

Atmospheric Precipitation as a Source of Nutrients in Chaparral Ecosystems¹

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During fires a large quantity of essential plant nutrients, particularly nitrogen, may be lost from terrestrial ecosystems to the atmosphere (Raison 1979). These losses have been quantified in chaparral ecosystems (DeBano and Conrad 1978, DeBano et al. 1979), as have the losses in erosion and runoff following fire (DeBano and Conrad 1976). The marked response of *Adenostoma* chaparral to nitrogen fertilization (Hellmers et al. 1955) has led to the widespread recognition of nutrient limitations to growth in chaparral soils. If fires are frequent, large losses could deplete chaparral sites of nitrogen at a more rapid rate than it is replenished by atmospheric deposition and by nitrogen-fixing species such as *Ceanothus*.

Over the past several years we have studied the rate of deposition of nutrients from the atmosphere in the chaparral near Santa Barbara, CA. The goal of these studies was to compare the annual deposition of nutrients to the typical losses in runoff and to the nutrient requirements for growth in mature chaparral. Our data also allow a calculation of the time needed to replenish the exacerbated losses which occur as a result of fire. In our early studies, we collected rainfall and dry fallout together in open funnels (Schlesinger and Hasey 1980); more recently we have separated these deposition processes by collections using an automatic rain collector. Here we report on our recent work, and we review sources of similar data in California.

METHODS AND MATERIALS

We established a research site on the south slope of the Santa Ynez Mountains (Los Padres

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Abstract: Precipitation and dry fallout were collected over a 2-year period at a remote site in the Santa Ynez Mountains, Santa Barbara County, California, USA and analyzed for nutrient content. Mean annual depositions of Ca (2.2 kg/ha), K (0.7 kg/ha), NH₄-N (0.5 kg/ha), and NO₃-N (1.5 kg/ha) were largely derived from dryfall; depositions of Na (7.2 kg/ha) and Mg (1.2 kg/ha) were important in both rainfall and dry fallout. These inputs are equal to or larger than the typical losses reported in runoff from mature chaparral, but these values imply that long periods are necessary to replace losses measured in volatilization and exacerbated runoff after fire.

National Forest) at 850 m elevation and approximately 10 km north of the Pacific Ocean near Santa Barbara, CA. The site was 3 km west of the transect of sites used for precipitation collections in related studies (Schlesinger and Hasey 1980, 1981). While these sites are close to the ocean, the south slope of this mountain range receives little direct deposition of salt spray and marine aerosols (Ogden 1975, p. 205-206). Direct on-shore winds are predominant only during the arrival of winter synoptic storms from the Pacific Ocean. The site is remote from anthropogenic sources of atmospheric constituents.

Over a 25-month period we measured precipitation in individual rainstorms using a standard U.S. Weather Bureau 8" (20.3 cm) diameter rain-gage. Monthly total airflow was measured with a recording 3-cup anemometer mounted 2 m above ground-level. A continuous record of air temperature and relative humidity was obtained using a sheltered hygrothermograph (Weathermeasure Model H311), but these data are not reported in the present paper.

We used an automatic rain collector (Aerochem Metrics Model 101), electronically sensitive to precipitation events, to collect nutrient deposition in rainfall and dry fallout in separate (28-cm diameter) plastic buckets. This rain collector was originally designed by the U.S. Atomic Energy Commission and tested favorably in the trials reported by Galloway and Likens (1976) and Bogen et al. (1980). The plastic buckets were washed with 50 percent HCl and rinsed 5 times with deionized water. They were transported to the field in plastic bags. At the end of each storm and at the end of each month, the wetfall bucket was replaced with a clean collector, the volume of precipitation was recorded, and an aliquot of the precipitation was saved for analysis. At the end of each month, the dryfall collector was rinsed with 250 ml of glass-distilled water which was saved for analysis; thus, our analyses include only those ions that are dissolved when dryfall is leached with distilled water (fraction 2 of Lewis and Grant 1978). A clean dryfall bucket was placed in the rain collector at this time.

