

Atmospheric Input of Some Cations and Anions to Forest Ecosystems in North Carolina and Tennessee

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The atmospheric contributions of elements in precipitation and dry fallout to forest ecosystems were measured at two sites in the southern Appalachians. At both sites, relative mean annual concentrations of cations in bulk precipitation were in the order $\text{Ca} > \text{Na} > \text{K} > \text{Mg}$. At the Coweeta Hydrologic Laboratory in North Carolina, average annual inputs of Ca^{++} , Na^+ , K^+ , Mg^{++} , and $\text{NH}_4\text{-N}$ in 1970–1973 were 4.88, 3.52, 1.62, 1.01, and 0.52 kg/ha/yr, respectively. At Walker Branch, Tennessee, the inputs of these elements during the same time period were 15.73, 3.89, 2.99, 2.94, and 2.37 kg/ha/yr. The inputs of $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, and Cl^- in 1972–1973 were 2.88, 0.19, and 8.53 kg/ha/yr at Coweeta. Inputs of $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ were 4.61 and 0.55 kg/ha at Walker Branch over the same period. One reason for differences in bulk precipitation chemistry was greater dry fallout for some cations at Walker Branch than at Coweeta. For both sites, dry fallout associated with local land use activities influenced seasonal concentrations of bulk precipitation except for Na^+ , which appeared to be partly derived from marine sources. Total inputs of elements are considered to be minimum estimates for both forest ecosystems due to sampling and analytical methods.

Experimental watersheds have been used to study biogeochemical processes within landscapes and for evaluating their response to manipulations by man [Likens et al., 1970; Johnson and Swank, 1973; Henderson and Harris, 1975]. A principal consideration in such studies is the chemical composition of the atmosphere because it contributes large quantities of materials to the land surface [Whitehead and Feth, 1964; Gambell and Fisher, 1966; Fisher et al., 1968].

As part of the U.S. International Biological Program in the Eastern Deciduous Biome, the U.S. Atomic Energy Commission and the U.S. Department of Agriculture (USDA) Forest Service are examining fluxes of nutrients in biotic and abiotic compartments of forest ecosystems on experimental watersheds. The overall objective is to quantitatively describe and account for the biogeochemical behavior of forest ecosystems at several scales of area and complexity [Burgess and Swank, 1972]. In this report we compare precipitation chemistry over 1- to 3-year periods at two sites in the southern Appalachian Mountains. The concentrations and weights of calcium, sodium, potassium, magnesium, ammonium and nitrate nitrogen, phosphorus, and chloride deposited by both rainfall and dry particulate fallout are reported.

SITE DESCRIPTION AND METHODS

Both experimental sites lie within the Appalachian Highlands Physiographic Division, but they are located in different physiographic provinces: The Coweeta Basin, a research facility of the Forest Service, USDA, is in the Blue Ridge Province. Elevations range from 685 to 1592 m, and the vegetation is predominantly an oak-hickory forest. Bedrock is Carolina gneiss of pre-Cambrian origin which includes granite, diorite, mica gneiss, and mica schist. The watershed is semi-isolated from urban and industrial activity, and the closest large city is Asheville, North Carolina, 80 km to the northeast (Figure 1). The Walker Branch catchment is a research site of the Oak

Ridge National Laboratory and is within the Ridge and Valley Province. Elevation ranges from 265 to 360 m. The watershed is predominantly forested, and oaks, hickories, yellow poplar, and pine account for over 75% of the 21-m²/ha basal area. It is underlain by a 1000-m-thick sequence of siliceous dolomite of the Knox group. The catchment lies 32 km west of Knoxville, Tennessee (Figure 1).

The climate at the two sites borders on the humid subtropical and marine classifications of Trewartha [1954]. Summers are moderately cool with higher temperatures at Walker Branch, and winters are mild with lower temperatures at Coweeta. The mean annual temperature is 12.8°C at Coweeta and 14.5°C at Walker Branch. Precipitation at both locations is distributed rather uniformly throughout the year and averages at least 7 cm each month. Mean annual precipitation at Coweeta varies from 250 cm on the upper slopes to 170 cm at the lower elevations in comparison to a 137-cm mean at Walker Branch. Snow typically comprises less than 5% of the annual precipitation at both sites.

