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Factors Affecting Anion Movement and Retention in Four Forest Soils¹

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ABSTRACT

Three hypotheses concerning the movement and retention of anions in forest soils were tested in a series of laboratory and field studies on two Tennessee Ultisols with mixed deciduous forest cover and two Washington Inceptisols, one with deciduous (red alder *Alnus rubra* Bong.) and one with coniferous [Douglas-fir, *Pseudotsuga menziesii* (Mirb.) Franco] forest cover. The first hypothesis, that sulfate and phosphate retention was related to adsorption to free Fe and Al oxides, which were in turn related to soil parent material and degree of weathering, was not supported by results of laboratory and field studies. The young, relatively unweathered Washington Inceptisols adsorbed more phosphate and sulfate than the older, highly weathered Tennessee Ultisols, apparently because of greater amorphous (oxalate-extractable) Fe and Al in the former. The second hypothesis, that NO₃⁻ retention was governed primarily by biological uptake, was supported. Nitrate adsorption by soils in laboratory column studies was negligible, but subsequent field studies showed that tree uptake in field plots greatly reduced the leaching of applied NO₃⁻ in all but the N-rich red alder plot. The third hypothesis, that inputs of mobile anions will reduce pH and concentrations of bicarbonate and adsorbing anions (e.g., sulfate), were supported by application of chloride as both acid and Na and Ca salts to soil columns in the laboratory. Sulfate concentration as well as bicarbonate concentrations in soil solutions were sensitive to solution pH.

Additional Index Words: bicarbonate, NO₃⁻, SO₄²⁻, chloride, phosphate, adsorption, uptake, leaching.

Johnson, D.W., D.W. Cole, H. Van Miegroet, and F.W. Horng. 1986. Factors affecting anion movement and retention in four forest soils. Soil Sci. Soc. Am. J. 50:776-783.

NYE AND GREENLAND (1960) first suggested that leaching in forest soils is limited by a lack of mobile anions in the soil. According to this concept, leaching cannot occur without an anion (or anions) to maintain electrochemical neutrality in soil solution. Cole and Gessel (1965) and McColl and Cole (1968) first applied Nye and Greenland's concept to describe carbonic acid leaching in undisturbed, fertilized, and harvested conditions in a forest soil. Subsequent studies confirmed the important influence of anion pro-

duction and mobility on nutrient leaching following harvesting, fire, fertilization, wastewater application, and atmospheric sulfuric acid inputs or "acid rain" (reviewed by Johnson and Cole, 1980).

Among the major anions in soil solutions that can be involved in leaching processes, there are large differences in terms of their biotic and abiotic chemical reactions. The production and mobility of NO₃⁻ is regulated almost entirely by biological processes (uptake, mineralization, nitrification), while for phosphate and sulfate soil chemical processes are more important. Anion adsorption (primarily to amorphous Fe and Al oxide surfaces) is a dominant mechanism for phosphate retention in soils and can be very important to sulfate mobility as well (Johnson and Cole, 1980). Both of these anions can enter into "specific" adsorption reactions on hydrous oxide surfaces (Hingston et al., 1967) in which anions enter into a coordination with a metal oxide and displace another anion (usually OH⁻). The latter is sometimes called ligand exchange (Hingston et al., 1967). Recent work by Rajan (1979) and Parfitt and Smart (1978) showed that ligand exchange is the dominant mechanism for SO₄²⁻ adsorption onto Fe and Al hydrous oxides.

Anion adsorption sites lie on the surfaces of colloids, and these surfaces can have a plus, minus, or zero charge depending upon pH (Yopps and Fuerstenaue, 1964). At low pH, surfaces become positively charged because of H⁺ adsorption, and anion adsorption is enhanced. At high pH, surfaces become negatively charged because of H⁺ dissociation (or OH⁻ adsorption), and anions may be repelled.

Bicarbonate is somewhat unique in that its production and mobility are affected by both chemical and biological processes. Equilibrium equations show that bicarbonate concentration in any solution is regulated by CO₂ pressure and pH. Carbon dioxide pressure is in turn affected by soil microbial and root respiration, soil porosity, soil moisture content, and soil depth (Wesseling, 1962). Soil solution pH can be affected by base saturation, the presence of buffering agents (such as organic acids), and the ionic strength of the soil solution (Reuss, 1978; 1983). The relationships between base saturation, ionic strength, and pH can be seen from a generalized selectivity coefficient that describes the exchange of cations and H⁺ on cation exchange sites (Stumm and Morgan, 1970)

$$Q = \frac{(H^+)^f [C^{r+}]}{(C^{r+}) [H^+]^f} \quad [1]$$

where Q = selectivity coefficient, $()$ = exchange phase,

¹ Research sponsored by the National Science Foundation's Ecosystem Studies Program (DEB-7824395) and Office of Health and Environmental Research, U. S. Dep. of Energy, under Contract no. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Publication no. 2642, Environmental Sciences Division, ORNL. Received 3 June 1985.

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[] = solution phase, C = cation, and r = valence of cation.

Solving for H^+ , we have

$$[H^+] = \left[\frac{(H^+)[C^{r+}]}{(C^{r+}) Q} \right]^{1/r} \quad [2]$$

This equation shows that we can change soil solution pH by changing exchangeable (H^+) or (C^{r+}) (e.g., by changing base saturation) or by changing solution cation concentration, $[C^{r+}]$. Generally, the pool of exchangeable cations or H^+ per unit of soil is much greater than the pool of solution cations of H^+ . Thus, changes in base saturation are more difficult to produce and longer in duration than those in solution concentrations, and for our purposes it is useful to separate the two into long- and short-term effects.

Since chloride is relatively unaffected by either biotic or abiotic chemical reactions in soils, it normally leaches through soils without reaction. However, the input of any mobile anion (such as Cl^-) should result in a short-term lower soil solution pH whether the anion is input as a salt or as an acid. This is because the concentration of cations $[C^{r+}]$ will be elevated concomitantly with the concentration of the introduced anion in soil solution, and this will in turn elevate $[H^+]$ according to Eq. [2]. In the case of an acid input, H^+ will displace exchange cations, lowering base saturation, and in this way induce a long-term decrease in pH and total ionic leaching following the passage of the initial flux. In the case of a salt addition, there should be some H^+ displacement by incoming cations (by mass action), resulting in a long-term increase in base saturation, pH, and total ionic leaching following the initial flux. Thus, although Cl^- (or any other mobile anion) itself may pass through the soil unaffected, it can have both short- and long-term effects on the mobilities of other anions and on total ionic flux.

