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Base cation and silicon biogeochemistry under pine and scrub oak monocultures: implications for weathering rates

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Abstract

Vegetation type has a profound influence over biogeochemical processes, including canopy leaching, stemflow, litterfall, and nutrient uptake. Understanding the relationship between plants and soil processes, such as mineral weathering, is a difficult task considering the interactions among biotic and abiotic soil-forming factors. In this study, soils planted with pure stands of scrub oak (*Quercus dumosa* Nutt.) and Coulter pine (*Pinus coulteri* B. Don) were used to identify key biogeochemical processes in each soil–plant system. The experimental design, a true biosequence, allowed an opportunity to link biogeochemical processes to mineral weathering. Precipitation, throughfall, litter leachate, and soil solutions were collected following rain events from November of 1996 to April of 1998. Relatively high Na and Ca concentrations in pine throughfall suggest that atmospheric deposition is a more important process within the pine canopy than is canopy leaching. In contrast to pine throughfall, mean K concentrations were higher than Ca in oak throughfall, reflecting the importance of canopy leaching. Nutrient cycling was more rapid within the scrub oak soil–plant system as evidenced by significantly reduced levels of cations in soil solution at the 7.5 cm depth compared to litter leachate. Mean Si concentrations at the 65 cm depth were 334 μmol L^{-1} under oak and 431 μmol L^{-1} under pine. Silicon and base cation fluxes indicate higher weathering rates under pine. Solution chemistry shows that canopy and nutrient cycling processes are different between the two species and are impacting the cation loss rates.

Keywords: Chaparral; Soil solution chemistry; Base cations; Atmospheric deposition; Mineral weathering

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1. Introduction

Base cation cycling and mineral weathering are related processes and are common topics addressed in current biogeochemical research. Documentation of soil acidification due to atmospheric deposition has resulted in numerous studies focused on base cations and mineral weathering. For example, several studies have related calcium depletion in forests of the northeastern USA to acid precipitation (Federer et al., 1989; Bailey et al., 1996; Likens et al., 1996, 1998). In some regions, in addition to serving as a source of acidity, atmospheric deposition may also provide base cations that are essential plant nutrients (Simonson, 1995). Lindberg et al. (1986) reported that atmospheric deposition of Ca supplied 40% of the annual requirement for a forest stand in eastern Tennessee. Likens et al. (1988) estimated that approximately 6% of the available Ca nutrient pool is from atmospheric deposition in a Hubbard Brook watershed study. Although the importance of atmospheric deposition of base cations has been increasingly acknowledged, its significance in relation to base cation biogeochemistry has not been extensively explored (Simonson, 1995; Stutter et al., 2003).

Plant growth can lead to soil acidification through the production of organic acids, respiration (carbonic acid production), and the uptake and storage of nutrients (Kelly et al., 1998; Jobbágy and Jackson, 2003). This biotically induced soil acidification can alter base cation cycling and mineral weathering (Augusto et al., 1998). Vegetation also exerts a strong control on biogeochemical function through its ability to alter the water budget and capture atmospheric deposition (Lelong et al., 1990). Through such interactions, vegetation may significantly influence the rate of loss of base cations from the soil–plant system.

Documented changes in pH (Nihlgård, 1971; Dahlgren et al., 1991; Richter et al., 1994; Johnson-Maynard et al., 1997; Hagen-Thorn et al., 2004) and the distribution of base cations (Jobbágy and Jackson, 2003) following vegetation conversion demonstrate that the processes through which plants alter soil properties are species specific. Understanding the influence of different plant species on soil pH and base cation cycling is important for determining the influence of atmospheric deposition and acidification on base cation biogeochemistry and future ecosystem productivity. Despite the recognized importance of vegetation on base cation cycling and mineral weathering, the more specific role of vegetation type in the biogeochemical functioning of terrestrial ecosystems is not well understood (Lelong et al., 1990).

The purpose of this study was to identify key biogeochemical processes and the controls over these processes within two different soil–plant systems. The original soil material in these systems was identical, but the imposed vegetation differed in that scrub oak was planted on one soil and Coulter pine on the other. These two species are very common components of the semiarid foothills of southern California. The influence of vegetation type on canopy processes, including the relative importance of the interception of atmospheric deposition, and soil biogeochemistry was determined, and estimates of weathering rates under each species were made.

