

Laboratory Investigation of Leachate Chemistry from Six Appalachian Forest Floor Types Subjected to Simulated Acid Rain¹

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ABSTRACT

In order to determine the role of the forest floor in neutralization of strong acidity in acid rain, simulated acid rain at pH 4.0 was applied under laboratory conditions to forest floor samples from six Appalachian forest types. Effects of forest type, storm size, and repeated storm applications on leachate chemistry were investigated. Forest floor leachate from a hemlock forest [*Tsuga canadensis* (L.) Carr.] showed significantly lower pH (mean pH 3.9) than other leachate types due to high concentrations of organic acids. Cove hardwood forest found in an area with calcareous soil parent material produced forest floor leachate with a significantly higher pH (mean pH 6.5) than other forest types. Forest floor leachates from mixed oak (*Quercus* spp.), northern hardwood, red pine (*Pinus resinosa* Ait.), and white pine (*P. strobus* L.) forests were intermediate in pH (mean pH 4.1-4.4) due to the acidifying influence of organic acid leaching balanced against the neutralizing effect of H⁺ exchange for Ca²⁺ in the forest floor. Weak acidity concentrations obtained by Gran plots were well correlated with 400-nm wavelength transmittance and anion deficits in the leachates. Organic anions dominated leachates from hemlock and mixed oak forest types. Increasing storm sizes caused reduced ionic concentrations, especially of H⁺, Mg²⁺, and Ca²⁺, but three repeated storms produced no consistent significant reductions in loads or concentrations.

Additional Index Words: weak acidity, Gran titrations, organic acids, 400-nm transmittance.

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Neutralization of strong mineral acids (H₂SO₄ and HNO₃) from the atmosphere in the soil can help prevent acidification of streams and creation of elevated dissolved Al concentrations toxic to fish. There is evidence (Sharpe et al., 1984) that forest soils typical of the Appalachian Plateau region in southwestern Pennsylvania only provide partial neutralization of atmospheric deposition and yield percolate with high concentrations of dissolved Al toxic to trout (*Salmonidae* sp.). Headwater streams that show signs of transient acidification and have no reproducing trout populations are common in this region of Pennsylvania. However, Appalachian streams originating on basins with similarly classified soils, which show little transient acidification, have been observed by the authors near Parsons, WV on the Fernow Experimental Forest. The hypothesis that differences in the species composition of the forest between the two areas may have caused differences in

neutralization of atmospheric deposition, prompted several studies including this study of the influence of the forest floor on simulated atmospheric deposition.

Studies by Richter et al. (1983), Cole and Johnson (1977), Stednick and Johnson (1982), Johnson et al. (1977, 1983), and Lee and Weber (1982) all have shown substantial decreases in the strong acidity and increases in basic cation concentrations in rainwater percolating through the forest floor. Leachates from forest floors in these studies were dominated by weak organic and/or carbonic acids and were relatively unaffected by strong mineral acids supplied from the atmosphere. In contrast, Cronan et al. (1978) observed acidic forest floor leachates in New Hampshire dominated by H⁺ and SO₄²⁻ supplied by atmospheric deposition. The question remains whether forest floors typical of Appalachian forest types behave similar to that observed by Cronan et al. (1978) or types that provide substantial neutralization.

Due to the variety of experimental conditions and techniques encountered in past studies, it is not possible to distinguish effects of forest type on forest floor leachate chemistry. Some studies employed simulated acid rain storms, while others relied on natural rainfall that varied in acidity geographically. Numbers, sizes, and intensities of storms sampled as well as the properties of the mineral soil and bedrock also varied. Since all of these factors could affect leachate chemistry as well as forest species composition itself, the role of the forest type was impossible to discern.

This study was primarily designed to determine the effects of forest types and secondarily the effects of storm size and repeated storm applications on the chemistry of leachate from forest floor samples subjected to simulated acid rain storms at pH 4.0. Forest floor samples from six different Appalachian forest types: cove hardwoods, northern hardwoods, mixed oak (*Quercus* spp.), red pine (*Pinus resinosa* Ait.), white pine (*P. strobus* L.), and hemlock [*Tsuga canadensis* (L.) Carr.] were tested. Short-term experiments were conducted under the same temperature and simulated rainfall conditions where the samples were isolated from the effects of root uptake and litter fall. Emphasis was placed on processes that affect the acidity of the resultant leachate in order to help determine effects of forest floors on acid rain.

SITE DESCRIPTION

Stands sampled were located in Tucker and northern Randolph counties in or near the Monongahela National Forest and Parsons, WV. Stands were geographically isolated from one another, except for the white pine and red pine stands, which were adjacent plantations on former agricultural land. All other stands were natural forest types.

