Nutrient and Trace Element Leaching following Mine Reclamation with Biosolids

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ABSTRACT

Mine reclamation with biosolids increases revegetation success but nutrient addition well in excess of vegetation requirements has the potential to increase leaching of NO_3 and other biosolids constituents. A 3-yr water quality monitoring study was conducted on a Pennsylvania mine site reclaimed with biosolids applied at the maximum permitted and standard loading rate of 134 Mg ha^{-1}. Zero-tension lysimeters were installed at 1-m depth 1 yr before reclamation: three in the biosolids application area, one in a control area (no biosolids). Before reclamation, all water samples had pH in the range 4.7 to 6.2, acidity <20 mg L^{-1}, and very low levels of all other measured parameters. Following reclamation, percolate water in the biosolids-treated area had lower pH and greater acidity than the control area. Acidity was greatest during the first winter following biosolids application, decreased during the spring, and showed a similar pattern but with much smaller concentrations the second year. Maximum first-year leachate NO_3 concentrations were ~300 mg L^{-1} and half as large the second year. Estimated inorganic N leaching loss during the first 2 yr after biosolids application was 2327 kg N ha^{-1}. Aluminum, Mn, Cu, Ni, Pb, and Zn followed similar leaching patterns as did acidity, and their mobilization appeared to be the result of the increased acidity. These results indicate that large applications of low-C/N-ratio biosolids could negatively impact area water quality and that biosolids reclamation practices should be modified to reduce this possibility.

BIOSOLIDS generated by municipal wastewater treatment facilities are commonly used for reclamation of surface-mined lands in the Appalachian Region of the USA. In a review of the literature, Haering et al. (2000) cited numerous studies documenting that the use of biosolids as a mine soil amendment increases the success of reclamation efforts relative to amendment with inorganic fertilizer and limestone, particularly if available topsoil is low in organic matter or if overburden materials are used as topsoil substitutes. Extensive research on the use of biosolids in mine reclamation in the Appalachian Region was conducted in Pennsylvania in the late 1970s and 1980s (Sopper, 1993; Sopper and Kerr, 1982) and also in Virginia (Roberts et al., 1988a, 1988b; Daniels and Haering, 1994).

In the Pennsylvania research, the biosolids application rates used were generally in the range of 80 of 134 Mg ha^{-1}, with most sites receiving amounts at the upper end of the range. Much of the research was conducted with a 1:1 (by volume) mixture of anaerobically digested biosolids cake and composted biosolids cake containing wood chips known as "mine mix" that was

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produced by the City of Philadelphia. These application rates were found to promote long-term plant growth by supplying inorganic and slow-release organic N and P to low-fertility mine soils. The large amount of added organic material was found to promote topsoil development, increase water holding capacity, and stimulate microbial activity and nutrient cycling (Seaker and Sopper, 1988a, 1988b). At these application rates, total N added was generally in the range of 650 to 1100 kg ha^{-1} (~0.8 as organic N, ~0.2 as NH_4, and only trace amounts of NO_3). Anaerobically digested biosolids cake generally has a C/N ratio <10:1 and it is generally assumed that 20% of organic N in anaerobically digested biosolids cake will be mineralized in the first year following application (USEPA, 1995). Composted biosolids mineralize more slowly and generally 10% availability of organic N is assumed for the first year. Because the "mine mix" used in most of this research also contains wood chips, the overall C/N ratio of the material is generally >25:1 and is expected to have slower mineralization rates and possibly some N immobilization due to the added organic C (Haering et al., 2000). While some evidence of NO_3 leaching following biosolids application at these rates was observed (Sopper and Kerr, 1982; Murray and Giddings, 1982; Carello, 1990; Cravotta, 1998), the increases were either relatively small or were limited to the first few months following biosolids application.

Research conducted in Virginia has largely corroborated the work done in Pennsylvania (Haering et al., 2000), where superior revegetation success (both quantity and diversity) and soil development were achieved with biosolids compared with inorganic fertilizer. Philadelphia mine mix material was used at rates up to 552 Mg ha^{-1} (equivalent to 150 Mg ha^{-1} of biosolids only) but only limited evidence of NO_3 leaching was observed and only during the first winter following application. The absence of significant N loss was attributed to the high C/N ratio of the mine mix and the added organic C provided by the wood chips. This was confirmed in later investigations of NO_3 leaching at gravel mines reclaimed with biosolids cake at rates up to 98 Mg ha^{-1} (Daniels et al., 2001; Schmidt et al., 2001). Leachate NO_3 concentrations increased up to 100 mg L^{-1} with increasing biosolids cake applications, but NO_3 leaching was greatly reduced when the biosolids was combined with sawdust to increase the C/N ratio to 20:1.

Based largely on the Pennsylvania research, the Pennsylvania Department of Environmental Protection presently allows a one-time application of biosolids for mine reclamation at rates up to 134 Mg ha^{-1} of biosolids (dry weight equivalent of biosolids excluding wood chips); however, this rule is applied to any biosolids, regardless of N content or C/N ratio, and most mine reclamation with biosolids in recent years has been done with anaerobically digested biosolids cake. Further-

