MASS OF IONS REMOVED BY LEACHING MINE SPOIL WITH SIMULATED PRECIPITATION[1]

by

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Abstract. A pyritic coal mine spoil was leached with simulated precipitation that was adjusted to pH values of 5.6, 5.0, 4.6, 4.2, and 3.8. Each mine spoil column contained 1500 g of recently dug, extremely acid mine spoil material. After being brought to field capacity (32 %by weight) with distilled water, 3 replicates of spoil were leached weekly using simulated precipitation at each pH level with a volume equivalent to 2.54 cm depth, and leachates were collected and analyzed. After 94 1-week leaching and drying cycles, the spoils released approximately 3.6 g Fe, 35 g SO_4, 0.6 g Al, 1.5 g Ca Kg^{-1} and smaller amounts of other elements. Patterns of release changed during the 94 weeks. Early in the study, sums of leached Fe and Ti showed significant differences among precipitation pH treatments. At the midpoint of the study, sums of leached Al, Ti, and Cr showed significant differences among treatments, but Fe did not. After 94 weeks, only the sums of leached Al, P, and Cr were significantly different among treatments. Leachate of all treatments was consistently about pH 2.1 for most of the 94 weeks, but it rose to about pH 2.3 near the end of this period. These results suggest that fresh spoil quickly contributes readily available ions to groundwater leachate. The pH of incident precipitation significantly affects leaching losses of some elements from mine spoils.

Additional key words: pH, acid mine drainage, acid-rain, mine soils.

Introduction

There has been increasing concern as well as controversy regarding the effect of acid deposition on terrestrial ecosystems, especially on surface mined areas in which ameliorative treatments are unlikely (Krug and Frink 1983; Likens et al. 1989). Neutralization of acid deposition is necessary to prevent acidification of streams and ground water, and creation of elevated, dissolved Al, Fe, and Mn concentrations that are toxic to fish and other animals and plants. Determining the effect of acid precipitation on strip mine spoil is a complex problem because of the heterogeneous composition of the spoil parent material.

Precipitation percolating through mine spoil dissolves and transports a variety of materials in the leachate water (Doepker 1988). The dissolved constituents may remain on-site and become part

of the ion balance of soil water and eventually affect plant establishment and growth. The dissolved material also can have off-site effects, either through addition to groundwaters, or by addition to surface runoff from the area. When the percolate enters the surface water system, it may be called mine drainage, or, if acidic, acid mine drainage.

Mine drainage is often severely contaminated, but the contaminant concentration can vary widely among different sources. Watzlaf (1988) worked with several mine waters with pH values as low as 2.0 and iron concentrations ranging from 7 to 7,000 mg L[1]. In general, contaminant concentration increased as pH declined. Mine drainage is often contaminated, but the water chemistry tends to be consistent with time (Halverson and Wade 1988).

In each of the studies of natural mine drainage or leaching, attention has centered on leachate chemistry rather than on the properties of the water used to leach the spoil. This procedure assumes the acid and contaminant potential in the spoil is so great that precipitation chemistry would not be important. In this study, a leaching liquid with a chemistry similar to natural precipitation and a pH adjusted to the range normally expected in rainfall was used. The objective was to determine if the chemistry of the leaching water, primarily pH, affected the leachate after the water percolated through a mine spoil.

Materials and Methods

Leaching Materials

Leaching solutions were based on distilled water to which reagent-grade chemicals were added to approximate the composition of natural rainfall. The compounds used to approximate rainfall chemistry and the mass of each chemical used are given in Table 1. Table 2 lists the ion concentration of the leaching material rather than compound concentration. Solution pH was adjusted to treatment levels by controlling the mass of sulfuric and nitric acids used in the formulation.

Spoil Materials

Fresh spoil material was collected from an active coal mine in southcentral Kentucky. The material was derived from shales located immediately above the coal. The spoil was acidic and contained significant amounts of pyritic sulfur (see Table 3). The high values for potential acidity are similar to values from other Appalachian spoils (Ammons and Shelton 1988). The comparatively high values for organic carbon and sulfur indicate the presence of coal wastes in the spoil material. The acid base account suggests that leachate from the spoil should be quite acidic.

Experimental Design

The spoil material was sieved (< 2 mm) to remove coarse fragments and was mixed well according to accepted procedures (Sobek et al. 1978). The mixed material was placed in 16 separate polyethylene leaching cylinders (10.4 cm diameter, 20.3 cm in length) and retained by an inert fiberglass mat at the bottom of each cylinder. Leaching columns were chosen over alternative methods because the technique has been shown to be the most representative of field conditions (Caruccio and Geidel 1986).