A survey of tree species and diameters within a 400 m² area was taken in each of the six forests stands at the site where forest floor samples were taken. The cove hardwood stand was comprised predominantly of yellow-poplar (*Liriodendron tulipifera* L.) in the overstory with sugar maple (*Acer saccharum* Marsh.) and yellow birch (*Betula alleghaniensis* Britton) in the understory. The northern hard-

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Table 1. Summary of chemical characteristics of humus and surface mineral soil by forest type.

Forest type	O2 Horizon						A1 Horizon					
	pH	P	CEC†	Ca ²⁺	Mg ²⁺	K ⁺	pH	P	CEC†	Ca ²⁺	Mg ²⁺	K ⁺
		g/m ²		mmol (p ⁺)/kg				g/m ²		mmol (p ⁺)/kg		
Cove hardwood												
Belmont soil series	6.7	1.12	138	11	10	3.1	6.4	0.53	153	115	10	2
Hemlock												
Gilpin soil series	3.8	2.83	250	25	5	8.3	4.2	1.33	180	8	1	8
Northern hardwood												
Dekalb soil series	4.1	1.34	202	32	6	5.6	4.2	0.75	165	21	2	3
Mixed oak												
Gilpin soil series	3.9	0.82	230	22	5	3.0	4.1	10.4	208	8	2	2
Red pine												
Gilpin soil series	4.3	17.1	209	47	4	2.8	4.2	0.90	198	28	3	4
White pine												
Gilpin soil series	4.0	1.71	207	21	3	4.2	4.1	2.24	192	9	1	2

†CEC = cation exchange capacity.

wood stand was dominated by black cherry (*Prunus serotina* Ehrh.), beech (*Fagus grandifolia* Ehrh.), and white ash (*Fraxinus americana* L.), with a sweet birch (*Betula lenta* L.) understory. The mixed oak stand had an overstory of white oak (*Quercus alba* L.), chestnut oak (*Q. prinus* L.), and red oak (*Q. rubra* L.), and an understory of sourwood (*Oxydendrum arboreum* (L.) DC.), dogwood (*Cornus* spp.), and red maple (*Acer rubrum* L.). The hemlock, red pine, and white pine stands were dominated by Eastern hemlock [*Tsuga canadensis* (L.) Carr.], red pine (*Pinus resinosa* Ait.), and Eastern white pine (*P. strobus* L.), respectively, with sweet birch prominent in the understory of the hemlock and red pine stands. The understory in the red pine stand also contained yellow-poplar, white oak, black gum (*Nyssa sylvatica* Marsh), and hickory (*Carya* spp.).

The thickness and mass of the forest floor varied considerably among forest types. Thickness and dry weight of samples were determined after the experiments were completed. Mean thickness of the forest floor for cove hardwood, hemlock, northern hardwood, mixed oak, red pine, and white pine samples were 18, 45, 20, 47, 56, and 40 mm, respectively. Mean dry weights of the samples were 1.44, 6.20, 1.63, 5.44, 5.43, and 5.30 kg/m², respectively. The forest floor in the cove hardwood stand was essentially only a litter layer without appreciable humus. Northern hardwood samples were also quite thin, but did include some humus. In contrast, the forest floor in the conifer and mixed oak stands was relatively thick with well-developed O1 and O2 horizons.

All forest stands sampled, except the cove hardwood stand, were growing in residual acid soils classified as loamy-skeletal, mixed mesic Typic Dystrachrepts (Dekalb series) or fine-loamy, mixed, mesic Typic Hapludults (Gilpin series) derived from shales, sandstone, and siltstone. The cove hardwood stand occurred on a Belmont series soil (fine-loamy, mixed, mesic Typic Hapludalfs) derived from shale, sandstone, and interbedded limestone. The influence of parent material is apparent in the significantly higher pH, Ca²⁺, and Mg²⁺ content in the O2 and A1 soil horizons in the cove hardwood stand than other forest stands (Table 1).

METHODS

Sample Collection

Six replicate forest floor samples were collected from each of the six forest types on 6-7 Feb. 1982. To collect the samples in an undisturbed condition, the forest floor was cut away from the edges of a rectangular 0.4 m by 0.24 m sample protected by a steel plate. The steel plate was then slipped under the sample, as near to the top of the mineral soil layer as possible. The sample was then lifted, placed into a plastic tray, and covered with a tightly fitting lid for storage. Sample disturbance during collection was lessened by the frozen condition of the forest floor. Upon return to the laboratory in State College, PA, the forest floor samples were kept in the trays and stored in a frozen condition until used in the experiment. At each site where forest floor samples were collected, three samples of humus (O2 horizon) and surface mineral soil (A1 horizon) were also collected for later chemical analysis.