more, essentially all reclamation with biosolids utilizes the maximum permissible application rate. The median total N content of anaerobically digested biosolids cake produced in Pennsylvania is 46 g kg^{-1} (36 g organic N, 9 g NH$_4$–N; Stehouwer, 1999). Thus application of 134 Mg ha^{-1} can be expected to add ~6140 kg N ha^{-1}, of which ~2100 kg ha^{-1} will be plant-available N in the first year following application (assumes 20% mineralization of organic N and availability of all NH$_4$–N). This is an N application rate almost six times larger than those used in the research on which these regulations are based, and estimated first-year plant-available N approximately 10 times larger than that suggested as an ideal target for mine reclamation in Pennsylvania (Sopper and Kerr, 1979; Sopper et al., 1982). Based on the work by Schmidt et al. (2001) and Daniels et al. (2001), these large N application rates with no added organic C to adjust the C/N ratio could result in greater N loss than was observed in previous studies. In addition to N loading of surface and ground water, leaching of NO$_3$ and other nutrients at a mine reclamation site may stimulate pyrite oxidation. Bos and Kuenen (1990) and Francis et al. (1989) showed that nutrient addition stimulated microbial pyrite oxidation in coal cleaning waste, and Cravotta (1998) reported evidence that leaching NO$_3$ may have stimulated pyrite oxidation at a mine site in Pennsylvania that was reclaimed with biosolids. In a laboratory incubation and leaching study with biosolids blended with glass beads, Qureshi et al. (2003) reported significant generation of acidity and mobilization of trace metals in the biosolids. They attributed the acid production to bacterially driven oxidation of primarily S compounds, and possibly also nitrification. Such acidification has not been reported with field-applied biosolids, but the large biosolids application rates used in Pennsylvania for mine reclamation could create conditions similar to this incubation study.

To determine the extent of NO$_3$ leaching as well as leaching of other nutrients and trace metals following mine reclamation with biosolids, a 3-yr water quality monitoring study was implemented on an abandoned mined land site in Pensylvania that was scheduled for reclamation with anaerobically digested biosolids cake applied at a target rate of 134 Mg ha^{-1}. All biosolids application and reclamation done at the study site were conducted by a commercial biosolids company.

MATERIALS AND METHODS

The monitoring study was conducted as part of the Tangascootack Creek Watershed Restoration program developed by the Hawk Run District Mining Office of the Pennsylvania Department of Environmental Protection. The study site is located in Clinton County in central Pennsylvania, within the bituminous coal field of the Appalachian Plateau. The study was conducted on a 6.2-ha tract that had been mined in the 1970s and reclaimed by backfilling with overburden material, treating the surface with inorganic fertilizer, and planting with cool-season grasses. Surface vegetation was sparse and the area was scheduled for reclamation with biosolids in 2001. The study area was relatively level, although there was a steep rise in elevation (10–15 m) on the south side

of the study area to the original contour and a more gradual downslope on the north side to a small perennial stream that drained the study area (Fig. 1). Approximately 1.2 ha at the west end of the tract was reserved as a control area and received no biosolids and was not tilled or replanted. One year before reclamation, water sampling instrumentation was installed at the site to collect surface runoff, vadose zone leachate water, and ground water. Because the focus of this study is on the leachate and ground water, only those collection devices will be described here.

Site Instrumentation

Zero-tension pan lysimeters and ground water wells were installed during April to May of 2000. Vadose zone percolate water was collected in four lysimeters: three located in the biosolids application area (denoted as L1, L2, and L3) and one in the control area (denoted as LC). Each lysimeter consisted of two 30 by 30 cm PVC pans that were installed side by side at a depth of 1 m and connected to a common drain line. The drain line from each lysimeter ran downslope (north) for ~25 m to 20-L collection bottles. Because of the unconsolidated nature of the overburden material in the study area, and the large amount of coarse fragments (shale and sandstone), we were unable to install the lysimeters by laterally excavating beneath undisturbed spoil material. Such attempts led to repeated collapse of the overlying material. Instead, the lysimeters were placed in the bottom of a 1-m-deep trench. The pans were filled with polystyrene beads and the drain lines installed. The trench above the pans was backfilled by first replacing and recompacting material excavated from the 15- to 100-cm depth, followed by material that had been removed from the 0- to 15-cm depth. Since the entire profile had already been excavated, mixed, and replaced by prior mining and reclamation activities, this method of lysimeter installation did not greatly alter profile characteristics.

Groundwater sampling wells were installed at four locations: three in the biosolids application area (denoted as W1, W2, and W3) and one in the control area (denoted as WC) (Fig. 1). Wells had 10-cm-diam. casings and were drilled to depths of 5.2, 9.4, 7.5, and 6.3 m for wells W1, W2, W3, and WC, respectively. Rain gauges were installed near lysimeters L1 and LC.

Sample Collection and Analysis

Surface soil samples (0- to 15-cm depth), corresponding to the locations of the four lysimeters, were collected during the summer of 2000 before biosolids application and twice in 2001: 2 d and again 2 mo after biosolids application. Each sample was a composite of 10 individual cores located randomly within a 15-m radius of the lysimeter location. Samples were analyzed for pH (potentiometric 1:2 soil/water); total N (combustion) and NH$_4$–N (2 M KCl extraction and specific ion electrode); Mehlich 3 extractable P, K, Ca, and Mg (inductively coupled plasma emission spectrophotometry [ICP] analysis); and total extractable (EPA Method 3051 digestion, USEPA, 1986) concentrations of Cd, Cu, Pb, Ni, Zn (ICP analysis), As, and Se (graphite furnace atomic absorption spectrophotometry [AA] analysis), and for Hg (EPA Method 7471, USEPA, 1986).

