

INFLUENCES OF HUMIC AND FULVIC ACIDS AND ORGANIC MATTER ON LEACHATE CHEMISTRY FROM ACID COAL SPOIL¹

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Abstract: Column-leaching experiments were conducted on an acid pyritic coal spoil to determine the influence of acid rain, humic acid (HA), fulvic acid (FA), and undecomposed organic matter (OM) on pH and Al, Fe, Mn, and SO₄ concentrations in the spoil leachate and on the spoil. Simulated acid rain of pH 4.0 was applied for 50 weeks under laboratory conditions to spoil columns modified with 0.5% FA or HA, or 2.0% OM from four forest trees and two herbs. Quality-control methods were used to evaluate treatment effects. Addition of HA and tall fescue leaf material to a Lily, KY, spoil created a greater and longer lasting desirable effect on leachate pH and Al, Fe, Mn, and SO₄ than additions of FA or OM of five other species. Results suggest that revegetation resulting in rapid production of matured soil OM may reduce the amount of some ions commonly leached from acid mine spoils.

Additional Key Words: simulated acid rain, quality-control statistics

Introduction

Acid atmospheric deposition probably has increased the rate of cation and anion dissolution and leaching in many strip mine spoils (Gentry et al. 1991), mine tailings (Doepker 1988), and soils (Bergkvist 1987). Neutralization by soils or mine soils of acids (H₂SO₄, HNO₃, and HCl) from the atmosphere can help to prevent acidification of streams, ground water, capillary water, or surface runoff and creation of heavy-metal concentrations that are toxic to fish (Sharpe et al. 1984), agricultural crops (Irving 1983), and microorganisms (Miller et al. 1991). Soil lacking natural buffering by alkaline earth carbonates and low-intensity management may be sensitive to acid rain (Reuss 1983). Therefore, surface mine spoils low in carbonates and with or without OM produced by reclamation and pioneer species warrant study with regard to acid rain.

Most mined areas in Appalachia have been revegetated naturally or through reclamation, but not all have been revegetated effectively. Many poorly vegetated surface mine spoils in the Appalachian area have extremely low pH (Davidson et al. 1988) and high concentrations of available Al (Berg and Vogel 1973) and Fe (Cummins et al. 1965).

This study was designed to investigate the effects of sources of raw and "matured" OM on the quality of leachates produced by simulated acid rain from an acid mine spoil and the composition of the spoil.

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Material and Methods

Spoil

An extremely acid (pH 3.8, 1:2 spoil-water) silty clay, pyritic spoil material from an unreclaimed surface mine that was mined in 1964 near Lily, KY, was selected for study. It had an electrical conductivity (EC) of 171.1 dS/m and a cation-exchange capacity (CEC) 32.4 of cmol/kg. Exchangeable ions included Al, Fe, Mn, and SO₄ at 223, 204, 141, and 4,700 mg/kg, respectively. Organic matter totaled 1.32%, HA was 0.38%, and FA was 0.27%. The spoil material was air-dried and passed through a 2-mm sieve. It was then well mixed according to the accepted procedures of Sobek et al. (1978).

Simulated Acid Rain

Simulated acid rain leaching solutions were based on the average chemical composition of natural precipitation in Berea, KY, from 1985 through 1990. The chemical composition of the simulated acid rain is NO₃ (0.836 mg/L), SO₄ (1.262 mg/L), Ca (0.186 mg/L), Mg (0.028 mg/L), K (0.156 mg/L), Na (0.176 mg/L), NH₄ (0.216 mg/L), and PO₄ (0.012 mg/L). It was acidified to pH 4.0 with HCl. Owing to the instability of the simulated acid rain, it was prepared with freshly distilled water at 21°C and applied to the soils within 2 h.

