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The *bio* in aluminum and silicon geochemistry

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Abstract. The translocation and transformation of Al and Si are of paramount importance in the processes of primary-mineral weathering, saprolite formation and soil formation. Geochemical mass balance studies of these processes have often not considered the important role of the biota in cycling of these omnipresent soil elements. In the Calhoun Experimental Forest, SC, we found a mean annual biological uptake of Al and Si of 2.28 and 15.8 kg ha^{-1} yr^{-1}, respectively, with a mean annual accumulation in aboveground biomass of 0.48 and 2.32 kg ha^{-1} yr^{-1}, respectively. In the case of Al, net soil leaching from 6 m depth is zero, thus biomass accumulation of Al accounts for the only removal from the soil system. There is an additional internal system mobilization of Al of 6.6 kg ha^{-1} yr^{-1}, in response to biotic inputs of dissolved organic carbon. In the case of Si, net soil leaching to groundwater is 17.26 kg ha^{-1} yr^{-1}. The accumulation of Si in aboveground biomass, 2.32 kg ha^{-1} yr^{-1}, and in forest floor organic matter, 11.95 kg ha^{-1} yr^{-1}, augments the annual weathering release estimate of Si by an additional 82%. The inclusion of biological cycling of both essential and non-essential mineral elements is important for properly evaluating the biogeochemistry of the earth's crust.

In forest ecosystems underlain by aluminosilicate rich rocks, the translocation and transformation of Al and Si are of paramount importance in the processes of primary-mineral weathering, saprolite formation and soil formation. Silicon and Al are the first and second most abundant oxides, by wt.%, respectively, in these rocks and as such their retention or mobilization affects important chemical and physical properties of the soil profile. The retention of Al as exchangeable Al or hydrous Al oxides affects the acid status, buffer capacity and exchange properties of the soil system (Jackson 1963; Thomas & Hargrove 1984). The loss of Si from rocks, the process of desilication, impacts both the nature of neoformed secondary minerals as well as the bulk density of the developing profile (Buol et al. 1989).

The rate of Al and Si mobilization from primary minerals, saprolites and soils has been estimated in some forest systems through use of geochemical mass balance, i.e. input-output budgeting (Cleaves et al. 1970, 1974; Creasey et al. 1986; Katz et al. 1985; Paces 1986; Pavich 1986; Rouston et al. 1977). As the name implies, *geochemical* mass balance studies have often not emphasized the important role of the biota in weathering and soil formation processes. In the case of nutrient cations, the omission of biotic uptake and accumulation can create errors of up to four-fold in estimates of mineral weathering rates (Taylor & Velbel 1991; Velbel 1985, 1986). In the case of the non-essential mineral elements of Al and Si, few biogeochemical data exist (Bartoli 1983; Cronan et al. 1990; Louvering 1959; Lucas et al. 1993; Vogt et al. 1987) to evaluate the effects of the biotic component on weathering and soil formation processes. The role of biological cycling of Al and Si needs to be more fully investigated to better appreciate the *bio* in the biogeochemistry of the earth's crust (Lucas et al. 1993; Richter & Markewitz 1995).

The objective of this paper is to report on the biogeochemical cycles of Al and Si in a 34-year-old loblolly pine ecosystem so as to assess the role of biota in cycling, mobilizing and accumulating these omnipresent soil elements.

Materials and methods

Research site

The research area (described fully in Richter et al. 1994) is located within the southeastern Piedmont of the USA in the Calhoun Experimental Forest of the Sumter National Forest in Union County, South Carolina (34.5°N, 82°W). Annual precipitation averages ~1170 mm (1950–1987) and temperature ~16°C. The study site is on gentling sloping terrain (<3%) that is covered by Appling and Cataula series soils (clayey, kaolinitic, thermic Typic Kanhapludults) that are derived directly from the granite-gneiss bedrock that underlies the site. After approximately 150 yrs of agriculture at the Calhoun Forest, the last crop of cotton in 1954 was followed by a 2-yr fallow, after which a loblolly pine (*Pinus taeda* L.) spacing study was planted in the winter of 1956–57. Loblolly pine is native to the area (Baker & Langdon 1990).

Biomass

Tree biomass, needed to estimate accumulation of Si and Al in aboveground tissues, was estimated from measurements of all trees on eight permanent plots, four planted at 2.4 × 2.4 m spacing and four at 3.0 × 3.0 m spacing. Diameter and height of all trees were measured most recently in 1991. Allometric equations were developed from a harvest of 10 trees that represented a range across the diameter distribution of the stand (Urrego 1993). Each of these ten trees was divided into stemwood, stembark, live branch, dead branch, and foliar components for determination of biomass content and nutrient concentration. The site specific allometric equations compared favorably to those of Van Lear et al. (1984) and Shelton et al. (1984) which were derived from other loblolly pine ecosystems in the southeastern United States.