Water sampling began in June 2000, 11 mo before biosolids were applied. Following each rainfall, the amount of precipitation in the rain gauges was recorded and the gauges were emptied. Samples of percolate water intercepted by the lysimeters were collected following precipitation or snowmelt events that were large enough to generate flow in the lysimeters. The volume of water collected by each lysimeter was
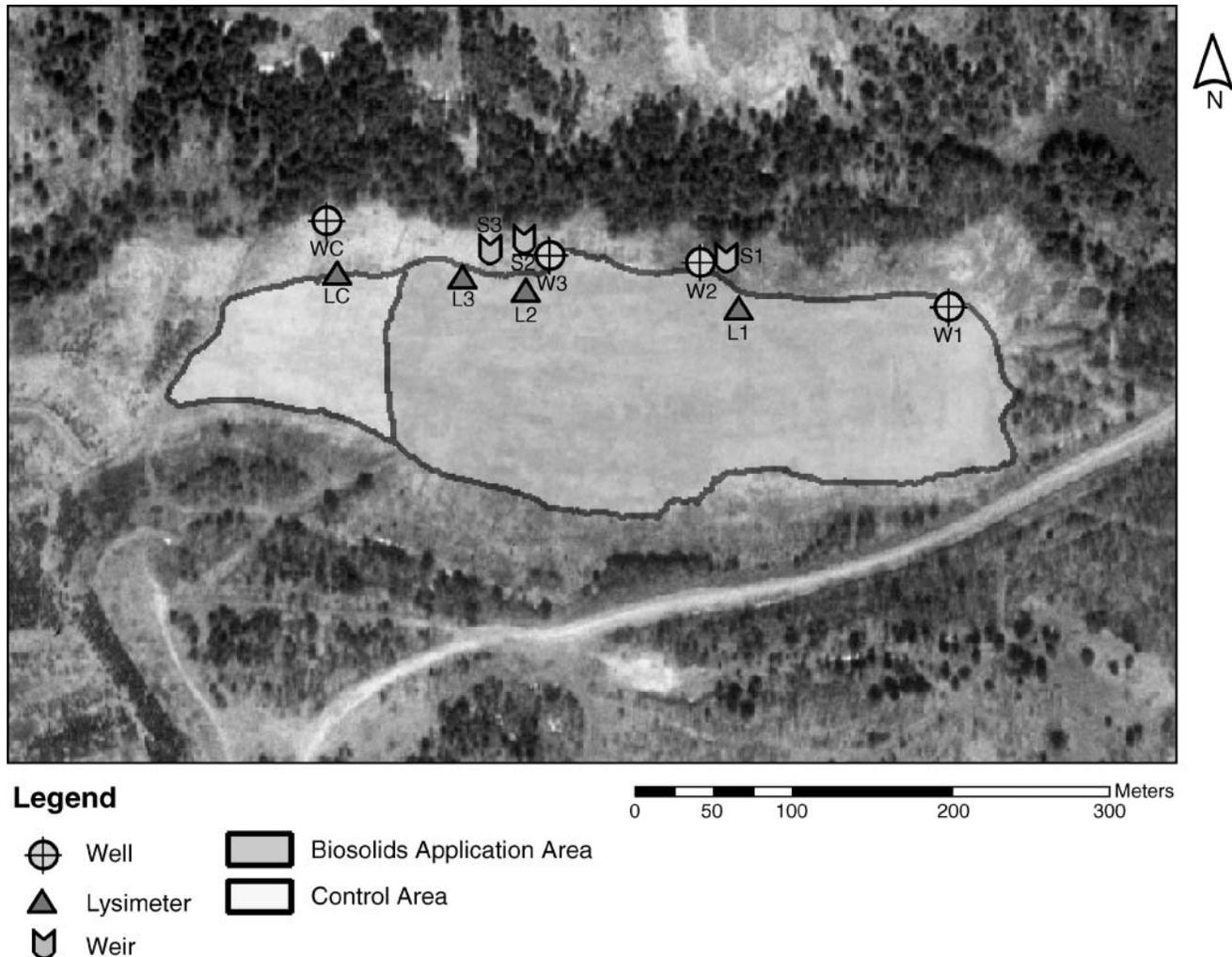
Fig. 1. Map of study area showing biosolids application area, control area, and locations of wells, lysimeters, and wiers.

measured in the field. Ground water samples were collected monthly. Wells were purged by pumping at least three times their storage volume before sample collection. Two aliquots of every water sample were obtained: a 125-mL field filtered (0.45-μm membrane filter) and acidified (2 mL concentrated HNO_3) aliquot, and a 500-mL unfiltered aliquot. Samples were packed in ice and transported to the laboratory for analysis. Unfiltered water samples were analyzed for pH (potentiometric), hot water acidity (titration), total Kjeldahl N (starting 13 Dec. 2001), NH_4 and NO_3 (colorimetric), total P (colorimetric following acid hydrolysis), and dissolved reactive P (colorimetric following filtration). Filtered and acidified samples were analyzed for Al, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, and Zn (ICP analysis), As and Se (graphite furnace AA analysis), and Hg (EPA Method 7471).

The total quantities of NO_3, NH_4, and trace metals collected by each lysimeter were determined from the product of the measured concentration and the corresponding volume of water collected for each sampling event. The total quantities of NO_3 and NH_4 leached per hectare were estimated by dividing the quantity for each lysimeter by the fractional hectare area of the lysimeters (1.8×10^{-5} ha).