2. Methods

The San Dimas Experimental Forest (SDEF) is a US Forest Service (Pacific Southwest Experiment Station) watershed research laboratory located in the San Gabriel Mountains about 56 km northeast of Los Angeles, CA. The climate is a Mediterranean type with warm, dry summers and mild, wet winters. The annual precipitation ranges from 292 to 1224 mm with an average value of 678 mm. Precipitation occurs as rain, with minimal snow, and most falls between December and March. The mean annual air temperature is 14.4 °C (Dunn et al., 1988). An experiment was started in 1937 to monitor changes in water availability under different plant communities. As part of this experiment “unconfined lysimeters,” which consist of earthen-walled pits ($5.3 \times 5.3 \times 2.1$ m deep) filled with soil material excavated on site, homogenized, and sieved to remove rock fragments and aggregates greater than 19 mm in diameter, were created. The fill material was fine sandy loam derived from the weathering of diorite. Mineralogical analysis of archived fill material shows that the dominant clay minerals in the parent material were kaolin, vermiculite, mica, and randomly interstratified vermiculite–mica (Tice et al., 1996). During the filling of the lysimeters, samples were taken from every 7.5 cm fill increment and archived. Analysis of these samples provided knowledge of the initial state of the system. After allowing for a settling period of 3 years (1937 to 1940), excess fill material was removed from the surface, a 5% slope to the south was imposed, and the lysimeters were planted with an annual grass (*Bromus mollis*). Six years later (1946), the grass was burned and replaced with monocultures of native species, including scrub oak (*Quercus dumosa*), and Coulter pine (*Pinus coulteri*). The design of the lysimeters minimized variation of all environmental conditions except vegetation (Colman and Hamilton, 1947; Patric, 1961), creating a true biosequence. The distance between the pine and oak lysimeters used in this study was approximately 18.5 m, thereby reducing any microclimatic effects. At the time of sampling, the pine lysimeter had minor amounts of grasses, while the scrub oak remained a monoculture with no understory vegetation.

3. Field methods

To minimize disturbance to this unique experiment, soil pits that were originally dug, described, and sampled in 1987 (Graham and Wood, 1991) were reexcavated to install monitoring and sampling equipment. Table 1 shows relevant solid-phase data from soils under pine and scrub oak. Walls of reexcavated soil pits were dug back to expose undisturbed soil, and at three depths, three replicate plastic porous plate lysimeters (12 cm in diameter) were inserted horizontally into the undisturbed soil on opposite sides and on one end of each soil pit. Plate lysimeters were installed at horizon boundaries to determine changes in soil solution chemistry from one horizon to the next. The corresponding depths are 10, 35, and 65 cm under pine and 7.5, 35, and 65 cm under oak. The 65 cm depth corresponds to the C3 horizon under each vegetation type and is relatively unaltered parent material. An on-site vacuum pump was used to supply a constant vacuum of 0.075 MPa for the collection of soil solutions. Four high-density polyethylene bottles with funnels attached were placed under the canopy of each

Table 1
Selected chemical and physical data from pedons under pine and oak

Horizon	Depth	Particle-size distribution[a]				Organic carbon	Exchangeable cations[b]				Exch. acidity[b]
	cm	Sand	Silt	Clay	pH[c]	%	Ca	Mg	Na	K	
		% (w/w) of <2 mm fraction					cmol kg^{-1}				
Pine											
Oi1	10–6	Fresh pine needles, twigs, some grass									
Oi2	6–4	Partially decomposed pine needles									
Oe	4–0	Mostly decomposed pine needles									
A	0–1	60.8	30.5	8.8	5.2	3.2	7.8	4.2	0.05	0.3	0.45
BAt	1–10	58.1	30.8	11.0	5.7	0.6	9.6	5.9	0.04	0.2	0.51
Bt	10–20	57.6	30.4	11.9	5.9	0.5	10.6	6.1	0.05	0.1	0.42
BCt	20–35	56.6	31.5	11.9	6.1	0.5	9.8	6.0	0.04	0.1	0.42
C1	35–50	56.7	31.1	12.1	6.1	0.3	10.6	6.3	0.05	0.1	0.37
C2	50–65	57.5	31.2	11.4	6.1	0.2	9.8	5.9	0.06	0.1	0.31
Oak											
Oi	7–0	Fresh oak leaves, twigs, and some pine needles; wormcasts									
A	0–7.5	54.3	32.1	13.6	5.7	2.5	14.5	6.8	0.05	0.3	0.13
AC	7.5–20	58.4	30.4	11.2	5.4	0.5	10.6	6.7	0.05	0.1	0.45
C1	20–35	57.6	31.1	11.4	5.4	0.3	9.7	6.5	0.08	0.1	0.46
C2	35–50	57.2	31.4	11.6	5.6	0.2	8.2	5.1	0.05	0.1	0.45
C3	50–65	57.7	30.9	11.4	5.6	0.2	10.1	5.8	0.06	0.1	0.44

[a] Reported by Graham and Wood (1991) for samples from 1987 sampling of the same pedons.

[b] Reported by Ulery et al. (1995) for samples from 1987 sampling of the same pedons.

[c] pH determined on 1:1 soil:water mixture.

site to catch throughfall. Throughfall amounts were recorded in 10 gauges separate from the throughfall collectors, randomly placed under each canopy. Litter leachate was collected by zero-tension lysimeters placed under the litter layer of each vegetation type. Two replicate samplers similar to those used to collect throughfall were placed on both the eastern and western ends of the biosequence away from the influence of vegetation canopies to collect bulk precipitation. A weather station located 200 m south of the biosequence recorded rainfall amounts. All solutions were collected within 24 h following a rainfall event. Solutions from replicate samples were collected and analyzed separately. Twenty-six events were sampled throughout the study period of November 1996 to April 1998.

