

Spatial and Temporal Variability of Phosphorus Retention in a Riparian Forest Soil

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ABSTRACT

Riparian zones remove P from surface runoff and can act as filters of nonpoint source (NPS) P pollution for surface waters. Riparian forest soils were investigated in spring and fall for their capacity to retain $\text{PO}_4^{3-}\text{-P}$. Samples (300 on each date) were taken from a soil drainage catena from moderately well (MWD), somewhat poorly (SPD), and poorly drained (PD) soil in May and November of 1995 to examine spatial and temporal variability of P retention and its relationship to soil properties. The equilibrium P concentration at zero sorption (EPC_0) was determined for each sampling point (lower EPC_0 = higher P retention capacity). Mean (coefficient of variation, CV) EPC_0 values were 3.8 (0.49) mg P L^{-1} in May and no P sorption was apparent in November for SPD soil, 1.0 (1.34) and 1.5 (1.03) mg P L^{-1} in May and November, respectively for MWD soil, and 0.5 (1.87) and 1.3 (1.13) mg P L^{-1} , respectively for PD soil. The EPC_0 was significantly and positively correlated to organic matter (OM) for all drainage classes on both dates. Low EPC_0 values—high P retention capacity—in MWD and PD soil corresponded with high Fe_{ox} and Al_{ox} values. For SPD soil, high mean EPC_0 corresponded with low mean Fe_{ox} and Al_{ox} values. The relationship between EPC_0 and Fe_{ox} and Al_{ox} was described by a hyperbolic function for MWD and PD soil, but not for SPD soil. The EPC_0 did not exhibit spatial structure at the sampling scale used for any of the drainage classes, even though Fe_{ox} , Al_{ox} , and OM content showed spatial structure.

NONPOINT source nutrient pollution is a leading cause of water quality problems in the USA (Novotny and Chesters, 1989; USEPA, 1973). Excessive nutrient loading from watersheds into surface waters can have negative ecological effects such as overstimulation of algal and aquatic plant growth in receiving waters (USEPA, 1992). Agricultural practices in upland areas are a leading contributor of NPS nutrient contamination, particularly P, to freshwater ecosystems (USEPA, 1992). Phosphorus is the limiting nutrient for primary productivity in most freshwater bodies (Schindler, 1977) and increased loading of P into these ecosystems often leads to accelerated eutrophication (Wetzel, 1983). More than 70% of the P load to freshwater systems is from land drainage via surface flow (Vought et al., 1994).

The interfaces between upland and freshwater ecosystems are known as riparian areas. These unique landscape features have distinct vegetation and soil characteristics. Their physical proximity results in extensive interaction with upland land uses and in filtering of nutrients moving from the upland areas to aquatic ecosystems (Lowrance, 1991). Nutrient retention varies within these zones depending on landscape position (Cooper and Gilliam, 1987; Simmons et al., 1992; Nelson et al., 1995). Removal mechanisms for P in riparian areas include sorption of soluble P by surface soils as

well as microbial and plant uptake (Lowrance et al., 1985; Richardson, 1985).

Riparian zones have been investigated for their ability to act as a nutrient buffer between these two ecosystems. Cooper and Gilliam (1987) found that about 50% of the P leaving agricultural fields appeared to be removed from runoff water in riparian areas. According to Lowrance et al. (1984), 30% of total P entering a forested riparian area is retained there. By contrast, Cooper et al. (1986) and Nixon and Lee (1986) found both removal and release of soluble P from wetland soils. Omernick et al. (1981) suggested that forested buffer strips can become saturated with nutrients, thus becoming ineffective buffers over time. Although the results from previous studies differ, removal of dissolved P in surface runoff in riparian areas is considered to be generally effective (Lowrance et al., 1995).

Soil properties known to influence P retention/release, such as OM, soil moisture, pH, and Fe and Al content, are known to exhibit spatial heterogeneity along the soil drainage gradient within riparian areas (e.g., Allen et al., 1989; Golet et al., 1993; Wright and Sautter, 1988). Seasonal changes in depth to water table, temperature, microbial activity, and litter and nutrient input can influence soil properties such as iron speciation, dissolved organic C levels, and pH. Thus, soils within a riparian zone may remove P to varying degrees, depending on landscape position and time of year. Knowledge of the spatial distribution of P removal capacity can be useful in identifying areas within riparian areas that can be targeted for protection because of their significance in attenuation of this nutrient.

A landscape-scale study was conducted within a riparian forest characterized by a soil drainage gradient to examine the spatial and temporal P retention/release capacity of the soils. We measured the capacity of riparian forest soils to retain $\text{PO}_4^{3-}\text{-P}$ using P adsorption isotherms in the spring and fall. Samples (300 on each date) were taken from a soil drainage catena in May and November of 1995 to examine the spatial and temporal variability of P retention. Three drainage classes were examined: MWD, SPD, and PD soil. The relationship between P retention capacity of the soil and soil properties measured at the same points, including soil OM, mass water content, pH, and oxalate-extractable Fe and Al content (Fe_{ox} and Al_{ox}) was determined.

We hypothesized that (i) the P retention capacity of the soil is spatially correlated to static soil properties that control P sorption, including soil OM, pH, and oxalate-extractable Fe and Al content, (ii) the P retention capacity of the soil varies among drainage classes because these soil properties vary within a soil drainage

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Abbreviations: NPS, nonpoint source; MWD, moderately well drained; SPD, somewhat poorly drained; PD, poorly drained; EPC_0 , equilibrium P concentration at zero sorption; CV, coefficient of variation; DP, dissolved phosphate; RSS, residual sum of square values; OM, organic matter.

catena, and (iii) the P retention capacity of the soil varies at different times of the year due to seasonal variations of P loading to the riparian zone, such as fertilizer applications and land management practices, as well as factors within the riparian zone, such as depth to the water table, temperature, and litter inputs, which can affect P retention.