Simulated Acid Rain

Simulated acid precipitation was produced according to formulae developed by Northrop Services, Inc., Research Triangle Park, NC (Lovitt, 1981). A concentrate was produced, as per their 2xxx series formula, for use in mixing batches of acid precipitation throughout the experiment. A target pH of 4.0 for the final solution was used as a control in the dilution of the concentrate. Due to problems with mixing and stability of the simulated acid rain, which were not discovered until later in the experiments, the chemistry of the applied rain varied among applications. Mean chemistry of the simulated acid precipitation based on samples collected after each of nine applied storms is summarized in Table 2. The simulated rain was similar to natural rainfall and throughfall for H⁺, Ca²⁺, Mg²⁺, and SO₄²⁻ concentrations, but high in concentrations of NO₃⁻ and Cl⁻. Chloride concentrations were particularly enriched and more closely approximated precipitation Cl⁻ at a coastal site.

Laboratory Procedures

Twelve forest floor samples were thawed at a time for use, two from each stand. After thawing, the sample trays were inclined at an angle of 10° and plastic drainage tubes were connected to the lower end of each tray. The tubes carried leachate from the trays to plastic sample collection bottles.

Each thawed forest floor sample was first saturated with simulated acid rain and allowed to drain for 12 h to equalize antecedent moisture content among samples. The lids were kept on the sample trays during drainage to prevent evaporation. After the initial wetting, each of the 12 samples received a simulated acid rain storm of specified amount. All storms were applied to samples at a shaded outdoor site from 17-27 May 1982. The storm was applied by hand with a watering can

Table 2. Chemical comparison of mean and range of chemical constituents of simulated acid rain with rain and hardwood forest throughfall measured during three growing seasons at Fernow Experimental Forest, Parsons, WV.

Ion	Simulated rain	Wet fallout	Throughfall
		μmol/L	
H ⁺	97 (76-209)	60	42
pH	4.01 (3.68-4.12)	4.22	4.38
Ca ²⁺	34 (19-52)	42	76
NH ₄ ⁺	55 (43-79)	-†	-
Mg ²⁺	17 (12-25)	6	18
K ⁺	32 (15-62)	--	--
Na ⁺	53 (28-105)	--	--
NO ₃ ⁻	77 (43-196)	29	34
SO ₄ ²⁻	61 (39-92)	69	100
Cl ⁻	170 (90-267)	2	2
<u>mol (p⁺) cations</u>	0.92	--	--
<u>mol (e⁻) anions</u>			

† No data.

over each sample in six equal increments during a 1-h period. After a 12-h drainage period with evaporation again prevented, a rain sample and the leachate samples from each tray were collected for chemical analysis. Twelve hours was sufficient time for drainage of water from all samples.

The same storm size and drainage cycle was repeated three times on each forest floor sample, generally with only 12 to 24 h between each application. After the application of all three replicate storms, the forest floor samples were weighed and their moisture content measured to determine dry weights. Also, the depth of each sample was measured. A fresh set of 12 samples, two from each stand, was then thawed for application of the next storm size to be applied. The three storm sizes applied were (i) 0.5 cm in 1 h, (ii) 1 cm in 1 h, and (iii) 2 cm in 1 h. These storms are all < 2 yr return period storms for this region and would be commonly encountered. Leachate volume recovery averaged 80, 90, and 96% of applied rainfall for 0.5-, 1.0-, and 2.0-cm storms, respectively.

Water and Soil Analysis

A total of 108 forest floor leachate samples and nine simulated acid rain samples were analyzed in the water lab of the Institute for Research on Land and Water Resources at The Pennsylvania State University. The analysis consisted of pH, NH_4^+ , NO_3^- plus NO_2^- , NO_2^- , SO_4^{2-} , Cl^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , 400-nm wavelength transmittance, strong acidity, and total acidity determinations.

Standard methods for collection, preservation, holding, and analysis of water samples were followed (USEPA, 1979). Samples were stored at 4°C and analyzed within recommended holding times. Subsamples for metals analysis were acidified with HNO_3 (Baker Instra-Analyzed® acid for trace metal analysis) to pH 2.0.

Analysis methods used refer to specific USEPA (1979) methodologies except for chlorides. Sample pH was measured potentiometrically, NO_2^- plus NO_3^- analysis involved the automated Cd reduction method and the Technicon Autoanalyzer II®, sulfates were analyzed turbidimetrically, conductance was measured with a Wheatstone bridge, transmittance was measured with a spectrophotometer, and NH_4^+ was determined using the automated phenate method. Analysis for NO_2^- concentration conducted on some samples was always below detection levels (1 $\mu\text{mol/L}$); thus, the analysis for NO_3^- plus NO_2^- was assumed to represent NO_3^- concentrations. Metals analysis for K^+ , Na^+ , Ca^{2+} , and Mg^{2+} was conducted using the flame atomic absorption spectrophotometer. Chlorides were measured using the automated silver chloride titration method with an Aminco Cotlove Chloride Titrator®.