Anaerobically digested biosolids cake was hauled to the study site and stockpiled during the winter and early spring of 2000 to 2001. In late April 2001, ground agricultural limestone was spread over the biosolids application area at a rate of 11.5 Mg ha^{-1} and incorporated to a depth of ~15 cm using a disk plow. On 15 May 2001, biosolids were spread at a target rate of 134 Mg ha^{-1} (dry weight basis) using a rear discharge manure spreader with a hydraulic push ram. Immediately after spreading, the biosolids were incorporated to an approximate depth of 15 cm using a disk plow. To achieve greater incorporation and mixing of the biosolids with the soil, the disk plow made at least four passes over the area in opposite and perpendicular directions. The actual biosolids application rate and variability was measured by spreading nine plastic tarps (each 2.31 m^2) on the soil surface before biosolids application. The tarps were distributed evenly along a transect running east to west across the application area. Immediately after the biosolids were applied, all biosolids on each tarp were weighed and a subsample was collected for solids content determination and chemical analysis. Solids content (drying at 105°C), total N (Kjeldahl), NH_4–N (ion selective electrode), organic N (subtraction of NH_4–N from total N), and total P and total K (EPA Method 3051 digestion, ICP analysis) were determined on all samples, and As, Cd, Cr, Cu, Pb, Mo, Ni, Se, and Zn (EPA Method 3051 digestion, graphite furnace AA for As and Se, ICP analysis for all other elements) and Hg (EPA Method 7471) were determined on a single composite sample. Vegetative growth was not measured as part of this water quality monitoring study. Vegetative cover was reestablished rapidly in the biosolids application area and essentially com-

Table 1. Results of *t*-tests conducted on log-transformed data comparing water quality parameters from each lysimeter in the biosolids application area with that from the control area. Data were analyzed separately for each year following biosolids application.

| Parameter | First year after biosolids application | | | Second year after biosolids application | | |
	Lysimeter 1	Lysimeter 2	Lysimeter 3	Lysimeter 1	Lysimeter 2	Lysimeter 3
			P > t			
pH	<0.004	<0.001	<0.001	<0.001	<0.001	<0.001
Acidity	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
NO$_3$–N	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
NH$_4$–N	<0.001	<0.001	<0.001	0.101	0.041	0.077
Organic N	<0.001	<0.001	<0.001	<0.001	<0.001	0.004
P (total)	<0.001	NS†	NS	<0.001	NS	NS
Al	0.027	<0.001	<0.001	NS	0.007	0.062
Cu	<0.001	<0.001	<0.001	<0.001	NS	NS
Fe	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Mn	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ni	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	<0.001	<0.001	<0.001	NS	NS	NS
Zn	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

† Not significant.

plete cover and good growth persisted throughout the monitoring period. Vegetative growth was clearly more abundant in the biosolids application area than in the control area.

Statistical Analysis

Because treatments were not randomized and there was no replication of the control treatment, analysis of variance could not be used to assess treatment effects on water quality parameters. To test for significance of differences due to biosolids application, data from each lysimeter in the biosolids application area were compared with the control-area lysimeter using a *t*-test. Data were normally distributed according to the Kolmogoroff–Smirnov test, but the Hartley *F*-max test (computed manually using a spreadsheet) showed that, for most parameters, variance in the control-area data was far smaller than in the biosolids area. Data were log-transformed to equalize variance and allow for use of a pooled *t*-test. Because treatment effects were expected to decay with time and also to follow a seasonal pattern, the data from each year following biosolids application were analyzed separately. Results of the *t*-test statistic are presented in Table 1. A significance level of $\alpha = 0.1$ (rather than the more traditional $\alpha = 0.05$) was selected to decrease β and the likelihood of a Type II error. In this study, we conclude that the consequences of making a Type II error (failing to conclude that biosolids changed the measured water quality parameter when they actually have) is at least as serious, if not more so, than a Type I error. Direct simple correlation of leachate acidity with leachate concentrations of several metals was computed. Except where noted, all statistical analysis was conducted using SAS Institute (2001).

RESULTS AND DISCUSSION

Soil Chemistry

Chemical characteristics of soil in the control and biosolids treatment areas were similar before biosolids application, and the soil in the control area remained relatively constant throughout the 3-yr study period (data not shown). The average amount of biosolids applied was 152 Mg ha^{-1}, only slightly above (1.13×) the target application rate of 134 Mg ha^{-1}; however, there was large variability in the amount of biosolids collected on each tarp (standard deviation = 72 Mg ha^{-1}), indicating that spreading was very uneven. The nonuniform application was in part due to the rough terrain that the spreading

equipment had to traverse. The tillage operation probably spread out some of the biosolids in high application areas and thus removed some of the spreading variability; however, even after tillage, differences in spreading uniformity were visually apparent. There was relatively low variability in the chemical characteristics of the nine biosolids samples we analyzed (Table 2). Thus the large variability in nutrient application (and presumably also trace element application) was due almost entirely to the nonuniform biosolids spreading. Some of this variability is also reflected in the large ranges for nutrients in the soil after biosolids application (Table 2). The apparent increases in soil organic C, total N, and all measured nutrients were consistent with the amounts of biosolids and nutrients applied (Table 2). Following biosolids application, there was large variability in soil trace element concentrations, and some indication that metals with the

Table 2. Biosolids characterization, loading of nutrients and trace elements with application of 152 Mg ha^{-1}, and measured concentrations in soil 2 mo after biosolids application.

| Parameter | Conc. in biosolids | Loading with 152 Mg ha^{-1} biosolids | Soil conc. 2 mo after biosolids application | |
			Biosolids area	Control area
pH	8.09 ± 0.04	–	5.5 ± 0.4	5.6
Nutrients	g kg^{-1}	kg ha^{-1}	g kg^{-1}	
Organic C			64.6 ± 15.2	48.6
Total N	34.8 ± 3.3	5277 ± 1924	6.3 ± 2.5	3.0
			mg kg^{-1}	
NH$_4$–N	8.6 ± 1.3	1300 ± 412	404 ± 304	38.3
NO$_3$–N	NA†	NA	415 ± 150	125
P	57.0 ± 3.4	3775 ± 1539	195 ± 37	16
K	3.2 ± 0.7	400 ± 178	124 ± 7	94
Ca	NA	NA	2564 ± 400	1874
Mg	NA	NA	407 ± 72	247
Trace elements	mg kg^{-1}	kg ha^{-1}	mg kg^{-1}	
As	12.2	1.85	NA	NA
Cd	4.67	0.72	0.86 ± 0.5	0.31
Cr	187	28.4	25.3 ± 9.1	10.1
Cu	529	80.2	101 ± 49	22.2
Pb	156	23.7	56.1 ± 37.2	20.8
Hg	2.08	0.32	NA	0.21
Mo	12.6	1.91	NA	NA
Ni	47.7	7.23	17.9 ± 2.9	15.3
Se	4.56	0.69	NA	NA
Zn	1086	165	287 ± 147	56.9

† Not analyzed.

largest loadings (Zn and Cu) had been increased (Table 2).