MATERIALS AND METHODS

Study Site

The study area is located at the Peckham Farm Research Area of the Univ. of Rhode Island (Kingston, RI) in the Chipuxet River watershed, within the larger Pawcatuck River Basin in southern Rhode Island. The area is forested and directly down gradient from a fallow field. The upland forest at the site is dominated by oak (*Quercus* sp.) grading to a red maple (*Acer rubrum*) swamp. The site is underlain by glacial outwash and contains a soil drainage catena. The soil in the upland portion of the site is mapped as a Hinkley sandy loam (a sandy-skeletal, mixed, mesic Typic Udorthent) and grades to a Walpole sandy loam (a sandy, mixed, mesic Aeric Haplaquept) and a Scarboro mucky sandy loam (a sandy, mixed, mesic Histic Humaquept) (Soil Survey Staff, 1981). Moderately well, SPD, and PD drainage classes were delineated using a modification of the criteria established by the Army Corps of Engineers (Wright and Sautter, 1988). Moderately well-drained soils have mottles common in the lower part of the subsoil, generally at a depth of 45 to 90 cm and remain wet and cold later in the spring. Somewhat PD soils have mottles common in the subsoil at a depth of 20 to 45 cm and remain wet for long periods as a result of slow removal of water caused by a high water table. Poorly drained soils have high water tables at or near the surface during a considerable part of the year, a thick, dark surface horizon, and mottles are frequently found within the top 20 cm of the soil surface (Amador et al., 1997).

Soil texture was found to be sandy loam, loam, and loam for MWD, SPD, and PD, respectively. Mean (%CV) soil available P ($n = 5$) determined by sodium bicarbonate extraction method (Schoenau and Karamanos, 1993) was 14.9 (8.8), 19.8 (8.0), and 10.2 (2.9) mg P/kg dry soil for MWD, SPD, and PD, respectively in November 1995 and 60.0 (40.1), 82.0 (24.7), and 27.7 (12.6) mg P/kg dry soil for MWD, SPD, and PD, respectively for May 1995.

Sampling

Soil samples were taken on 9 May and 8 Nov. 1995 using a nested random stratified sampling scheme. An area 24 m in length by 15 m downslope was delineated to include the three drainage classes. The sampling scheme covered a 24 by 5 m area in each drainage class, which was divided into five, 5 by 5 m subplots per drainage class. A total of 300 samples were taken at each sampling date, 100 samples per drainage class. Within each drainage class, 20 random samples from each subplot were taken, 10 of which were taken from two areas of 1 by 1 m chosen randomly within each subplot. Nested samples were taken to capture spatial variations at a small scale. Sample points were surveyed to a common benchmark using a transit. The distance between samples for all drainage classes ranged from 7 cm to 24 m. The litter layer was removed and soil cores (5 cm diam.) were taken from the top 5 cm, placed in sealable plastic bags, and kept on ice in a cooler until transported to the laboratory, where they were stored in the dark at 4°C.

Soil Physical and Chemical Properties

Soil pH, OM content, and moisture content were determined within 7 d after the sampling date. Soil samples were homogenized manually by shaking before soil properties were determined. Soil moisture content was determined gravimetrically after oven drying a 5.0 g sample of moist soil at 105°C for 6 h. Soil pH was determined using a 1:2 soil/water ratio and a pH meter (Hendershot et al., 1993). Soil OM content was determined by loss on ignition at 550°C for 4 h (Karam, 1993). Particle-size distribution was determined after removal of OM using the hydrometer method (Sheldrick and Wang, 1993). Soil available P was determined by sodium bicarbonate extraction (Schoenau and Karamanos, 1993), followed by colorimetric analysis using an automated nutrient analyzer (model RFA-300, Alpkem, Clackamas, OR).

For determination of oxalate-extractable Fe and Al, soil samples were air dried for 3 d, sieved to pass a 2-mm mesh sieve, and homogenized manually by shaking. For each sample, 1.0 g of air-dry soil was placed in a 250-mL plastic bottle and 100 mL of extractant was added. The extractant was a 0.2 M ammonium oxalate solution, adjusted to a pH of 3.0 with oxalic acid. The bottles were capped and shaken for 4 h at 175 rpm in the dark at room temperature (20–23°C). The resulting mixture was passed through a Whatman no. 42 filter, the filtrate placed in a plastic vial, and stored in the dark at room temperature for later analysis. Oxalate-extractable Al and Fe (Al_{ox} and Fe_{ox}) were determined by atomic adsorption spectroscopy (Soil Conservation Service Staff, 1972).

Phosphorus Retention/Release Capacity

Phosphorus adsorption isotherms were used to determine the ability of the soil to remove P according to the method of Guertal et al. (1991). Soil samples were air dried for 3 d, sieved to pass a 2-mm mesh sieve, and homogenized manually by shaking. For each sample, 1.0 g of air-dry soil was placed in a 20-mL plastic vial and 15 mL of a solution containing 0, 1, 3, 5, or 7 mg P L⁻¹ was added. Phosphorus solutions were prepared using NaH₂PO₄ in 0.5 M NaNO₃. The vials were capped and shaken for 24 h at 100 rpm in the dark at room temperature. The mixture was passed through a Whatman no. 42 filter and the filtrate analyzed for soluble reactive P colorimetrically using an automated nutrient analyzer (model RFA-300, Alpkem, Clackamas, OR).

Sorption isotherms were used to evaluate P removal capacity for each sampling point by plotting solution concentration after equilibration vs. amount of P sorbed. From these data, the EPC₀ was determined for each sampling point at the point where the isotherm crosses the x-axis.