Since many of the water samples analyzed were colored due to dissolved organic acids and laboratory analysis for SO_4^{2-} , NO_3^- , and NH_4^+ concentrations can be affected by sample color, special precautions were taken to avoid errors in analysis for these ions. As prescribed by USEPA (1979) for SO_4^{2-} analysis with colored water samples using the turbidimetric method, sample turbidity measured before addition of BaCl_2 was subtracted from the turbidity measurement after formation of BaSO_4 precipitate to directly adjust for the effects of color. Color effects on NO_3^- and NH_4^+ analysis were checked by reanalysis of selected highly colored samples with deionized water instead of standard reagents on the Technicon Autoanalyzer II®. For 17 leachate samples the error in NH_4^+ concentration due to sample color averaged only 0.65% with a range of 0 to 2.41%. Errors due to sample color for NO_3^- determination were less, averaging 0.32% with a range of 0 to 2.94% for 12 samples. Thus, errors in NH_4^+ and NO_3^- determinations were judged to be negligible in this study. In other studies where samples have greater organic discoloration or lower 400-nm transmittance than in this study and low NH_4^+ or NO_3^- concentrations, such errors could be significant.

Determination of strong and total acidity was accomplished using Gran's procedure (Rossotti and Rossotti, 1965; Galloway et al., 1979). To analyze acidity via the Gran's method, N_2 was bubbled through a sample for approximately 20 min or until pH stabilized to eliminate the effect of H_2CO_3 . Also during the titration, N_2 was continuously bubbled through the sample.

The construction of a Gran's titration curve is necessary to determine the strong and total acidity and hence the weak acidity by difference. The Gran's plot consists of a horizontal axis defined as the volume of base added, and two vertical axes (ϕ and ϕ') defined as

$$\phi = (V + v) 10^{-\text{pH}}$$

$$\phi' = (V + v) 10^{\text{pH}}$$

where V is the initial sample volume, v is the volume of base added, and pH is the pH of the sample after the addition of the base. With small volumes of base added, an extension of the linear portion of a plot of ϕ vs. v intersects the horizontal axis at a volume corresponding to the strong acidity. Conversely, with larger volumes of base added, an extension of the linear portion of θ' vs. v intersects the horizontal axis at a volume corresponding to the total acidity. Weak acidity is obtained as the difference between total and strong acidity and is used in this study as an index of organic acids present in the leachate. Since organic acids also cause discoloration of the leachate, transmittance of the leachate samples at the 400-nm wavelength (Lee and Brosset, 1978) was also measured for use as an index to organic acid concentrations.

Soil chemical analysis was conducted at Merkle Soil Testing Laboratory, The Pennsylvania State University. Analyses were performed to determine soil pH, cation exchange capacity, and concentrations of P, Ca^{2+} , Mg^{2+} , and K^+ in the humus and mineral soil. Soil pH was measured on a 1:1 soil-distilled water mixture, soil Ca^{2+} , K^+ , and Mg^{2+} content were determined by extraction with NH_4OAc and use of the atomic absorption spectrophotometer, soil P was determined photometrically after extraction with NH_4F and HCl solution, and the cation exchange capacity was determined from the measured cation concentrations and exchangeable H^+ determined using a mixture of soil and SMP (Shoemaker et al., 1961) buffer solution.

Statistical Methods

Statistical analysis for each chemical parameter involved three-way analysis of variance using the SAS General Linear Model (Statistical Analysis Systems Institute, Inc., Cary, NC) for effects of forest type, storm size, and repeated storm sequence nested within storm size. Analysis was performed on leachate concentrations ($\mu\text{mol/L}$) and leachate loads (concentration \times volume, μmol) for each constituent. Loading data are stressed later in the paper.

Because the concentration of some ions varied in the input rainfall, concentrations were tested as a covariate in the analysis of variance of leachate concentrations. Mean separation tests were performed to determine significant differences among adjusted means using the SAS, GLM least squares means routine by forest floor type, storm size, and repeated storm application. Although comparisons among forest types were not affected by covariate adjustments because all types were exposed simultaneously to the same simulated rainfall, leachate concentrations of NH_4^+ , Na^+ , K^+ , SO_4^{2-} , and Cl^- reported later were corrected for a significant covariate effect. Regardless, covariate adjustments to means were small and only occasionally affected significant differences among means for storm sizes and repeated application.

RESULTS AND DISCUSSION

Effects of Forest Floor Type

The mean pH of the leachate was significantly lower in the hemlock type (pH 3.88) and significantly higher in the cove hardwood type (pH 6.52) than in other forest types (Table 3). Low pH in hemlock forest floor leachate appeared to be associated with high weak acidity concentrations. Hemlock and mixed oak forest floor leachates exhibited significantly greater weak acidity than leachate from the other forest types, presumably due to greater production and leaching of organic acids. The significantly lower 400-nm transmittance for leachate from these two forest types also attests to discoloration of these samples by organic acids. Dissociation of weak organic acids could release sufficient H^+ to reduce leachate pH, barring influences from other processes. This apparently explains the low pH in the hem-

Table 3. Mean ionic loads and chemical composition of leachate from six forest types and simulated acid rain storms.