Prior to elemental analysis, samples were oven-dried (70 °C) and ground in a Wiley Mill to pass a 40-mesh screen. Samples were digested for Al analysis with nitric-perchloric acid (Thorton et al. 1985). Analysis of the digestate was by atomic absorbtion spectrophotometry using a nitrous oxide flame. Sample digestion for Si closely followed the method of Fox et al. (1969), and analysis of the digestate was by molybdenum blue colorimetry.

To estimate Si and Al return to the forest floor, litterfall was collected from 40 samplers (five in each of 8 permanent plots) on a monthly basis. Samplers were 0.7 m^2 in area and samples were divided between foliar and non-foliar material. Elemental concentrations were determined with the same methods as those for forest floor and tree biomass.

Fine root (<2 mm) biomass in the 0 to 30 cm mineral soil was determined by tri-weekly coring from March 1994 to March 1995 with a 6-cm diameter corer. One core was collected in each plot (n = 8) per sample period. The mineral soils were immersed in water to float out organic material. The resulting soil-slurry supernatant was passed through a 140-mesh screen to retain all organic material and fine roots which were then separated by hand. Aluminum and Si concentrations were not determined on this component.

Soil analyses

The Si and Al accumulated in soil O horizons were estimated in the spring of 1992 from samples in each of the eight permanent plots. Organic matter accumulation in soil O horizons were estimated using 36 sampling points (each 0.13 m^2 in area) with three to six samples collected from within each plot. An additional 1-m radius was established around each of the 36 forest floor sampling points (3.14 m^2 in area) for collection of large woody material (>1 cm). Elemental concentrations of Al and Si were determined on a separate collection of O horizon material in which areas of prior forest floor disturbance were avoided and care was taken to minimize mixing Oa horizon material with mineral soil. After collection, samples were scrutinized for macrosize mineral contaminants which were removed during sample preparation. This second collection was a composite of three samples (0.0625 m^2 in area) in each plot. The average percent ash for Oi, Oe, and Oa horizons for the second collection prior to removal of macrosize mineral contaminants was 2.08 ± 0.20, 6.95 ± 2.90 and 21.44 ± 7.77% (mean ± 1 SD), respectively. Analytical methods for Si and Al were the same as those used for biomass samples. Forest floor mass (which includes fine roots) and Al and Si content estimates were made on an ash-free basis.

The soil profiles were examined in 1990 by excavating four large soil pits, one per block, to 1.65 m and by augering with a 10-cm diameter bucket auger to 3 m. In each soil pit, volumetric samples (0.3 L) were taken by 6-cm diameter corer from each horizon to 1.65-m depth to estimate bulk density, chemistry, and mineralogy with $n > 12$ per horizon. Below the 1.65-m depth, samples were collected from 0.5-m layers within the lower B horizon and saprolite. In 1994, three additional deep pits of approximate 4.5-meters depth were dug on the site to examine soils in greater detail. Deeper soil materials were sampled by augering from the bottom of the freshly dug pit to a total depth of 8.25 m. In two pits volumetric samples were taken at 50-cm increments from a depth of 2.0 to 4.5 m to estimate bulk density. Measurements of bulk density from 4.5 to 7.75 m were made using the soil clod method (Brasher et al. 1966). Paired samples were collected with all bulk density samples for further chemical analyses. Total elemental digestion for Al and Si were by $LiBO_2$ fusion with analysis by directly coupled plasma emission (Klein et al. 1991).

In this soil the A horizon is only weakly expressed due to its sandy texture and long-term cultivation. Eluvial E horizons have sandy loam textures that overlie kandic (low CEC) B horizons whose mineralogy are dominated by kaolinite. The B horizons have an average CEC (at soil pH) of 7.35 $cmol_c\ kg^{-1}$ of clay and $CEC_{8.2}$ (at pH 8.2) of 15.68 $cmol_c\ kg^{-1}$ clay which gives them the kandic status (CEC < 12.0 $cmol_c\ kg^{-1}$ of clay and $CEC_{8.2} <$ 16 $cmol_c\ kg^{-1}$ clay [Moorman 1985; Soil Survey Staff 1987]). The upper BC horizon is about 2.0 m from the soil surface and grades to a CB horizon by 4.0 m from the soil surface. The saprolite is highly weathered and acidic throughout, with pH < 4.2 in $CaCl_2$ and an acid saturation that is commonly greater than 90% or base saturation $<10\%$. Exchangeable base cations are low throughout much of the profile with slight increases in the lowest portions of the profile. These increases in the lower C horizon potentially express a weathering front above bedrock (Calvert et al. 1980; Stolt et al. 1991).