For each drainage class, five sample points were chosen randomly and analyzed in triplicate for evaluation of analytical uncertainty of EPC₀ determinations.

Statistical Analysis

Mean, median, standard deviation (SD), and CV were determined for all physical and chemical soil properties and EPC₀ values for each drainage class. Normality of the data was determined using the Kolmogorov-Smirnov test. For data sets that were not normally distributed, nonparametric statistical tests were used. An unpaired *t*-test or a Mann-Whitney rank sum test was used to assess differences in soil properties and EPC₀ values between seasons. A Kruskal-Wallis analysis of variance (ANOVA) on ranks was used to assess differences in soil properties and EPC₀ values among drainage classes. Multiple comparisons procedures were used to isolate differences among EPC₀ values and soil properties—Dunn's method

was used for EPC_0 values and the Student-Newman-Keuls method was used for other soil properties. Significant differences were evaluated at the 95% confidence level unless otherwise specified.

Scatter plots were created by plotting EPC_0 values against individual soil properties for each drainage class. Linear and nonlinear regression analysis were performed using SigmaPlot (version 5.0, Jandel Scientific, Corte Madera, CA). Stepwise multiple regression analysis of soil properties and EPC_0 values was performed to determine which combination of soil properties best explained variability in retention of P for each drainage class.

Geostatistical Analysis

Geostatistical analysis was used to model the spatial structure of EPC_0 and soil properties that affect P retention. Geostatistics assumes spatial dependence among sample points, which traditional statistical analyses tend to ignore (Rossi et al., 1992). This is important when investigating soil properties known to vary spatially and in identifying spatial distribution patterns that may exist in the field. The semivariogram is used to describe the spatial autocorrelation for a particular random variable measured on a sample spatial data set (Trangmar et al., 1985). It displays the change in the semivariance between two sample points as the distance between them increases. Semivariograms were calculated using the equation

$$\gamma(h) = 1/2E [z(x_i) - z(x_i + h)]^2 \quad [1]$$

where $\gamma(h)$ is the semivariance, E is the expected squared distance between values of samples separated by lag distance h , and $z(x_i)$ and $z(x_i + h)$ are measured values at points x_i and $x_i + h$ (Trangmar et al., 1985).

Semivariograms were computed for each spatially referenced soil property and EPC_0 values for each drainage class. GS+ (version 1.21, Gamma Design Software, Plainwell, MI), the geostatistical analysis program used, evaluates the semivariogram and suggests the model that best fits the data. In all cases, the spherical model, the most common variogram model used (Isaaks and Srivastava, 1989), was used to fit the data. A lag spacing of 0.3 m, the average distance between sampling

points (Isaaks and Srivastava, 1989), was used in determining semivariograms for all soil properties for each of the three drainage classes.

RESULTS

Soil Physical and Chemical Properties

Soil physical and chemical properties were examined for temporal variation (Table 1). No significant differences were observed in mass water content, OM, Al_{ox} , and Fe_{ox} in MWD soil between May and November. For SPD soil, OM, Al_{ox} , and Fe_{ox} did not differ significantly between sampling dates, but mass water content was significantly lower and pH was significantly higher in November. No significant differences in Al_{ox} and Fe_{ox} content between sampling dates were observed for PD soil. Otherwise, PD soil appeared to be more dynamic than the other drainage classes, with significantly lower mass water content, higher OM content, and higher pH in November than May.

Differences among drainage classes for each sampling date were also examined. Except for pH, all other soil properties differed significantly among drainage classes in both May and November (Table 1).

Distribution of Phosphorus Retention Capacity

Phosphorus retention capacity of the soil was determined for all three drainage classes using P adsorption isotherms from which the EPC_0 was calculated. The EPC_0 is the point at which the isotherm crosses the x-axis and represents the solution P concentration at which P adsorbs and desorbs at the same rate. A low EPC_0 represents a high P retention capacity; conversely, a high EPC_0 represents a low P retention capacity.

Significant differences in mean EPC_0 were observed between sampling dates for MWD and PD soils, with

Table 1. Mean, median, and coefficient of variation (CV) of soil properties for MWD, SPD, and PD soil in May and November.

Soil drainage class	Date		Mass water content	OM content	pH	Al_{ox}	Fe_{ox}
			%		g kg ⁻¹		
MWD†	May	Mean‡	87.5†§,a	33.8†,a	3.8†,a	2.19†,a	2.16†,a
		Median	76.4	72.7	3.8	2.14	1.84
		CV	0.5	0.50	0.1	0.28	0.43
	Nov.	Mean	79.1†,x	35.5†,x	4.1‡,x	2.18†,x	2.58†,x
		Median	72.7	32.8	4.2	2.13	2.46
		CV	0.5	0.4	0.1	0.24	0.3
SPD	May	Mean	191.0†,b	63.1†,b	3.8†,a	1.97†,b	1.63†,b
		Median	195.1	66.0	3.8	1.96	1.62
		CV	0.23	0.19	0.1	0.1	0.33
	Nov.	Mean	155.8‡,y	61.9†,y	4.0‡,y	2.04†,y	1.92†,y
		Median	157.9	63.9	4.0	2.06	1.92
		CV	0.2	0.2	0.1	0.25	0.24
PD	May	Mean	241.8†,c	59.8†,c	3.7†,c	5.16†,c	3.51†,c
		Median	245.4	59.7	3.6	5.07	3.38
		CV	0.15	0.12	0.1	0.36	0.33
	Nov.	Mean	219.9‡,z	62.3‡,z	4.2†,z	5.60†,z	4.14†,z
		Median	212.5	62.5	4.2	5.46	3.9
		CV	0.2	0.1	0.05	0.35	0.37

† MWD = moderately well drained, SPD = somewhat poorly drained, PD = poorly drained.