As a result of the considerations outlined above, we constructed the following hypotheses concerning anion mobility in forest soils:

Hypothesis I:

The mobility of sulfate and phosphate in soil is related to the free Fe and Al content of the soil which, in turn, is a function of the original chemical composition of the soil and the degree to which it has been weathered.

Hypothesis II:

The mobility of NO_3^- is controlled by biological uptake rather than abiotic chemical processes.

Hypothesis III:

Although mobile, biologically inactive anions such as Cl^- will pass through the soil unaffected, the additions of such anions as salts or acids will have both short- and long-term effects on soil solution pH and on the mobilities of other anions, thus effecting an increase or decrease in net ionic flux from the soil.

These hypotheses were tested in a variety of laboratory and field experiments on two Ultisols with

mixed deciduous forest cover in eastern Tennessee and two Inceptisols, one with coniferous [Douglas-fir, *Pseudotsuga menziesii* (Mirb.) Franco] and one with deciduous (red alder, *Alnus rubra* Bong.) cover in western Washington. Results of these tests are summarized in this paper.

SITES

Walker Branch Watershed, Tennessee

Walker Branch Watershed is situated in the ridge and valley physiographic province near Oak Ridge, TN (Grigal and Goldstein, 1971). The climate type is humid mesothermal with moderate summer and winter temperatures. Mean annual temperature is 14.3°C and precipitation averages 151 cm/yr, mostly as rain (Henderson et al., 1977). Soils of the watershed are primarily Ultisols derived from Knox dolomite, a cherty, dense to coarsely crystalline rock of late Cambrian to early Ordovician age. Soil coarse fractions consist of chert, Fe-Mn nodules, and quartz. Clay fractions consist primarily of kaolinite with lesser amounts of vermiculite, hydrous micas, and quartz, (Peters et al., 1970). In a nearby site with similar parent material, Lee et al. (1984) concluded that kaolinite was weathering to Al hydroxy-interlayered vermiculite in surface horizons.

The chestnut oak (*Quercus prinus* L.) stand on Walker Branch is located on a ridgetop on the Fullerton series soil, a Typic Paleudult. Coarse fragments range from 30% in E horizons to 17 to 18%, in Bt horizons and clay content ranges from 3 to 12% in E horizons to 40 to 50% in Bt horizons (Peters et al., 1970). Vegetation type is chestnut oak, described by Grigal and Goldstein (1971). Species consist primarily of chestnut oak, hickory (*Carya* spp.), red maple (*Acer rubrum* L.), white oak (*Quercus alba* L.), black oak (*Q. velutina* Lam.), blackgum (*Nyssa sylvatica* Marsh.), sourwood (*Oxydendrum arboreum* L.), and yellow-poplar (*Liriodendron tulipifera* L.), with occasional dogwood (*Cornus florida* L.) and northern red oak (*Q. rubra* L.). Understory is absent.

The yellow-poplar stand is located in a sinkhole depression on the Tarklin series soil, a Typic Fragiudult. Coarse fragments range from 7% in Ap horizons to 12 to 17% in Bt horizons and clay content ranges from 4 to 7% in Ap horizons to 12 to 17% in Bt horizons (Peters et al., 1970). Vegetation type is yellow-poplar, described by Grigal and Goldstein (1971). Species consist primarily of yellow-poplar with occasional red maple, white oak, black locust (*Robinia pseudoacacia* L.), persimmon (*Diospyros virginiana* L.), black cherry (*Prunus serotina* Ehrh.), and Carolina buckthorn (*Rhamnus caroliniana* D.C.). Understory consists of dogwood, occasional eastern red cedar (*Juniperus virginiana* L.), and Japanese honeysuckle (*Lonicera japonica* Thunb.).

Thompson Site, Washington

The Thompson site is located in the western foothills of the Cascade Mountains near Landsburg, WA. The climate type is maritime with cool, dry summers, and wet, moderate winters. Mean annual temperature is 9.8°C and mean annual precipitation is 136 cm, most of which falls as rain between October and March. The soil at the study site belongs to the Alderwood series, a Dystric Entic Durochrept, and is composed of loosely consolidated ablation till of varying depth over a compacted basal till. Brackett (1966) found a predominance of quartz and feldspar with lesser amounts of chlorite, plagioclase, and chalcedony in the very fine sand fraction of this soil. The predominant clay mineral was found to be vermiculite.

The research plots are located in a naturally regenerated 48-yr-old stand of red alder and in an immediately adjacent 48-yr-old plantation of Douglas-fir. The understory in the

Table 1. Some chemical properties of soils from the study sites. (Standard deviations are given.)

