

Alteration of Soil Phosphorus Pools from Coal Mining and Reclamation

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2005 Annual Proceedings of the West Virginia Academy of Science, In review June 2005

ABSTRACT

Surface mining of coal converts large areas of forest in the Appalachian region to other land uses such as pasture. Mining radically alters the soil and vegetation of a site so there is potential for substantial alteration of nutrient pools and fluxes. The objective of this study was to compare the soil phosphorus pools of a reclaimed mine site and a nearby forested site.

Organic horizon material and mineral soil cores were collected at 3-m intervals along three transects that were established at random in a 14- to 17-year-old surface mine reclaimed to pasture and in a mature hardwood forest. Soil samples were analyzed for total P, organic P, and bicarbonate-extractable P. Phosphate adsorption isotherms were used to assess the soils' ability to retain P. Soil solutions were collected in tension lysimeters to evaluate soil solution P.

All three forms of soil P plus soil solution P were significantly lower in the mined soil than in the forested soil and in the mineral horizon versus the organic horizon ($p < 0.05$). Adsorption isotherms suggested that the organic horizon of the mined site had a smaller capacity to adsorb periodic pulses of phosphate. On an areal basis, the mined site contained significantly less P than the forested site (1,230 vs. 1,810 kg P ha⁻¹; $p < 0.05$). In summary, the reclaimed mine site contained 32% less phosphorus overall and much less plant-available phosphorus compared to a managed forest, which could have long-term implications for plant nutrition and ecosystem development.

INTRODUCTION

Surface mining of coal is widespread in the central Appalachian region and the practice converts large areas of forest to other land uses, mainly pasture. From 1930 to 1980 1,454 square miles of forest were strip mined for coal in KY, WV, VA, and TN (Hopps 1994). At the landscape level the result is a patchwork of contrasting soil types supporting ecosystems with very different biological and geochemical characteristics. It is important to understand the implications of this large scale alteration on nutrient cycles in light of the nationwide problem of nutrient pollution. This is especially critical within the Chesapeake Bay watershed where 69% of the nutrient load to the Bay comes from the watersheds of the four main tributaries.

The soils that result from the mining and reclamation process are fundamentally different from undisturbed, native soils in a variety of ways. The native forest soil is typically the product of thousands of years of soil development and has well-defined horizons with a surface horizon characterized by a high organic matter content which leads to a low bulk density, high water-holding capacity, high cation and anion exchange capacity, and good aggregate structure. During the mining process the native soil (called “topsoil”) is removed, mixed, and piled to the side for a period of weeks to months. After mining is complete, a layer of homogeneous spoil material (overburden) is laid down and the “topsoil” is spread on top using heavy equipment. Thus, a typical minesoil has a 20- to 30-cm thick surface layer of mixed, compacted native soil material over a thicker homogeneous layer of spoil material (Doll 1988). Consequently young minesoils tend to have a high bulk density, little aggregate structure, low carbon content, and often a low pH or high toxic metal concentration (Johnson and Skousen 1995; Bradshaw 1997; Akala and Lal 2001; Ramsey et al. 2001).

The low carbon content, likely a result of rapid decomposition of organic matter due to soil disturbance during mining and reclamation, leads to other changes in the soil including a higher bulk density, lower cation and anion exchange capacities, poor aggregate structure, and smaller microbial populations (Lyons et al. 1998; Ramsey et al. 2001; McDowell and Sharpley 2003). As a result of these changes one would expect that organic phosphorus and exchangeable phosphorus in young minesoils would be lower, which potentially could lead to reductions in net primary productivity. Indeed, P deficiency is cited as a common problem of minesoils that must be overcome in order to establish vegetation on a site (Plass and Vogel 1973; Barnhisel 1988; Bradshaw 1997).

The objectives of this study were to determine how conversion of forest to pasture via coal surface mining and reclamation affects P pools and P availability. We hypothesized that P pools would be reduced in the reclaimed mine soils as a result of the disturbance and the reduction in soil carbon. To accomplish this we compared the soil of a 14-17 year-old reclaimed mine watershed with the soil of a nearby forested watershed.