After each column was filled with 1.5 Kg[1] of spoil, 15 cylinders were randomly assigned to 5 treatments in groups of 3 replications per treatment. The remaining cylinder was used to check the response of spoil material to an initial leaching with unmodified distilled water at a pH of 6.5. Spoil in each treatment column was brought to field capacity with distilled water.

Treatments

The treatments consisted of leaching the material with artificial precipitation adjusted to pH 5.6, 5.0, 4.6, 4.2, and 3.8. Each of the 3 replications was irrigated at weekly intervals with 2.54 cm of water and allowed to drain freely. Leachate water from each column was collected in a new polyethylene

Table 1. Chemical Composition of Rain Simulants (mg L^{-1})

Compound	Formula Wt	Leaching Solution				
		5.6	5.0	4.6	4.2	3.8
NaCl	58.42	0.176				
$CaSO_4.2H_2O$	172.17	0.709				
$MgSO_4.7H_2O$	246.47	0.355				
K_2SO_4	174.27	0.069	Same for all solutions			
$NaNO_3$	84.99	0.368				
$(NH_4)_2SO_4$	132.14	0.746				
NH_4NO_3	80.04	0.243				
H_3PO_4 (85.2%)	97.98	0.008				
H_2SO_4 (96.7%)	98.07	0	0.383	0.987	2.451	5.948
HNO_3 (70%)	63.00	0	0.221	0.554	1.377	3.460

Table 2. Ion Concentrations for Precipitation Simulants (mg L^{-1})

pH	H^+	Ca^{++}	Mg^{++}	K^+	Na^+	NH_4^+	NO_3^-	$SO_4^=$	Cl^-	PO_4^{-3}
5.6	0.0025	0.165	0.035	0.031	0.169	0.258	0.457	1.114	0.107	0.007
5.0	0.010						0.610	1.476		
4.6	0.025		Same for all solutions				0.839	2.015		
4.2	0.063						1.406	3.422		
3.8	0.158						2.841	6.737		

Table 3. Properties of Spoil Material used in Leaching Study Based on Total Sulfur and Pyritic Sulfur

Variable	Units	Value
(Values based on total sulfur)		
pH, paste method	pH units	3.84
Neutralization Potential	$CaCO_3$ equivalent per 1,000 parts material	11.73
Potential Acidity	$CaCO_3$ equivalent per 1,000 parts material	41.25
Net Neutralization Potential		-29.55
Total Sulfur	%	1.32
Total Carbon	%	11.34
(Values based on pyritic sulfur)		
Neutralization Potential	$CaCO_3$ equivalent per 100 parts material	11.73
Potential Acidity	$CaCO_3$ equivalent per 100 parts material	26.88
Net Neutralization Potential		-15.15
Sulfate	%	0.09
Pyritic Sulfur	%	0.86
Organic Sulfur	%	0.37

bottle each week, and analyzed the following day. Treatments began on August 11, 1988, and continued until June 17, 1990, for a total of 94 weeks.

The treatment columns were covered with a watch glass during the 6-day period between irrigations to prevent excessive drying of the spoil. Although the columns were protected, the seal was not complete; so, many spoil pores drained and a definite drying cycle was established with air introduced into each column between leaching treatments. Approximately 50 ml of solution was required to restore the spoil to field capacity prior to leaching. Channel formation in the sample was prevented during percolation by a second fiberglass pad used to distribute the irrigation water over the spoil surface. Also, the columns were rotated each week. Treatment columns were located in a climate controlled area to remove any effects of temperature changes.

Chemical Analyses

The leachate samples were taken to the USDA Forest Service laboratory immediately after collection, and analyses were normally performed the next day. Each leachate sample was subjected to a thorough analysis using standard methods and appropriate reference standards (see Table 4). Data analyses were captured in a data file and formatted for statistical analyses with a computer system dedicated to laboratory control.

Statistical Analyses

Data analyses were accomplished by utilizing various statistical subroutines (Wilkinson 1988). The primary method utilized was an analysis of covariance. Covariance techniques were used to evaluate the effect of treatment pH while removing the effect of the sequential leachings. The effect of sequential leaching was isolated by using both week number and log week number as covariates. This technique identified both linear and curvilinear week effects. The model expressed each variable as a function of a constant, the treatment, log of the week number, the interaction, and error. Interactions, when significant, suggest that coefficients for slope are due to treat-

Table 4. Analyses Methods Used to Determine Contaminants in Mine Spoil Leachate

Variable	Method Type	EPA Reference Number
AcidityTitrimetric	305	
Alkalinity	Titrimetric	310.1
Metals and related elements including:	Argon Plasma Emission Spec.	AES0029
B Si Zn		
P Fe Cu		
Mn Mg Na		
Co Al Ni		
Ca K Ti		
Cr Pb		
pH	Potentiometric	150.1
Specific Conductance	Potentiometric	120.1
Sulfate	Turbidometric	300
Sediment, >0.45 micron	Gravimetric	160.2
Total Dissolved Solids	Computer	

ment beyond that expected by chance.