‡ $n = 100$ for all soil properties for all drainage classes on both sampling dates.

§ Values within a drainage class followed by the same symbol within a column are not significantly different, using a *t*-test for mass water content (SPD), bulk density (SPD), Al_{ox} (SPD, PD), and Fe_{ox} (SPD, PD), otherwise a Mann-Whitney rank sum test was used.

|| Values among drainage classes for each date followed by the same letter within a column are not significantly different, using a Kruskal-Wallis ANOVA on ranks test.

Table 2. Mean, median, standard deviation (SD), and coefficient of variation (CV) of EPC₀ for moderately well drained (MWD), somewhat poorly drained (SPD), and poorly drained (PD) in May and November 1995.

	MWD		SPD		PD	
	May	November	May	November	May	November
	EPC ₀ , mg P L ⁻¹					
Mean	1.01 ^{†,a†,‡}	1.53 ^{‡,x}	3.90 ^b	ND [§]	0.52 ^{†,c}	1.26 ^{‡,y}
Median	0.36	1.09	3.93	ND	0.17	0.55
CV	1.34	1.03	0.49	ND	1.87	1.13
n	80	66	61	ND	74	82

[†] Values within a drainage class followed by the same symbol are not significantly different.

[‡] Values among drainage classes for each date followed by the same letter are not significantly different.

[§] Not determined.

higher values observed in November (Table 2). We were not able to determine EPC₀ values for SPD soil in November because the initial P concentration of the soil exceeded the P concentration of the solutions added to the soil, indicating that during the equilibration process, P was released from the soil into solution. Although the absence of P sorption by soil in November indicates that there was a difference in P sorption between sampling dates in SPD soil, we were not able to determine its magnitude or statistical significance.

Poorly drained soil had a significantly lower mean EPC₀ in May and November than MWD and SPD soils (Table 2). Somewhat PD soil had the highest EPC₀ in May compared to MWD and PD soils. Overall, retention capacity of all three drainage classes was less in November than in May.

Triplicate analyses of samples were performed on five sampling points per drainage class to evaluate analytical uncertainty in the determination of EPC₀ values. The mean CV for MWD and PD soil ranged from 0.17 to 0.44, respectively (data not shown). These values are two to six times lower than the CVs observed for a drainage class (Table 2).

Relationship Between EPC₀ and Soil Properties

The EPC₀ was plotted against mass water content, OM, pH, Fe_{ox}, and Al_{ox} to investigate relationships between P retention and soil physical and chemical properties. Soil OM was significantly and positively correlated to EPC₀ for all three drainage classes on both sampling dates (Table 3), whereas Fe_{ox} and Al_{ox} were significantly and negatively correlated to EPC₀ for all drainage classes on both sampling dates, except for Al_{ox} in MWD soil in May.

Stepwise linear regression analysis was performed on

data for each drainage class on both sampling dates to determine which combination of soil properties best predicted EPC₀. In no case was the inclusion of more than one variable found to improve predictions of EPC₀ significantly.

Plots of EPC₀ vs. Fe_{ox} and Al_{ox} suggested a nonlinear relationship existed between these variables, as shown for PD soil in November (Fig. 1). These data are representative of what was observed in MWD and PD soil on both sampling dates (data not shown). In general, EPC₀ appeared to be insensitive to changes in Fe_{ox} and Al_{ox} at low concentrations of these metals. There seemed to be a range of these metals above which EPC₀ declined with increasing Fe_{ox} and Al_{ox}. This appeared to be the case for MWD and PD soil in May and November. The SPD soil did not exhibit a similar relationship between EPC₀ and Fe_{ox} and Al_{ox}. The data were fit to the equation

$$EPC_0 = [1/(x^2 - a)]^{1/2} \quad [2]$$

where $x = Fe_{ox}, Al_{ox},$ or $Fe_{ox} + Al_{ox}$ (g kg⁻¹) and $a =$ a constant (g² kg⁻²). Parameter estimates and residual sum of squares values (RSS) are shown in Table 4. Similarly good fits were obtained whether Fe_{ox}, Al_{ox}, or the sum of Fe_{ox} and Al_{ox} were fit to Eq. [2], as indicated by similar RSS values.

The nonlinearity of the relationship between EPC₀ values and Fe_{ox} and Al_{ox} suggested that perhaps another soil property was affecting P retention. We examined the possible involvement of OM using three-dimensional plots to investigate the relationship between EPC₀, OM content, and Fe_{ox} + Al_{ox} (Fig. 2) for all drainage classes. Although data are shown for PD soil in November for the sake of brevity, the trend observed is representative of MWD and PD soil on both dates. Higher EPC₀ values generally occurred at high OM con-

Table 3. Coefficient of determination (r²) of EPC₀ vs. individual soil physical and chemical properties for moderately well drained (MWD), somewhat poorly drained (SPD), and poorly drained (PD) soil.

Soil drainage class	Date	Mass water content	OM content	pH	Al _{ox}	Fe _{ox}
		g kg ⁻¹				
MWD	May	0.170***	0.151***	0.009	0.037	0.105*
	Nov.	0.154*	0.226***	0.175***	0.249***	0.299***
SPD	May	0.303***	0.199***	0.064	0.348***	0.234***
	Nov.	ND [†]	ND	ND	ND	ND
PD	May	0	0.109*	0	0.317***	0.287***
	Nov.	0	0.073*	0.064	0.508***	0.417***

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†] OM = organic matter; ND = not determined.