METHODS

Site

The two study sites were located on Dans Mountain ($N79^{\circ} 02'$, $W39^{\circ} 40'$), just south of Frostburg in western Maryland. NEF watershed is a small (3.0 ha) forested subwatershed of Neff Run covered with mixed conifers and hardwoods at an elevation of 2,200 – 2,520 ft. and northwest aspect. Most of the subwatershed was selectively logged in 1980 according to aerial photos (K. Kuers, personal communication). MAT is a 27.2-ha subwatershed of Matthews Creek, with an elevation of 2,540 – 2,740 and west aspect. Prior to 1981 MAT was covered with

mixed conifer hardwood forest. Virtually all of MAT was clearcut in 1981 according to aerial photographs and permit records (K. Kuers, personal communication). These records also indicate that approximately one-half the area of MAT (12.5 ha) was surface mined for coal from 1981-1985. We refer to the reclaimed mine portion of the watershed as MAT-R. The upper portion of MAT-R was reclaimed to pasture in 1983 and the lower half in 1986. Reclamation included reapplying approximately 30 cm of topsoil that was scraped from the site, amending with fertilizer, and seeding with a mixture of grasses. The two watersheds, which are approximately 0.5 km apart, are described in more detail in Negley and Eshleman (2005).

Sampling

Three permanent, 100-m transects were established in both MAT-R and NEF at random locations and with orientations of either 0, 120, or 240 degrees. Soil samples were collected at approximately 3-m intervals along the length of each transect in August 1999 in NEF and in August 2000 in MAT-R. Oe/Oa horizons were collected quantitatively using a 10 x 10 cm template. At MAT-R there was only a thin Oe horizon. Mineral horizon material was collected by taking two 5-cm diameter bulk density cores to a depth of 20 cm.

In 2001 tension lysimeters were installed in both watersheds within three randomly-located, permanent plots at depths of 10 cm (shallow) and 40 cm (deep). Three lysimeters at each depth were located in each plot for a total of 18 per watershed. Lysimeters were sampled once per month during the growing season of 2000 and 2001 by establishing a partial vacuum in the lysimeters, waiting 24 hours, and then removing the sample.

Analysis

Soil samples were sieved through a 2-mm mesh and both fractions weighed for bulk density. The remaining analyses were conducted on the <2 mm fraction only. Soil pH (in 0.01 M CaCl₂) and ammonium-acetate-extractable Fe, Al, and Ca were measured (Thomas 1982). Total C was determined using a CHN analyzer (Carlo-Erba, Inc.). Plant-available P was measured using a bicarbonate extraction and total and organic P by dry-ashing (Olsen and Sommers 1982). P adsorption was measured by adding 30 mL of extracting solution (0, 10, 30, 50, 70 and 90 mg P L⁻¹) to 3 g of soil, letting it equilibrate for 24 hours, and then vacuum filtering. The P adsorption procedure was conducted in triplicate on 12 randomly-selected samples from each horizon from MAT-R and NEF. Adsorption isotherms were calculated from these results. Carbon and phosphorus pools were calculated for each sampling location by multiplying the total C or total P concentration by the bulk density corrected for the mass of stones and then extrapolated to 30 cm depth.

Lysimeter samples were filtered (0.45 µm) and subsamples frozen until analysis for dissolved reactive P and total dissolved P (alkaline persulfate digestion). Dissolved organic P was calculated by difference (APHA 1995).

Statistics

A two-way ANOVA was used to identify site, horizon and interaction effects for the P fractions and soil physico-chemical characteristics. Horizon effects were not of concern for the phosphate adsorption data, so a simple t-test was used to examine differences between watersheds. A repeated measures ANOVA was used to test for site, horizon, and sampling date effects on lysimeter data. There were no significant date effects so data from all dates was pooled

and analyzed with a two-way ANOVA. All statistical analyses were performed using SPSS v.13.0 (SPSS, Inc.) with an alpha of 0.05.

RESULTS

Because of the manipulation of the soil in MAT-R during the mining operation 14 to 17 years previously, the soil exhibited very little horizon development. A thin Oe horizon (mean thickness 0.9 cm) had formed in the years since reclamation, which was significantly thinner than the Oe/Oa horizon of NEF (6.4 cm; $p < 0.01$). Compared to the forested NEF watershed, both horizons in the reclaimed mine site had a significantly higher pH but lower percent carbon (Table 1). Also the bulk densities of both horizons in MAT-R were significantly greater. In the mineral horizon this was probably due to compaction by heavy equipment during reclamation. The greater density of the Oe horizon, which formed after reclamation, was probably a result of the lower carbon content of that horizon.