During 15 months of the study, we also collected bulk precipitation using the rain collector designed and tested by Likens et al. (1967, 1977) to collect a composite sample of rainfall and dry fallout at the Hubbard Brook Ecosystem in New Hampshire. This collector consisted of a 10-cm diameter polypropylene funnel connected to a 1-liter polypropylene bottle with tygon tubing. It was acid-washed, rinsed, and replaced in the field after each storm. It was also rinsed at the end of each month.

The various samples were analyzed for Ca, Mg, K, and Na as described in Schlesinger and Hasey (1980). During the second year of study, the samples were also analyzed for NH_4^+ -N and NO_3^- -N as described in Schlesinger and Hasey (1980). Analyses for the nitrogen constituents were performed as soon as possible after collection, usually within 24 hours; thus, no preservatives were used in the collectors. For each rainfall event, concentrations of ions (mg/l) in the wetfall and in the Hubbard Brook collector were multiplied by the volume of precipitation, converted to $1/\text{m}^2$ based on the area of the collector surface, to calculate total deposition (mg/m^2). Concentrations in the water used to rinse the dryfall collector were converted to dry deposition based on the volume of rinse water and the area of the collector.

In this paper we use the term "bulk precipitation" to refer to collections made using the Hubbard Brook collector. "Total deposition" refers to the sum of "wet deposition (wetfall)" and "dry deposition (dry fall)," as collected in the automatic rain collector. When data are treated as monthly depositions, it should be remembered that these are derived from summing the collections and calculations for the individual rainstorms during the month.

RESULTS AND DISCUSSION

Long-term measurements compiled by the National Oceanic and Atmospheric Administration for Santa Barbara (elevation 3 m) indicate a mean annual rainfall of 45 cm. Sites in the coastal mountains of southern California generally receive greater rainfall than lower elevations along the coast (Bauer 1936, Miller and Poole 1979, Schlesinger and Hasey 1980), but the influence of local topography on rainfall patterns often results in only a weak correlation of increasing rainfall with increasing elevation in the mountains. Santa Barbara County records show a mean annual rainfall of 77 cm for a 33-year period at San Marcos Pass (700 m elevation), along the ridgetop of the Santa Ynez Mountains 2.5 km west of our study site. During the 2 years of study, we recorded 76 and 111 cm of rainfall in the U.S. Weather Bureau gage.

Because of progressive atmospheric cleansing during large storms, the concentrations of ions in precipitation often decrease during the dura-

tion of rainfall (Junge 1963, Georgii and Wotzel 1970, Gatz and Dingle 1971, Kennedy et al. 1979). Thus, concentrations are higher in rainfall collections from small storms than from larger storms. To express rainfall concentrations, many workers use weighted average concentrations, calculated by dividing the total deposition in a collection period (mg/m^2) by the total volume of precipitation recorded ($1/\text{m}^2$). Table 1 shows the annual weighted average concentrations (mg/l) in wetfall for the various ions for the 2 years of study. Not surprisingly for this coastal site, Na and Mg are dominant ions, reflecting their abundance in sea water from which aerosols and rainfall nuclei are commonly formed (Gorham 1961).

We found only non-significant negative linear correlations between the ionic concentrations in the wetfall collections and increasing precipitation volume. The correlations between log-concentration and precipitation were usually stronger (higher r); these correlation coefficients (r) were -0.60^* for Ca, -0.01 for Mg, -0.53^* for K, $+0.12$ for Na, -0.82^* for NH_4^+ -N and -0.60 for NO_3^- -N. Thus, those ions derived from continental and terrestrial sources (e.g., Ca and K, Gorham 1961) show a stronger tendency to be cleansed from the atmosphere during rainfall than those derived from the ocean. This conclusion is directly opposite from that of Kennedy et al. (1979) in an analysis of rainfall chemistry in northern California; however, we feel that our results are likely to be more typical for precipitation derived from maritime aerosols.