Factor analysis procedures were used to identify groups of contaminants that responded to the treatments in a similar fashion. Factor analysis does not identify the factors causing the response, but can be used to suggest reasons for an observed result. Factor analysis is not based on a model. Analysis of variance (ANOVA) was used to determine statistical difference among means due to treatment.

Results and Discussion

Mean loads of all chemical constituents in leachates from a toxic strip mine spoil decreased significantly with sequential, simulated acid-rain irrigations (see Table 5). The leachate chemistry with fresh distilled water was compared periodically with percolate from leaching with simulated acid-rain at various acidity levels. The results for the major potential phytotoxic chemical factors do

not indicate a highly statistically significant difference among simulated acid-rain treatments, but they do illustrate that significant changes occurred with each leaching. Concentrations of leachate chemical components consistently declined. Other parameters, including the control samples, except pH, also declined in concentrations as a result of sequential leaching with simulated acid-rain irrigations. Patterns of release changed during the 94 weekly leaching cycles. They illustrated a pattern of high output early in the leaching cycle, followed by declining values for succeeding weeks during the first year (Halverson et al. 1990). Thereafter, much smaller declines occurred in chemical composition with each additional leaching.

The leachate mean pH values averaged over 94 weekly applications of simulated acid-rain did not decrease with decreasing solution pH (see Table 6). All leachate pH values were considerably less than the pH of the solutions applied. Lilieholm and Feagley (1988) found the leachate pH values of soil

Table 5. Chemistry of minespoil leachate from fresh distilled water at pH 6.5 compared to the mean chemistry of leachates from simulated precipitation water at pH values of 5.6 and below.

Weeks	Treatment	EC	pH	Fe	Al	Mn	SO_4	TDS
	pH	ds/m						
1	6.5	11.1	2.2	4,999	370	378	30,700	37,762
	<5.6	10.7	2.1	4,027	321	353	24,880	30,607
2	6.5	6.4	2.2	1,255	205	205	11,600	16,645
	<5.6	7.0	2.2	1,354	172	177	10,750	19,754
20	6.5	4.1	2.1	178	47	28	3,150	3,697
	<5.6	4.7	2.1	328	54	37	3,841	4,528
46	6.5	2.9	2.2	50	10	3	572	665
	<5.6	3.2	2.1	70	22	6	881	1,069
94	6.5	1.8	2.3	10	10	0.41	425	486
	<5.6	2.0	2.2	12	12	0.79	478	554

The header spanning "Leachate" covers Fe, Al, Mn, SO_4, TDS with units "- - - - - - - - - - - - mg /L - - - - - - - - - -".

to be higher than the pH of solution applied. They also found that the leachate pH value from soil decreased with decreasing leaching solution pH. These data indicate that the buffering capacity of the spoil was very low, and that it had been depleted by simulated acid-rain treatments, because it was unable to accept H+ions. Since all leachate pH values in this study were lower than the leaching solutions, the simulated acid-rain solutions brought about additional chemical weathering and leaching. Chemical weathering is a part of natural soil development from spoil material (Struthers 1964).

The lowest leachate pH value was found for the first application of simulated acid-rain solution (see Table 5). The pH of the leachates showed little variation with successive leachings and was not responsive to the acidity of irrigation solutions during the first year. The pH of the leachate for all treatments began to rise gradually with successive leachings during the second year. Leachate pH values were not responsive to acidity of the irrigating solutions but to mine spoil and leachate chemistry.

Mean leachate electrical conductivity (EC) was significantly influenced by leaching solution pH. The pH 4.6 solution had the highest leachate EC value and the 5.6 pH solution the lowest value (see Table 6). This relationship was obtained throughout the greater part of the experiment. A maximum release of ions occurred from spoils receiving the 4.6 pH leaching solution. The pH 4.6 leaching solution produced the greatest EC and the lowest mean pH leachates.

Mean Al concentrations were significantly affected by leaching solutions pH. The 4.6 pH solution produced the highest concentration of Al in the leachates. These responses correlated well with Fe, EC, and leachate pH, and indicate steady mineral dissolution. However, smaller concentrations of Al, Fe, and acidity occurred with the pH 3.8 leaching solution. These factors suggest that mine spoil pH may be lowered by leaching with solutions below pH 5.6 or by acid-rain. Also, mine spoil mineral and chemical composition and weathering properties are contributing factors to leachate chemistry. All leachates contained sufficient concentrations of heavy metals and soluble salts to create potentially toxic conditions, so they would be classified as phytotoxicant for most organisms.