Samples were brought back to the laboratory and stored at 4 °C until analyzed. Once in the laboratory, all solutions were treated in the same manner. The pH of samples was measured with a standard pH meter. The samples were then filtered through a 0.45-μm filter. A subsample was collected and acidified to pH<2 with HNO_3 for measurement of Ca, Mg, Na, K, and Si concentrations by inductively coupled plasma optical emission spectroscopy (ICP-OES). A second filtered and acidified subsample was analyzed for dissolved organic carbon (DOC) on a Dorhman TOC analyzer. Data were analyzed by the general linear model procedure of SAS (SAS, 1987).

Drainage estimates were obtained by calculating drainage flux rates based on volumetric water contents at 65 cm (measured hourly during winter and three times a day during dry periods) by TDR. Drainage flux was equated to unsaturated hydraulic conductivity ($K(\theta)$), assuming that drainage is gravity driven. Simulations using the Hydrus 1-D model (Šimůnek et al., 1998) have indicated that this is a reasonable assumption for the biosequence soils and boundary conditions (T. Skaggs, personal communication, 1999).

Drainage flux (Jw) was calculated using Eq. (1).

$$\mathrm{Jw} = K(\theta) = \mathrm{Ks}((\theta - \theta\mathrm{r})/(\theta s - \theta\mathrm{r}))^{1/2} * [1 - (1 - ((\theta - \theta\mathrm{r})/(\theta\mathrm{s} - \theta\mathrm{r}))1/m)m]^2 \tag{1}$$

(van Genuchten, 1980) where θ is the measured water content at any time at 65 cm, θr is the residual water content at 65 cm, θs is the saturated water content at 65 cm, Ks is the measured saturated hydraulic conductivity, m=1−1/n, n is the empirical constant that affects the shape of the retention curve.

Residual water content (θr), θs, and n were estimated using the RETC program (van Genuchten et al., 1991). The RETC program uses the VG equation (van Genuchten, 1980) to model the water retention curve. The pore size distribution model of Mualem (1976) and Burdine (1953) in conjunction with measured soil water retention data is used to predict unsaturated hydraulic conductivity. Drainage was calculated by

$$D = \mathrm{Jw} * T \tag{2}$$

where D is drainage, Jw is the drainage flux calculated by Eq. (1), T is time.

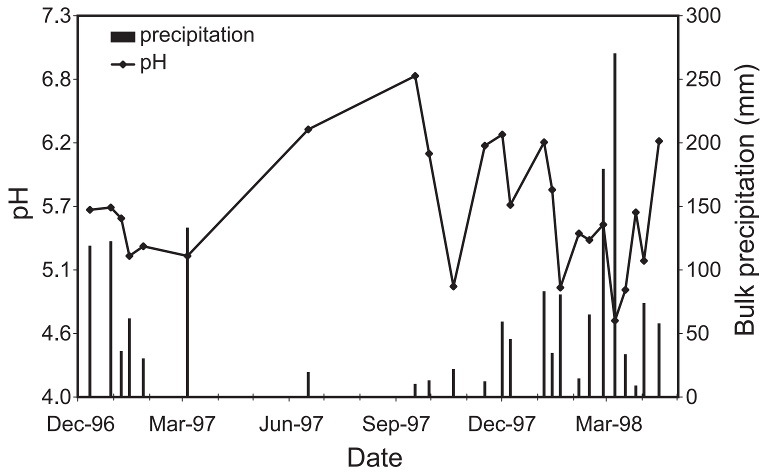

Fig. 1. Amount of precipitation (mm) and the pH of rainfall for every sampling date.

Table 2
Mean values of pH and cation and Si concentrations in solution samples

	pH	Ca	Mg	K	Na	Si	DOC
		μmolL^{-1}					
Bulk precipitation	5.6bc	22.2b	10.0d	20.7c	75.0a	5.2f	288c
Pine							
Throughfall	4.9d	91.7b	47.0cd	82.5bc	175.1a	11.4f	1499cd
Litter leachate	5.7bc	79.4b	89.9bcd	191.1bc	76.2a	34.5f	6194ab
10 cm	5.7abc	119.0b	109.8bc	17.9bc	64.5a	143.2de	2779bcd
35 cm	5.9ab	90.7b	95.9bcd	11.5bc	81.4a	180.9d	1288bcd
65 cm	6.0ab	159.3ab	183.1ab	12.5bc	173.5a	431.1a	960cd
Oak							
Throughfall	5.5c	85.4b	60.9cd	167.9b	144.2a	11.3f	2083d
Litter leachate	5.6bc	304.0a	242.8a	430.6a	107.9a	114.8e	9351a
7.5 cm	6.1a	102.7b	91.8bcd	19.2bc	37.7a	256.5c	2363cd
35 cm	6.1a	62.4b	66.4bcd	9.9bc	79.2a	408.8ab	2403cd
65 cm	5.9ab	72.3b	74.6bcd	7.7bc	70.7a	333.5b	3096cd

Reported values are means from November 1996 to April 1998. Like letters within a column indicate values that are not statistically significantly different at alpha=0.05.

The calculated drainage flux was used to determine the flux of cations from the 65 cm depth using measured concentrations.