Nutrient input to a watershed is measured as the dissolved form in precipitation (wetfall) and as dry particulate fallout (dryfall) or a combination of these two sources, referred to as bulk precipitation [Whitehead and Feth, 1964]. Bulk precipitation samples at Coweeta are collected weekly from modified water trap-type gages [Likens et al., 1967] which are 1.25 m above the ground and located at standard precipitation gaging sites that have a 45° sky view from the gage orifice. The water trap was eliminated and the collection vessel insulated and buried in the ground to prevent concentration of samples by evaporation. Also, an aluminum screen (7 mesh per cm, rinsed in 5% acetic acid and then in distilled water) was inserted in the funnel drain to reduce contamination problems associated with debris collecting in the traps. During warm months, 1 ml of a 1000-ppm solution of phenylmercuric acetate is added to each gage. Field tests show that the preservative inhibited biological transformations. Precipitation samples are collected over the entire 2185-ha Coweeta Basin, but for this report,

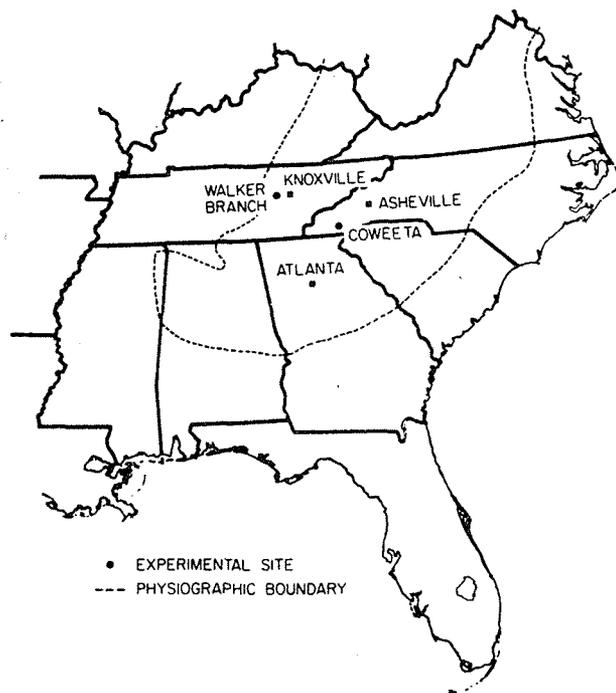


Fig. 1. Location of the two experimental sites within the Appalachian Highlands and the closest cities.

average concentrations are given for eight gages from four different locations at the lower elevations. Previous analysis showed that it is appropriate to average gage values to determine bulk precipitation chemistry for a watershed at Coweeta [Johnson and Swank, 1973]. Areal precipitation received by an experimental watershed at Coweeta is estimated by an isohyetal weighting method [Swift, 1968]. Dryfall is collected in two Wong Model ARC Mark V collectors which automatically close to exclude rain or snow. These gages are located at the base of the Coweeta Basin. Samples are recovered weekly in 500 ml of deionized water by scrubbing and rinsing the collection vessel. Total nutrient input to a watershed is taken as the product of precipitation volumes and chemical concentrations. Precipitation values reported in this paper are for watershed 18, a 12.5-ha control watershed covered with a mixed deciduous forest.

At Walker Branch, samples of materials from dryfall and precipitation are collected at five sites over the 97.5-ha catchment area. The samples are collected with modified Wong samplers. These samplers are 1.25 m above the ground and 17–21 m from the nearest trees. Dryfall collectors remain open at all times except when it rains, whereas the precipitation (wetfall) collectors are open only when it is raining. The dryfall collectors contain about 250 ml (500 ml during the summer) of 0.1 N HCl to prevent resuspension of deposited materials. Samples are collected weekly, and precipitation collections are filtered through Whatman number 1 filter paper prior to chemical analysis. Dryfall samples are digested with hydrogen peroxide (H_2O_2) to oxidize organic materials, and cations are acid extracted with 1.0 N HCl. The sample is passed through a Millipore filter prior to analysis, and the residue is dried and weighed. The weighted average precipitation received on the catchment is estimated by the Thiessen [1911] polygon method. Bulk precipitation concentrations are calculated from dryfall and wetfall determinations.