In most regions the concentrations of Na and Cl in precipitation can be used as an index of the relative importance of the sea as a source of dissolved constituents in rain and of aerosols for raindrop nuclei. Sodium may be slightly preferred over Cl, for some Cl is apparently also derived from continental or anthropogenic sources (Likens et al. 1977, Kennedy et al. 1979). Recognizing the possibility that various ions might be fractionated during the production of marine aerosols (e.g., Glass and Matteson 1973), one assumes that all Na is ocean-derived and that the oceanic contribution of other ions will be in a ratio similar to sea water. In the present study the Ca/Na ratio for the weighted average concentrations of these ions in wetfall suggests slight enrichment of the Ca ion in rainfall; Ca/Na is 0.06 in wetfall vs. 0.04 in sea water (Mason 1966, p. 195). Ratios for Mg/Na (0.13) and K/Na (0.03) in wetfall show no indication of enrichment of these ions compared to sea water ratios of 0.13 and 0.04, respectively. Comparisons using ratios of nitrogen are not usually made because of the labile nature of these constituents. Further indication of the enrichment of Ca from continental sources is shown in figure 1, which includes the concentrations of Ca and Na in individual wetfall samples. For most samples, the Ca values lie above a line representing the Ca/Na ratio in sea water, especially in small storms with rela-

* significant at $P < 0.05$

Table 1--Concentrations and depositions of nutrient ions in wet- and dryfall from the atmosphere in the Santa Ynez Mountains. All calculations have been rounded.

	Rainfall	Ca	Mg	K	Na	NH ₄ ⁺ -N	NO ₃ ⁻ -N
Weighted average concentrations in wetfall (mg/l)							
1978-1979		0.03	0.06	0.01	0.44	-	-
1979-1980		0.03	0.06	0.02	0.49	0.02	0.03
Annual depositions in wetfall (mg/m ²)							
1978-1979	76	24	43	5	336	-	-
1979-1980	111	28	70	24	542	17	25
Annual deposition in dryfall (mg/m ²)							
1978-1979		123	45	46	185	-	-
1979-1980		256	74	60	384	35	128
Total deposition (mg/m ² /yr)							
1978-1979		147	88	51	521	-	-
1979-1980		284	144	84	926	52	153
Mean annual deposition, this study (mg/m ²)		216	116	68	724	52	153
Mean annual deposition, extrapolated from Schlesinger and Hasey (1980) (mg/m ²)		140	80	40	610	10	90
Overall mean annual deposition (mg/m ²)- 3 years		190	104	58	688	31	121

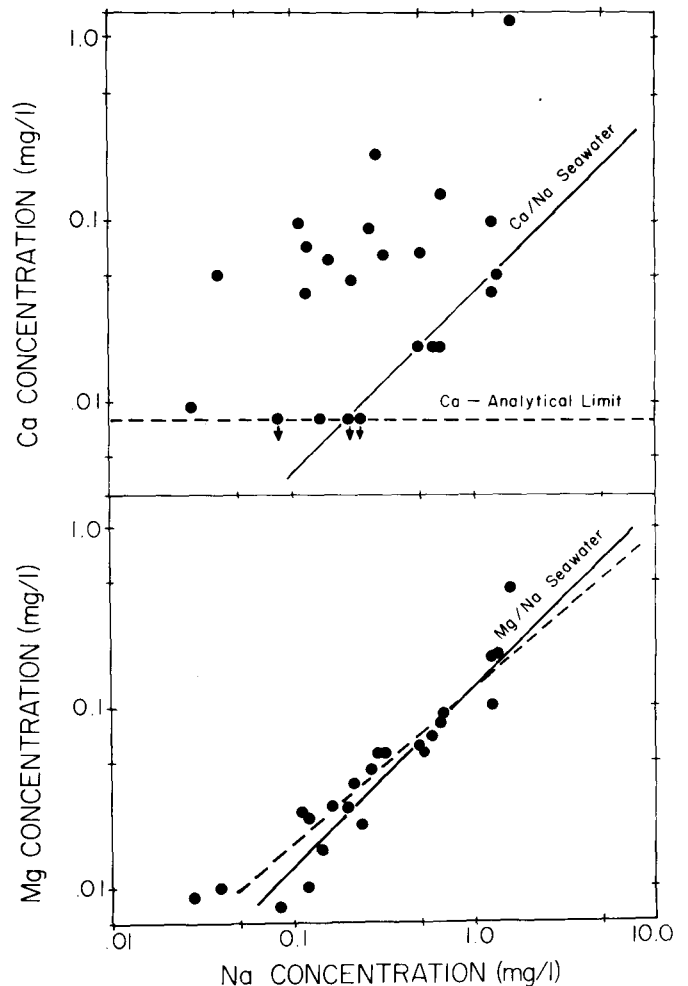
¹ data in cm.