The iron content (ammonium-acetate extractable) of the mined soil was significantly greater than that of the forested site ($p < 0.01$; Table 1). The higher metal concentration likely came from the incorporation of pulverized minerals (like pyrite, FeS_2) during the mining and reclamation process that rapidly oxidize when exposed to air and water. The extractable aluminum and calcium concentrations of the two soils were not significantly different.

The two-way ANOVA for soil total P and organic P showed significant site, horizon, and interaction effects (Table 2). Both total P and organic P were significantly greater at NEF than at MAT-R (Table 2; Figure 1). Mineral soil horizons contained only about half the concentration of total P and organic P as the surface horizons. In contrast, there were no differences in organic

P expressed as a percentage of total P between the two sites, only between horizons. The percent organic P averaged 71% in the Oe/Oa horizons and 57% in the mineral horizons at both sites.

Bicarbonate-extractable P, which represents the plant-available fraction, showed a similar pattern with significant differences by site, horizon, and interaction (Table 2). Bicarbonate-extractable P was significantly lower in MAT-R than in NEF. In its organic horizon MAT-R contained only 37% as much bicarbonate-extractable P and in the A horizon only 17% as much.

To determine if there were significant changes in the absolute amount of P in the soil column as a result of the mining and reclamation process we calculated the C and P pools at each site on an areal basis. The P pool was significantly smaller in MAT-R ($1,230 \text{ kg P ha}^{-1}$) than in NEF ($1,810 \text{ kg P ha}^{-1}$; Figure 2). In contrast to the P pool results and to the dramatic difference in percent carbon between MAT-R and NEF, the total C pools were not different mainly because of the high bulk density of MAT-R soil which offset its lower carbon concentration. For both elements, the quantities in the mineral horizons exceeded those in the organic horizons by a factor of 10 or more because of the greater thickness and density of the former.

We also examined the capacity of the soil to retain P by using adsorption isotherms to calculate EPC_0 . EPC_0 is the solution phosphate concentration at which phosphate is adsorbed and desorbed at the same rate. Graphically, it is the point at which the isotherm crosses the x-axis. High EPC_0 values correspond to low retention ability. The soil's ability to buffer against increases in soil solution P can be estimated from the slope of the isotherm at the point that it crosses the EPC_0 point. A low slope means the soil has little capacity to adsorb additional P when soil solution P increases.

The reclaimed mine site had a significantly lower EPC_0 than the forested site but only in the organic horizon (Table 3). This indicates that the reclaimed mine soil had a greater P

retention ability in this horizon. Since the reclaimed mine site has a much lower phosphorus concentration, this makes sense. The smaller concentration of available P in the reclaimed mine soil could lead to many unoccupied exchange sites. However, because this horizon is so thin, the absolute capacity of this layer to adsorb phosphate will be limited.

At the same time the buffering capacity of the MAT-R organic horizon, as represented by the slope of the adsorption isotherm, was significantly lower than that of NEF. Thus, increases in soil solution P, such as might occur after plant senescence and leaf drop in autumn, will lead to relatively little P retention in the reclaimed mine soil. Instead, a large portion will remain in labile and solution phases where it may be leached to lower horizons. In contrast, the forested site's organic horizon will tend to retain more of the added P. In the mineral horizon there were no significant differences in the EPC₀ or slope between sites.

Soil solution P data exhibited a significant site and date effect but no effect of horizon (Figure 2). Both total dissolved P (TDP) and dissolved organic P (DOP) were significantly lower in MAT-R than in NEF. DOP contributed approximately 26 to 56% of the TDP.