Solutions

To estimate solution fluxes for Si and Al, continuous biweekly collections of wet-only precipitation, bulk throughfall, and soil solutions, using procedures employed previously (Richter et al. 1983; Richter & Lindberg 1988), were made for the period March 1992 to March 1994. Solutions for precipitation were collected with a battery operated Aerochem Metrics (Bushnell, FL) wet-only rainfall collector. On each of the eight permanent plots, three bulk throughfall bottles with funnels (16-cm diameter) collected canopy throughfall (Richter & Lindberg 1988). Plot bottles were composited for chemical analysis. Two tension-free lysimeters of 64-cm^2 area (constructed from

PVC tubing) sampled soil water that drained the O horizons and through 15-cm mineral soil layers (middle E horizon) in each of the eight plots. The two tension-free lysimeters in each horizon drained to a single bottle which provided a sample for analysis. A single Superquartz® lysimeter (Prenart Equipment ApS, Frederiksberg, Denmark) at both 60- and 175-cm depths was placed under vacuum, 0.08 MPa, to collect soil solutions from each of the eight plots. Buried PVC wells with polypropylene tubing extending to the surface collected solutions from the saprolite at six meters depth. These deep solution collections were made in one plot within each of the four experimental blocks. Collections at six meters started in December 1992. Solutions were analyzed after filtration through a 0.40-um polycarbonate filter (Nucleopore, Pleasanton, CA). Analysis for Al was by graphite furnace (Perkin Elmer 5100) and for Si by the molybdate blue method on a Scientific auto-analyzer (Westco, CT). Solutions were also analyzed for conductivity (Wheatstone bridge), pH (glass electrode), HCO_3^- alkalinity (1 mM HCl to an endpoint pH of 5.0), Ca^{+2}, Mg^{+2}, Na^+ (atomic absorption), K^+(flame emission), NH_4^+ (indophenol blue colorimetry), Cl^-, NO_3^-, SO_4^{-2} (ion chromatography), and dissolved organic carbon (Shimadzu TOC 5000). In addition, water samples were equilibrated to atmospheric CO_2 concentration prior to pH measurement. Equilibration required approximately 12 minutes of vigorous stirring for soil solutions from 60 cm or below. Bicarbonate alkalinity is conserved during CO_2 degassing and was thus also measured after equilibration to atmospheric CO_2 concentration. For water samples with pH below 5.0, bicarbonate alkalinity was zero and negative alkalinities were not measured. In solutions that generally have pH < 5 such as bulk precipitation, throughfall, and O horizon and 0.15 m soil leachates the distribution of measured alkalinities are strongly right-hand skewed with 73, 88, 82 and 52% of all measured alkalinities being zero, respectively. Thus, for these solutions medians are presented as a better representation of the central tendency than the mean (Steel & Torrie 1980). For DOC measurement, samples were acidified and sparged with N_2 gas to promote the complete removal of dissolved CO_2 prior to samples analysis.

The fluxes of ions through the ecosystem were estimated from the products of volume-weighted ion concentrations in the 1992 through 1994 collections, and drainage estimates for the Calhoun Forest. Drainage estimates were obtained from a combination of 15-yr hydrologic simulations with the PROSPER model using a daily time step (Gnau 1992; Vose & Swank 1992) and the solution Cl^- budget (Lockwood et al. 1995).

Table 1. Si and Al concentrations, contents and molar ratio in a 34-year-old loblolly pine ecosystem in the Calhoun Experimental Forest, SC

Component	Biomass	Si	Al	Si	Al	Si:Al
		Concentration		Contents		molar ratio
	kg ha^{-1}	—mg kg^{-1}—		—kg ha^{-1}—		
Foliage	3934	2597.4[1]	389.1	10.19	1.53	6.4
		351.0[2]	98.7			
Live Branch	8963	351.0	222.7	3.14	2.00	1.5
		220.6	47.8			
Dead Branch	1740	270.7	125.5	0.47	0.22	2.1
		180.5	36.3			
Stemwood	148565	130.4	15.5	19.31	2.31	8.1
		150.4	13.7			
Stembark	19932	2306.6	457.7	45.84	9.13	4.8
		1644.7	89.6			
Oi	20692		595.2		12.32	
			55.9			
Oe	36500		1935.2		70.69	
			938.2			
Oa	6731		3878.0		26.12	
			1084.4			
Oi,Oe,Oa	63923	47936.5[3]	1708.7[4]	3055.52	109.14	27.0
		25462.6				
Foliar Litterfall[5]	4100	3349.6	426.6	13.69	1.76	7.5
		1063.0	96.3			

[1] Mean concentration.
[2] Standard deviation of the mean.
[3] Forest floor organic layers digested as a single composite.
[4] Weighted mean of individual organic layer concentrations.
[5] Litterfall contents are equivalent to the annual litterfall flux.