tively high concentrations of Ca. In comparison, the Mg values lie closer to the Mg/Na ratio in seawater over the full range of concentrations recorded.

In an earlier study (Schlesinger and Hasey 1980), very strong enrichment of Ca and K and slight enrichment of Mg were observed in bulk precipitation (rainfall + dry fallout) collections in the Santa Ynez Mountains. While our present data for wetfall show enrichment for Ca, it is now obvious that most of the enrichment in the bulk precipitation values was due to contributions from dryfall in those collections.

Total annual deposition of ions in wetfall and dryfall collections is given for the 2 years of study in table 1. In accordance with our interpretation of the sources of ions in wetfall collections, the depositions of Ca, K, NH₄⁺-N and NO₃⁻-N in dry fallout are much larger than the deposition in wetfall, while for Na and Mg the opposite is true. The semi-arid climate of southern California allows for long periods of

Figure 1--(Right) Concentrations of Ca and Mg in the wetfall precipitation of individual storms in the Santa Ynez Mountains, California, plotted as a logarithmic function of Na concentrations. In both cases the solid line represents the ratio of these ions to Na in seawater. For Mg, the dashed line is the least-squares-fit linear regression to the data (F = 143, P(0.0001, r²=0.88). The equivalent regression for Ca is not significant.



soil drying and dispersion of soil dust by wind. Thus, there is a strong terrestrial influence on deposition which is manifest in the abundance of dryfall as well as in the enrichment of Ca and K in wet deposition. The large amount of NO_3^- -N in dryfall confirms earlier reports of its importance as a form of nutrient deposition from the atmosphere in chaparral systems (Christensen 1973, Schlesinger and Hasey 1980, also Hart and Parent 1973).

Dry fallout is derived from a number of processes including long range atmospheric transport and the suspension of soil particles from the local environment. We attempted to separate the importance of the suspension of soil dust from the local area, by expressing monthly dryfall deposition as a function of monthly windflow and using the Y-intercept of this regression to represent dry sedimentation in conditions of no wind (cf. Munn and Rodhe 1971). Unfortunately, none of these regressions was statistically significant. During the course of our study there were few fires in the Santa Ynez Mountains; we noted no unusual depositions of nutrients during one large fire in October 1979, such as have been reported in studies in other regions (Clayton 1976).

Monthly deposition in wetfall and dryfall is summed to give monthly total deposition. Total monthly depositions are significantly correlated with monthly precipitation for most ions; the correlation coefficients are higher for Mg ($\underline{r} = 0.89^* \pm .17$) and Na ($\underline{r} = 0.93^* \pm .12$) than for Ca ($\underline{r} = -0.06 \pm .20$), K ($\underline{r} = 0.77^* \pm .12$), NH_4^+ -N ($\underline{r} = 0.52 \pm .30$) and NO_3^- -N ($\underline{r} = 0.69^* \pm .20$), though the 95 percent confidence intervals show overlap among some pair-wise comparisons. The magnitude of these coefficients suggests the extent to which monthly depositions vary between the wet and dry seasons in California. Thus, Na and Mg, which are not diluted by increasing rainfall volume, tend to be derived from precipitation in winter storms, whereas dryfall is important for the latter group. The low correlation coefficient for Ca suggests substantial deposition in months with little or no rain, presumably as a result of more airborne dust from local soils.