DISCUSSION

Our results demonstrate a substantial decrease in soil P after mining and reclamation at MAT-R which could negatively affect plant productivity. In particular plant growth rate may be negatively affected by the lower concentration of available P and soil solution P (Table 2; Figure 3). Whether or not plant production in MAT-R was actually limited by P, plants will need to allocate more resources to roots and mycorrhizal associations than those in NEF to obtain the same amount of P (Geissler et al. 2004). In a soil with low P concentration there is the potential for a negative feedback on the P cycle. Low soil P concentrations can lead to reduced uptake and

consequently lower foliage P concentrations. This, in turn, can lead to lower concentrations of P in soil organic matter. If the C:P ratio is high enough it is possible that P can become limiting to microbial decomposers who will conserve it tightly at the expense of plant uptake (Gallardo and Schlesinger 1994; Cross and Schlesinger 1995). Thus, available P concentrations (bicarbonate-extractable and soil solution P) in such a soil will remain low until organic P has accumulated sufficiently to reduce the soil C:P ratio to the point that microorganisms are saturated.

MAT-R soil has been changed in other ways as well. Compaction by heavy equipment increased the bulk density of the soil which was shown to decrease soil aeration and infiltration rate (Negley and Eshleman 2005). The organic horizon of MAT-R is very thin and does not serve as a nutrient reservoir for plants as the thick humus layer in NEF does. Physical and chemical limitations of minesoils such as these can limit the species of plants that can invade and establish themselves (Johnson and Skousen 1995). Visual inspection of the site showed an incomplete plant cover consisting mostly of perennial plants and virtually no tree species present. This suggests less than ideal growing conditions were present.

A contributing factor to the low P concentrations in MAT-R is the soil's reduced ability to retain P. At the higher pH that exists in the reclaimed soil a lower number of pH-dependent anion exchange sites would be expected. As a result the exchange capacity of the soil is likely to be lower as well as the ability of the soil to adsorb seasonal pulses of P. The low EPC_0 values in the reclaimed mine site's soils suggests a P retention ability that is not being realized and reflects a relatively low long-term soil solution concentration of P (Table 3; Figure 3). A difference in iron concentrations could explain differences in P retention ability; however, iron concentrations were higher in MAT-R and should have led to a greater ability to retain P. The fact that they did not implies that the difference in iron concentration was not substantial.

The lower concentration of total P in MAT-R means that the soil has a limited capacity to replenish the available P pool during seasonal lows or after a disturbance like fire or harvesting. Over the long-term reduced plant growth and increased competition for P may affect succession by slowing it or by altering the species that can survive and compete there.

The reduction in total P concentration in soil horizons was mirrored by a reduction in total P per hectare. We can estimate the total amount of P lost from the reclaimed mine watershed if we assume that MAT-R soil prior to the disturbance was similar to the soil that exists currently in NEF. There is reason to accept this assumption. First, aerial photos and permits for the operation confirm the existence of mature forest on the site before 1980, meaning that a hardwood forest soil similar to that in NEF existed on the site and that it likely had some degree of horizon development. Second, the P pools in NEF are unlikely to have changed much during the past 14-17 years as the forest has recovered from the relatively minor disturbance of selective logging. P inputs from weathering and deposition are typically small and mostly offset by small leaching losses of P in highly conservative, aggrading forest systems (Newman 1995; Yanai 1998).

With the aforementioned assumption we estimate a net change of $-580 \text{ kg P ha}^{-1}$ in total soil P (Figure 2). Reclamation records indicate that 90 kg P ha^{-1} of fertilizer was applied just before revegetation. Thus, we estimate a gross change of $-670 \text{ kg P ha}^{-1}$, or -37%, during the mining and reclamation process. At the ecosystem level the loss of P is probably even greater because of the removal of P in aboveground biomass (trees) prior to mining. It is unlikely that much of the P was lost during the 14-17 years of recovery because once vegetative growth, and consequently nutrient cycles, were established P losses due to leaching would be minimal (Bradshaw 1997; Yanai 1998).

Rapid loss of P, as well as carbon, nitrogen, and other nutrients, during mining and reclamation could occur at several steps in the process although we know of no investigations of this process. Immediately after clearcutting the forest the cessation of plant uptake could lead to increased leaching losses. During mining when the native soil was removed and stored in spoil piles, decomposition of soil organic carbon would be stimulated with a concomitant loss of organic P. After replacement of the soil material and before establishment of vegetation, decomposition would again be stimulated by the disturbance, releasing organic P which would be rapidly leached without plant uptake to prevent it. Finally, erosional losses of bulk soil from spoil piles and unvegetated soil would contribute to the loss of P (Udawatta et al. 2004). P losses from all or some of these processes could be responsible for the observed decreases in soil P.