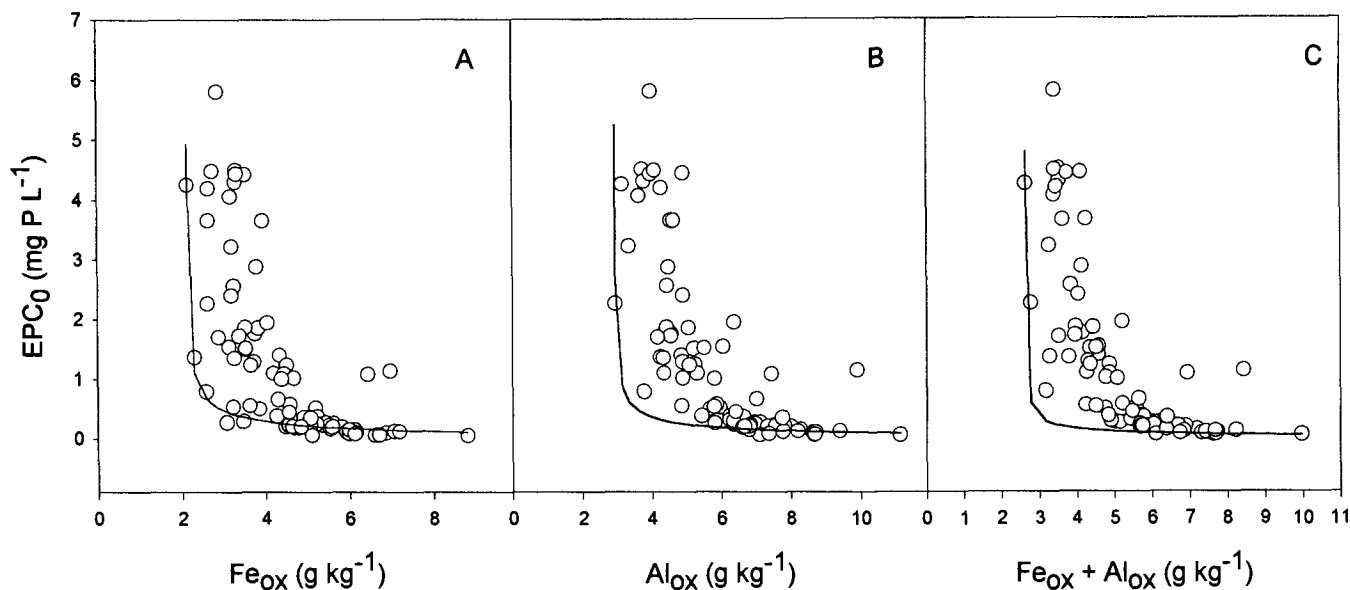


Fig. 1. Relationship between EPC_0 and Fe_{ox} (A), Al_{ox} (B), and $Fe_{ox} + Al_{ox}$ (C) for poorly drained (PD) soil in November. Line represents best fit of data to Eq. [2].

tent and low levels of $Fe_{ox} + Al_{ox}$ and decreased with decreasing amounts of OM and increasing amounts of $Fe_{ox} + Al_{ox}$.

Spatial Analysis of EPC_0 and Soil Properties

Geostatistics was used to analyze the spatial structure of EPC_0 and soil physical and chemical properties for all drainage classes. Because we observed a significant relationship between EPC_0 and OM, Fe_{ox} , and Al_{ox} , spatial analysis was performed to examine possible spatial relationships among these properties. Model parameters, including range, sill, nugget, Q , and r^2 are presented in Table 5. The nugget (C_0) represents unexplained variability attributable to analytical error or the chosen sampling scale. The sill (C), the value at which the semivariogram levels off, is the sample variance. This constant value occurs at a given separation distance known as the range. The ratio of the sill to the sum of the sill and nugget variance, Q , can be used to indicate the level of spatial structure that exists at the sampling

scale used. Q is given by

$$Q = C / (C + C_0) \quad [3]$$

where C = sill and C_0 = nugget. The ratio ranges from 0 to 1; a value of 0 indicates that the variability is driven by the nugget variance—a lack of spatial structure. As Q increases, more of the variance is explained by the semivariogram.

EPC_0 did not exhibit spatial structure at the sampling scale used for any of the drainage classes studied. The semivariograms had a weak fit (low r^2 ; Table 5) and did not follow the general pattern of increasing semivariance with increasing distance (Fig. 3). Semivariograms are shown for Fe_{ox} for all three drainage classes in Fig. 3 and are representative of the general pattern exhibited for Al_{ox} and OM content. The spatial structure of Fe_{ox}

Table 4. Parameter estimates for a nonlinear model (Eq. [2]) describing the relationship between EPC_0 and Fe_{ox} , Al_{ox} , + Al_{ox} for moderately well drained (MWD), somewhat poorly drained (SPD), and poorly drained (PD) soil.

Soil drainage class	Date	Variables included	a	RSS†
MWD	May	Fe_{ox}	1.14	11.71
		Al_{ox}	1.82	11.45
		$Fe_{ox} + Al_{ox}$	8.77	11.81
	Nov.	Fe_{ox}	1.55	14.38
		Al_{ox}	1.71	13.81
		$Fe_{ox} + Al_{ox}$	7.58	15.54
PD	May	Fe_{ox}	2.68	6.73
		Al_{ox}	4.54	6.78
		$Fe_{ox} + Al_{ox}$	21.41	8.13
	Nov.	Fe_{ox}	4.53	14.37
		Al_{ox}	8.49	15.16
		$Fe_{ox} + Al_{ox}$	27.93	15.58

† Residual sum of squares.