Analytical procedures are similar at both sites. Concentra-

tions of Ca^{++} , Mg^{++} , K^+ , and Na^+ are determined by atomic absorption spectrophotometry following standard procedures. Lanthanum or strontium is added to samples prior to Ca^{++} and Mg^{++} determinations to eliminate interference with these cations. The automated spectrophotometric methods used for anion determinations are ammonium nitrogen by the Berthelot reaction at Coweeta and indophenol blue at Walker Branch, nitrate by reduction to nitrite and reaction with sulfanilamide, orthophosphorus by the molybdate blue method, and chloride by the ferricyanide method (all of these according to the Technicon autoanalyzer methodology [Technicon Industrial Systems, 1971] or the Environmental Protection Agency [1971]). Most methods referenced have been modified to improve detection of low anion concentrations [McSwain, 1973].

Dry fallout samples at Coweeta are extracted with water, while Walker Branch dry fallout is digested and extracted with acid. Thus it was important in the interpretation of results to define the effect of differences in sample preparation on chemical concentrations. The H_2O_2 digestion-HCl extraction method was applied to dry fallout samples at Coweeta over a 3-month period, and Ca^{++} , Mg^{++} , K^+ , Na^+ , and PO_4-P concentrations were compared to water-extracted determinations. Nitrate nitrogen and NH_4-N were not compared because these ions are not measured in dry fallout at Walker Branch. The digestion procedure gave concentration values about double the water soluble concentrations for Ca^{++} , Mg^{++} , and K^+ , but no change in Na^+ was observed. Since dry fallout of these materials comprises a relatively small portion of the bulk precipitation chemistry at Coweeta, differences between sites due to sample treatment are of minor significance when considering the large contrasts in precipitation chemistry between sites. However, the digestion treatment increased PO_4-P concentrations ninefold and is a primary reason for site differences in P described later.

RESULTS AND DISCUSSION

Site comparisons on annual basis. Annual precipitation and input of elements for both sites are given in Table 1. The 189 cm of precipitation at Coweeta in 1971–1972 was slightly above the 30-year average of 181 cm on watershed 18. The other 2 years are much wetter than average; the 245 cm in 1972–1973 is the wettest year on record. Most of the excess rain came during the spring months. At Walker Branch the 138 cm of precipitation during 1970–1971 and 1971–1972 was close to the annual average of 137 cm, but like Coweeta, the 183 cm in 1972–1973 was the wettest year on record since 1948.

The relative contribution of cation input at each site was similar, with $Ca > Na > K > Mg > NH_4-N$ (Table 1). However, inputs of most cations were considerably greater at Walker Branch than at Coweeta. At Walker Branch the quantity of Ca^{++} was about 3 times that at Coweeta; multiples for Mg^{++} , K^+ , NH_4-N , and Na^+ were 2.5, 2, 5, and 1, respectively. Site differences are even greater when weighted concentrations are compared because of differences in annual precipitation. Except for Na^+ the concentrations of cations in bulk precipitation at Walker Branch were 2.5–6 times greater than concentrations at Coweeta. Less anion data are available, but the relative inputs of anions at both sites were $NO_3-N > PO_4-P$ (Table 1). Concentrations of these anions at Walker Branch were 2–5 times those at Coweeta. Of all ions considered at Coweeta, Cl^- was the most abundant.

A major reason for the difference in the chemistry of bulk precipitation between sites is found in dry fallout contributions (Table 2). Dry fallout of Ca^{++} , K^+ , and Mg^{++} at Walker

TABLE 1. Annual Precipitation, Elemental Input, and Weighted Concentration of Elements in Bulk Precipitation (Wetfall and Dryfall) on Coweeta, North Carolina, and Walker Branch, Tennessee, Catchments

Water Year (June-May)	Annual Precipitation, cm	Ca		Na		K		Mg		NO ₃ -N		NH ₄ -N		PO ₄ -P		Cl	
		kg/ha	mg/l	kg/ha	mg/l	kg/ha	mg/l	kg/ha	mg/l	kg/ha	mg/l	kg/ha	mg/l	kg/ha	mg/l	kg/ha	mg/l
<i>Coweeta</i>																	
1970-1971	204	6.83	0.33	3.85	0.19	2.16	0.11	1.46	0.07
1971-1972	189	3.21	0.17	1.58	0.08	0.90	0.05	0.98	0.05
1972-1973	245	4.61	0.19	5.12	0.21	1.79	0.07	0.90	0.04	2.88	0.12	0.52	0.02	0.19	0.007	8.59	0.35
	213*	4.88*	0.23*	3.52*	0.17*	1.62*	0.08*	1.11*	0.05*
<i>Walker Branch</i>																	
1970-1971	138	13.74	1.00	3.52	0.26	3.06	0.22	2.46	0.18	0.48	0.04
1971-1972	138	14.35	1.04	2.81	0.20	2.43	0.18	1.94	0.14	0.50	0.04
1972-1973	183	19.09	1.04	5.31	0.29	3.48	0.19	4.42	0.24	4.61	0.25	2.37	0.13	0.68	0.04
	153*	15.73*	1.03*	3.89*	0.25*	2.99*	0.20*	2.94*	0.19*	0.55*	0.04*