Vadose Zone Water Chemistry

Precipitation at the site was near normal for the region during the study period: 456 mm from June to December 2000; 835 mm in 2001; 905 mm in 2002; and 490 mm from January to June 2003. It should be noted that the rain gauges at the study site did not accurately collect snowfall, thus total precipitation amounts were probably somewhat larger than reported here. Rainfall distribution was also relatively normal, with the exception of summer 2002 when only 66 mm of rainfall was recorded between 18 June and 26 September and occurred in showers of 12 mm or less. Because of the low rainfall during the warm summer months when vegetative water demand was high, no water was collected by the lysimeters during this period.

Percolate water collected in the lysimeters showed very similar water quality parameters for all lysimeter samples before biosolids application, little change in the control-area water samples throughout the monitoring period, and large changes in biosolids-area water samples for several parameters. The changes in the biosolids-area samples typically were first observed within 2 to 3 mo following reclamation and the largest effects were observed during the first winter following reclamation. The effects of biosolids application tended to decrease during the first spring following reclamation (~9–12 mo after biosolids application). For many water quality parameters. a similar though smaller effect from biosolids application was observed in the second winter following reclamation.

pH and Acidity

Before limestone and biosolids application, percolate water collected in all lysimeters was only mildly acidic (Fig. 2, Table 1) with pH values mostly in the range of 4.7 to 6.2 (Fig. 3). Within 1 mo of biosolids application, there was a sharp increase in the acidity of water collected from two lysimeters, and within 3 mo, percolate water acidity at all three lysimeters had clearly increased. With only a few exceptions, the acidity of percolate water collected in the biosolids application area remained greater than that collected in the control area throughout the first winter and spring following biosolids application. In late spring and early summer of 2002, the acidity levels decreased to that of the control area. Acidity of percolate water in the biosolids application area increased again during the second winter, although the magnitude was somewhat smaller than that observed during the first winter. Although the acidity of percolate water collected from the biosolids application area decreased again in the second spring after application, it remained above that of the control area when monitoring ceased. Percolate water pH followed a similar though less clear-cut pattern (Fig. 3, Table 1) as that observed with acidity. There were dips in the pH of water collected in the biosolids application area (relative to the control area) during the first winter following rec-
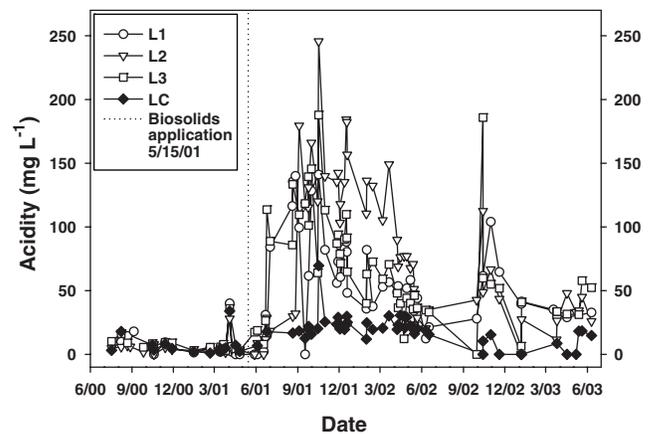

Fig. 2. Acidity of percolate water collected in zero-tension lysimeters (L1, L2, and L3 in the biosolids application area and LC in the control area) before and after reclamation with biosolids.

lamation. During the second winter after biosolids application, the pH of all percolate water samples appeared to increase but the pH of biosolids-area samples remained below that of control-area samples at the end of the monitoring period.

The increased acidity and decreased pH appear to have been caused by mineralization and oxidation reactions occurring in the applied biosolids. Mineralization of organic N to NH_4, followed by nitrification to NO_3, are net acid-generating processes if the NO_3 is leached (as will be shown below) rather than taken up by plant roots (Essington, 2004). Although we did not specifically monitor these reactions in this study, it is clear from the data in Table 2 that biosolids addition greatly increased both NH_4 and NO_3 in the soil. Qureshi et al. (2003) reported generation of significant amounts of acidity in a laboratory incubation and leaching study with biosolids, and attributed the acidity primarily to oxidation of S in the biosolids. We did not measure S in biosolids, soil, or water in this study; however, it is possible that oxidation of reduced S in the biosolids also contributed to the increased acidity of percolate water.
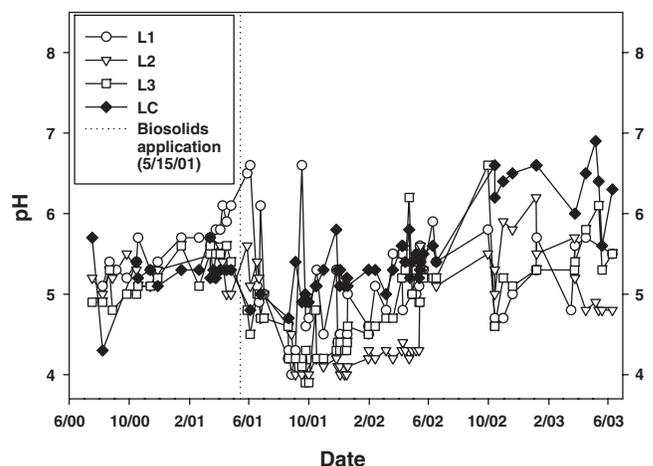

Fig. 3. pH of percolate water collected in zero-tension lysimeters (L1, L2, and L3 in the biosolids application area and LC in the control area) before and after reclamation with biosolids.