4. Results

4.1. Canopy processes

The pH of bulk precipitation over the sampling period ranged from 4.7 on 8 March 1998 to 6.8 on 17 September 1997, with a mean value of 5.6 (Fig. 1 and Table 2). The pH of rainfall tended to increase for rainfall events following substantial dry periods (Fig. 1a and b). Solution pH significantly decreased as the rainwater leached the pine canopy, yielding a mean throughfall pH value of 4.9 (Table 2). The mean pH of oak throughfall was not significantly different from that of rainfall. Sodium (Na) was the most concentrated cation in bulk precipitation with a mean value of 75 μmol L^{-1}, followed by Ca (22 μmol L^{-1}), K (21 μmol L^{-1}), and Mg (10 μmol L^{-1}) (Table 2). The relative concentrations of Ca, Na, K, and Mg were the same in pine throughfall and bulk rainfall (Na>Ca>K>Mg; Table 3). Mean K concentration of oak throughfall was almost twice that of pine, with a mean value of 168 μmol L^{-1} (Table 2). Seasonally, combined cation concentrations of both precipitation and throughfall (Fig. 2) were higher in the spring and summer of 1997 when rainfall events were separated by dry periods (Fig. 1a). During winter and early spring of 1998, El Niño conditions prevailed, and cation concentrations were relatively stable.

4.2. The influence of vegetation on soil biogeochemistry

As pine throughfall leached the 10-cm-thick litter layer, becoming litter leachate, the order of cation concentration changed. In the leachate from pine litter, K was the most concentrated (191 μmol L^{-1}), followed by Mg (90 μmol L^{-1}), Ca (79 μmol L^{-1}), and Na (76 μmol L^{-1}; Tables 2 and 3). Mean concentrations of Ca, Mg, and K in the oak litter leachate were all approximately four times greater than in the throughfall (Table 2).

Mean concentrations of Ca, Mg, and K under oak significantly decreased from the litter leachate to the

Table 3
Ranking of base cations by mean concentrations over the entire study period

	Pine	Oak
Bulk Precipitation	Na>Ca>K>Mg	Na>Ca>K>Mg
Throughfall	Na>Ca>K>Mg	K>Na>Ca>Mg
Litter leachate	K>Mg>Ca>Na	K>Ca>Mg>Na

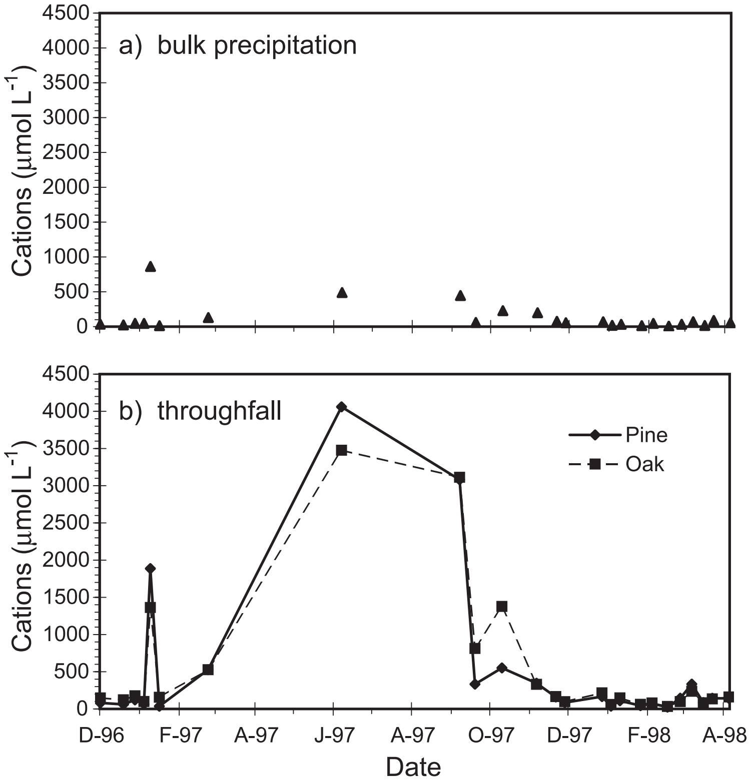

Fig. 2. Sum of cations (Ca, Mg, K, and Na) in (a) bulk precipitation and (b) throughfall from under pine and oak.

7.5 cm depth (Table 2). Mean concentrations of Ca, Mg, and K were not significantly different between litter leachate and soil solution at any depth under pine. Mean soil solution Ca, Mg, K, and Na concentrations were not statistically significantly different among the three depths under either vegetation type. The highest concentrations of Si were found in the soil solutions of each soil–plant system. Within the soil supporting pine, mean Si solution concentrations significantly increased from 143 μmol L^{-1} at the 10 cm depth to 433 μmol L^{-1} at 65 cm (Table 2). The highest concentration of Si in soil solution from under oak (409 μmol L^{-1}) was found at the 35 cm depth (Table 2). Mean DOC concentrations significantly increased as throughfall leached the litter layers of each vegetation type and significantly decreased as it moved through the top 10 cm of soil. Soil solutions from 7.5 cm under oak were often amber to brown in color compared to light yellow to colorless under pine.