*Annual mean.

Branch exceeded the total input of these ions from all sources at Coweeta. Dry fallout contributed 28-64% of the cation input of Walker Branch compared to 19-31% at Coweeta. The percent differences in dry fallout contributions between sites would be smaller if methods of sample preparation were the same. The Walker Branch watershed is near electric generating plants that burn coal, and microscopic examination of the residue from filtered samples showed that dryfall contains siliceous fly ash. Although the chemical composition of coal varies with source, the concentration of metals is high [Capes *et al.*, 1974]. Furthermore, the quantity of dry fallout deposition at Walker Branch is quite large. Following dryfall digestion and extraction, the residue input over a 2-year period averaged 78 kg/ha/yr compared to preliminary estimates of 14 kg/ha/yr at Coweeta. This dry fallout input at Walker Branch is about double the sediment losses from undisturbed watersheds at Coweeta [Johnson and Swank, 1973].

Coweeta data show that dry fallout contributes only 7-12% of the anion input. Only PO₄-P data are available at Walker Branch; 90% of the total input of this element is from dry fallout. This is in contrast to only 10% for PO₄-P at Coweeta and partly reflects the difference in sample treatment; i.e., the H₂O₂ digestion at Walker Branch probably oxidizes the organic forms of P, and the acid treatment dissolves some mineral P.

Seasonal site comparisons. Seasonal distributions for the

ions were initially examined by correlating the monthly input of each element in bulk precipitation with the total monthly precipitation. At Coweeta the only cation that consistently showed strong correlation over the 3-year period was Na⁺ with *r* values ranging from 0.65 to 0.73. Correlations for the other cations were inconsistent between years, and *r* values were generally less than 0.50. For anions the quantity of Cl⁻ and NO₃-N was strongly correlated with precipitation quantities (*r* values of 0.74 and 0.84), but only 1 year of data was available for the analysis. Correlation for all ions was poorer at Walker Branch than at Coweeta. Sodium had the highest *r* values, but they ranged from 0.33 to 0.63. Collectively, the results of correlation analysis suggest that, except for Na⁺, the monthly deposition of cations is weakly associated with monthly precipitation at both sites. Furthermore, it appears that when dry fallout is a major constituent of bulk precipitation chemistry, the association between amount of precipitation and element input is poorer. These results partly agree with findings in the northeastern United States [Pearson and Fisher, 1971]. Based on the annual relationship between element input versus yearly precipitation they found that the quantity of ions such as Ca⁺⁺, K⁺, and Mg⁺⁺, which enter bulk precipitation primarily as dry fallout, were independent of precipitation amount. Also, the input of dissolved substances such as Na⁺ and Cl⁻ from sea-salt aerosols varied regularly with precipitation amount near the coast, but further

TABLE 2. Annual Input in Kilograms per Hectare of Elements in Dry Fallout to Forest Ecosystems at Coweeta and Walker Branch Catchments

Water Year (June-May)	Ca	Na	K	Mg	NO ₃ -N	NH ₄ -N	PO ₄ -P	Cl
<i>Coweeta</i>								
1970-1971	0.83(12)	0.52(14)	0.59(27)	0.15(10)				
1971-1972	0.64(20)	0.46(29)	0.30(33)	0.18(18)				
1972-1973	1.40(30)	0.72(14)	0.61(34)	0.27(30)	0.21(7)	0.11(21)	0.02(10)	1.02(12)
	0.96(21)*	0.61(19)*	0.51(31)*	0.20(19)*				
<i>Walker Branch</i>								
1970-1971	5.21(38)	0.99(28)	1.83(60)	1.32(54)			0.42(88)	
1971-1972	6.57(46)	0.99(35)	1.75(72)	1.06(55)			0.45(91)	
1972-1973	5.69(30)	1.11(21)	2.13(61)	1.34(30)			0.60(88)	
	5.82(38)*	1.03(28)*	1.90(64)*	1.24(46)*			0.49(89)*	

Values in parentheses are percent dryfall in bulk precipitation.