It has been suggested that mine reclamation with biosolids could reduce the generation of acidity at mine reclamation sites in the Appalachian Region of the USA by inhibiting oxidation of reduced FeS minerals present in the mine spoil (Cravotta, 1998). Such a reduction would be the indirect result of biosolids stimulating a vigorous vegetative and microbial community in the surface soil that would strip O_2 from percolate water and thus prevent the oxidizing agent from reaching reduced FeS minerals. Our observation that biosolids generated acidity does not contradict this hypothesis. This is because conditions at our study site were only mildly acidic and there appeared to be little, if any, acidity being generated in the upper 1 m from oxidation of FeS. At mine reclamation sites where significant amounts of reduced FeS minerals are present, the amount of acidity that could be generated from oxidation of these minerals would far exceed that from biosolids mineralization. Our data clearly show, however, that biosolids applied at the high rate used in this study will be a source of acidity for at least 2 yr.

Nitrogen and Phosphorus

Large amounts of N were leached from the surface during the 2 yr of monitoring following biosolids application. Most of the loss occurred as NO_3 (Fig. 4, Table 1) and much smaller quantities as NH_4 (Tables 1 and 3) and organic N (data not shown). Nitrate leaching response to biosolids application followed a temporal pattern similar to that observed with acidity. There were very large increases in NO_3 concentrations within 2 to 3 mo after application and concentrations in samples collected from all three lysimeters in the biosolids application area approached or exceeded 300 mg L^{-1}. Concentrations gradually decreased from this maximum during the first winter and early spring but, 1 yr after biosolids application, were still clearly greater than concentrations in the control area. Beginning in the fall of the second year after biosolids application, a distinct but smaller pulse of NO_3 leaching was observed with maximum concentrations approximately half as large as the

prior year. This second pulse also decreased during late winter and early spring. Although concentrations remained greater than those in the control area at the end of the monitoring period, the final samples collected were below the 10 mg NO_3–N L^{-1} drinking water standard.

During the first 2 yr following reclamation, the estimated total amount of inorganic N leached from the biosolids application area was vastly greater than that leached from the control area (Table 3). Although there was considerable variability among the lysimeters in our estimates of N loss, it appears that more than one-third of the N applied in the biosolids was lost from the soil surface by leaching of inorganic N. The data in Table 3 must be considered loss estimates because of two opposing errors in measurement of leachate volume, each of unknown magnitude. First, following some prolonged rainfall or snowmelt events, particularly when antecedent soil moisture content was high, the collection carboys overflowed, resulting in an underestimation of leachate volume. On the other hand, these same conditions possibly led to some funneling of flow into the lysimeters, thereby causing an overestimation of leachate volume.

Leachate NO_3 concentrations observed in our study were far greater than was reported in early biosolids research in Pennsylvania (Sopper and Kerr, 1982; Murray and Giddings, 1982; Carello, 1990) and also greater than the 100 mg NO_3–N L^{-1} reported in more recent work by Cravotta (1998). Experiments with biosolids application to gravel mines in Virginia reported by Daniels et al. (2001) showed significant NO_3 leaching during the first winter following application. Maximum NO_3–N concentrations in 50-cm-deep lysimeter samples steadily increased from ~20 to ~130 mg N L^{-1} as biosolids cake applications increased from 14 to 98 Mg ha^{-1}. The biosolids application rate in our monitoring study was $1.5\times$ greater than the maximum used by Daniels et al. (2001) and resulted in maximum NO_3 concentrations more than $2\times$ greater. Daniels et al. (2001) found little evidence for second-year NO_3 leaching, whereas in our study there was very clear second-year leaching. It is clear that the application of 152 Mg ha^{-1} of biosolids cake (5160 kg total N ha^{-1}) at the mined land site we monitored greatly exceeded the capacity of the vegetation to accumulate N and of the soil to retain the added N.
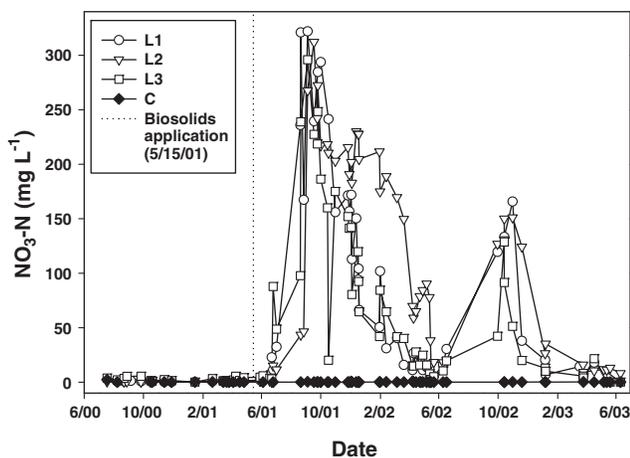

Fig. 4. Nitrate concentrations in percolate water collected in zero-tension lysimeters (L1, L2, and L3 in the biosolids application area and LC in the control area) before and after reclamation with biosolids.

Table 3. Estimated quantities of inorganic N and trace metals leached during the first 2 yr following reclamation with biosolids.