5. Discussion

5.1. Canopy processes

The rise in rainfall pH when there is considerable time between rain events may be due to the accumulation of dry deposition in the form of oxides, hydroxides, carbonates, and salts on precipitation collectors (Figs. 1b and 2a). The bulk precipitation collectors used in this study were constantly open to the atmosphere and therefore collected dry as well as wet deposition. Sodium was the dominant base cation in bulk precipitation, followed by Ca, K, and Mg (Table 3). The abundance of Na is probably due to the proximity (35 km) of the site to the Pacific Ocean (Quideau et al., 1996). Comparisons of Mg:Na, Ca:Na, and K:Na ratios have been used to determine the source of atmospheric deposition (Schlesinger et al., 1982), where ratios higher than expected for seawater are attributed to continental sources. The ratio of Mg:Na (volume-weighted average concentrations) in bulk precipitation collected during this study was 0.19, higher than the 0.13 reported for seawater (Holland, 1978; Fig. 3a). Ratios of Ca:Na (0.54; Fig. 3b) and K:Na (1.1; Fig. 3c) were both higher than their reported value of 0.04 in seawater (Holland, 1978). The comparison of cation ratios in bulk precipitation to those found in seawater therefore suggests an important source of dry deposition to the SDEF. A likely source of cations in dry deposition is dust from the Mojave Desert carried by the Santa Ana winds (Reheis and Kihl, 1995). The importance of dry deposition at the SDEF is also evident in the increased concentrations of cations in the bulk precipitation (Fig. 2a) during the driest part of the sampling period. This may be explained by the accumulation of dry deposition on the open collectors during the approximately 3-month dry period between storms (97 March to 97 June and 97 June to 97 September). Dry deposition can make significant contributions toward the nutritional requirement of plants, as well as influence pedogenic processes in some soils (Simonson, 1995). Estimates of the annual accumulation of base cations in aboveground biomass and dry deposition (estimated as total atmospheric deposition−wet only) were reported by Quideau et al.

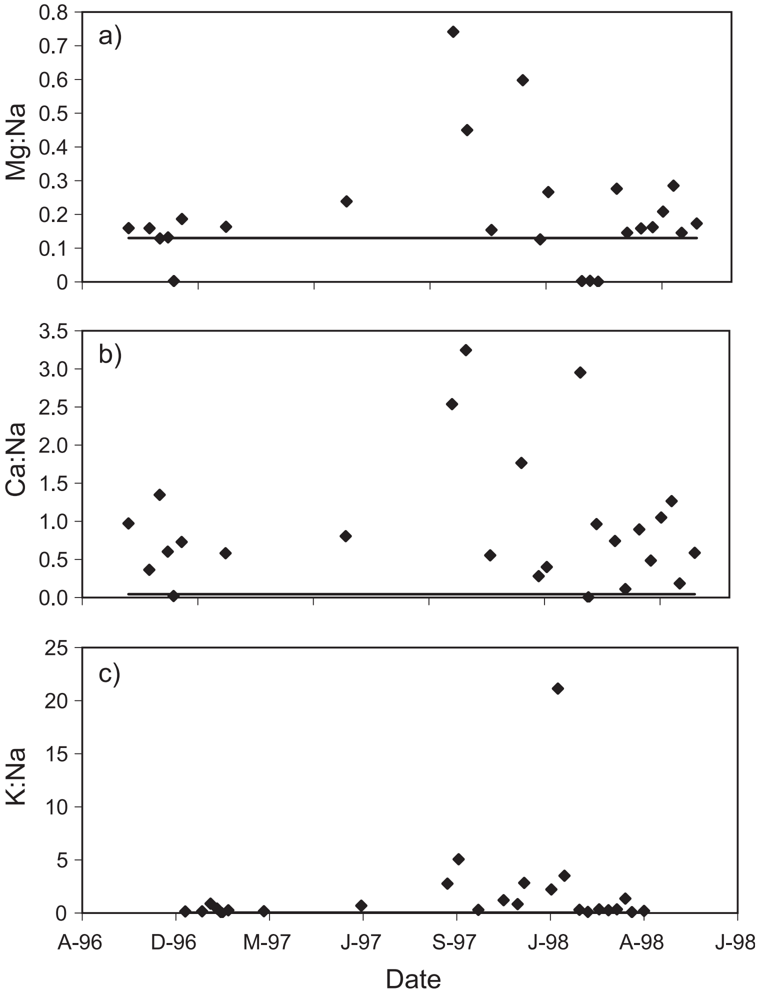

Fig. 3. The ratio of (a) Mg:Na, (b) Ca:Na, and (c) K:Na in bulk precipitation (weighted average concentrations). Solid lines represent values reported for seawater (Mg:Na=0.13, Ca:Na=K:Na=0.04; Holland, 1978).

(1996). The relative importance of dry deposition to plant uptake can be assessed by dividing deposition by the annual plant uptake for a given ion. Based on the data from Quideau et al. (1996), dry deposition equals 29% of the Ca, 13% of the Mg, and 17% of the K accumulated within the aboveground oak system each year. Within the pine system, dry atmospheric deposition could supply 121% of the Ca, 19% of the Mg, and 30% of the K taken-up by the plant. Based on these estimates, which assume that plant uptake has been constant since planting and that base cations in dry deposition are soluble and plant available, atmospheric deposition of base cations within the lysimeters makes a significant contribution toward meeting the nutritional requirements of the plants. The overall importance of dry deposition reflects the efficiency of the canopy in capturing dryfall. The pine canopy, with its greater height and potential for greater surface area, likely captures more dry deposition than does oak (Quideau et al., 1996). Dry deposition, therefore, may represent a more important input of base cations to the pine soil than to the oak.