Horizon and depth cm	pH†	C†	Dithionite-extractable		Oxalate-extractable		Dithionite-citrate minus oxalate extractable			Water-extractable		NH ₄ F:HCl extractable PO ₄ ³⁻	NaH ₂ PO ₄ † extractable SO ₄ ²⁻	
			Fe _d	Al _d	Fe _o	Al _o	Fe _c	Al _c	Fe _d /Fe _c	Al _d /Al _c	PO ₄ ³⁻			SO ₄ ²⁻
mmol kg ⁻¹														
Fullerton (Chestnut oak)														
A (0-7)	4.6 ± 0.11	2580 ± 190	168 ± 14	144 ± 11	7.7 ± ND	56.7 ± ND	161 ± ND	87 ± ND	0.05	0.40	0.007 ± 0.004	2.1 ± 0.2	0.22 ± 0.04	0.55 ± 0.15
E (7-38)	4.9 ± 0.05	550 ± 78	88 ± 5	63 ± 4	5.6 ± 1.7	27.8 ± 19.2	82 ± 4	35 ± 14	0.07	0.44	0.004 ± 0.003	1.0 ± 0.2	0.07 ± 0.01	1.92 ± 0.33
BE (38-50)	4.6 ± 0.04	150 ± 14	197 ± 16	74 ± 7	0.9 ± 0.2	7.6 ± 1.8	196 ± 11	66 ± 5	0.005	0.10	0.001 ± 0.0002	0.6 ± 0.1	<0.01	3.98 ± 0.63
Bt (50-80)	4.8 ± 0.17	120 ± 7	445 ± 25	122 ± 3	1.1 ± 0.2	19.2 ± 2.8	444 ± 18	103 ± 3	0.003	0.16	0.003 ± 0.003	0.3 ± 0.1	<0.01	5.90 ± 1.47
Tarklin (Yellow-poplar)														
A (0-7)	4.6 ± 0.05	2290 ± 107	91 ± 2	56 ± 1	15.3 ± 10.7	30.9 ± 4.3	76 ± 8	25 ± 3	0.17	0.55	0.013 ± 0.004	2.0 ± 0.2	0.43 ± 0.06	0.18 ± 0.08
Ap (7-18)	5.0 ± 0.19	1180 ± 129	84 ± 2	67 ± 1	5.3 ± 0.4	23.3 ± 0.4	79 ± 1	44 ± 0.8	0.06	0.35	0.025 ± 0.008	1.4 ± 0.4	0.90 ± 0.34	0.10 ± 0.10
B (18-32)	4.7 ± 0.06	390 ± 43	113 ± 5	67 ± 2	2.5 ± 1.2	11.7 ± 2.9	110 ± 4	55 ± 3	0.02	0.17	0.017 ± 0.008	1.7 ± 0.6	0.09 ± 0.02	1.26 ± 0.62
Bt (32-50)	4.7 ± 0.08	180 ± 21	134 ± 9	63 ± 4	1.3 ± 0.2	12.4 ± 3.3	133 ± 6	51 ± 4	0.01	0.20	0.003 ± 0.002	0.7 ± 0.1	0.09 ± 0.07	2.66 ± 0.50
Alderwood (red alder)														
A (0-15)	4.7 ± 0.16	2650 ± 354	253 ± 27	324 ± 20	31.3 ± 10.7	240 ± 36	222 ± 21	84 ± 29	0.12	0.74	0.002 ± 0.001	0.2 ± 0.08	0.35 ± 0.12	0.61 ± 0.29
B (15-45)	5.2 ± 0.09	1460 ± 254	201 ± 22	204 ± 19	7.1 ± 2.3	167 ± 14	194 ± 16	37 ± 17	0.04	0.82	0.002 ± 0.0006	0.17 ± 0.03	0.05 ± 0.02	1.20 ± 0.54
B (45-75)	5.2 ± 0.14	920 ± 105	177 ± 22	157 ± 12	7.1 ± 3.6	134 ± 14	170 ± 16	23 ± 12	0.04	0.85	0.001 ± 0.0004	0.15 ± 0.03	0.04 ± 0.02	1.80 ± 1.00
BC (75-90)	5.1 ± 0.12	970 ± 171	175 ± 7	167 ± 7	7.4 ± 3.3	141 ± 20	168 ± 5.5	26 ± 15	0.04	0.85	0.001 ± 0.0004	0.15 ± 0.02	0.04 ± 0.005	2.25 ± 1.28
Alderwood (Douglas-fir)														
A (0-15)	5.1 ± 0.06	2460 ± 200	253 ± 31	309 ± 61	32.6 ± ND	213 ± ND	220 ± ND	96 ± ND	0.13	0.75	0.036 ± 0.027	0.3 ± 0.17	0.50 ± 0.12	0.82 ± 0.43
B (15-45)	5.1 ± 0.03	1180 ± 114	182 ± 15	182 ± 17	7.8 ± 3.2	130 ± 22	174 ± 11	52 ± 20	0.04	0.71	0.003 ± 0.002	0.2 ± 0.06	0.11 ± 0.01	3.60 ± 1.08
B (45-75)	5.2 ± 0.08	530 ± 73	157 ± 18	111 ± 7	4.1 ± 1.5	94 ± 6	153 ± 13	17 ± 6.5	0.03	0.85	0.001 ± 0.0003	0.13 ± 0.05	0.09 ± 0.02	1.49 ± 0.28
BC (75-90)	5.1 ± 0.08	350 ± 21	140 ± 14	96 ± 4	3.3 ± 1.5	77 ± 7	136 ± 10	19 ± 6	0.02	0.80	0.0003 ± 0.00003	0.16 ± 0.07	0.18 ± 0.04	1.28 ± 0.64

† From Johnson et al. (1981)

‡ ND = not determined.

red alder stand is dominated by sword fern [*Polystichum munitum* (Kaulf.) Presl.] intermixed with occasional western hemlock [*Tsuga heterophylla* (Raf.) Sarg.], huckleberry (*Vaccinium parviflorum* Smith), vine maple (*Acer circinatum* Pursh.), Oregon grape [*Berberis nervosa* (Pursh.) Nutt.], and elderberry (*Sambucus callicarpa* Pursh.). Understory in the Douglas-fir stand is much less predominant and consists of salal (*Gaultheria shallon* Pursh.), Oregon grape, huckleberry, and mosses.

METHODS

Field Studies

At each of the four study sites, four 6- by 6-m plots were laid out. At Walker Branch, a soil pit (approximately 0.5 by 0.75 m at the surface) was dug in the center of each plot; at the Thompson site, a larger soil pit (approximately 1 by 2.5 m at the surface) was dug between pairs of plots. Soil samples were taken proportionally by horizon (i.e., a column of soil was taken from the entire horizon depth) from the pit walls prior to lysimeter installation. Soils were analyzed for a number of chemical and physical properties (Johnson et al., 1981). Those relevant to this study included pH (1:1 ratio in water); total C (LECO combustion), dithionite-citrate and oxalate-extractable Fe and Al (USDA, 1972), NH₄F/HCl-extractable PO₄³⁻ (Olson and Sommers, 1982), NaH₂PO₄-extractable SO₄²⁻ (Johnson and Henderson, 1979), and water-extractable PO₄³⁻ and SO₄²⁻ (1:20 soil solution ratio; shaking for 1 h). Iron and Al in the extractant solutions were analyzed by atomic absorption, PO₄³⁻ in the NH₄F/HCl extractant solution was analyzed by Technicon Autoanalyzer, SO₄²⁻ in the NaH₂PO₄ extract solution was analyzed by the Ba chloranilate procedure of Bertolacini and Barney (1957), and PO₄³⁻ and SO₄²⁻ in the water extracts were analyzed by Technicon Autoanalyzer. Detection limits are <0.1 mmol kg⁻¹ for C, <0.002 mmol kg⁻¹ for citrate-dithionite Fe and Al, <0.2 and <0.7 mmol kg⁻¹ for oxalate-extractable Fe and Al (respectively), <0.01 mmol kg⁻¹ for NH₄F/HCl-extractable PO₄³⁻, <0.05 mmol kg⁻¹ for NaH₂PO₄-extractable SO₄²⁻, and <0.01 mmol kg⁻¹ for water-extractable PO₄³⁻ and SO₄²⁻.