Nutrient or trace metal	Control area	Biosolids area		
		Mean	SD	Leaching loss as fraction of quantity applied in biosolids
		kg ha^{-1}		
NO_3–N	3.5	2078	439	0.40†
NH_4–N	0.9	250	245	0.05†
Sum of inorganic N	4.4	2327	676	0.45†
Cu	0.26	1.48	0.75	0.018
Ni	0.69	5.7	1.18	0.79
Pb	0.03	0.13	0.04	0.004
Zn	0.95	31.2	7.25	0.19

† Fraction of total N applied.

Despite this large flux of N through the vadose zone, there was very little evidence that N reached the ground water in the application area. Very small and brief increases in ground water NO_3 (data not shown, maximum concentration 6.5 mg NO_3–N L^{-1}) in two of the three wells within the application area indicated that either very little of the NO_3 observed at 1-m depth moved to the ground water, or that there was a large amount of dilution in the aquifer. Nitrate was the only measured parameter in ground water that showed any response to biosolids application. The appearance of numerous seeps on the northern downslope edge of the study area (between the biosolids application area and the receiving stream) during periods of high precipitation or snowmelt indicated that there was significant lateral flow of percolate water in the study area. These seeps also suggest the possible presence of an aquitard at some depth between the lysimeters and the ground water. Ground water sampling wells W3 and WC became artesian during high moisture periods, again suggesting the presence of a relatively impervious layer between the ground water and surface percolate.

Biosolids application increased P leaching in just one of the three lysimeters (Fig. 5, Table 1). In contrast to N leaching, total P concentrations remained very low throughout the study period, as would be expected based on P mobility in soil. On average, ortho-P concentrations were 25% of total P concentrations (data not shown), so some P was being transported as sediment-bound P and organic P. Thus relative to the addition of 3.7 Mg P ha^{-1} in the biosolids, the leaching loss of P was very small. Biosolids application did not change P concentrations in the ground water.

Metals

The solubility of most metals in soil systems is greatest under acidic conditions (McBride, 1994). This effect was very apparent in the case of Al (Fig. 6) and Mn (data not shown), both of which increased in percolate water as pH decreased and acidity increased. Both Al ($R^2 = 0.65$) and Mn ($R^2 = 0.56$) were positively and signif-

Fig. 6. Aluminum concentrations in percolate water collected in zero-tension lysimeters (L1, L2, and L3 in the biosolids application area and LC in the control area) before and after reclamation with biosolids.

icantly correlated with acidity. Increased proton activity could have solubilized Al and Mn either from the added biosolids or from minerals in the soil and mine spoil. Iron, however, behaved just the opposite of what was observed with Al and Mn (data not shown). Although Fe concentrations in the percolate water were lower than Al and much lower than Mn, and changes in Fe were small relative to variability, it was clear that Fe concentrations decreased following biosolids application when acidity increased (Table 1). In acidic systems, increased concentrations of these metals often leads to phytotoxicity. We did not measure vegetative growth as part of this study, but vegetative growth in the biosolids area was vigorous and there was no visual indication toxicity from Al or Mn, despite the large increases in soluble Al and Mn. Presumably the biosolids also increased soluble organic C concentrations and complexation with these metals would have decreased their phytotoxicity.

The effect of increased acidity on mobilization of metals was also observed with Cu, Ni, Pb, and Zn (Table 1), but not with the other trace elements that were analyzed (As, Cd, Co, Cr, Hg, Mo, and Se; data not shown). Leachate concentrations are shown only for Zn (Fig. 7) because the patterns of mobilization (but not concentrations) were similar to Cu, Ni, and Pb. Before biosolids application, concentrations of these metals were extremely low and they remained at very low concentrations throughout the monitoring period in control-area percolate samples. Very clear increases in concentrations of Cu, Ni, Pb, and Zn were observed in all three lysimeters in the biosolids application area in the first year following application. Percolate concentrations were the largest for Zn, intermediate for Ni and Cu, and smallest for Pb. In the second year following biosolids application, the increases were much smaller and were significantly larger than the control area percolate only for Ni and Zn. The increases and subsequent decreases paralleled very closely the changes in percolate pH and acidity described above. All four of these trace metals were significantly and positively correlated with acidity (Cu, $R^2 = 0.33$; Ni, $R^2 = 0.43$; Pb,
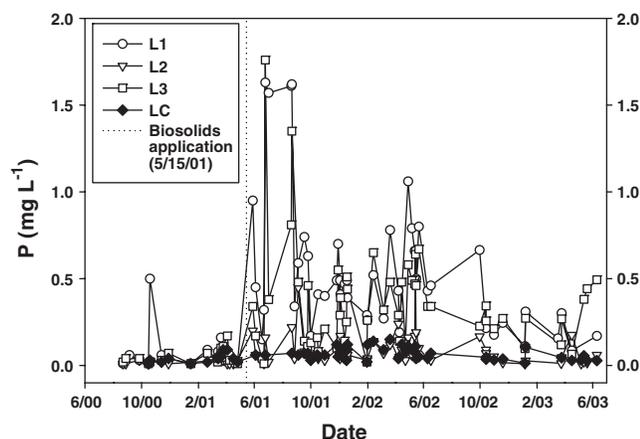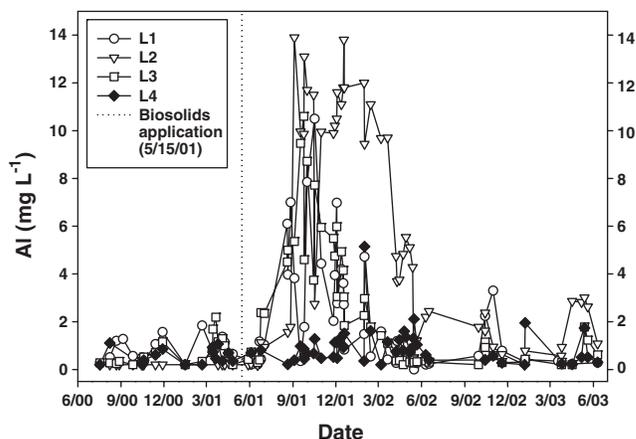