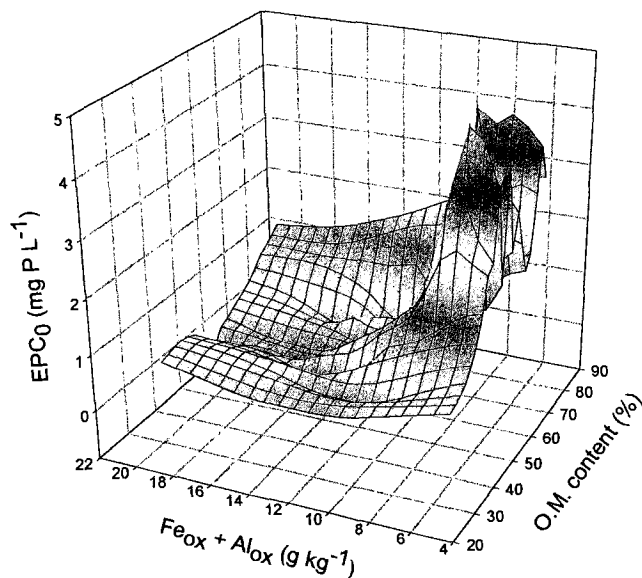


Fig. 2. Three-dimensional mesh plot of EPC_0 vs. organic matter (OM) content and $Fe_{ox} + Al_{ox}$ for poorly drained (PD) soil in November.

Table 5. Geostatistical properties of organic matter (OM), Fe_{ox}, and Al_{ox} content in soil from different drainage classes.

Drainage class	Soil property	Range	Sill† (C ₀ + C)	Nugget‡ (C ₀)	Q (C/C ₀ + C)	r ²
MWD§	OM	8.7	312.5	188.4	0.40	0.45
	Fe _{ox}	3.45	1.14	0.26	0.77	0.70
	Al _{ox}	0.54	0.367	0.001	0.99	0.16
SPD	OM	2.99	134.4	68.6	0.49	0.53
	Fe _{ox}	4.33	0.26	0.08	0.69	0.80
	Al _{ox}	8.78	0.31	0.20	0.36	0.34
PD	OM	0.51	45.7	0.1	1.0	0.26
	Fe _{ox}	2.97	1.41	0.03	0.98	0.87
	Al _{ox}	3.55	2.95	0.03	0.99	0.63

† Units for sill are %OM² for OM and g²/kg² for Al_{ox} and Fe_{ox}.

‡ Units for nugget are %OM² for OM and g²/kg² for Fe_{ox} and Al_{ox}.

§ MWD = moderately well drained; SPD = somewhat poorly drained; PD = poorly drained.

was similar in all three drainage classes. The semivariograms had similar characteristics (Fig. 3) and the range was similar among drainage classes (2.97, 3.45, and 4.33 m for PD, MWD, and SPD soil, respectively) (Table 5). Values of Q for Fe_{ox} were 0.77, 0.69, and 0.98 for MWD, SPD, and PD soil, respectively. By contrast, the spatial structure of Al_{ox} differed among drainage classes (Table 5). The value of Q was 0.36 for SPD soil, with

a value of 0.99 for both MWD and PD soil. The highest range (8.78 m) was observed for SPD soil, followed by PD (3.55 m) and MWD soil (0.54 m) (Table 5). The spatial structure of soil OM also varied among drainage classes. Range values decreased in the order MWD (8.65 m), SPD (2.99 m), and PD soil (0.51 m) (Table 5). Lower values of Q were observed for MWD (0.40) and SPD (0.49) soil than in PD (1.0) soil.