During the 14 to 17 years since reclamation successional processes have been active at MAT-R. Akala and Lal (2001) documented changes in soil carbon in a chronosequence of reclaimed soils in Ohio. Soil organic carbon levels were low for the first 5 years and then C fixation by plants caused it to increase rapidly to nearly the pre-mining level by year 20. In a plot-level study in western Virginia soil carbon levels, which were initially low, returned to pre-mining levels after 16 years (Bendfeldt et al. 2001). Comparable rates of carbon accumulation were reported in an abandoned agricultural field chronosequence (Knops and Tilman 2000). A similar process may have occurred at MAT-R. In 2000 the C content of MAT-R was comparable to that of its pre-mining level; however, we do not know how far it was reduced immediately after reclamation.

Although C pools can be replenished in as little as 20 years, P accumulation is much slower. P accumulates through weathering and deposition at extremely low rates on the order of 1 to 2 kg ha⁻¹ yr⁻¹ (Newman 1995; Yanai 1998). Leaching losses of P in the eastern U.S. are on

the order of 0.1 to 1.0 kg ha⁻¹ yr⁻¹ (Newman 1995; Yanai 1998). At these rates it would take over 300 years for the total P pool to return to its pre-mining level. Thus, in the short term P will remain in short supply. This underscores the importance of taking a long-term view in the design phase of the reclamation project. Decisions made regarding spoil materials used and configuration of those spoils will determine the long-term successional trajectory of the site (Chichester and Hauser 1991; Johnson and Skousen 1995).

If the results from this case study are typical of surface mines in Appalachia then we can expect mined watersheds to have much less P compared to surrounding forested ecosystems. Replenishment of that P from natural processes may take centuries and as such represents an essentially irrecoverable loss of this important nutrient. Nutrient management should be an integral part of ecosystem management but it is often overlooked in mining reclamation perhaps because reclamation, by definition, is a short term objective (Bradshaw 1997). A potential solution to this problem is amending the soil with fertilizer. However, additions of chemical fertilizers will be most effective 5 to 10 years after reclamation when the system's ability to retain phosphorus has been established. The fertilizer at our study site was applied when no vegetation was present and as a result much of the P was probably leached from the system.

Another implication of this loss of P from terrestrial ecosystems is that some portion of that loss is translocated to the aquatic realm. At any given time, numerous surface mining operations are active in the Potomac River basin and could be acting as sources of P inputs to the river. Quantifying the size and significance of this source is not possible with current information, but it should be a priority for research in the next few years.

In summary, the reclaimed mine soil in this case study exhibited significantly smaller P pools and less available P than the forested soil. Furthermore the ability of the soil to retain P

was reduced. It will likely take centuries for the P pool to recover to pre-disturbance levels. This underscores the importance of nutrient management as a part of ecosystem management.

ACKNOWLEDGMENTS

We wish to acknowledge the help of Z. Dragan, G. Frech, C. Giffen, A. Nakai, T. Negley, and M. Ramsey for field and lab assistance. K. Kuers provided information on site history and vegetation characteristics. We are grateful for the leadership of L. Pitelka on this project which was funded by a grant from the A.W. Mellon Foundation to the Appalachian Laboratory and the Appalachian College Association.

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Tables

Table 1. Mean (standard deviation) characteristics of soil from an 18-yr-old selectively logged forest (NEF) and a 14- to 17-yr-old reclaimed coal mine (MAT-R). All sites were located within the Georges Creek watershed in western, MD. Two-way ANOVA results are presented at the bottom of each column. * and ** indicate that the effect was significant with $p < 0.05$ or 0.01 , respectively; ns = not significant. N= 30 for each parameter in each watershed.