Effects of Fulvic and Humic Acids on Leachate Chemistry

To investigate the effects of humic and fulvic acids, 1.6 kg lots of Lily spoil were carefully mixed with 8 g of FA or HA (5 g/kg or 0.5%) and then passed through a soil splitter 25 times to ensure an even mix. The FA and HA were extracted from a Pennsylvania revegetated mine soil (Gentry et al. 1993) and purified by the method of Schnitzer (1982). Control spoils received no organic acids. The amended spoils were placed into 20.3-cm-long, 10.4-cm-diameter polyethylene leaching columns of spoil packed (avoiding stratification) to a bulk density of approximately 1.45 g/cm³, and retained by an inert fiberglass mat at the bottom of each column. Columns were placed inside a Buchner funnel on a leaching rack. Three columns were prepared for each treatment.

Weekly, each column was brought to field capacity with distilled water, then irrigated with 200 mL freshly prepared pH 4.0 simulated acid rain (2.54-cm equivalent) from a 250-mL plastic bottle at a constant drip rate of 50 mL/h. Spoil columns were treated every Thursday for 50 weeks beginning on August 13, 1991, and allowed to drain freely. Leachate water from each column was collected in a new sterile polyethylene bottle every other week. The collected leachate was analyzed for pH and SO₄ immediately, and within 36 h for the other constituents.

Effects of Organic Matter Source on Leachate Chemistry

Leaf materials were collected at Lily on August 5, 1991, from six naturally established plant species growing in the immediate area surrounding the unvegetated spoil source--tall fescue (*Festuca arundinacea* Schreb.), pokeweed (*Phytolacca americana* L.), black cherry (*Prunus serotina* Ehrh.), Virginia pine (*Pinus virginiana* P. Mill.), red pine (*P. resinosa* Ait.), and white pine (*P. strobus* L.). The leaves were rinsed with 0.01M HCl solution and distilled water, dried for 48 h at 68°C in a forced-air oven, and ground to pass through a 2-mm screen. The ground tissue was mixed by hand and passed through a soil splitter.

Seven soil organic-matter treatments were set up: none (no OM), tall fescue, poke, Virginia pine, red pine, black cherry, and white pine. Thirty-two g of plant tissue were added to 1.6 kg of the Lily spoil and mixed, then mixed again by passing the material 25 times through a soil splitter to ensure an even mix of spoil and OM. Spoil from each treatment was added to a randomly assigned leaching column. For 50 weeks beginning on August 13, 1991, each column received weekly applications of pH 4.0 simulated acid rain as described earlier.

Spoil and Leachate Analysis

Spoil material was analyzed in the soil laboratory at Berea (KY) College. It was air-dried, passed through a 2-mm sieve to separate coarse fragments, and analyzed for particle-size distribution by the hydrometer method. Spoil pH was determined in a 1:2 soil-water mixture with a glass electrode. Soluble salts were determined by measuring the EC of a 1:5 soil-water extract (Bower and Wilcox 1965). Organic carbon content was determined by the Walkley-Black Method (Nelson and Sommers 1982); FA and HA were determined by the method of Schnitzer (1982). Cation-exchange capacity was determined by the Gillman method for acid soils (Rhoades 1982). Aluminum was determined colorimetrically (Barnhisel and Bertsch 1982), total Fe by the O-phenanthroline method (Olson and Ellis 1982), and Mn by the periodate oxidation method (Gambrell and Patrick 1982). Sulfate was measured turbidimetrically (Rhoades 1982).

All leachates were analyzed immediately for pH by the potentiometric method (EPA 150.1) and for sulfate by the Turbidimetric Method (EPA 300). Aluminum, total Fe, and Mn were determined by the colorometric procedures described for spoils.

Statistical Methods

The experimental design is completely randomized except for weekly treatment effects on leachate composition. One-way ANOVA was used to evaluate effects that were measured at the end of the study period. Treatment effects on leachate quality could not be analyzed by ANOVA because serial observations were not independent. Time series methods, though effective for describing time dependence, are poorly suited for evaluating treatment effects. Instead, we adapted Shewart control-chart methods that have long been used to study industrial processes.

