grass in Minnesota, USA, 0.18-0.98 mg L⁻¹ for grass in New Zealand (Sharpley

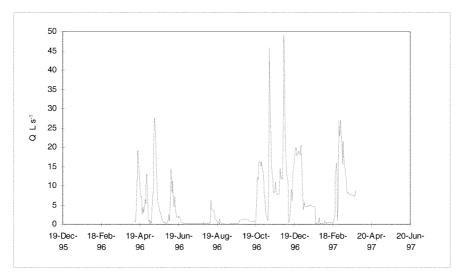


Figure 4. Runoff hydrograph showing spring and fall peaks.

et al. 1995), and 0.3 mg L^{-1} for pasture (Haith & Tubbs 1981). All reported pasture runoff concentrations, however, appear to exceed the SRP_{mean} found in this study. As a result, successional forest resulting from land abandonment undoubtedly produces lower P loading to receiving waters than pasture or manured land prior to abandonment.

Phosphorus source material assay

The results of the assay for TP are shown in Figure 5. Flowpath TP matched outflow TP closely, indicating that 3,000 mg kg⁻¹ is a robust measure of persulfate-extractable P in solids that are prone to runoff transport from this site. Given that both outflow and flowpath materials were composites of biomass and mineral soil, we reason that the three remaining material types represent the primary P sources from which outflow and flowpath TP must be derived.

It is clear that Bh mineral soil cannot account for TP levels greater than several hundred mg kg⁻¹. Of the two remaining sources, regrowth biomass mean TP and old growth biomass mean TP were 3% and 19% lower than outflow mean TP respectively. With the same entrainment and SRP dissolution processes applying for both sources, it is clear that the concentrations in runoff measured at the outflow are strongly influenced by regrowth biomass, although the outflow signal was undoubtedly a composite of multiple sources.

Mineralized P is available as $H_2PO_4^{2-}$ or HPO_4^{-} (Illmer & Schinner 1992) or in readily available labile fractions (Gressel et al. 1996). As a result, runoff

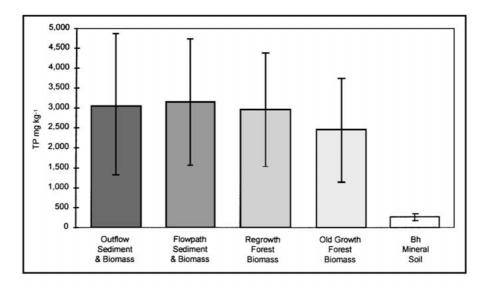


Figure 5. Total P by source type (error bars ± 1 standard deviation).

SRP levels result primarily from biomass entrainment and dissolution, and only limited desorption. Related laboratory work on the kinetics of P desorption using rainwater and field soil samples (Scott 1998a) indicated that for SRP concentrations in the range measured for this site, sorbed-solute equilibrium is reached within hours after initial mixing, with 50% SRP_{equilibrium} reached within 3 hr, indicating that for typical transport times shorter than this, it is likely that SRP primarily reflects soluble P fractions.

Accordingly, we examined the fraction of TP that is made up of SRP (see Figure 6). Outflow SRP/TP was the lowest of the P sources assayed. It is suggested that the flowpath value was significantly higher because the flowpath bed material had a higher sediment:biomass ratio than the outflow material. Again, Bh material could not account for the SRP signal measured at the outflow, given that virtually all P was available as SRP after complete (72 hr) mixing. Finally, regrowth biomass SRP/TP and old growth biomass mean SRP/TP were 22% and 44% higher than outflow SRP/TP, respectively, strengthening the conclusion that outflow SRP is primarily derived from regrowth biomass that reflects residual P effects.