Potassium is usually highly concentrated in throughfall samples because it is highly soluble and concentrated in cells near leaf surfaces (Schlesinger, 1997). Calcium is typically less concentrated but was more concentrated in pine throughfall even though aboveground pine biomass contains more K than Ca (Table 4), and K is more soluble. Calcium was found to be the dominant cation in dry deposition within the SDEF (Reheis and Kihl, 1995; Quideau et al., 1996). Dry deposition within the pine canopy is eventually washed off by precipitation and incorporated in the throughfall. This results in throughfall that reflects the cationic signature of both wet and dry deposition. Throughfall under pine has the same cationic signature as the bulk precipitation from the collectors used in this study, which were constantly open to the atmosphere (Table 3), suggesting that interception of atmospheric deposition and the subsequent washing of foliage by rainfall, is a more important process than the leaching of foliage in the pine canopy. As rainfall leached the pine canopy becoming throughfall, the pH significantly decreased (Table 2). Ugolini et al. (1977) reported a decrease of almost 1 pH unit between rainfall and throughfall in a conifer forest and attributed the decrease to low molecular weight acids leached from the canopy. The pine canopy appears to be a net source of soluble organic acids and/or H^+.

Table 4
Total cation composition of aboveground plant and litter nutrient pools

	Ca	Mg	K	Na
	kg ha^{-1}			
Pine				
Plant[a]	352	148	409	5
Litter[b]	86	27	15	1
Oak				
Plant[a]	1625	248	729	22
Litter[b]	153	24	22	1

[a] Reported by Milone (1994).

[b] Reported by Quideau et al. (1996).

Mean cation concentrations in oak throughfall are similar to those of pine with the exception of K. The mean K concentration of oak throughfall is twice that of pine throughfall (Table 2). This difference could be due to higher levels of K within the oak foliage (Table 4) combined with higher leaching rates due to differences in leaf morphology (e.g., shape, thickness; Luxmoore et al., 1981; Schlesinger, 1997). Despite higher leaching rates expected under oak due to its leaf morphology and higher Ca and Na contents of the aboveground biomass (Table 4), Ca and Na concentrations in oak throughfall were slightly lower than in pine throughfall. A likely source of Ca and Na in pine throughfall is dry atmospheric deposition.

While leaching of each canopy resulted in higher concentrations of base cations in throughfall than in rain, the additions under pine did not alter the cationic signature from that of rain (Table 3). Within the oak system, K became the dominant cation in throughfall. Comparison of base cation chemistry of rain and throughfall suggests that the capture of dry atmospheric deposition is an important process under pine while leaching of the canopy foliage is more important under oak.

5.2. The influence of vegetation on soil biogeochemistry

Once pine throughfall leaches the 10-cm-thick O horizon, the order of cation concentration changes. Potassium becomes the dominant cation, increasing from an average concentration of 83 μmol L^{-1} in throughfall to 191 μmol L^{-1} in litter leachate (Table 2). This results in a large flux of K, an essential nutrient element, into the mineral soil that is then available for root uptake and/or fixation by minerals. The 10-fold decrease in concentration of K from the pine litter layer to the 10 cm depth indicates that K coming out of the litter layer is utilized or immobilized within the first 10 cm of soil. Mean K concentrations in pine soil solution were similar at all depths. Intrasystem cycling of Ca and Mg are somewhat different than that of K under pine. Calcium and Mg concentrations remain relatively constant and reach their maximum concentrations at the 65 cm depth.

Mean cation concentrations in the oak litter leachate were 3 to 4 times greater than those in the throughfall except for that of Na, which was slightly lower (Table 2). The litter layer under oak contained higher concentrations of cations than did the pine litter (Table 4), which is reflected in the higher concentrations of cations in oak litter leachate. With relatively high concentrations of K and Ca, litter leachate under oak serves as an important source of these nutrients to the mineral soil. Within the oak system, mean concentrations of Ca, Mg, and K in soil solution collected from the 7.5 cm depth (Table 2) were significantly lower than in litter leachate. The abrupt decrease in concentration within the first 7.5 cm of soil under oak shows that base cations are quickly recycled via root uptake, incorporated into minerals, or leached. Mineralogical data indicate that K is immobilized in the A horizons under oak and pine by fixation in vermiculite (Tice et al., 1996). Since Ca and Mg are not usually incorporated into secondary minerals (Schlesinger, 1997) and have lower concentrations in drainage water under oak, the main fate of these elements is plant uptake. Quideau et al. (1996) reported higher incorporation of Ca, Mg, and K in the aboveground biomass (wood+foliage+litter) and soil exchangeable pools in the oak system than in the pine system at the SDEF biosequence. Comparison of litter leachate and soil solution indicates that nutrient cycling of Ca, Mg, and K is much tighter under oak as compared to pine. Rapid nutrient cycling under oak is likely a combination of litter quality and the relatively large earthworm community that encourages decomposition (Quideau et al., 2001; Johnson-Maynard et al., 2004).