A process is "in control" if the fluctuation of means of a control variable, plotted over time, is "reasonably explained" by the "inherent variability" of the observations. Inherent variability (homogeneity of variation is assumed) is based on the variation between sample units taken from the process at the same time, which is analogous to our "between replicates" variation, for which we used the square-root transformation on all variables but pH to impose homogeneity of variance. By using the difference between the treatment and the control, we ensured that observations would fluctuate about zero in the absence of treatment effects. As with conventional hypothesis testing, Shewart control charts are chary of claiming that a process is "out of control" without substantial evidence. (A 1/20 type II error rate prevails for processes disturbed by normally distributed white noise.) However, the control-chart criteria include trend influences; a process is considered out of control when eight consecutive observations are on the same side of the center line, as well as when the observation deviates greatly (three standard errors) from the control line. The criteria for control using these X-bar Shewart control charts are found in the quality control literature (Western Electric 1958).

For an example using the data from this study, see figure 1 in which the initially large and negative influence of HA on leachate Fe is evident (the 'x' points "out of control"); this influence diminishes up to week 40, where it becomes questionable and data points '.' are "in control."

Results

Effects of Fulvic and Humic Acids on Leachate Chemistry

Additions of HA, FA, and fresh OM caused pH, Al, Fe, Mn, and SO₄ leachate concentrations to deviate from the control conditions, but the results were not uniform. Plots of FA and HA treatment means versus controls are shown in figure 2, and fresh OM treatment results are similarly shown in figure 3. Table 1 summarizes the OM treatment effect on column leachate and specifies in which time periods the treatment effects were outside the limits of the control.

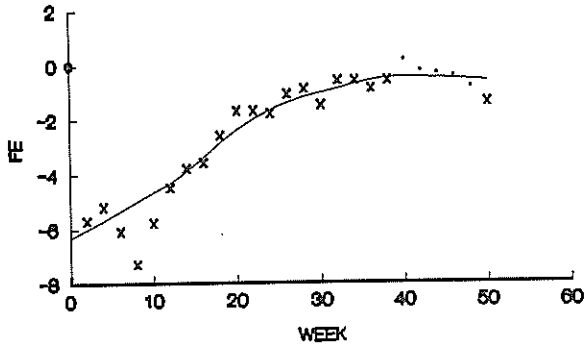


Figure 1. A Shewart control chart showing leachate Fe response to HA in spoil.

In general, HA had a greater and longer lasting beneficial effect on pH, Al, Fe, Mn, and SO_4 of mine spoil leachates than FA. Of the raw additions of organic matter, tall fescue had the greatest and longest lasting beneficial effect on leachate quality.

Changes in Spoil Organic Matter Over Time

Addition of FA resulted in FA fraction that was still significantly above that of the control spoil 50 weeks later (table 2). Addition of HA resulted in significantly higher HA and total OM at the end of the study.

Addition of raw OM resulted in an increased FA fraction in spoils in all treatments, increased HA for all but poke and white pine, and increased total OM in all but poke (table 3).

Discussion

The mine spoil used in this study was not sterilized so transformations of fresh OM, HA, and FA took place. Losses of OM indicate a significant amount of respiration loss of carbon as CO_2 , transformation by soil microbial populations, and leaching. The high amount of variability within and among fresh OM addition treatments is likely due to successive transformations of fresh OM into various forms at different rates, which made leachate-chemistry responses complex.

That some fractions of OM are efficient in sequestering metal ions and some anions is well known.