Results and discussion

Biological cycling

Biomass aluminum

The total content of Al in aboveground biomass and forest floor at the Calhoun forest is 124.3 kg ha^{-1} (Table 1). Of the total accumulation of Al, 12.2% (15.2 kg ha^{-1}) resides in the aboveground components and 87.8% (109.1 kg ha^{-1}) resides in the forest floor. This partitioning of Al in the ecosystem is in contrast to that for organic matter in which 74.2% is in the aboveground component and only 25.8% is in the forest floor. The mean annual accumulation of Al for aboveground biomass and forest floor is 0.5 and 3.2 kg ha^{-1} yr^{-1}, respectively. The 0 to 30 cm fine root biomass (1940 ± 768 kg ha^{-1}), using an assumed concentration of 1000 mg kg^{-1} (Rodin & Bazilevich 1965; Rustad & Cronan 1995; Vogt et al. 1987), would accumulate an additional 1.9 kg ha^{-1} yr^{-1} of Al.

In the aboveground loblolly pine ecosystem the highest concentrations of Al are in foliage, 389.1 ± 98.7 mg kg^{-1} (mean ± 1 SD) and stembark, 457.7 ± 89.6 mg kg^{-1}. The stembark component has accumulated the largest content of Al in the aboveground biomass at 9.1 kg ha^{-1}. This high stembark accumulation is consistent with a recent study in a *Picea rubens* ecosystem (Rustad & Cronan 1995) but differs from earlier studies in *Abies amabillis* (Vogt et al. 1987) and *Pinus rigida* (Turner et al. 1985) ecosystems where highest accumulations were in wood tissues.

In the forest floor, the total content of Al, 109.1 kg ha^{-1}, exceeds a hypothetical retention of all Al inputs from foliar litterfall and gross throughfall (based on current input rates of 1.9 kg ha^{-1} yr^{-1}) over the 34 yrs of forest growth, Tables 1 and 2. This excess of Al necessitates an additional input of Al to forest floor. Potential sources include a greater rate of Al input earlier in the life of the forest stand possibly due to higher levels of atmospheric dust, an additional pathway for Al input potentially from root translocation (Rustad & Cronan 1995) or water table rise (Lawrence et al. 1995), or an upward mixing of mineral components into the forest floor through processes of bioturbation such as burrowing animals or insects, treethrow, or anthropogenic disturbances. As previously stated by Rustad and Cronan (1995), given the high concentration of Al in mineral soil relative to organic materials even small contributions of mineral soil added to the O horizon could dramatically increase the total Al content of the forest floor.

The annual biological uptake of Al by the forest at Calhoun can be estimated from the aboveground input of Al to the forest floor (i.e., litterfall and net throughfall) plus the mean annual increment of Al in woody biomass (i.e., live and dead branch, stemwood and stembark but excluding fine roots). This calculation follows that of Cole and Rapp (1981) and others (Johnson & Lindberg 1992) where

$$U = FL + NTF + \Delta W$$

U is mean annual uptake, FL is foliar litterfall, NTF is net throughfall (that represents leaching of foliar contents) and ΔW is the mean annual increment in wood. Based on this definition, Al uptake is 2.3 kg ha^{-1} yr^{-1}. The annual

Table 2. Volume-weighted mean concentrations and annual fluxes for Si and total Al between March 1992–March 1994 from eight sample plots in the Calhoun Experimental Forest, SC. Values presented below means are one standard deviation

Component	Hydrologic Flux	pH[1]	Alk[2]	Si concentration	Al_t concentration	Si Flux	Al_t Flux	Si:Al_t molar ratio	DOC[5]
	cm		ueq L^{-}	—μmol L^{-1}—		—kg ha^{-1}—			μmol L^{-1}
Wet-Only Ppt[3]	123	4.52	0.0	0.2	0.1	0.04	0.04	1.5	153.3
Bulk Ppt[3]	123	4.91	0.0[4]	0.3	0.2	0.01	0.07	1.5	281.7
Throughfall	105	4.50	0.0[4]	0.8[3]	0.6	0.22	0.17	1.4	644.2
				0.2[4]	0.2				84.2
O horizon Leachate	101	4.77	0.0[4]	7.0	9.7	1.96	2.64	0.7	2615.0
				2.3	5.0				735.8
0.15 m – middle E horizon	97	5.01	2.4[4]	18.8	25.3	5.10	6.61	0.7	1600.8
				7.7	16.4				551.7
0.50 m – middle Bt horizon	71	6.11	32.92	60.7	0.2	12.03	0.04	273.0	115.8
			18.17	6.5	0.1				22.5
1.75 m – middle BC horizon	39	6.06	28.31	90.7	0.3	10.01	0.04	272.0	81.7
			10.69	23.3	0.3				16.7
6.0 m – lower C horizon	36	6.21	33.40	169.8	0.3	17.30	0.03	655.0	69.2
			8.16	47.0	0.2				18.0

[1] pH was measured in solution after equilibration with atmospheric CO_2 concentration.

[2] Alk is HCO_3^- alkalinity measured by titration to an endpoint pH of 5.0.

[3] Precipitation inputs were measured at a single location within the research site.