Parameter (μmol)	Forest type						Simulated acid rain
	Cove hardwoods	Hemlock	Northern hardwoods	Mixed oak	Red pine	White pine	
H ⁺	0.4a*	107b	60c	56c	45c	62c	100
pH	6.52a	3.88b	4.24cd	4.26cd	4.36cd	4.11d	4.01
NH ₄ ⁺	24a	93b	81b	238c	92b	197d	64
Ca ²⁺	228a	59b	92c	68b	144d	153d	37
Mg ²⁺	77a	39b	64c	42b	54d	73d	32
K ⁺	91a	195b	71a	199b	132c	90a	33
Na ⁺	47a	38bc	48a	37b	50a	40b	54
SO ₄ ²⁻	43ab	44ab	32a	43ab	90c	53b	68
Cl ⁻	160ad	135b	151ac	145bc	168d	140b	176
NO ₃ ⁻	133a	56b	156b	60b	58b	343c	79
Weak acidity	—	309a	134b	337a	237c	250c	73
400-nm transmittance (%)	70a	28b	69a	25b	44c	57d	100
Mean leachate volume (mL)	1165a	1106b	1151ac	1139cd	1122bd	1128d	

* Values in rows followed by the same letter are not significantly different among forest types at the 95% confidence level.

lock forest floor leachate, but other factors also control leachate pH.

Greater leaching of organic acids from the forest floor in the hemlock and mixed oak stands is related to the greater mass of forest floor in these forest types and the "leachability" of the material. Using weak acidity as an index to organic acids produced, the ratios of mean weak acidity loads (Table 3) to mean mass of forest floor per unit area (given previously) could be used as an "organic acidity leachability" index. These ratios are 473, 776, 587, 417, and 445 $\mu\text{mol}/\text{kg}$ for hemlock, northern hardwood, mixed oak, red pine, and white pine forests, respectively. On this basis, forest floor "leachability" in the hemlock stand was actually lower than in northern hardwood and mixed oak forest. Northern hardwood forest floor had the highest leachability ratio, probably because a greater proportion of the samples were freshly fallen leaves rather than humus. However, northern hardwood forest floor produced the lowest measured weak acidity loads due to the small mass of material. Mixed oak forest floor leachability and mass were both high and produced a high organic acid concentration in leachate.

The major factor affecting pH in the cove hardwood leachate was Ca²⁺ content of the forest floor. The significantly higher leachate pH in cove hardwoods was accompanied by significantly higher leachate Ca loads than found in any other leachate type (Table 3). Belmont soil at the cove hardwood site also had significantly higher Ca²⁺ and Mg²⁺ concentrations and pH than soil at the other sites. Cove hardwood forest was dominated by tree species, such as yellow-poplar and sugar maple known to accumulate Ca²⁺ in foliage (Lutz and Chandler, 1946). Thus, Ca²⁺ and Mg²⁺ were available in the cove hardwood forest floor to exchange with H⁺, producing a higher pH.

Some exchange of H⁺ for Ca²⁺ and Mg²⁺ probably also occurred in other forest types, since mean pH for red pine, white pine, northern hardwood, and mixed oak were above that in the applied rain. For these forest types, the increase in Ca²⁺ and Mg²⁺ concentrations as water passed through the forest floor were much greater on a charge equivalent basis than needed to account for the reduction in H⁺ concentration.

Leachate Ca²⁺ loads were high for the red and white pine sites (Table 3), perhaps due to the past agricultural

use at these sites. However, surface mineral soil and humus did not consistently show significantly higher Ca²⁺ concentrations at these sites (Table 1), although red pine humus did exhibit the second highest Ca²⁺ concentration.

Large increases in the pH of water percolating through the forest floor similar to those found for cove hardwoods have been reported previously. For example, Stednick and Johnson (1982) report forest floor leachate pH of 5.5 at an Indian River, AK spruce-hemlock forest site with limestone and marble soil parent material; Richter et al. (1983) reported a pH of 6.0 in forest floor leachate at two Tennessee hardwood forest sites (Fullerton and Tarklin) with dolomitic soil parent material and A1 horizon base saturation of 61 to 74%. Cole and Johnson (1977) also reported forest floor leachate of pH 6 to 7 in a Washington Douglas-fir forest with Everett series soil (loamy-skeletal, mixed, mesic Dystric Xerochrepts) derived from coarse glacial outwash and with A horizon base saturation of 39%. It appears that forest floors with pools of exchangeable cations, such as the cove hardwood site with > 80% base saturation in the O2 horizon, can provide considerable neutralization capability to reduce strong mineral acidity. In contrast, the base saturation of O2 and A1 horizons from the other forest types in this study were < 20% and leachate pH remained < 4.4.