5.3. Implications for weathering rates

By far, the largest concentrations of Si measured in this study occur in soil solutions (Table 2). Both vegetation types had significantly higher mean concentrations of Si at the 65 cm depth than at the 7 to 10 cm depths (Table 2). Although the concentrations found at the San Dimas biosequence were much lower, the pattern with depth is similar to what was reported by Markewitz and Richter (1998) in a 34-year-old loblolly pine forest in South Carolina. Since the atmospheric contribution of Si is very minor and the main source is mineral dissolution, Si is often used as an indicator of mineral weathering (Schlesinger, 1997). Significantly higher Si concentrations in drainage water (65 cm depth) under pine indicate higher weathering rates than under oak. The Si loss rate reported for pine in this study (Table 5) is similar to the value of 615 mol ha^{-1} $year^{-1}$ reported by Markewitz and Richter (1998) for a loblolly pine forest and to the 850 mol ha^{-1} yr^{-1} reported for Hubbard Brook (Likens et al., 1977). The rate of Si loss from the oak system is approximately 20 to 30 times lower than these estimates.

The estimated loss of Ca (precipitation drainage) was 222 mol ha^{-1} under pine (Table 5). The flux of Ca at 65 cm under oak was less than Ca input by bulk precipitation, indicating a net gain of 35 mol $ha^{-1}year^{-1}$. Small gains of Ca under oak compared

Table 5
Cation fluxes through each soil–plant system for 1998

	Ca	Mg	K	Na	Si
	mol ha^{-1}				
Bulk precipitation (*P*)	40	10	40	160	10
Pine					
Plant uptake[a]	230	160	230	10	n.d.
Drainage (*D*)	262	292	16	293	759
Δ system (*P*−*D*)	−222	−282	24	−133	−749
Oak					
Plant uptake[a]	950	240	410	20	n.d.
Drainage	5	5	1	3	26
Δ system (*P*−*D*)	35	5	39	157	−16

n.d.—not determined.

[a] Estimates of annual plant uptake reported in Quideau et al. (1996).

to losses under pine reflect greater plant uptake and extremely efficient Ca cycling under oak. The creation of islands of fertility around oaks in the California oak woodlands has been reported (Kay, 1987; Dahlgren et al., 1997) and attributed to the return of nutrients by litterfall and throughfall (Dahlgren et al., 1997). Potassium was accumulating in both systems. Solution data indicated that the largest accumulation of K was within the first 10 cm of each soil. Tice et al. (1996) reported increases in nonexchangeable K of 23% in the clay fraction of the A horizon under oak and 5% in the clay fraction of the A horizon under pine relative to the archived parent material. The increase in nonexchangeable K was accompanied by evidence of the alteration of vermiculite to mica in the A horizons under oak and pine. The solution data presented here indicate higher K levels released from the oak litter layer, as compared to pine, as a driving force of this mineralogical alteration in the A horizons.

The net export of Ca and Na can be used to estimate weathering rates because the main source of these elements is primary minerals, and they are not commonly fixed in secondary minerals when released (Schlesinger, 1997). The loss of Ca indicates different weathering rates under each vegetation type with the higher rates under pine. It is also important to consider plant uptake and storage. Assuming that growth has been constant throughout the experiment, annual plant uptake can be estimated by dividing the total cation content of the above ground biomass by the number of years since planting. Except for Na and K, atmospheric inputs are less than plant demand (Table 5). Plant uptake results in lowering of soil solution concentrations of base cations, with consequential loss from the exchangeable and nonexchangeable pools to help meet the nutritional need. Although plant uptake is greatest under oak, more cations are returned to the soil each year through litterfall and throughfall, as evidenced by higher cation concentration in litter (Table 4) and the throughfall and litter leachate base cation chemistry. The rate of oak litter decomposition, as measured by ^{14}C, is more rapid than that of pine litter (Quideau et al., 2001), resulting in a more rapid cycling of nutrients through the oak system. Nutrient uptake, therefore, cannot be considered a true loss from the system. The rapid return of nutrients through biogeochemical processes supports new growth, while limiting losses from the soil profile (Dahlgren and Singer, 1991). In general, California soils supporting chaparral communities are considered relatively nutrient poor (Vlamis et al., 1954). High nutrient return by litterfall and relatively rapid decomposition rates may therefore play an important role in maintaining the productivity of these ecosystems (Schlesinger and Gill, 1980).

The Ca release rates from the pine (-222 mol ha^{-1}) system (Table 5) are similar to the 290 mol ha^{-1} reported for a watershed in Hubbard Brook (Likens et al., 1977) and the 220 mol ha^{-1} reported for a red pine site in Wisconsin (Quideau et al., 1996) but are slightly higher than those reported for adjacent beech forest and grass catchments in France (Lelong et al., 1990). The vegetation in that Mediterranean climate appeared to have a large impact on weathering rates, with Ca losses of 67.5 mol Ca ha^{-1} under beech and 182.5 mol ha^{-1} under grass.