Tension lysimeters were installed in the A (8 cm) and B horizons (50-80 cm) of each plot. Solutions were collected continuously at 10-kPa tension and sampled on approximately a 30-d basis (more frequently during rainy periods and less frequently during droughty periods).

After 120 d of monitoring the lysimeter waters, one of the four plots was treated with 0.5 mol(-) m⁻² of NaH₂PO₄, Na₂SO₄, NaCl, and NaNO₃ salts as a test of Hypotheses I and II.

Water samples were analyzed at each institution separately (Analytical Chemistry Division at ORNL and the College of Forest Resources at the Univ. of Washington, Seattle). Cross comparisons between laboratories were made and results were comparable. All waters were analyzed for pH, conductivity, Ca²⁺, Mg²⁺, K⁺, and Na⁺ (the latter four by atomic absorption); for NH₄⁺, NO₃⁻, PO₄³⁻, Cl⁻, and SO₄²⁻ (by Technicon Autoanalyzer); and for alkalinity by titration. Detection limits were <0.005 mmol L⁻¹ in all cases. Further checks of analyses were made by charge balance between cations and anions and by comparing calculated with measured conductivity (Golterman and Clymo, 1969).

Laboratory Studies

As additional tests of Hypotheses I and II, anion adsorption isotherms were determined at ORNL on the soils from the four sites before treatment (one each per horizon and treatment plot, giving four replicates per horizon per site). Successive 50-mL aliquots of 0.5, 1.0, 2.5, and 5.0 mmol(-) L⁻¹ of Cl⁻, NO₃⁻, H₂PO₄⁻ as Na⁺ salts, and SO₄²⁻ as Na⁺

and Ca^{2+} salts (using separate soil samples for each salt) were applied to 5-g air-dried, sieved (<2 mm) soil in a mechanical vacuum extractor (Concept Engineering, Inc.) at a 1-h extraction time setting. Each column (2.5-cm diam by 13.2-cm length) was prepacked with 1 g of ashless filter pulp, and two columns were left without soils (as blanks). Adsorption or desorption of anions was calculated by disappearance or appearance of anions in the eluent solution (after accounting for interstitial water and blank adsorption-desorption) as described by Johnson and Henderson (1979). Calculated soil anion contents during adsorption studies included pretreatment soil anion previously determined as described above. Anion adsorption studies originally done with Na^+ salts gave extremely variable results except in the case of phosphate. Sulfate adsorption was done again using Ca^{2+} salts with much more satisfactory results (i.e., less variation and more differentiation among soils). No Cl^- or NO_3^- adsorption was noted in any soil, and thus only phosphate and SO_4^{2-} adsorption results are shown here.

A final test of Hypotheses I and II was made by setting up a column study to duplicate field Na^+ salt applications. Triplicate columns of the type described above were filled with 30-g samples of air-dried, sieved A and B horizon soils sampled before treatment from each salt-treated plot. The A horizon columns were pretreated with approximately 250 $\mu\text{mol}(-)$ each of Cl^- , NO_3^- , H_2PO_4^- , and SO_4^- as Na^+ salts. (Actual input values as determined by outputs from columns without soil, varied from 235 $\mu\text{mol}(-)$ to 280 $\mu\text{mol}(-)$ per column). These columns were then leached with four 150-mL aliquots of distilled water, of which 75 mL was kept for analysis and 75 mL was leached through B horizon columns. All waters were analyzed for pH, HCO_3^- , H_2PO_4^- , SO_4^{2-} , Cl^- , NO_3^- , and conductivity.

A second column study was set up to test Hypothesis III using soils from the Fullerton and Douglas-fir control plots. The A and B horizon columns were set up as described above. Triplicate A horizon columns were leached with 4 150-mL aliquots of H_2O , HCl , NaCl , and CaCl_2 , the latter at concentrations of 1.0 $\text{mmol}(-) \text{L}^{-1}$. The B-horizon columns were leached with 75-mL of the 150-mL A-horizon leachates. All waters were analyzed for pH, HCO_3^- , SO_4^{2-} , NO_3^- , H_2PO_4^- , Cl^- , conductivity and Al^{3+} (the latter by atomic absorption).

Statistical analyses (standard deviation calculations, Duncan's multiple range test) were performed using SAS (SAS Institute, 1982).

RESULTS AND DISCUSSION

With one exception (dithionite-citrate-extractable Fe [Fe_d] in the Fullerton Bt horizon), the Washington (Alderwood) soils were as high or higher in Fe and Al hydrous oxides than the Tennessee (Fullerton and Tarklin) soils (Table 1). This was especially so for oxalate-extractable Al (Al_o) where the Washington soils had 4 to 10 times greater contents than the Tennessee soils (Table 1). The Washington soils also had approximately 1.5 to 4 times greater oxalate-extractable Fe (Fe_o) contents and approximately two times greater surface soil dithionite-extractable Al (Al_d) contents than the Tennessee soils (Table 1).