[4] Median value presented for significantly right-hand skewed distribution.

[5] Dissolved organic carbon.

Table 3. Estimate of the annual content of Al and Si available in the mass-flow of soil water driven by plant transpiration. Hydrologic flux is estimated from a combination of direct observation for aboveground inputs, and mechanistic and Cl^- budget models for belowground flows. All solution concentrations were measured March 1992 to March 1994 at the Calhoun Experimental Forest, SC

	Estimated Flux	Flux Difference	Si Solution Concentration	Al Solution Concentration	Si Mass-Flow Uptake	Al Mass-Flow Uptake
	cm yr^{-1}		—μmol L^{-1}—		—kg ha^{-1}—	
Wet-only Precipitation	123					
Throughfall	105	4	0.8	0.6	0.01	0.01
Litter Leachate	101	4	7.0	9.7	0.08	0.11
0.15 m Soil Solution	97	26	18.8	25.3	1.37	1.78
0.60 m Soil Solution	71	32	60.7	0.2	5.44	0.02
1.75 m Soil Solution	39	3	90.7	0.3	0.77	0.00
6.00 m Soil Solution	36		169.8	0.3		
Total					7.7	1.9

plant uptake of Al is similar to the estimated annual content of Al available in the mass-flow of soil water driven by plant transpiration, 1.9 kg ha^{-1} (Table 3). This similarity indicates that the pines at Calhoun are not actively accumulating Al nor are they Al excluders. The portion of Al uptake that is retained in wood storage, ΔW, plus any potential root translocation of Al from lower to upper soil horizons, equals the annual biomass sink of Al which effects estimates of mineral weathering or soil formation.

Biomass silicon

The total content of Si in the aboveground biomass and forest floor at the Calhoun Forest is 3135.1 kg ha^{-1} (Table 1). Of the total accumulation of Si, 4.5% (79.0 kg ha^{-1}) resides in the aboveground components and 95.5% (3055.5 kg ha^{-1}) resides in the forest floor. This partitioning of Si indicates a preferential accumulation of Si in forest floor organic matter. The mean annual accumulation of Si for biomass and forest floor over the 34-yrs of forest growth is 2.3 and 89.9 kg ha^{-1} yr^{-1}, respectively. The 0 to 30 cm fine roots, using an assumed Si concentration of 1400 mg kg^{-1} (Rodin & Bazilevich 1965), would add an additional 2.7 kg ha^{-1} yr^{-1} of Si accumulation.

In aboveground biomass the highest concentrations of Si in loblolly pine tissues are in foliage, 2597.4 ± 351.0 mg kg^{-1} (mean ± 1 SD) and stembark, 2306.6 ± 1644.7 mg kg^{-1}. As for Al, stembark has accumulated the largest content of Si in the biomass, 45.8 kg ha^{-1}. The concentrations of Si in foliage and stembark are substantial and rival those of Ca within these same components, 1800 and 2200 mg kg^{-1} Ca, respectively. Both these elements are used in cell wall construction although Si is a beneficial not an essential element like Ca (Marschner 1986). The above concentrations and contents of Si in the forest at Calhoun indicate the importance of incorporating the biological component in the biogeochemical cycle of this element.

The large contents of Si in the forest floor of 3056.2 kg ha^{-1} indicate some additional input of Si into the O horizon besides those from litterfall and throughfall. The complete immobilization of Si inputs from foliar litterfall and gross throughfall over 34 years, based on current input rates of 13.9 kg ha^{-1}, could account for 472.9 kg ha^{-1} of accumulated forest floor Si. Some additional component has been added to forest floor Si contents.

The annual biological uptake of Si into accumulating biomass in the forest at Calhoun (estimated as for Al) is 15.8 kg ha^{-1} yr^{-1}. An estimate of the annual content of Si available in the mass-flow of soil water driven by plant transpiration, 7.7 kg ha^{-1} (Table 3) indicates an excess uptake of Si to plant biomass. This excess uptake of Si indicates loblolly pines on this site are apparent accumulators of Si. The portion of annual Si uptake which is accumulating in forest organic matter must be incorporated into estimates of mineral weathering or soil formation.

Biomass Si:Al ratio

The SiO_2:Al_2O_3 molar ratio has been used in soil systems to investigate processes of accumulation and depletion within various regions of the soil profile (Birkeland 1984; Tan & Troth 1982). In a similar fashion use is made of the Si:Al molar ratio within the organic matter (and the following solution) components. Within these components there is no reason to assume an oxidized state for these elements thus we have used the elemental form. The Si:Al molar ratio ranges from 1.5 in live branch tissues to 27.0 in forest floor indicating a clear abundance of Si in relation to Al in all organic matter components (Table 1). The low ratio within live and dead branches indicates a relative accumulation of Al within these tissues. The ratio in foliar tissues, 6.4, is greater than that in branches but less than that in litterfall, 7.5. The increase in Si:Al from foliage to foliar litterfall necessitates the accumulation of Si or the removal of Al during needle abscission. Monthly concentrations of Al and Si in needlefall collections (Figure 1), however, have similar annual cycles and indicate no clear difference in retranslocation processes.