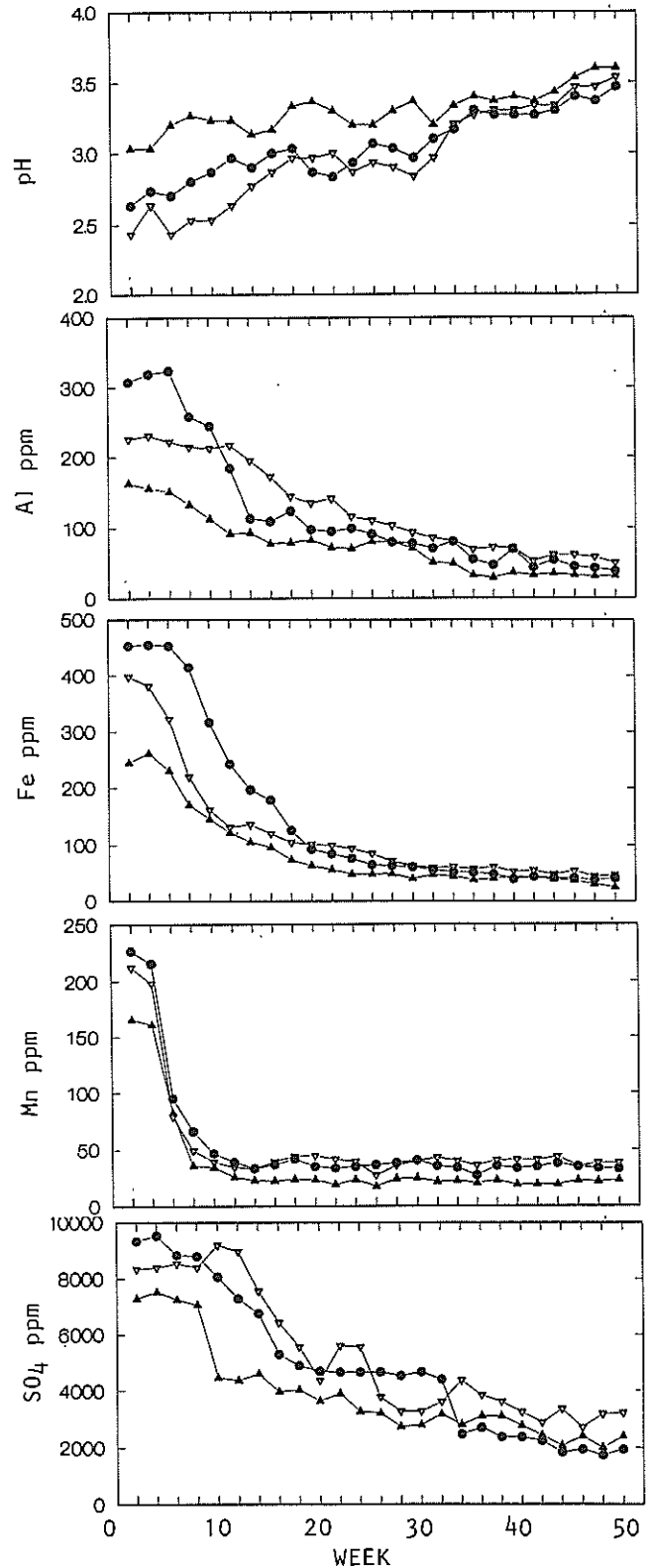


Figure 2. Effects of FA and HA on spoil leachate chemistry. ●-●-control, ▼-▼-FA, ▲-▲-HA.