*Annual mean.

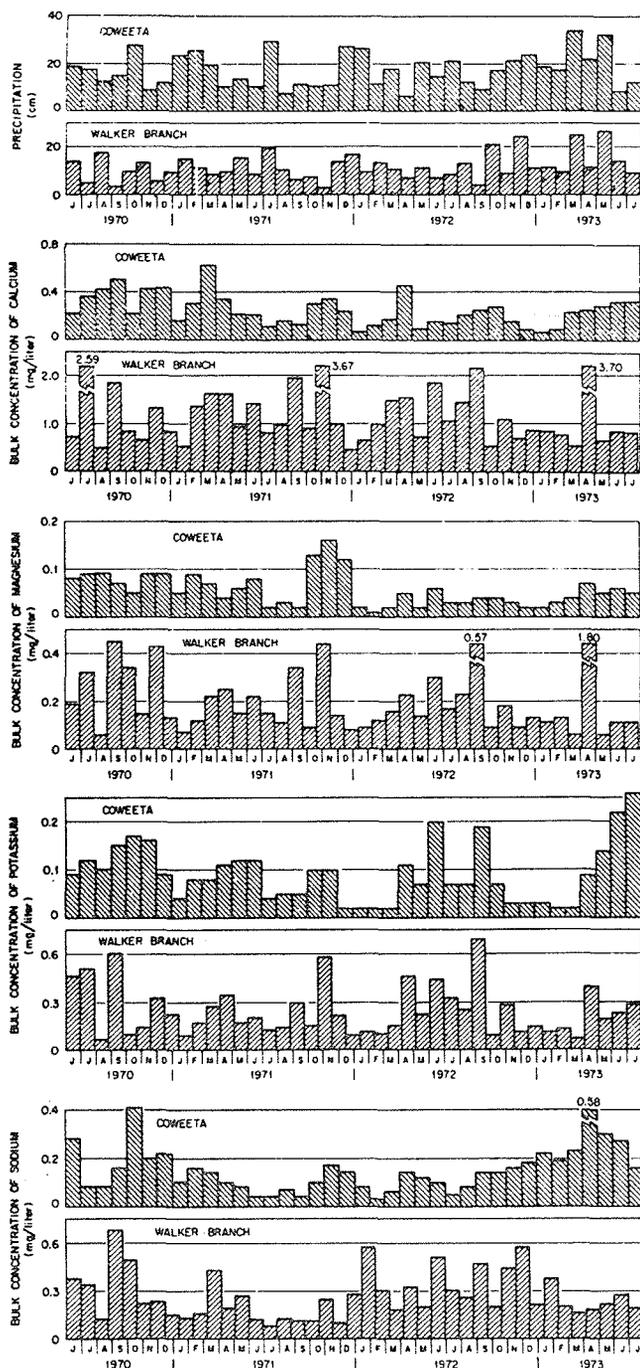


Fig. 2. Periodic weighted concentration of cations in bulk precipitation at Coweeta and Walker Branch. Concentration scales are different at the two sites.

inland these two ions were independent of precipitation amounts. Although Coweeta is located about 450 km from the ocean, sea-salt aerosols may be a primary source of Na^+ and Cl^- at the site and could also be a source of Na^+ at Walker Branch.

The seasonal pattern of bulk precipitation chemistry was further examined by plotting periodic, weighted average concentrations of cations at both sites (Figure 2). Coweeta data are monthly values (12/yr), while the Walker Branch data are for 4-week periods (13/yr). Although the data appear to be highly variable, trends in concentrations were observed at both sites. Calcium, Mg^{++} , and K^+ concentrations were generally highest during March–June and lowest during Decem-

ber–February. A second peak concentration also occurred for some of these cations during the fall. Sodium concentrations were more variable at both sites and did not show a consistent year-to-year pattern. High Na^+ concentrations frequently occurred during winter but also occurred at other times of the year. *Gambell and Fisher* [1966] reported similar seasonal patterns of Ca^{++} concentrations in eastern North Carolina and southeastern Virginia but found higher K^+ concentrations during the summer and highest Mg^{++} concentrations during late fall and early spring. The concentrations at Walker Branch were higher and more variable than those at Coweeta. This greater variability appears to be due to the relatively greater influence of dry fallout at Walker Branch (Table 2). The influence is especially evident during periods which receive little precipitation (e.g., July and September 1970, October and November 1971, and September 1972), an observation similar to that of *Gambell and Fisher* [1966]. The higher precipitation and smaller dry fallout at Coweeta resulted in smaller monthly variations and lower concentrations.