Soil contents

Concentrations of Al_2O_3 and SiO_2 in rock samples from the vicinity of the research site are 16.65 and 69.50 wt.%, respectively (Table 4). These

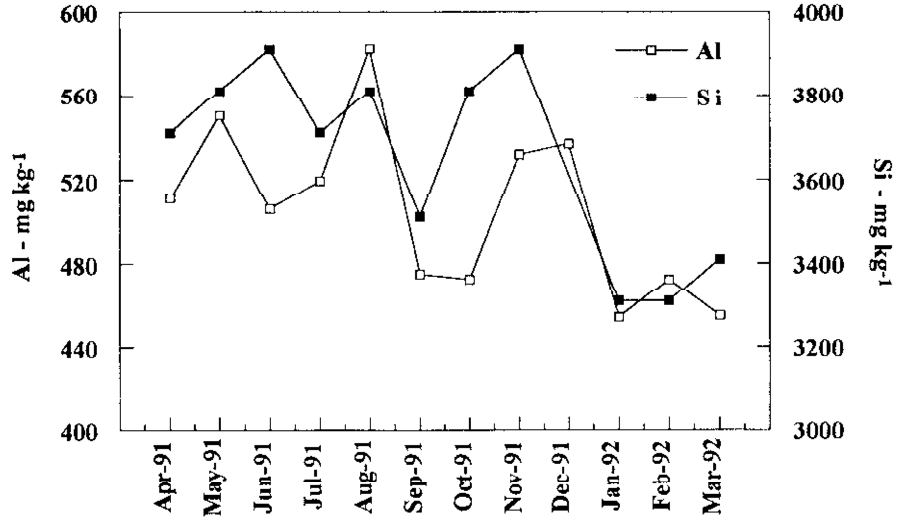

Figure 1. Al and Si concentrations in monthly needlefall collections (composite of 40 samples) between April 1991 and March 1992 in the Calhoun Experimental Forest, SC.

Table 4. Si and Al concentration, contents and molar ratio for a Typic Kanhapludult in the Calhoun Experimental Forest, SC

Depth	Horizon	Bulk Density	SiO_2	Al_2O_3	Si	Al	SiO_2:Al_2O_3 molar ratio
cm		$Mg\ m^{-3}$	—wt%—		—$Mg\ ha^{-1}$—		
0–15	A/E	1.52	92.52	2.48	984	29	63.3
15–35	BE	1.52	89.57	5.10	1270	82	29.9
35–60	Bt1	1.44	76.27	16.37	1281	312	7.9
60–100	Bt2	1.44	65.27	24.48	1754	746	4.5
100–150[1]	Bt3	1.41	65.12	24.14	4284	1801	4.6
200–250	BC1	1.33	67.47	23.73	4187	1670	4.8
300–350	BC2	1.28	66.93	23.86	3982	1610	4.8
400–450	CB1	1.28	70.73	19.00	4224	1287	6.3
500–550	CB2	1.33	71.07	18.53	4394	1299	6.5
600–700	C1	1.42	70.51	18.68	4672	1404	6.4
700–800	C2	1.36	69.82	18.84	4431	1356	6.3
Rock[2]	R	2.52	69.50	16.65	8172	2221	7.1

[1] Si and Al contents are expanded by two for the 100 to 500 cm samples to estimate total contents.

[2] Rock samples were collected near a streambed < 0.1-km from the research site, rock contents are based on 100 cm depth of bedrock.

concentrations are consistent with the granite-gneiss and granite geology for the Southeastern Peidmont (Overstreet & Bell 1965). Al_2O_3 concentrations are highest at a maximum 24.48 wt.% in the clay enriched B horizon and are minimum at 2.48 wt.% in surficial horizons. Concentrations of SiO_2 are relatively high throughout the profile but range from a low of 65.1 wt.% in the clay-enriched B horizon to a high of 92.5 wt.% in the sandy loam surface horizon. High surface soil concentrations of Si in A and E horizons are due to the eluviation of other mineral components and the concentration of SiO_2-rich sand particles.

Soil SiO_2:Al_2O_3 ratio

The SiO_2:Al_2O_3 ratio fluctuates accordingly with the above concentrations from 7.1 in the rock sample, to a low of 4.5 in the B horizon, and to a high of 63.3 in the surface soils. On a whole-soil basis the decrease in the SiO_2:Al_2O_3 ratio moving up the profile is consistent with a pattern of increasing weathering (Birkeland 1984). In the surface, the high ratios are the result of both chelation and mobilization of Al into solution as well as eluviation of clay particles from surficial horizons into the B horizon. The ratio of SiO_2:Al_2O_3 for kaolinite, the predominant clay mineral in this soil profile (Markewitz 1996), is 2 to 3 (Tan & Troth 1982). Thus eluviation of these clay components into the B horizon would serve to lower the bulk soil SiO_2:Al_2O_3 ratio.