	<u>pH^a</u>	Bulk <u>Density</u> (g cm ⁻³)	Total <u>Carbon</u> (%)	Extractable Cations ^b Fe (mg g ⁻¹)	Al (mg g ⁻¹)	Ca (mg g ⁻¹)
<i>Oe/Oa Horizon^c</i>						
NEF	4.21 ^d	0.032 (0.015)	32.9 (6.6)	1.1 (0.6)	0.88 (0.53)	2.3 (0.8)
MAT-R	5.59	0.128 (0.091)	15.5 (5.2)	2.2 (0.9)	1.04 (0.61)	2.4 (1.2)
<i>Mineral Horizon</i>						
NEF	3.99	0.824 (0.201)	4.80 (2.9)	5.3 (1.8)	2.3 (1.2)	2.2 (0.9)
MAT-R	5.15	1.26 (0.152)	1.95 (0.3)	6.7 (2.8)	2.4 (1.7)	2.1 (0.9)
<i>Significant effect</i>						
watershed	**	**	**	**	ns	ns
horizon	**	**	**	**	*	ns
interaction	ns	**	**	ns	ns	ns

^apH measured in 0.01 CaCl₂.

^bFe, Al, and Ca extracted in 1N ammonium acetate (Thomas, 1982)

^cIn MAT-R only an Oe horizon was present

^dpH values were back calculated from the mean H⁺ concentrations; therefore standard deviations could not be calculated

Table 2. Mean (standard deviation) total, organic, and bicarbonate-extractable P from soils at a selectively-logged forest (NEF) and reclaimed mine (MAT-R) in western Maryland. Two-way ANOVA results are presented at the bottom of each column. * and ** indicate that the effect was significant with $p < 0.05$ or 0.01 , respectively. ns = not significant.

	<u>Total P</u> (mg g ⁻¹)	<u>Organic P</u> (mg g ⁻¹)	<u>Organic P^a</u> (%)	<u>Extractable P</u> (μg g ⁻¹)
<i>Oe/Oa Horizon^b</i>				
NEF	2.50 (0.587)	1.81 (0.49)	69.8 (7.07)	129 (85.1)
MAT-R	0.371 (0.093)	0.29 (0.47)	74.0 (6.93)	48.0 (24.3)
<i>Mineral Horizon</i>				
NEF	1.24 (0.758)	0.73 (0.51)	58.2 (10.4)	79.0 (42.0)
MAT-R	0.375 (0.165)	0.22 (0.11)	56.7 (13.6)	13.4 (11.5)
<i>Significant effect</i>				
watershed	**	**	ns	**
horizon	**	**	**	**
interaction	*	**	ns	**

^aOrganic P as a percentage of the total P

^bIn MAT-R only an Oe horizon was present

Table 3. EPC₀ (mg L⁻¹) and slope of phosphorus adsorption isotherms using equilibration solutions of 0, 10, 30, 50, 70 and 90 mg P L⁻¹. The mean and standard deviation of 12 replicate samples per watershed and horizon are presented. Asterisks indicate significant differences between watersheds ($p < 0.05$).

	EPC ₀		Slope	
	<u>Mean</u>	<u>SD</u>	<u>Mean</u>	<u>SD</u>
<i>Oe/Oa Horizon^a</i>				
NEF	3.20	(0.119)	2.12	(0.54)
MAT-R	0.158*	(0.68)	0.269*	(0.061)
<i>Mineral Horizon</i>				
NEF	0.121	(0.113)	0.932	(0.517)
MAT-R	0.029	(0.021)	0.633	(0.262)

^aIn MAT-R only an Oe horizon was present

Figure Legends

Figure 1. Total and organic P concentrations in (a) Oe/Oa horizons and (b) mineral horizons (0-20 cm) at the forested watershed (NEF) and the reclaimed mine watershed (MAT-R). Bars represent the mean of 30 replicate soil samples taken along three transects. Error bars show the standard deviation. Two-way ANOVA indicated significant watershed, horizon, and interaction effects (Table 2).

Figure 2. Total element pools per hectare in the forested watershed (NEF) and the reclaimed mine watershed (MAT-R) for (a) carbon and (b) phosphorus. Asterisks indicate a significant difference between the watersheds (t-test; $p < 0.01$).

Figure 3. Mean total dissolved phosphorus (TDP) and dissolved organic phosphorus (DOP) concentrations in lysimeter solutions at the forested watershed (NEF) and the reclaimed mine watershed (MAT-R) at (a) 10 cm depth and (b) 40 cm depth. Bars represent the volume-weighted mean values of eight collections made monthly during the growing seasons of 2000 and 2001. Error bars represent one standard deviation.