The seasonal input of elements contained in dry fallout (Figure 3) is similar in pattern to concentration trends of bulk precipitation. Inputs of Ca^{++} , Mg^{++} , and K^+ as dry fallout to Walker Branch were generally higher during spring and summer than during fall and winter. At Coweeta, inputs of these elements peaked in spring and fall. We suggest that these patterns of dry fallout deposition are related to local activities induced by man. Since one source of dry fallout at Walker Branch is fly ash, the seasonal inputs may be associated with demands for electricity. On the land surrounding Coweeta, agricultural practices dominate land use. Spring plowing usually begins in the latter part of February if weather permits, peaks in March, and is largely complete by May or early June. Light burning of fields to eliminate weeds is common in spring; burning of fields, brush, and leaves in the fall months is also common. Specific examples of the impact of these practices on elemental input have been observed. March of 1973 was extremely wet, with 34 cm of rainfall. Many of the plowing and burning activities were delayed until late spring and early summer when high loads of dry fallout deposition were observed. In June and July, Ca^{++} and K^+ inputs averaged about 0.11 and 0.09 kg/ha, respectively, some of the highest values recorded for that time of year. During the last week of June, heavy ash fallout accompanied brush burning in the valley below the experimental basin. This event produced the highest observed concentrations of K^+ in bulk precipitation and dry fallout.

Our seasonal data on bulk precipitation concentrations and dry fallout inputs support the hypothesis that nonmarine processes largely control the deposition of Ca^{++} , Mg^{++} , and K^+ but have less influence on Na^+ in this region of the United States [*Gambell and Fisher*, 1966]. Other investigators have discussed factors influencing ions in the atmosphere [*Gorham*, 1961; *Junge*, 1963] and the need to separate local deviations in precipitation chemistry from the background chemistry [*Voronkov*, 1968; *Selezneva*, 1972]. Our results emphasize the need to carefully examine the contributions of dry fallout to the chemical loads in forested ecosystems. Total inputs presented for Walker Branch and Coweeta are considered to represent minimum values at these sites for two reasons. First, it is apparent for some elements that digestion and acid extraction of dry fallout samples yield higher concentrations than water extraction. Since large quantities of particulates are scavenged during rainfall, digestion would elevate concentrations for this component of atmospheric input. Second, most of the dry