Solution fluxes

Aluminum

Atmospheric inputs of total Al (Al_t) in wet-only precipitation to the forest system at Calhoun are 0.04 kg ha^{-1} yr^{-1} (Table 2). The flux of Al_t in throughfall solutions increases to 0.17 kg ha^{-1} yr^{-1}, a relatively small increase, that indicates a minor role for dry deposition or canopy leaching. The flux of Al_t from the forest floor in litter leachate increases an order of magnitude to 2.64 ± 0.66 kg ha^{-1} yr^{-1} (mean ± 1 SD). This flux of Al_t from forest floors is approximately equal to inputs to the forest floor from foliar litterfall plus throughfall, 1.9 kg ha^{-1} yr^{-1}. This balance in inputs and outputs suggests that currently Al is cycling rapidly through this loblolly pine forest floor with little apparent Al accumulation.

Below the forest floor, the flux of Al_t in soil solutions increases to 6.61 ± 4.30 kg ha^{-1} yr^{-1} at 0.15 m (middle E horizon) in the soil profile. This increase in Al_t flux is rapidly diminished such that at 0.60 m (middle Bt horizon) only 0.04 ± 0.02 kg ha^{-1} yr^{-1} of Al_t are moving through the soil profile. The increase in Al_t concentration and flux in the surface horizon is correlated to concentration patterns in DOC (Table 2 and Figure 2). These patterns suggest a chelating and mobilization effect by DOC in surface solutions (Cronan et

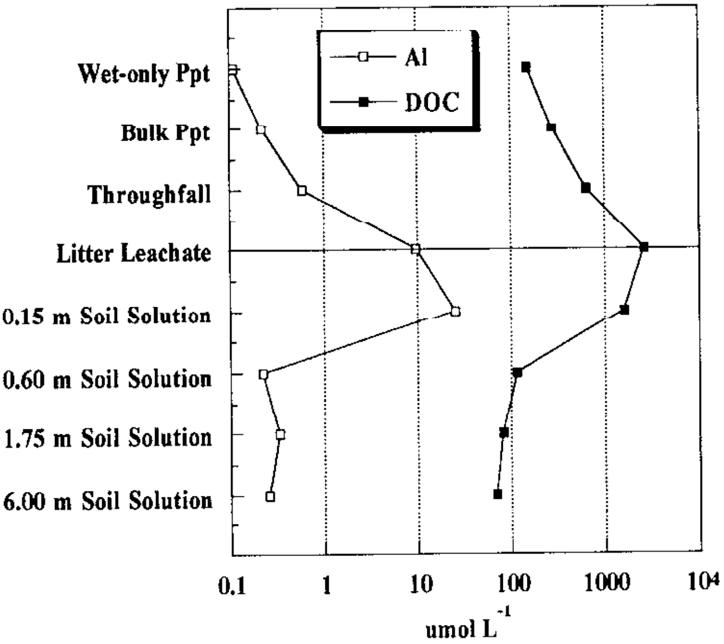

Figure 2. Volume-weighted mean annual concentrations of total Al and dissolved organic carbon (DOC) in solutions from the Calhoun Experimental Forest, SC for the period March 1992 to March 1994.

al. 1978; Gerke 1994; Sposito 1989; Tan 1980). Subsequent adsorption or decomposition of DOC leads to a concurrent decrease in Al_t concentration in upper B horizon solutions. Below the upper B horizon at 0.60 m, the flux of Al_t in soil solutions remains constant at approximately 0.04 kg ha^{-1} yr^{-1} to a depth of 6.0 m.

The flux of Al_t at 6.0 m in the soil profile at Calhoun, 0.04 kg ha^{-1} yr^{-1}, is equivalent to the input of Al_t in wet-only precipitation, 0.04 kg ha^{-1} yr^{-1}. The equivalence in solution inputs and outputs indicates a current steady-state for Al in the soil system according to the geochemical mass balance, i.e. without considering biotic removals,. Internal soil-solution processes, however, mobilize >6 kg ha^{-1} yr^{-1} of Al, mainly in response to biotic inputs of DOC, and indicate a net transport of Al from the surficial soil horizons, 0–0.15 m, to lower soil horizons.