The ratio Fe_o/Fe_d gives an index of the crystallinity of Fe hydrous oxides, which in turn provides an index of the degree of aging (Blume and Schwertmann, 1966). According to this index, Fe hydrous oxides in the Washington soils are only slightly less crystalline than those in the Tennessee soils (Table 1). The meaning of the Al_o/Al_d ratio in terms of Al crystallinity is not well-defined (Blume and Schwertmann, 1966; Mc-

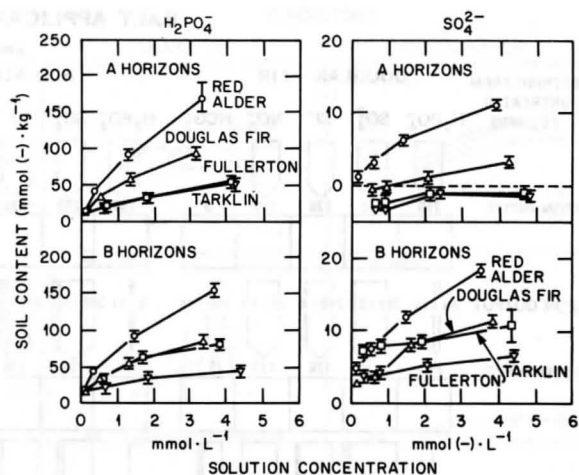


Fig. 1. Phosphate and sulfate adsorption isotherms for the four study soils. (Standard deviations are given.)

Keague and Day, 1966), but it is worth noting that these ratios are considerably higher for the Washington than for the Tennessee soils (Table 1).

McKeague and Day (1966) note that the difference between Fe_d and Fe_o , or $\text{Fe}_c = \text{Fe}_d - \text{Fe}_o$ provided a good chemical index of crystalline Fe hydrous oxide content. Again, the meaning of $\text{Al}_c = \text{Al}_d - \text{Al}_o$ is less clear. In any event, the Washington soils have higher Fe_c and Al_c contents in surface horizons but lower Al_c contents in subsurface horizons than the Tennessee soils (Table 1). For subsurface horizon Fe_c , the Fullerton soil was by far the highest and the other soils were about equal.

The phosphate and sulfate adsorption isotherms were very similar to one another in terms of relative curve positions and shapes for the various soils (Fig. 1). For both anions, the A horizon adsorption capacities were (in decreasing order) Red alder > Douglas-fir > Fullerton \approx Tarklin. In the B horizons, the capacities were Red alder > Douglas-fir \approx Fullerton > Tarklin. These patterns were most closely correlated with Al_d and, to some extent, with Al_o but not particularly well with Fe_o , Fe_d , Al_c , or Fe_c (Table 1).

Johnson and Todd (1983) found that Fe_c was most closely correlated with sulfate adsorption among a variety of forest soils. On the other hand, Parfitt and Smart (1978), in a more rigorous, mechanistic study, found that more highly crystalline Fe hydrous oxides (such as goethite and hematite) have lower sulfate adsorption capacities than less crystalline Fe hydrous oxides because of fewer singly-coordinated surface hydroxyl ions in the former. The results of the current study tend to support the view that highly crystalline Fe hydrous oxides are not particularly efficient at either sulfate or phosphate adsorption (in comparison, at least, to seemingly less crystalline Al hydrous oxides). This implies that Hypothesis I is false and leads to the alternative hypothesis that the most highly-weathered soils, with the most crystalline Fe and Al hydrous oxides, will have lower anion adsorption capacities than less weathered soils with lower Fe and Al hydrous oxide crystallinity.

The question remains as to the effect of organic matter. Some studies have shown that organic matter in-

SALT APPLICATION - COLUMN STUDY

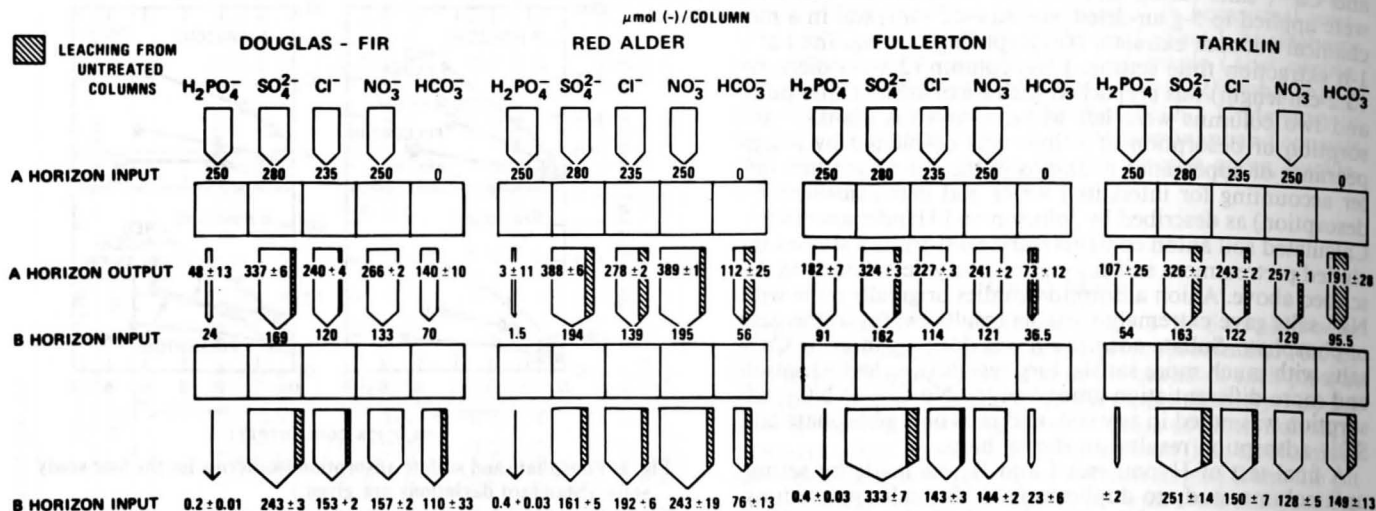


Fig. 2. Inputs and exports of anions from soil columns (30 g soil/column) treated with H_2PO_4^- , SO_4^{2-} , NO_3^- , and Cl^- as Na^+ salts. The A horizon columns were treated with salts and leached with 150 mL of distilled water; B horizon columns were leached with 75 mL of A horizon leachate. Values for control columns leached with H_2O only are shown at the right side of each output arrow. All values are in $\mu\text{mol (-)}$ per column. (Standard deviations are given.)