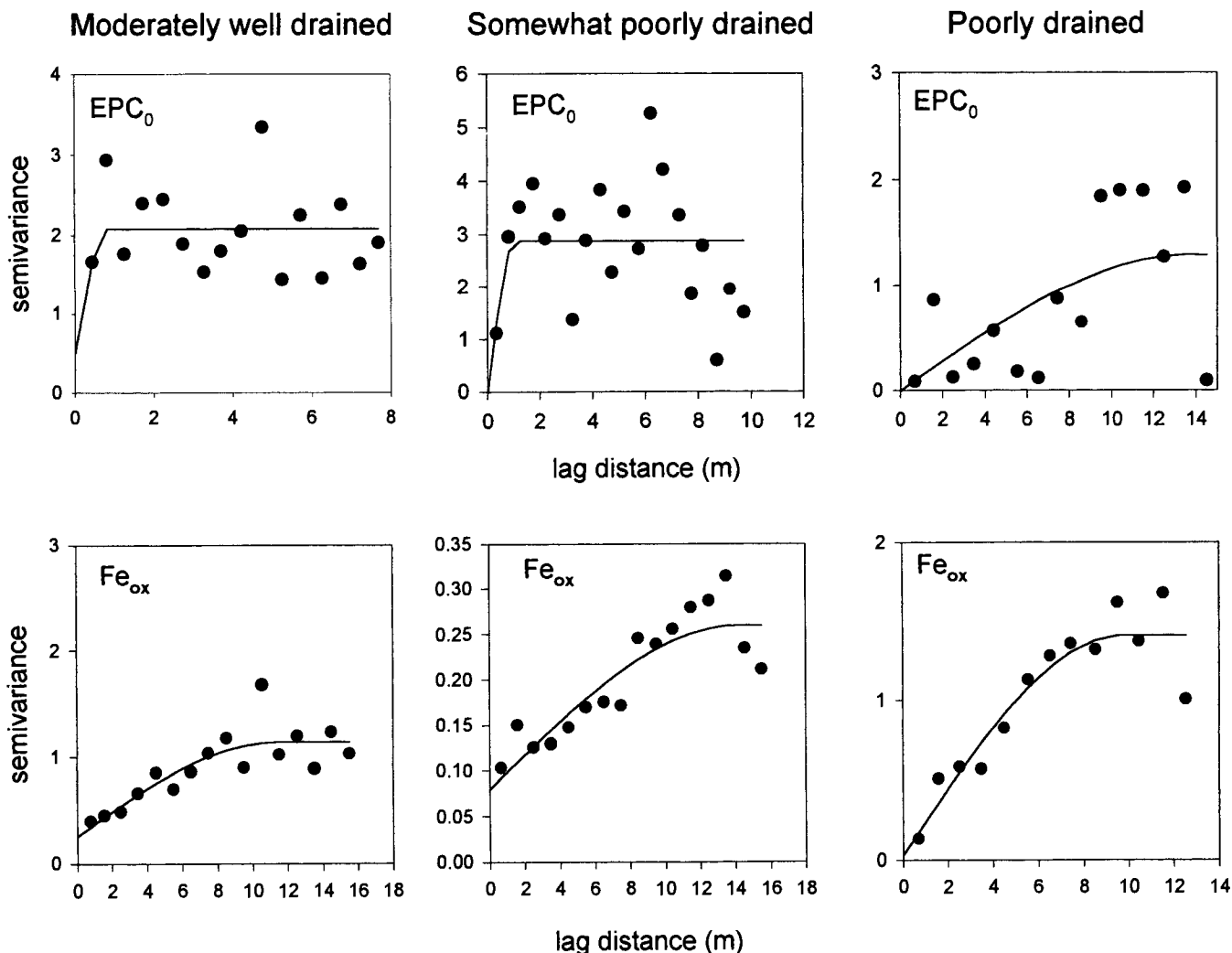


Fig. 3. Semivariograms of EPC₀ and Fe_{ox} for moderately well drained (MWD), somewhat poorly drained (SPD), and poorly drained (PD) soil in May.

DISCUSSION

The higher retention capacity—low EPC_0 values—of MWD and PD soils indicates that larger amounts of P could be removed from solution by soil in these two drainage classes compared to SPD soil. The range of EPC_0 values observed in the present study (0.52–1.53 mg P L⁻¹) is within that observed for soils from other ecosystems. For example, using the same methodology as in the present study, Guertal et al. (1991) found EPC_0 values of 2 and 3 mg P L⁻¹ for the top 2 cm of field soils for a Hoytville silty clay loam (a fine, illitic, mesic Mollic Ochraqualf) and a Canfield silt loam (a fine-loamy, mixed, mesic Aquic Fragiudalf), respectively. By contrast, in a riparian forest in North Carolina, Cooper and Gilliam (1987) observed mean (CV) EPC_0 values that ranged from 8.99 (0.34) in the forest edge to 31 (0.61) $\mu\text{g P L}^{-1}$ in the flood plain swamp. These values are much lower than the EPC_0 values observed in MWD, SPD, and PD soil in both May and November in our study (Table 2). Differences in EPC_0 values compared to those observed in our study could be attributed to differences in vegetative cover or soil properties. In the study by Cooper and Gilliam (1987), selective cutting of trees allowed the growth of a thick understory and floor vegetation. These management techniques have been suggested to maintain the successional stage and maintain nutrient filtering (Lowrance et al., 1983). Plant uptake removes a portion of the inorganic P in the soil solution, thus increasing the availability of adsorption sites and resulting in a higher P retention capacity. Alternatively, the lower EPC_0 values reported by Cooper and Gilliam (1987) could also be attributed to differences in clay mineral content. The clay content of soils in their study ranged from 6 to 24%, whereas clay minerals are found in negligible quantities in Rhode Island soils (Wright and Sautter, 1988). Differences in EPC_0 values could also be attributed to the P status of the soil, as well as the ionic strength of the supporting electrolyte. A lower level of P already in the soil or an increase in concentration of the supporting electrolyte would cause an increase in P retention, resulting in a lower EPC_0 value.

The P retention capacity of soil is generally closely associated with the acid-extractable Fe and Al content of the soil (e.g. Karim and Adams, 1983; Richardson, 1985; Abrams and Jarrell, 1995). Extraction by ammonium oxalate is known to dissolve primarily the amorphous and poorly crystalline oxides of Fe and Al, which sorb large quantities of P from soil solution (Karim and Adams, 1983; Sanyal et al., 1993; Abrams and Jarrell, 1995). In the present study, the Fe_{ox} and Al_{ox} content of the soil seems to exert a strong control on P removal. Low mean EPC_0 values—high retention capacity—in PD and MWD soil corresponded with higher mean values of Fe_{ox} and Al_{ox} compared to SPD soil. Poorly drained soil, with the lowest mean EPC_0 for both sampling dates, had the highest mean Fe_{ox} and Al_{ox} , while the lower P retention capacity in SPD soil was associated with lower mean Fe_{ox} and Al_{ox} values.

The relationship between Fe_{ox} and Al_{ox} and EPC_0

within a drainage class was not linear; rather, a hyperbolic function appeared to best describe the data. Such a relationship suggests that metals exert little control on P retention below a certain concentration of Fe_{ox} and/or Al_{ox} . For MWD and PD soils, Fe_{ox} and Al_{ox} did not appear to affect EPC_0 below a range of 2 to 4 g kg⁻¹ of these metals. When the levels of Fe_{ox} and Al_{ox} exceed this range, P retention appeared to be controlled directly by these properties. By contrast, the plot of EPC_0 vs. Fe_{ox} or Al_{ox} for SPD soil showed much more scatter (data not shown) and a range of values for either Fe_{ox} or Al_{ox} , below which EPC_0 was not affected, was not apparent. The relatively low levels of Fe_{ox} and Al_{ox} found in soil from this drainage class (Table 1) may be responsible for the absence of a hyperbolic relationship with EPC_0 .