Weak acidity and 400-nm transmittance data are consistent with the hypothesis that greatest leaching of organic acids occurs in samples with low transmittance and high weak acidity concentrations. Weak acidity was linearly related to 400-nm transmittance (Fig. 1) for all samples combined except white pine. The difference in weak acidity between the applied rain and leachate was used in Fig. 1, since the applied simulated rain exhibited an important weak acidity component.

White pine leachate data were significantly different in the relationship between weak acidity and transmittance (Fig. 1). This difference appeared to be caused mainly by high NH₄⁺ concentrations in the white pine leachate (Table 3), which causes higher weak acidity rather than differences in organic acid leaching. Weak acidity was significantly and positively correlated with NH₄⁺ concentrations in leachate ($R^2 = 42\%$).

Differences in nitrification rates among the forest types during the experiments are also suspected of in-

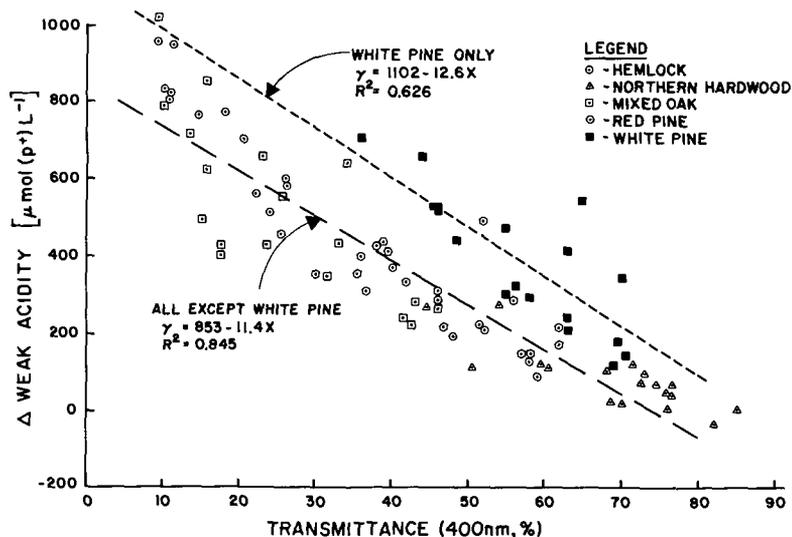


Fig. 1. Relationship between transmittance of leachate samples at 400-nm wavelength and the change in weak acidity concentration as simulated acid rain passes through the forest floor.

fluencing leachate pH. For example, mixed oak forest floor produced leachate with the highest average weak acidity and lowest 400-nm transmittance, indicating high organic acid concentration, but mixed oak leachate had a significantly higher pH than hemlock leachate. One reason for the intermediate pH for mixed oak may be low rates of conversion of NH_4^+ to NO_3^- , which could also have an acidifying effect on the leachates. Mixed oak leachate exhibited significantly higher $[\text{NH}_4^+]$ and among the lowest $[\text{NO}_3^-]$ compared with other forest types, which could indicate that nitrification rates were lowest in mixed oak. Without direct measurement of nitrification, this hypothesis cannot be tested, but it is important to note that nitrification could have also influenced leachate acidity.

Mean volumes of leachate recovered did vary significantly among forest types (Table 3), ranging from 90 to 95% of mean volumes of applied rainfall. Highest leachate volumes were recovered from the thinner forest floor types with low mass per unit area (cove hardwoods and northern hardwoods) and lowest volumes were recovered from the thicker, higher mass per unit area forest floors (hemlock, red pine, and white pine). Despite occurrence of significant differences among species in leachate recovery, relative differences in leachate volumes were small. Analysis of variance gave the same significant differences among forest types for all chemical parameters using either ionic concentrations or loads.

Although there were significant differences in leachate samples from all six forest types studied, there were also marked similarities between several of the types. For example, the leachate samples from cove hardwood and northern hardwood were statistically similar in mean loads of Na^+ , K^+ , NO_3^- , SO_4^{2-} , Cl^- , and 400-nm transmittance at the 0.95 confidence level. In a like manner, samples from hemlock and mixed oak were similar in mean loads of Na^+ , Mg^{2+} , K^+ , NO_3^- , SO_4^{2-} , Cl^- , weak acidity, and 400-nm transmittance.

The role of organic anions from dissociation of weak organic acids in the ion charge balance in leachate among the forest types can be examined by totaling

equivalent weights of measured anions and cations. Although organic anion concentrations were not measured, any anion deficit can be taken as a measure of organic anion concentrations. Due to the low pH of the leachates, HCO_3^- concentrations can be assumed negligible for all types except cove hardwood. Comparison of anion deficits with weak acidity concentrations (Fig. 2), indicates significant correlation ($R^2 = 0.93$) and the fact that organic anions are approximately equal to 59% of weak acidity. Using this relationship to estimate organic anion concentrations (Table 4), we see organic anions in leachate from hemlock and mixed oak contributed over 50% of the anions in forest floor leachate. Cove hardwood and northern hardwood leachate was least dominated by organic anions. Leachate from pine stands was intermediate in organic anion dominance.