hibits phosphate and sulfate adsorption (Guar, 1969; Larsen et al., 1959; Singh, 1984; Johnson and Todd, 1983). Other studies have shown that organic matter may enhance phosphate adsorption (Harter, 1969; Singh and Jones, 1976). Harter (1969) suggests that orthophosphate exchanges for OH^- on organic matter as an initial reaction, following which Fe and Al complexes form. Singh and Jones (1976) found that organic matter low in phosphorus enhances orthophosphate adsorption, whereas the reverse is true for organic matter high in P. One possible explanation for these apparently contradictory results may be the inhibition of hydrous oxide crystallization by organic matter, as noted for Fe hydrous oxides by Schwertmann (1966) and Kodama and Schnitzer (1977). This inhibitory effect may maintain greater soil anion adsorption capacity by maintaining higher levels of amorphous, noncrystalline Fe and Al hydrous oxides (Parfitt and Smart, 1978). Counteracting this would

be the negative (blocking) effect of organic ligand adsorption on phosphate and sulfate adsorption (Struth and Sieling, 1950; Larsen, et al., 1959; Singh, 1984), making the situation quite complex.

The negative effect of organic matter on Fe and Al crystallinity (as indexed by the Fe_0/Fe_d and Al_0/Al_d ratios) is evident in Table 1, both between horizons of a soil and within similar horizons (e.g., B horizons) among all four soils. B horizon carbon contents, Fe_0/Fe_d and Al_0/Al_d ratios all follow the pattern red alder > Douglas-fir > Tarklin > Fullerton; nearly the same pattern noted for sulfate and phosphate adsorption. Thus, we hypothesize that the blocking effects of organic matter on anion adsorption in this case are outweighed by the enhancing effects of maintaining noncrystalline Fe and Al hydrous oxides.

The results of both the laboratory column and field salt application studies corroborated the results of the adsorption isotherms. The red alder soil retained the

Table 2. Fluxes of anions in soil solution in control and salt-treated [$0.5 \text{ mol (-) m}^{-2}$ each of H_2PO_4^- , SO_4^{2-} , NO_3^- , and Cl^- as Na^+ salts] plots over a 2-yr period.

Site and horizon	Phosphate		Sulfate		Nitrate		Chloride		Bicarbonate	
	Control	Salts	Control	Salts	Control	Salts	Control	Salts	Control	Salts
mol (-) m^{-2}										
Washington†										
Red Alder										
A (8 cm)	0.00006	0.0061	0.11	1.07	1.03	1.63	0.13	0.58	0.05	0.38
B (40 cm)	0.00012	0.0002	0.06	0.06	0.96	2.45	0.11	0.94	0.16	0.22
Douglas-fir										
A (8 cm)	0.0004	0.007	0.17	1.09	0.01	0.56	0.11	0.57	0.16	0.44
B (40 cm)	0.00008	0.0004	0.14	0.38	0.04	0.05	0.12	0.35	0.25	0.30
Tennessee‡										
Fullerton										
A (8 cm)	0.0002	0.0122	0.36	1.47	0.001	0.60	0.04	1.18	0.10	0.36
Bt (80 cm)	0.0004	0.0002	0.25	0.90	0.003	0.10	0.07	0.69	0.12	0.11
Tarklin										
A (8 cm)	0.002	0.07	0.50	1.51	0.01	0.62	0.04	1.55	0.08	0.32
Bt (50 cm)	0.001	0.0003	0.46	1.30	0.01	0.06	0.05	1.29	0.11	0.11

† Calculated water flux = 280 cm (Knutsen, 1965).

‡ Calculated water flux = 130 cm (Luxmore, 1983).

most phosphate, followed by the Douglas-fir, Fullerton, and Tarklin soils, respectively (Fig. 2 and Table 2). Phosphate adsorption apparently caused net desorption of native soil sulfate from A horizons of salt-treated soils, both in laboratory column and field studies (Fig. 2 and Table 2). There also was a net sulfate release from all but the red alder B horizon in the column studies, apparently a result of phosphate inputs from A horizon leachates (Fig. 2). In the red alder soil, B horizon columns showed a net retention of sulfate, presumably due to the lower phosphate inputs from A horizon leachates and the greater sulfate adsorption capacity of this soil.

Both of the Washington Inceptisols retained applied sulfate in field studies, whereas neither of the Tennessee Ultisols did (Fig. 3). After 2 yr (and approximately 280 cm of leaching), the red alder soil showed no net sulfate export (in excess of control plots) and the Douglas-fir soil showed a net export (in excess of control) of only $0.24 \text{ mol}(-) \text{ m}^{-2}$, or roughly 50% of applied sulfate (Table 2). On the other hand, the Fullerton and Tarklin soils showed net exports (in excess of control) of 0.65 and $0.84 \text{ mol}(-) \text{ m}^{-2}$ (130 and 168% of applied sulfate) after only 130 cm of leaching (Table 2). (Annual leaching rates were lower in the Tennessee soils due primarily to higher evapotranspiration.)

Flux calculations in field lysimeter plots are subject to many uncertainties (one of which is the appropriate water flux to apply), and thus the apparent release of native soil sulfate from the Tennessee soils may have been an artifact. This was not the case in the laboratory column studies, however, where fluxes were accurately measured and clearly showed net sulfate release due to phosphate adsorption. In any case, the patterns of sulfate retention in B horizons in the field studies followed those of the adsorption isotherms, namely red alder > Douglas-fir > Fullerton > Tarklin.

Hypothesis II was supported by the results of the laboratory and field salt application studies. No net NO_3^- retention was observed in any of the soils in the column studies (Fig. 2). The N-rich red alder soil showed a net release of NO_3^- in both the laboratory column and field salt application studies (Fig. 2 and Table 2). This was likely due to release of native soil NO_3^- in the column studies (Fig. 2) and nitrification in excess of NO_3^- uptake in field studies (Van Miegroet and Cole, 1984). In contrast, the NO_3^- applied to the N-limited Douglas-fir, Fullerton, and Tarklin plots in the field studies was almost completely retained in B horizons (Table 2). The differences in NO_3^- mobility in laboratory vs. field studies in the latter soils appear to be due primarily to tree uptake because there was little net NO_3^- retention in the organic matter-rich surface horizons in the field studies (Table 2). The possibility of microbial uptake in B horizons cannot be excluded, however.