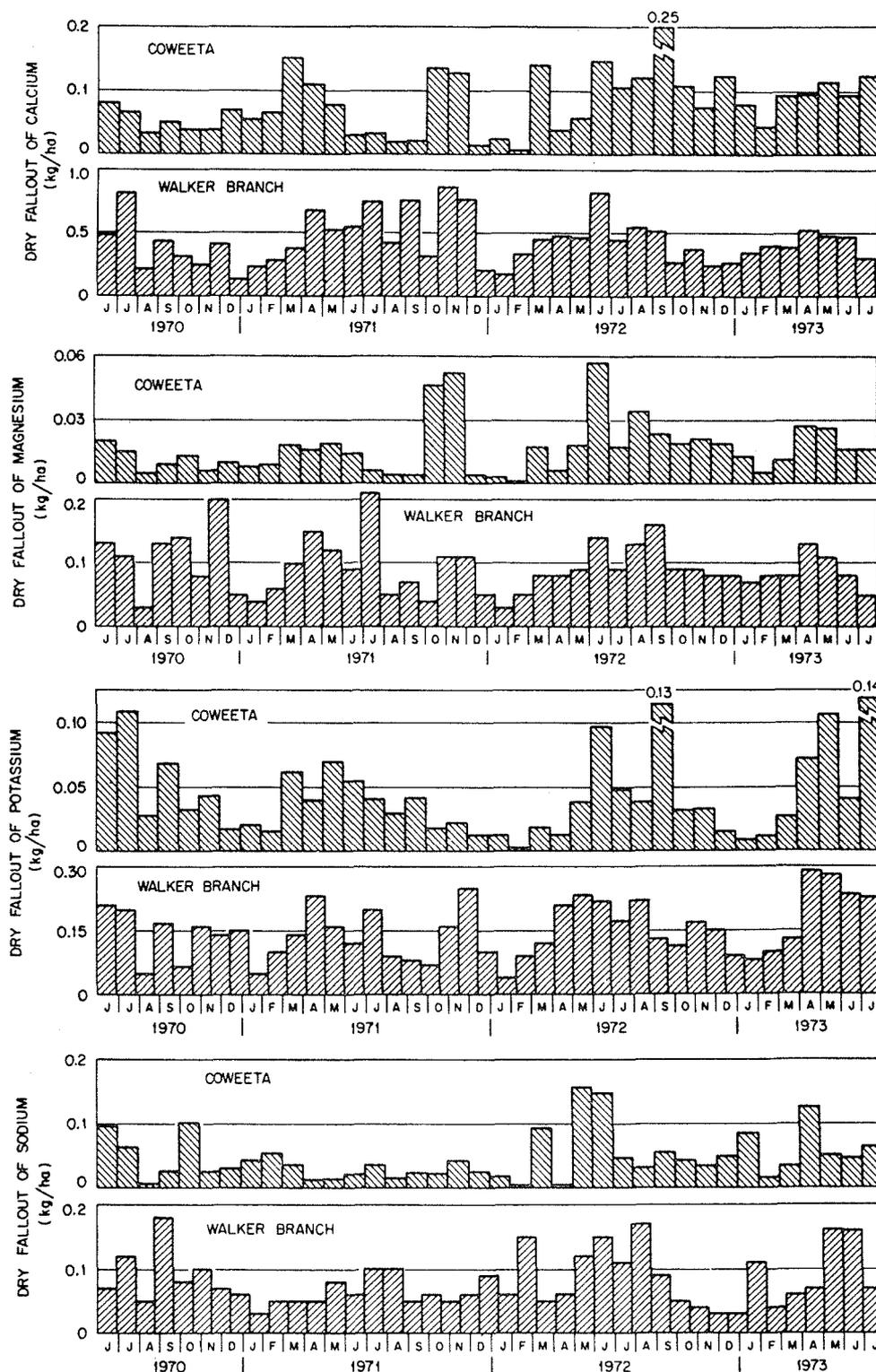


Fig. 3. Periodic input of cations in dry fallout at Coweeta and Walker Branch. Input scales are different at the two sites.

fallout deposited in collectors is probably through the process of gravitational settling and represents only one mechanism for deposition of materials on surfaces [George and Poehlein, 1974]. Since the ratio of forest vegetation surface to ground surface ranges between 5 and 20 to 1 [Swank and Schreuder, 1973], aerosol impaction on vegetation [Eriksson, 1955] could account for large inputs not measured in this study.

In view of the dry fallout contribution noted at Walker Branch and the effect of dry fallout on seasonal concentrations

of bulk precipitation at both sites, it is desirable to quantify other processes that remove aerosols from the lower atmosphere.

CONCLUSIONS

The chemistry of bulk precipitation at two sites in the southern Appalachians showed that the relative contributions of cations were similar, with $\text{Ca}^{++} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{++} > \text{NH}_4\text{-N}$; for anions measured at both sites, $\text{NO}_3\text{-N} > \text{PO}_4\text{-P}$. At

Walker Branch, Tennessee, however, the average annual weighted concentrations of ions were 2–6 times greater than at Coweeta Hydrologic Laboratory, North Carolina. A major reason for higher concentrations at Walker Branch was the large dry fallout inputs, some in the form of fly ash produced by coal-burning power-generating plants. The impact of land use activities such as plowing and burning on precipitation chemistry was observed at Coweeta. Seasonal data on bulk precipitation concentrations and dry fallout inputs suggest that nonmarine processes largely control the deposition of Ca^{++} , Mg^{++} , and K^+ , while Na^+ is primarily of marine origin in this region of the United States. Our results show the importance of quantifying the contributions of dry fallout to the chemical loads in forest ecosystems and suggest the need to examine the magnitude and chemical composition of aerosol impaction on vegetation surfaces.

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