Forest floors where organic anions are least important, such as northern hardwoods in this study, are probably more susceptible to effects of acidic atmospheric deposition. Sulfates added from acid deposition in this type of forest floor could provide relatively large percentage increases in negative charge for cation transport than in forest floors where organic anions naturally dominate the cation leaching. Although cove-hardwood forest floor leachate was low in organic anions, high Ca^{2+} in this forest floor produced high neutralizing capacity, high pH, and probably dominance by HCO_3^- among anions.

Cronan et al. (1978) found forest floor leachate pH averaged 4.1 and was dominated by SO_4^{2-} in a Mt. Moosilauke, NH balsam fir [*Abies balsamea* (L.) Mill.] forest influenced by acid precipitation. In contrast, Stednick and Johnson (1982) show forest floor leachate pH of 4.2 and organic anion dominance in a Findley Lake, WA silver fir [*Abies amabilis* (Doug.) Forbus] forest not exposed to acid precipitation. A study by Leibfried (1982) conducted on Laurel Hill in southwestern Pennsylvania in a forest dominated by red maple, sugar maple, red oak, and black cherry trees showed forest floor leachate with an average pH of 3.8 during winter rain and snowmelt, which added water at

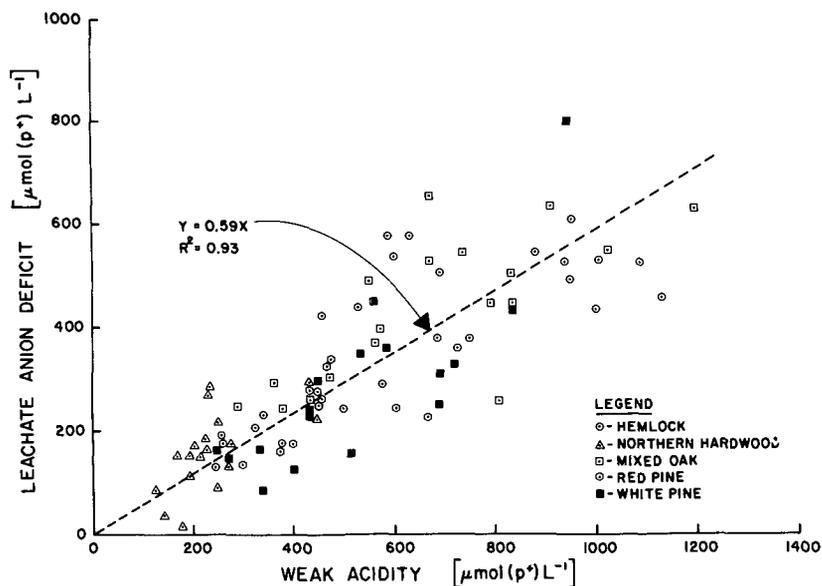


Fig. 2. Relationship between the deficit of measured anion concentrations and weak acidity concentrations in the forest floor leachate.

pH 4.0. These studies show leachate pH in the range found for noncalcareous sites (pH 3.9 to 4.4) in our study and illustrate (Stednick and Johnson, 1982) that low leachate pH does not necessarily indicate effects of acid precipitation. Leaching of organic acids and neutralization by H^+ exchange for Ca^{2+} must also be considered.

Acidic leachates from the forest floor may be neutralized in the mineral soil below. Mineral horizons with high exchangeable Ca^{2+} or Mg^{2+} could provide neutralization needed to protect aquatic ecosystem from flushes of acidic water with high dissolved Al concentrations. However, Sharpe et al. (1984) found that for soils on the Laurel Hill in southwestern Pennsylvania mineral forest soil horizons exhibited base saturations < 10% and leachate collected below B horizons had pH < 4.5 and high dissolved Al concentrations. Thus, neutralization of acidic leachates in mineral soil horizons can occur, but it has not been observed in Laurel Hill forest soils, at least.

Effects of Storm Size and Repeated Storm Applications

Mean loads of all chemical constituents in forest floor leachate increased significantly as storm size increased

Table 4. Comparison of the role of organic anions in leachate from six forest floor types.

Ions	Cove	Northern	Mixed	Red	White	
	hardwood	hemlock	oak	pine	pine	
	$\mu\text{mol (p}^+ \text{ or e}^- \text{)/L}$					
Cations†	736	679	552	742	730	984
Anions†	425	193	392	307	412	720
Anion deficit	311	386	160	435	318	263
Organic anions‡	123§	423	140	400	282	317
(Percent of total anions)	22	69	26	56	41	30

† Cations = H^+ , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ ; anions = SO_4^{2-} , NO_3^- , Cl^- .