Chloride was mobile in all soils in both laboratory and field salt studies (Fig. 2 and Table 3), confirming its chemical and biological inertness. The Na^+ -salt application studies do not provide adequate tests of Hypothesis III, however, because of the confounding effects of phosphate and sulfate adsorption on soil

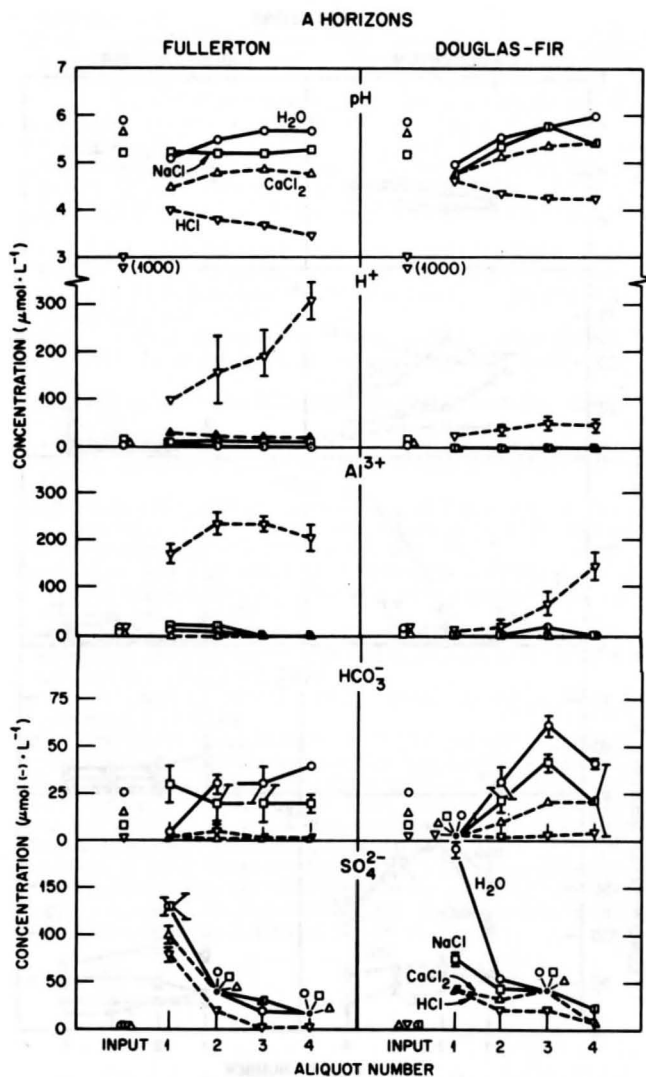


Fig. 3. pH, H^+ , Al^{3+} , HCO_3^- , and SO_4^{2-} concentrations in leachates from A horizon soil columns treated with H_2O , NaCl , CaCl_2 , and HCl at $1.0 \text{ mmol}(-) \text{ L}^{-1}$. (Standard deviations are given.)

solution pH. Thus, Hypothesis III was tested in a series of column studies on the Douglas-fir and Fullerton soils involving chloride applications as NaCl , CaCl_2 , and HCl .

Table 3. Net export of HCO_3^- and SO_4^{2-} with H_2O , NaCl , CaCl_2 , and HCl treatments [$1 \text{ mmol}(-) \text{ L}^{-1}$] to soil columns.†

Soil	Horizon	Treatment			
		H_2O	NaCl	CaCl_2	HCl
— $\mu\text{mol}(-)$ per column —					
HCO_3^-					
Fullerton	A	$16 \pm 3a$	$14 \pm 6a$	$0.5 \pm 0.5b$	$0b$
	Bt	0	0	0	0
Alderwood-Douglas-fir	A	$20 \pm 4a$	$13 \pm 5b$	$14 \pm 1b$	$0c$
	B	$24 \pm 4a$	$10 \pm 1b$	$4 \pm 2c$	$0d$
SO_4^{2-}					
Fullerton	A	$32 \pm 2a$	$35 \pm 1b$	$30 \pm 2a$	$18 \pm 1c$
	Bt	$107 \pm 10a$	$98 \pm 11a$	$42 \pm 5b$	$32 \pm 2c$
Alderwood-Douglas-fir	A	$48 \pm 4a$	$27 \pm 1b$	$18 \pm 1c$	$14 \pm 1d$
	B	$51 \pm 1a$	$32 \pm 2b$	$21 \pm 2c$	$16 \pm 2d$

† Numbers not sharing the same letters are statistically different from one another, Duncan's Multiple Range Test, 95% level.

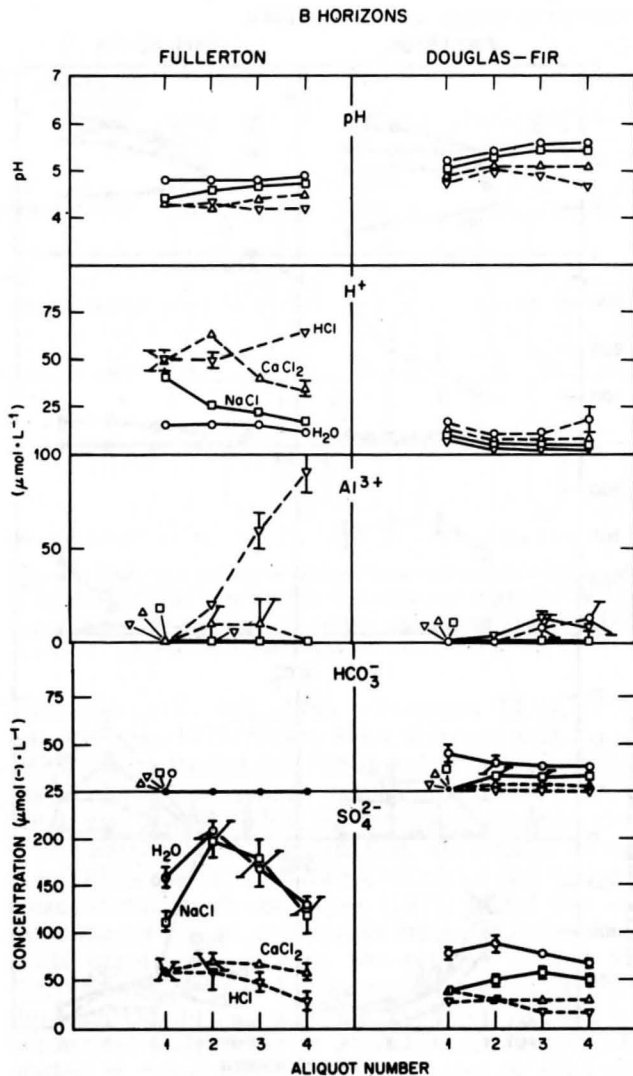


Fig. 4. pH, H^+ , Al^{3+} , HCO_3^- , and SO_4^{2-} concentrations in leachates from B horizon soil columns treated with H_2O , NaCl, $CaCl_2$, and HCl at $1.0 \text{ mmol}(-) \text{ L}^{-1}$. (Standard deviations are given.)