Fig. 5. Total P concentrations in percolate water collected in zero-tension lysimeters (L1, L2, and L3 in the biosolids application area and LC in the control area) before and after reclamation with biosolids.
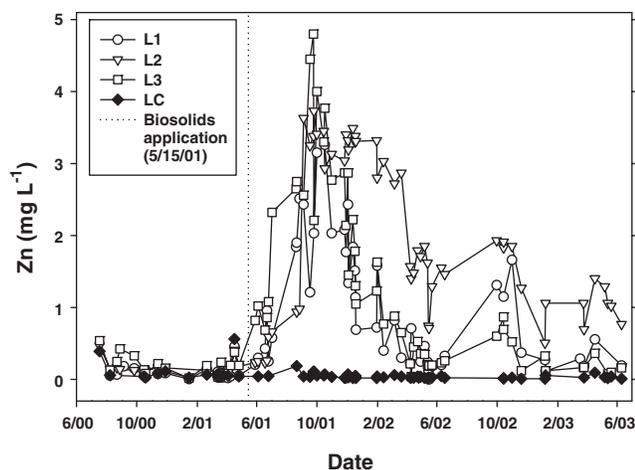
Fig. 7. Zinc concentrations in percolate water collected in zero-tension lysimeters (L1, L2, and L3 in the biosolids application area and LC in the control area) before and after reclamation with biosolids.

$R^2 = 0.46$; Zn, $R^2 = 0.71$). With the exception of Cr, loading of Cu, Ni, Pb, and Zn in the added biosolids were larger than any of the other trace elements (Table 2). Our estimates of the quantity of metals leached decreased in the order Zn > Ni > Cu > Pb (Table 3). Relative to the amounts of these metals applied in the biosolids, the amount of Ni leached was very large, the amount of Zn was intermediate, and the amounts of Cu and Pb were small (Table 3). From our data we cannot partition the source of mobilized metals between those added in biosolids and those present in the native soil material. In their laboratory incubation and leaching study, Qureshi et al. (2003) observed mobilization of biosolids Zn, Ni, and Cu and attributed it to the acidic conditions that had been generated in the nonsoil system. Since biosolids also generated acidic conditions in our field study, it appears possible that there was mobilization of biosolids Ni and Zn.

The question of loss of biosolids-applied trace metals from the application zone has been much debated in recent years in the scientific literature. Several studies have documented near-total recovery of added metals several years after application (Granato et al., 2004; Sloan et al., 1998), while other studies have reported loss of added metals (McBride et al., 1997; Richards et al., 2000). Studies reporting mobilization of biosolids trace elements have been criticized because either the biosolids used contained much greater concentrations of trace elements than are found in contemporary biosolids, or because the application rates were much greater than would be used in actual practice. Our results demonstrate that mobilization can occur with contemporary, low-metals-content biosolids applied at permitted and frequently used rates. It should be noted that although we observed evidence that biosolids trace elements were mobilized, the concentrations remained quite low relative to U.S. drinking water standards: Cu remained well below the maximum contaminant goal level of 1.3 mg L^{-1}, Zn approached but did not exceed the secondary maximum contaminant level of 5 mg L^{-1}, and Pb only

briefly exceeded the treatment technique action level of 15 $\mu g\ L^{-1}$.

CONCLUSIONS

Mine reclamation with biosolids in Pennsylvania at the currently allowed application rate of 134 Mg ha^{-1} was found to have several negative effects on vadose zone water quality that could potentially impact area ground or surface water. The effects of such a large application of biosolids were manifested most strongly in the first year following reclamation, though most continued at an abated level in the second year following reclamation. The greatest impact is on leaching of NO$_3$ and to a much lesser extent leaching of NH$_4$. Percolate water NO$_3$ concentrations exceeded the primary maximum contaminant level of 10 mg N L^{-1} almost continually for 2 yr following reclamation. Estimated leaching loss of as much as 2.3 Mg inorganic N ha^{-1} in the 2 yr following reclamation indicates the potential for significant loading of local ground or surface waters depending on hydrologic conditions and the fraction of the watershed to which biosolids are applied. Given the hydrologic conditions at this study site, however, the only measured effects on ground water were extremely small and short-lived increases in NO$_3$.

Application of biosolids at this rate also increased the acidity and decreased the pH of vadose zone water during the first 2 yr following biosolids application, presumably from nitrification coupled with extensive NO$_3$ leaching and biosolids S oxidation. Thus, rather than mitigating low pH and acidic conditions in vadose zone spoil material, this practice could possibly contribute to acidity in the soil and spoil profile; however, generation of acidity from biosolids probably does not persist much beyond the 2-yr observation period of this study. Another consequence of the biosolids-generated acidity is the mobilization of Zn, Ni, Cu, and Pb, the more abundant trace elements present in the biosolids, and their transport to a depth of at least 1 m.

While the nutrients and organic C in biosolids unquestionably increase the likelihood of achieving successful and sustained revegetation of drastically disturbed sites such as mined lands, the potential for adverse impacts on water quality should not be overlooked in developing reclamation programs and strategies. Reclamation programs that allow large one-time application of biosolids should consider alternative approaches that maintain biosolids benefits but decrease the potential for nutrient and trace metal losses. This could possibly be achieved by adopting relatively simple changes such as reducing application rates, combining application with high-C/N-ratio organic material, and increasing lime application to counter acid generation. These and possibly other alternatives warrant investigation and adoption if found effective.

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