Silicon

The input of Si in wet-only precipitation, 0.04 kg ha^{-1} yr^{-1}, is equal to that of Al. Si flux increases to 0.22 kg ha^{-1} yr^{-1} in throughfall solutions, again, suggesting only a small amount of Si is entering the system through dry deposition or cycling through canopy interception. The flux of Si from the forest floor in litter leachate increases an order of magnitude to 1.96 kg ha^{-1} yr^{-1}. In the case of Si, however, this loss from the forest floor accounts for only a small percent, 11.7%, of the current inputs from foliar litterfall plus throughfall, 13.9 kg ha^{-1} yr^{-1}. This excess of inputs to outputs for the forest floor indicates a continued accumulation of Si in the O horizon. Below the forest floor, the flux of Si in soil solutions increases with depth from 5.10 kg ha^{-1} yr^{-1} at 0.15 m to a maximum of 17.3 kg ha^{-1} yr^{-1} at 6.0 m (Table 2).

The flux of Si from 6.0 m in the forest soils at Calhoun, 17.3 kg ha^{-1} yr^{-1}, is 400-fold greater than inputs from wet-only precipitation, 0.04 kg ha^{-1} yr^{-1}. Thus, according to the geochemical mass balance the soil system is losing 17.26 kg ha^{-1} $yr^{-1}$of Si to groundwaters and desilication is an active soil process. In addition to this loss from net soil leaching, however, is an additional 15.8 kg ha^{-1} yr^{-1} of Si removal from the soil system through biological uptake. This plant uptake accounts for nearly as large a mobilization of Si from the soil as does net soil leaching. These processes do differ, however, in that 100% of net soil leaching is a loss from the soil system whereas only that portion of biological uptake accumulating in organic matter can be considered a loss. Currently at Calhoun, 2.3 kg ha^{-1} yr^{-1} are accumulating in aboveground biomass and in the forest floor current needlefall inputs exceed solution outputs by 12.0 kg ha^{-1} yr^{-1}. Thus, 90.3% of biological uptake, 14.3 kg ha^{-1} yr^{-1}, can be considered a loss from the soil system.

Solution Si:Al ratio

Solution ratios of Si:Al vary widely from 0.7 in forest floor litter leachate to 655.1 in soil solutions at 6.0 m (Table 2). The initial Si:Al ratio for solutions input to the forest system including wet-only precipitation, bulk precipitation and canopy throughfall are all similar near 1.5. The decrease in the Si:Al ratio in the litter leachate and 0.15 m solutions is a result of Al mobilization in relatively DOC-enriched solutions. Si concentrations also increase in these solutions but at a lesser rate. The order of magnitude increase in the Si:Al ratio in the lower soil solutions is a function of both the nearly complete loss of Al from solution and the continued increase in Si concentration. This preponderance of Si to Al in deep soil solution indicates a retention of Al relative to Si in the residual mineral components.

Conclusion

The biogeochemical mass balances for Al and Si differ in magnitude and in process but both indicate an important role for biotic cycling. In the case of Al, the balance between system inputs, 0.04 kg ha^{-1} yr^{-1}, and outputs from 0.60 m, 0.04 kg ha^{-1} yr^{-1}, as well as, from 6.0 m, 0.03 kg ha^{-1} yr^{-1}

(Table 2) indicates relatively low rates of weathering loss of Al from soil or saprolite. There is, however, evidence for an internal system mobilization of Al in the 0.60 m layer (the upper 10% of the 6-m soil profile) on the order of 6.6 kg ha^{-1} yr^{-1} in response to biotic inputs of DOC. In addition, the biotic uptake of Al serves to mobilize 2.3 kg ha^{-1} $yr^{-1}$from the soil reservoir, a 35% increase in Al mobilization.

Of the total biotic uptake of Al, that portion which accumulates in organic matter is currently the sole removal from the soil reservoir. In this study, the Al accumulation in aboveground biomass, 0.5 kg ha^{-1} yr^{-1}, is clearly a result of biotic uptake and defines the lower limit of soil loss of Al as a result of biological cycling. The additional 3.2 kg ha^{-1} yr^{-1} of Al accumulating in forest floor organic matter may be a result of biotic uptake but may also result from bioturbation. The bioturbation process does not result in a removal of Al from the soil system and thus does not represent a chemical weathering release of Al. On the contrary, any portion of Al accumulation in the forest floor due directly to plant uptake would serve to increase the role of biota in weathering and in removing Al from the soil system.

In the case of Si, solution outputs at 6.0 m, 17.3 kg ha^{-1} yr^{-1}, greatly exceed atmospheric inputs, 0.04 kg ha^{-1} yr^{-1}, to the soil system. In a purely geochemical model this excess flux, 17.26 kg ha^{-1} yr^{-1}, from the soil reservoir would estimate the rate of Si weathering. However, the Si accumulating in aboveground biomass, 2.3 kg ha^{-1} yr^{-1}, as a result of biotic uptake, serves to increase the weathering release estimate by 13% annually. The current retention of Si in forest floor organic matter of 12.0 kg ha^{-1} yr^{-1} indicates a continued biomass accumulation of Si also as a result of biotic uptake. Inclusion of this biological Si removal from soil further augments the weathering release estimate by 62%. Thus, the omission of biological cycling of Si creates a substantial error in the estimate of current Si weathering.

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