The chloride application studies supported Hypothesis III in that inputs of chloride, as salt or acid, caused lowered pH, HCO_3^- , and SO_4^{2-} concentrations in leachates as compared to water applications (Fig. 3 and 4). The effects depended on the cation associated with chloride input, with the degree of effect being $HCl > CaCl_2 > NaCl > H_2O$. The HCl and, to a lesser extent, the $CaCl_2$ treatments also stimulated Al leaching (most markedly in the more acid Fullerton soil and more markedly in A horizons than in B horizons for both soils). No effects of chloride input on NO_3^- were noted, and no significant net retention or release of chloride was noted except for that accounted for from control (H_2O -treated) columns. Phosphate was assumed to be a minor contributor to total anion concentration and, therefore, was not determined in this particular study.

Treatments with chloride caused reductions in the net export of bicarbonate and sulfate with the level of reduction being $HCl > CaCl_2 > NaCl$ in most cases (Table 3). No net change in chloride export could be detected, due in part to the large background chloride

(and background Cl^- variability) in chloride-treated columns. Nitrate export was low ($< 1 \text{ mmol/column}$) and not affected by treatment.

SUMMARY AND CONCLUSIONS

Laboratory and field studies tested hypotheses concerning anion movement and retention in forest soils. Two Ultisols (Fullerton and Tarklin series), both with deciduous forest cover in eastern Tennessee, and two Inceptisols (both Alderwood series), one with Douglas-fir and one with red alder forest cover in western Washington were studied. We hypothesized that sulfate and phosphate retention in the four forest soils would be related to Fe and Al oxide content, which in turn would be related to soil parent material and degree of weathering. This hypothesis was not supported by results of soil Fe and Al hydrous oxide analyses, adsorption isotherm determinations, or applications of sulfate and phosphate as Na^+ salts to laboratory columns and field plots. The Washington Inceptisols (especially the red alder site) adsorbed more sulfate and phosphate than the Tennessee Ultisols. Apparently, this was due to greater amorphous hydrous Fe and Al oxide contents in the former. Hydrous Fe and Al oxides in the Tennessee subsoils appeared to be more crystalline. Consequently, they were less able to adsorb sulfate and phosphate.

A second hypothesis that NO_3^- retention was governed by biological processes was supported by laboratory and field results of $NaNO_3$ application. No soil retained NO_3^- in laboratory studies where forest floor and trees were excluded, but most of the applied NO_3^- was retained in B horizons of all but the N-rich red alder soil, suggesting tree uptake as a major cause of NO_3^- immobilization in the ecosystem.

The third hypothesis stated that manipulations causing solution pH to rise would increase leaching of bicarbonate and adsorbed anions (and vice versa) and that inputs of mobile anions like chloride would lower solution pH and cause net anion retention. This hypothesis was supported by applications of HCl, NaCl, and $CaCl_2$ (compared to H_2O only) to soil columns. Chloride applications lowered solution pH and reduced the leaching bicarbonate and sulfate with the order of effectiveness being $HCl > CaCl_2 > NaCl$ for a given chloride concentration.

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Physical and Chemical Soil Properties of Three Big Sagebrush Subspecies¹

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ABSTRACT

The three subspecies of *Artemisia tridentata* Nutt. typically occupy qualitatively different sites. Wyoming big sagebrush, *A. t. ssp. wyomingensis*, commonly grows in Aridisols; mountain big sagebrush, *A. t. ssp. vaseyana*, commonly lives in Mollisols at a higher average elevation; and basin big sagebrush, *A. t. ssp. tridentata*, occurs in deep soils of either order. This study evaluated some physical and chemical characteristics of surface and subsurface soil horizons of soils occupied by each subspecies in four widely spaced Oregon locations. Most soil chemical characteristics showed no significant differences between subspecies. Interaction between location and subspecies often indicated that analysis should proceed at each individual location. The Frenchglen location had the greatest elevational differences between sites and also had most statistically significant soil differences between subspecies. Many of the measured characteristics are interrelated and differences in them prob-

ably are influenced by elevation-related variation in climate. Surface horizons of Frenchglen, *A. t. ssp. vaseyana* sites had lower pH, base saturation, and exchangeable Na^+ and higher organic matter, cation exchange capacity, and water retention at -1.50 MPa than surface horizons of *A. t. ssp. wyomingensis* sites. Fewer surface soil characteristics of *A. t. ssp. tridentata* sites were significantly different. In deeper soil horizons at Frenchglen, *A. t. ssp. vaseyana* sites had lower pH and base saturation than *A. t. ssp. tridentata* sites.

Additional Index Words: *Artemisia tridentata*, organic matter, cation exchange capacity, base saturation, soil depth, soil texture, soil-water retention.

Swanson, S.R., G.H. Simonson, and J.C. Buckhouse. 1986. Physical and chemical soil properties of three big sagebrush subspecies. *Soil Sci. Soc. Am. J.* 50:783-787.

¹ Research was supported through funding provided by USDA-ARS and the Eastern Oregon Agricultural Research Center. Technical Paper no. 6920. Oregon Agricultural Experiment Station, Corvallis. Received 31 Dec. 1984.

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VEGETATION AND SOIL CHARACTERISTICS are interdependent integrators of environmental factors. Understanding the indicator value of vegetation can be useful to land managers, especially where soil and vegetation are correlated over broad areas of the