Based on Si release rates, the process of desilication is affecting soil genesis under each vegetation type. The order of weathering rates, based on Si fluxes, corresponds to base cation fluxes in that the highest rates are under pine. The magnitude of weathering may correspond to nutrient cycling strategy. Oak appears to be a conservative species exhibiting tight nutrient cycling with lower leaching rates. The constant supply and availability of recycled cations to the plant may reduce the requirement from the nonexchangeable or mineral phase resulting in lower weathering and Si loss rates.

It is important to recognize that the cation and Si fluxes, reported in Table 5, are estimates. Errors involved in this simple mass balance approach (inputs–outputs) include those associated with water content measurements, modeled drainage, and laboratory analyses. The method used to calculate drainage utilizes changes in volumetric water content as measured by TDR. Time domain reflectrometery has been shown to have a reproducibility of ±0.01 (Topp and Davis, 1985). Paired waveguides in agricultural fields have been reported as measuring volumetric water contents with standard deviations ranging from ±0.004 to ±0.008 (Baker and Allmaras, 1990). Regression analysis showed that the R^2 values for the observed versus fitted conductivity data obtained from the RETC Model range from 0.989 to 0.999, indicating that the model accurately described each system. The inherent variability of biogeochemical cycling within each system must also be considered. One of the most extensive biogeochemical data sets available is from the Hubbard Brook Experimental Forest. Based on an 11-year data set, Likens et al. (1977) concluded that 1 to 3 years of measurements are adequate to characterize the magnitude of loss or gain of Ca^{+2}, Mg^{+2}, Na^{+}, Al^{+3}, NH_4^{+}, H^{+}, SiO_2, and HCO_3^{-}. Nitrate, Cl^{-}, and K^{+} require longer data sets because of the higher variability in annual inputs. The weathering rates calculated in this study are based on 1998 data only and should be regarded as preliminary estimates of cation and Si fluxes within the SDEF, especially when the variability of atmospheric inputs are taken into account.

Base cation and Si loss rates reported here are approximately two to three orders of magnitude lower than those reported for the SDEF oak and pine soils by Quideau et al. (1996) using a mass-balance, solid-phase approach. Including plant uptake values reported in that study would still result in weathering rates at least an order of magnitude lower than those reported by Quideau et al. (1996). The disparity may result from differences in the temporal scale addressed by the studies. The previous study based weathering rates on changes in the exchangeable, nonexchangeable, and aboveground biomass pools over the entire life of the experiment. The data may reflect extremely high initial weathering rates of minerals with fresh surfaces exposed by mixing of the fill material during construction of the lysimeters (Quideau et al., 1996). The solution data presented here reflect current processes and indicate that the weathering rate has drastically decreased over the 50 years since vegetation was established on the biosequence soils.

Large fluxes of dissolved organic carbon (DOC) are also important because organic acids affect mineral weathering. Increased rates of mineral weathering have been reported in the presence of low molecular weight organic acids (Amrhein and Suarez, 1988; Lundström and Öhman, 1990), larger molecules such as fulvic acid extracted from soil (Kodama et al., 1983), organic acids from pine roots and fungi grown in the laboratory (Boyle and Voigt, 1973), DOC in stream and soil water (Lundström and Öhman, 1990), and DOC in soil and peat extracts (Lundström and Öhman, 1990; Heyes and Moore, 1992). Although the mean DOC concentrations at 7.5 cm under oak and 10 cm under pine were not significantly different, differences in mean pH (5.7 for pine and 6.1 under oak) and color of the soil solutions suggest that the organic compounds present in each solution are of different composition. Dissolved organic carbon may contribute to increased mineral weathering under pine and/or a difference in the stoichiometry of weathering between pine and oak (Quideau et al., 1996). Higher weathering rates under pine, despite larger inputs of base cations in atmospheric deposition, which helps meet plant demand, suggest that organic acids play a large role in weathering reactions within the pine soil. The composition of DOC in soil solutions, as influenced by vegetation type, was not addressed by this study but deserves further attention with regard to its effect on mineral weathering.

6. Conclusions

Canopy processes are different between the vegetation types. Within the pine canopy, the interception of atmospheric deposition is a more important process than canopy leaching, and composition of the pine throughfall reflects the cationic signature of precipitation. Within the oak canopy, leaching alters the base cation composition compared to bulk precipitation. Litter leachate provides nutrients to the soil surface that appear to be quickly recycled within the oak system. The fluxes of K from the litter layer to the mineral soil are responsible for an increase in mica relative to vermiculite within the clay fraction of the A horizons over a 40-year period.

The rapid return of nutrients under oak decreases the release of base cations from the exchangeable and nonexchangeable pools, thereby resulting in weathering rates that are almost 40 times less (based on Si fluxes) than under pine. Tight nutrient cycling would give chaparral species, such as scrub oak that have evolved on soils that are relatively nutrient poor, a competitive advantage, suggesting a strong positive interaction between plant survival strategy and mineral weathering. Together, the data show that through biogeochemical processes, vegetation type can have a profound impact on nutrient loss. Differences in base cation cycling within oak and pine systems strongly suggests that the impact of atmospheric deposition may differ between species and may lead to relatively fine-scale differences in soil fertility.

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