Phosphorus removal in soil is known to be affected by OM (Sanyal et al., 1993). Organic matter may coat Fe and Al oxides, thus blocking potential sorption sites and decreasing P adsorption (Stevenson, 1994). Competition between humates and phosphate for adsorption sites may also decrease P adsorption (Stevenson, 1994). López-Hernández et al. (1986) found phosphate adsorption by tropical soils is reduced in the presence of organic anions. Guertal et al. (1991) investigated the depth dependence of P retention in soil and attributed the lower retention of P at the soil surface partly to higher OM content. Reddy et al. (1980) found increased EPC_0 values with increased application rates of organic residues in the form of animal wastes. Struthers and Sieling (1950) showed that, under acidic conditions, organic anions greatly reduced the amount of P adsorbed by Fe and Al. Ohno and Erich (1997) observed that dissolved OM isolated from corn (*Zea mays* L. Merr.) and wheat (*Triticum aestivum* L.) residue decreased adsorption of P onto soil surfaces.

For all drainage classes on both sampling dates, EPC_0 exhibited a significant, positive correlation with OM content, indicating that OM had a negative effect on P sorption capacity of the soil. The hyperbolic relationship between EPC_0 and Fe_{ox} or Al_{ox} could result from the interactions of OM with Fe_{ox} and Al_{ox} . The nonlinear relationship between $Fe_{ox} + Al_{ox}$ and EPC_0 is most apparent at higher amounts of OM (Fig. 2). At lower levels of Fe_{ox} and Al_{ox} , the effects of OM on P retention—high EPC_0 values—are apparent, whereas at higher levels of Fe_{ox} and Al_{ox} OM appears to have no effect. At low levels of Fe_{ox} and Al_{ox} , organic acids could out-compete phosphate for adsorption sites (Struthers and Sieling, 1950), whereas at higher levels of Fe_{ox} and Al_{ox} more adsorption sites may be available, thus reducing competition between OM and phosphate.

Spatial and Temporal Variability

EPC_0 does not exhibit spatial structure among the drainage classes as described by the semivariogram (Fig. 3), even though Fe_{ox} , Al_{ox} , and OM are significantly correlated with EPC_0 (Table 3) and these soil properties did show spatial structure (Fig. 3). The sampling scale and/or the size of the sample itself may not have been

sufficiently small to capture the spatial structure of EPC_0 . This suggests that perhaps additional properties affecting P retention may vary at a smaller scale. For example, organic acids or particle-size distribution may show variation at a smaller scale, possibly adding to the complexity of the spatial distribution of EPC_0 .

Seasonal variations in rainfall (intensity and duration), length of time between runoff events, depth to water table, and degree of vegetative cover may cause differences in P removal/release. These factors influence the relative magnitude of physical and chemical processes determining the fate of P. Although retention capacity remained higher in MWD and PD than in SPD soil, there were differences between sampling dates. In November, P retention was lower for all drainage classes as indicated by higher EPC_0 values. As mentioned previously, no P sorption occurred in SPD soil in November. The lower P retention capacity could be driven by an increase in the level of organic acids in the soil from leaching of forest litter in the fall when precipitation is high. Total precipitation was 77.2 and 151.6 mm in April and October, respectively (NOAA, 1996). The greater total precipitation on the month prior to sampling in the fall coupled with newly deposited leaf litter, tends to support the contention that organic acid concentrations in the soil could be higher in the autumn and that leached organic anions could outcompete phosphate anions for sorption sites (López-Hernández et al., 1986; Stevenson, 1994; Kaiser and Zech, 1996). Other studies in riparian forests have found no difference in P retention between seasons. Lowrance et al. (1984) found total P and dissolved phosphate (DP) showed almost no change between seasons for a riparian forest in an agricultural watershed in Georgia. Osborne and Kovacic (1993) found no effect of season on the mean concentration of DP in a riparian forest in Illinois. However, Peterjohn and Correll (1984) observed that peak output of orthophosphate for a watershed in Maryland occurred in the spring.

CONCLUSIONS AND IMPLICATIONS

The P retention capacity of the soil (EPC_0) appeared to be controlled by OM and Fe- and Al- oxides. A significant positive relationship was observed between EPC_0 and OM, whereas the relationship between EPC_0 and Fe_{ox} and Al_{ox} was nonlinear. There appeared to be a range of concentrations of these metals above which EPC_0 exhibited consistently low values. Higher values of EPC_0 occurred with high amounts of OM and low levels of Fe_{ox} and Al_{ox} . The pH of the soil, mass water content, and bulk density did not prove to be useful indicators of P retention capacity in this study.

As we hypothesized, the P retention capacity of the soil varied not only among drainage classes, but between sampling dates. Poorly drained soil, with the lowest mean EPC_0 in May and November, had the highest P retention capacity in the soil drainage catena. Moderately well drained soil also had potential to act as a sink for P. However, once the concentration of the surface water exceeds the EPC_0 , the soil may contribute P to

the overlying water. The EPC_0 for SPD soil in May, although much higher than MWD and PD, indicated this drainage class as a sink for P. However, this area may have become saturated with P and no longer acts as a sink but rather a source of P. The P retention capacity of MWD and PD decreased in November.

Knowledge of the P retention capacity of riparian zones has useful applications in water quality management. For example, the role of riparian forests as sinks and sources of P can be incorporated into P-loading models, thus improving their accuracy. Identifying areas within riparian forest zones with the greatest removal can allow for more efficient use of these landscape features for water quality improvement. Furthermore, improved understanding of relationships of OM content, Fe_{ox} , and Al_{ox} content with EPC_0 will facilitate targeting specific areas within a catena for maximum P removal.

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