Mean loads of all chemical constituents in mine

Table 6. Mean of leachate pH, electrical conductivity, and aluminum and iron concentrations as influenced by pH leaching solutions for 94 weeks.*

pH		EC ds/m		Al. mg L^{-1}		Fe mg L^{-1}	
pH	Mean	pH	Mean	pH	Mean	pH	Mean
5.6	2.12	5.6	3.78a	5.6	41a	5.6	2.28a
5.0	2.10	5.0	3.82ab	5.0	42a	5.0	2.25a
4.6	2.06	4.6	4.06b	4.6	45b	4.6	2.84c
4.2	2.11	4.2	3.90ab	4.2	49c	4.2	2.49b
3.8	2.14	3.8	3.86ab	3.8	39a	3.8	2.35a

* Column means with the same letter are not significantly different using Duncan's multiple range (0.05).

spoil leachate increased significantly as the acidity level increased in simulated acid-rains from pH 5.6 to 4.6. Total dissolved solids, (TDS), decreased with leaching solutions less than 4.6 pH (see Table 7). After 94 weekly leachings with 2.54 cm of simulated acid-rain at a pH of 4.6, the spoil released approximately 35 g of sulfate, 3.6 g of iron, 0.6 g Al, 1.5 g Ca, and smaller amounts of other elements per kg of mine spoil. Approximately 42 g of total dissolved solids per kg of spoil were released.

Patterns of release of the chemical constituents changed during the 94 weeks. Early in the study, sums of leached Na, Al, Fe, Ti, Mn, and P showed significant differences among simulated acid-rain treatments. At the midpoint of the study, sums of leached

Al, Ti, and Cr showed significant differences among treatments, but iron did not. After 94 weeks, Al, P, Cr, and TDS were significantly different among treatments. The companion control samples leached with fresh distilled water (pH 6.5) showed a similar declining pattern, but the absolute values of chemicals leached were always slightly lower than those derived with acidified leaching materials (see Table 7). Except for the control leach material at pH 6.5, lower pH levels of 5.6 and below, all seemed to accelerate leaching of contaminants from the spoil, with a peak efficiency when the leaching solution was at a pH of 4.6. Leachates from all treatments were consistently about pH 2.1 for most of the 94 weeks, but it rose to about 2.3 near the end of this period. All leachates had

Table 7. Mass of ions removed and chemical composition of leachate from minespoil with 94 simulated acid-rains.*

Parameter mg Kg^{-1}	Simulated Rain				
	pH 5.6	pH 5.0	pH 4.6	pH 4.2	pH 3.8
SO$_4$	33,467	32,080	34,799	32,590	30,173
Acid	18,814	19,052	20,547	19,097	18,354
Fe	2,855	2,820	3,569	3,080	2,952
Mn	377	361	383	359	337
Al	521.ab*	527 ab	566.a	535.a	497.b
Mg	460	469	482	453	431
Ca	1,369	1,312	1,518	1,412	1,169
Si	226	277	270	281	263
P	14.2ab	13.0ab	15.2a	12.9ab	12.4b
K	8.3	6.0	5.0	4.2	5.9
B	1.7	1.8	1.7	1.8	1.7
Zn	21.7	22.7	23.6	22.9	24.2
Cu	6.7	6.5	7.0	6.6	6.5
Na	12.3	12.4	10.8	12.3	11.3
Co	5.6	5.6	5.8	6.3	5.8
Ni	14.2	14.4	15.1	15.1	13.8
Ti	1.8	1.8	2.3	1.5	1.79
Cr	2.0ab	2.0ab	2.1ab	2.2a	1.9b
Pb	8.2	8.2	9.0	8.8	8.2
TDS	39,927.ab	38,294.bc	41,669.a	38,788.b	35,906.c

*Values in rows followed by the same letter are not significantly different among acid-rain treatments at the 95% confidence level.

lower mean pH and higher mean acidity levels than the leaching solutions.

Conclusions

These results imply that fresh spoil quickly contributes readily available ions to groundwater leachate. The materials in the leachate are produced by weathering of rock and minerals in the spoil after repeated leaching with simulated acid-rain. The large amount of SO_4, Fe, Al, Mn, and TDS removed by leaching could contaminate and produce phytotoxicity in ground or surface water. Nevertheless, it is clear that the hydrologic regime within mine spoil can also affect leachate and ground water chemistry. Acidification by simulated acid-rain depleted the low buffering capacity of the spoil and increased weathering, resulting in leachate pH values lower than the pH of the applied simulated acid-rain. The pH of incident precipitation modestly, but significantly, affects leaching losses of some elements from mine soils. Further studies in the field and laboratory are needed to fully evaluate the state of spoil (mine soil) - plant - water - environments the stress of acid precipitation.

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