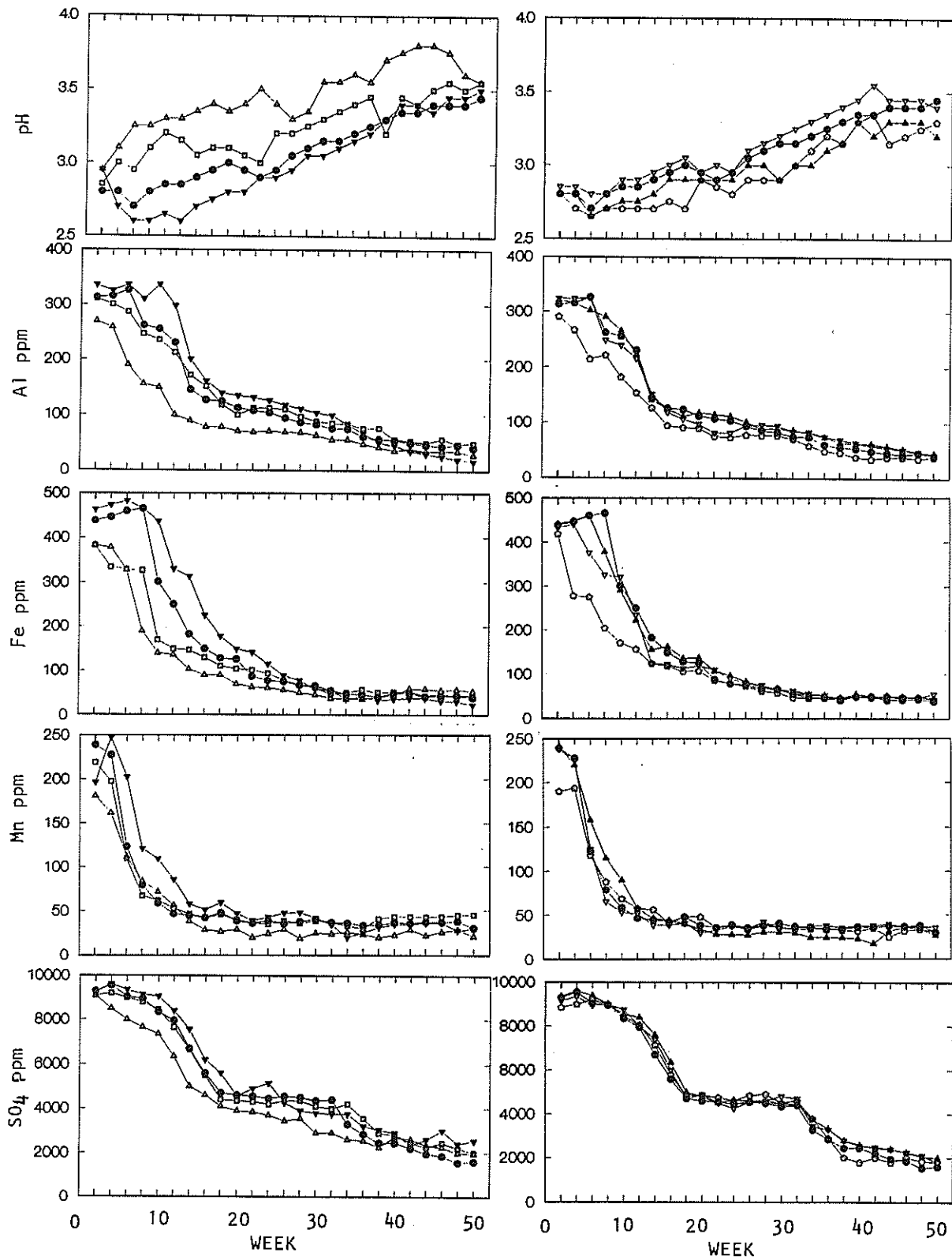


Figure 3. Effects of raw OM on spoil leachate chemistry. -●- control, ▲-▲ fescue, ▼-▼ poke, □-□ black cherry, △-△ Virginia pine, ▽-▽ red pine, ○-○ white pine.

Table 1. Organic matter treatment effects on ions in column leachate. Values in this table are the weeks in which the treatment effects were outside the control limits. Underlined values were above the control; values not underlined were below the control.

Treatment	pH	Al	Fe	Mn	SO ₄
Fulvic acid	2-18	2-10	2-18	4-14	2-6
	<u>22</u>	<u>12-50</u>	<u>26-30</u>	<u>20-24</u>	<u>10-20</u>
	28-32		<u>34-50</u>	26	22-24
				<u>34-44</u>	<u>34-50</u>
				46	<u>48-50</u>
Humic acid	<u>2-50</u>	2-50	2-40	2-50	2-32
			52		38-50
Fescue	<u>2-50</u>	2-50	2-40	2-4	4-38
			<u>44-50</u>	<u>12</u>	<u>44-50</u>
Poke	2	<u>8-36</u>	<u>10-28</u>	2	<u>10</u>
	4-20	42-50	40-42	<u>6-30</u>	<u>14</u>
	30-36		46-50	34	<u>16</u>
				46-50	<u>24</u>
					28-32
Black cherry	<u>4-36</u>	2	4-20	4-8	24-32
	38	6	<u>24</u>	<u>40-50</u>	<u>34-50</u>
	<u>40-50</u>	10-12			
		<u>14-16</u>			
		<u>18-20</u>			
Virginia pine	10-20	<u>8</u>	8	<u>6-12</u>	<u>14-20</u>
	30-50	<u>28-50</u>	14	24-50	36-50
			<u>26-50</u>		
Red pine	<u>10-30</u>	18-24	6	20	<u>38-50</u>
	<u>36-48</u>	<u>32-50</u>	8	22	
	50		18		
			20		
			<u>24</u>		
White pine	<u>2</u>	4-50	2-22	4	2
	8-40			6	<u>22-36</u>
	44-50			<u>14-16</u>	38-44

Table 2. Organic matter fractions in Lily spoil containing 0.5 percent added ferulic acid or humic acid after 50 weeks of leaching with pH 4.0 simulated acid rain. Values are means of 3 replications. Standard errors of means are in parentheses under controls.