‡ Estimated as 0.59 times mean weak acidity from Fig. 2.

§ Estimated using leachate transmittance, Fig. 1 and Fig. 2.

due to the larger volumes of leachate involved, with few exceptions. Loads of K^+ , NO_3^- , and SO_4^{2-} between the 0.5- and 1.0-cm storms were not significantly different. Interestingly, load increases were always less than expected due to increased amounts of applied water; indicating concentrations declined as storm size increased. As can be seen in Table 5, concentrations of H^+ , Ca^{2+} , and Mg^{2+} in the leachates significantly and consistently declined, while transmittance increased, as storm size increased. Other parameters, except Cl^- and SO_4^{2-} , also showed some significant decline in concentrations with increasing storm size.

The implication of these results is that storm size controlled the percolation rate of simulated rain through the forest floors and consequently affected time available for reactions between the applied water and organic materials. The decline in H^+ concentrations with increasing storm size must be caused by reduced leaching of organic acids with increasing storm size, since reduced concentrations of Ca^{2+} with increasing storm size implies reduced H^+ exchange and more H^+ available for leaching. Other parameters are apparently less affected by the storm sizes applied due to the rapid reaction

Table 5. Mean chemical composition of forest floor leachate for three simulated acid rain storm sizes (all sites).

Parameter ($\mu\text{mol/L}$)	Storm size		
	0.5 cm	1.0 cm	2.0 cm
H^+	82a*	63b	37c
pH	4.08	4.20	4.44
NH_4^+	140a	135a	104b
Ca^{2+}	200a	126b	82c
Mg^{2+}	51a	33b	25c
K^+	153a	152a	103b
Na^+	50a	41b	39b
SO_4^{2-}	59a	48a	53a
Cl^-	170a	146a	131a
NO_3^-	317a	106b	86b
Weak acidity	316a	313a	167b
400-nm transmittance (%)	47a	40b	61c

* Values in row followed by the same letter are not significantly different among storm sizes at the 95% confidence level.

within the forest floor or, as in the case of Cl^- , the fact that the ion is only slightly absorbed and remains near the concentration in the applied rain. Regardless, it is clear that the hydrologic regime within the forest floor can also affect leachate chemistry.

Three repeated storm applications at the same rate did not produce consistent significant changes in forest floor leachate chemistry. Repeated applications would eventually be expected to cause reduced concentrations and loads of ions due to depletion of supply within the forest floor samples. The lack of any significant trend may only indicate that three repeated storms did not cause sufficient leaching to produce a detectable depletion. For short-term studies such as this, depletion of elements for chemical exchange in the forest floor appears to be negligible.

CONCLUSIONS

Only cove hardwoods of six Appalachian forest floor types tested neutralized strong mineral acidity in simulated acid (pH 4.0) rainfall to a level that would help prevent soil acidification of aquatic ecosystems. Cove hardwood forest floor samples produced leachate with mean pH of 6.5, which was attributed to calcareous soil parent material and a base saturation in the O2 and A1 soil horizons > 80%. Hemlock, mixed oak, red pine, white pine, and northern hardwood forest floor samples collected in areas with sandstone and shale parent materials and soil base saturation in O2 and A1 horizons of < 20% produced leachates with mean pH < 4.4. Leachate acidity from these forest floor types was influenced by leaching of organic acids and possibly nitrification.

Leaching of organic acids was controlled by the mass of forest floor as well as the "leachability" of available material, with the thick forest floors and those with a higher proportion of fresh litter contributing greater amounts of organic acids. Relative rankings of organic acid leaching from forest floors, from high to low, were:

(Hemlock + Mixed oak) > (Red pine + White pine)
> (Cove hardwoods + Northern hardwoods).

Consequently, organic anions were found to represent the majority of anions in leachate from hemlock and mixed oak forest floors, but $\leq 26\%$ of anions in cove hardwood and northern hardwood leachate. Forest floor types with low concentrations of organic anions and without calcareous bedrock, such as the northern hardwoods in this study, were judged most susceptible to leaching by increased acidic atmospheric deposition.

Leachate transmittance at 400 nm wavelength was found to be linearly related to weak acidity contributed by forest floor material. It may be feasible to routinely

measure soil leachate transmittance to ascertain weak and organic acidity concentrations, after empirically establishing the transmittance-weak acidity relationship on a limited number of samples.

Larger storm sizes significantly increased forest floor leachate loads (concentration \times volume), but caused concentrations of ions—especially H^+ , Ca^{2+} , and Mg^{2+} —to decline. Thus, larger storms produced higher leachate pH. Three repeated storm applications did not generally produce a significant change in leachate chemistry.

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