Surface vs. soil profile P sources

SRP(t) increases with increasing Q during events, then falls rapidly suggesting that concentrations at the outflow appear to be derived primarily from forest floor surface sources. Ohrui and Mitchell (1998) found positive

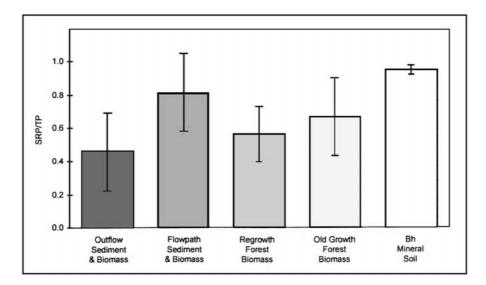


Figure 6. SRP as a fraction of total P by source type (error bars ± 1 standard deviation).

correlations for Ca²⁺ and NO₃⁻ with Q, but inverse correlations for Na⁺, HCO₃⁻ and SiO₂. Anderson et al. (1997) observed inverse trends for all major ion species (except hydrogen ion) in their study, which did not test for SRP, leading to the conclusion that low concentration ('old') water stored in the catchment dominates runoff and dilutes the solute signal.

Where changes in soil moisture storage can be shown to account for runoff volumes generated during storm events, soil water may represent the major portion of runoff as described by Rice and Hornberger (1998); hence, solute concentrations may be reasoned to derive primarily from soil profile sources. We consider this process to apply for solutes released from a relatively uniform concentration gradient throughout the entire soil profile.

The sorption characteristics of P as confirmed by the difference between observed organic matter and mineral soil levels of TP, however, lead us to conclude that desorption equilibrium cannot explain event SRP concentrations. Phosphorus is released to runoff in elevated concentrations when the saturated zone rises to the soil surface and surface layer mixing occurs as a result of overland flow, as described separately for dissolved inorganic and organic nitrogen by Creed and Band (1998). These processes support our interpretation that elevated SRP concentrations during events are derived from mobilization of P from sources primarily at the soil surface, not throughout the soil profile.

Two possible explanations exist for the pronounced seasonal SRP trends observed in Figure 3. The first is that SRP is dependent on soil moisture that would be at concentration equilibrium with soil-sorbed P. Equilibrium soil profile SRP ambient concentration (C_a) is determined from sorbed concentration, S, by:

$$C_{a} = \frac{S}{K_{d}} \tag{1}$$

Taking S as the average of the three $P_{available}$ values reported in Table 1 and 143.8 L kg⁻¹ as the value of K_d , the distribution (desorption-partition) coefficient based on Morgan's solution extraction (Scott 1998a), yields $C_a = 0.0115 \text{ mg L}^{-1}$. We reported above that sorbed-solute equilibrium is reached within hours after initial mixing and concluded that typical transport times are shorter than this. It appears unlikely that sorbed P can account for the SRP values observed. It should be noted that K_d is dependent on the clay content of the soil, among other factors, and variation in the value used here might increase C_a . Hutson et al. (1997) use a generalized K_d value of 100 L kg⁻¹ for similar conditions.

This raises the second possibility; one we suggest would form an important applied research question, that runoff SRP on abandoned land may be linked to microbial mineralization of organic P in surface litter. This contention is based on the earlier observation that SRP appears to be primarily from surface-derived P sources and that the SRP flush starts in late spring and peaks in early summer. SRP mineralized on the forest floor and transported in surface runoff bypasses the mineral layers of the soil, which would result in unavoidable loss to re-adsorption. Thus elevated SRP concentrations are maintained into the stream system.

Microbially mineralized P is generated in readily available labile fractions (Gressel et al. 1996; Fabre et al. 1996) or as $\rm H_2PO_4^{2-}$ or $\rm HPO_4^{-}$ (Illmer & Schinner 1992), which would allow for SRP concentrations higher than possible through desorption. Studies by Cross and Schlesinger (2001), Compton and Cole (1998), Díaz-Raviña et al. (1995), Antibus et al. (1992), Gillespie and Pope (1991), and Pang and Kolenko (1986) support this hypothesis, with some indicating that microbial processes appear to operate within the SRP concentration range observed.

Conclusion

Based on continuous runoff data, event and grab sample SRP concentrations, and P source material assays for a forest stand on abandoned agricultural land in the Catskill Mountains of New York State, USA, this paper strongly suggests that residual P from past agriculture is detectable as runoff-transported SRP approximately 40 years into forest succession. It was shown that the SRP signal in runoff events primarily reflects soil surface — not profile-derived sources. This was corroborated by a P source material assay establishing forest surface litter as the primary source of SRP in runoff. Microbial mineralization was postulated to influence the marked seasonal SRP trend observed.

Acknowledgements

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