	Fulvic Acid %	Humic Acid %	Total O.M. %
Initial condition	0.27	0.38	1.32
<u>Treatment</u>			
Control	0.19 (0.02)	0.35 (0.02)	1.21 (0.04)
+ FA	0.29*	0.36	1.34
+ HA	0.22	0.48*	1.49*

*Significantly different from the control, P = 0.05, using Bonferroni's inequality applied to t-tests in the ANOVA.

Table 3. Spoil OM fractions in Lily mine spoil containing 2 percent added OM of different species after 50 weeks of leaching with pH 4.0 simulated acid rain. Values are means of 2 replications with 2 analyses per replication. Standard errors of means are in parentheses under controls.

	Fulvic Acid %	Humic Acid %	Total O.M. %
Initial condition	0.27	0.38	1.32
<u>Treatment</u>			
Control	0.20 (0.02)	0.33 (0.03)	1.19 (0.06)
Fescue	0.38*	0.78*	1.71*
Poke	0.45*	0.36	1.36
Black cherry	0.39*	0.41*	1.35*
Virginia pine	0.53*	0.46*	1.86*
Red pine	0.47*	0.46*	1.66*
White pine	0.57*	0.45	1.79*

*Significantly different from the control, P = 0.05, using Bonferroni's inequality applied to t-tests in the ANOVA.

Decreasing treatment effects over time may be due to saturation of OM exchange sites, microbial or transformation of active OM fractions and leaching of organic compounds.

Treated spoils and leachates both showed marked similarities and differences in overall results. Leachate pH generally increased in all treatments throughout both studies. Concentrations of Al, Fe, Mn, and SO₄ in soil leachates showed marked decrease over time. At the end of the study, pH and Al, Fe, Mn, and SO₄ leachate concentrations were virtually the same in all treatments in both studies. Additions of FA and HA to the mine spoil generally had immediate effects on leachate chemistry, which dissipated gradually. By contrast, effects due to addition of fresh OM took time to develop.

There were marked differences in the cumulative effects of treatments in both studies (table 4). Addition of HA and fescue leaf material significantly decreased total amounts of Al, Fe, Mn, and SO₄ leached from the spoils. The sums of ions leached from the fescue treatment are similar to those of the HA treatment, and the poststudy HA fraction of the fescue treatment was elevated well above that of other treatments. This suggests that fescue material may have been rapidly converted to the HA class of organic matter.

Among the three angiosperms (fescue, poke, and black cherry), there was a general inverse relationship of leachate pH and concentrations of the other ions. There was a less obvious difference between treatments among gymnosperms (pines). Different amounts of acidity produced during decomposition of various plant materials may reinforce or counteract the ion-complexing roles of some OM fractions in soils.

Table 4. Milligrams of Al, Fe, Mn, and SO₄ leached from 1.6 kg of Lily spoil with a variety of organic matter treatments over a 50 week period. Standard errors of the means are in parentheses.

Treatment	Al	Fe	Mn	SO ₄
<u>Raw O.M.</u>				
None	1291 (14)	1510 (14)	593 (9)	48700 (402)
Fescue	869*	1063*	455*	42460*
Poke	1453*	1743*	678*	52100
Black cherry	1310	1226*	585	49280
Virginia pine	1340	1499	583	51580
Red pine	1292	1411	580	50700
White pine	1023*	1113*	562	49340
<u>Mature OM</u>				
None	1228 (33)	1496 (11)	543 (11)	48280 (277)
HA	750*	859*	366*	38547*
FA	1276	1214*	540	52453*

*Significantly different from the control, P = 0.05, using Bonferroni's inequality applied to t-tests in the ANOVA.

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