Total monthly deposition values were summed to give yearly deposition (table 1). Depositions are higher during 1979-1980, reflecting the greater rainfall received, but also as a result of greater dryfall. Together with the annual deposition values extrapolated from 1977 collections by Schlesinger and Hasey (1980), these values give an indication of the annual range in deposition to be expected in the chaparral of the Santa Ynez Mountains. As shown later, the variation is relatively insignificant when the importance of atmospheric deposition is assessed in terms of other nutrient fluxes in these ecosystems.

*P < 0.05

Comparison Between Collectors

The Hubbard Brook collector as developed by Likens et al. (1967, 1977) has been widely used in their ecosystem studies in New Hampshire to collect "bulk precipitation," the composite of wet and dry processes as defined by Whitehead and Feth (1964). As a result of the reliability of the Hubbard Brook collector and other advantages, Galloway and Likens (1976, 1978) advocate its use and employ it as a standard for the comparison of more elegant collectors. In the present study, the volume of precipitation per storm measured by the U.S. Weather Bureau raingage was highly correlated with the volume measured by both the wetfall bucket of the automatic rain collector ($\underline{r} = 0.99$) and the Hubbard Brook collector ($\underline{r} = 0.99$), but these collectors underestimated the volume by an average of 6 percent and 8 percent, respectively, over the range of storms sampled. In a recent comparative study, Bogen et al. (1980) also found that this model of automatic rain collector underestimated rainfall by 4 percent.

For ions other than Na and Mg, we found poor correlations between the total monthly deposition as measured in the Hubbard Brook collector and the sum of wet and dry depositions in the automatic rain collector (table 2). An initial interpretation of the data suggests that the Hubbard Brook gage and the automatic rain collector differ mainly as a result of different efficiency of collection for elements with a strong dryfall component. For most ions the automatic rain collector records higher depositions at the lower range of depositions, but the opposite is true at higher levels of deposition (cf. magnitudes of slope and intercept

Table 2-- Correlation between monthly depositions (mg/m^2) received in the Hubbard Brook collector (bulk precipitation) and in the sum of wet and dry fall (total deposition) in the automatic raingage. Slope and intercept are the factors "m" and "b" in the linear equation:

$$\text{"Total deposition} = m (\text{bulk precipitation}) + b."$$

The converse model offers no different interpretations of data. Also given are weighted average concentrations (mg/l) in bulk precipitation.

	Ca	Mg	K	Na	NH_4^+ -N	NO_3^- -N
r	0.48	0.98*	-0.10	0.95*	0.48	0.84*
Slope	0.32	0.70*	-0.03	0.79*	1.17	0.84*
Intercept	13.44	2.10	7.51	2.16	1.49	4.07
Weighted Average Concentrations	0.20	0.15	0.14	0.94	0.02	0.12

* P < 0.05

Table 3-- Sources and loss of nutrients from chaparral ecosystems.

Process	Ca	Mg	K	N	P
Input:	-----kg/ha/yr-----				
Precipitation ¹	1.9	1.0	0.6	1.5	-
N-fixation ²	-	-	-	1.1	-
Outputs, mature stand:					
Runoff ³	0.9	0.6	0.6	0.3	0.1
Outputs, post-fire:					
Runoff ³	67	32	27	15	3.5
Volatilization ⁴	-	-	48	146	-
Indicated Replacement time for first year losses after fire (yr)	35	32	125	62	

¹Present Study

²Kummerow et al., 1978; Ellis, pers. comm., 1980

³DeBano and Conrad 1976

⁴DeBano and Conrad 1978

in table 2). For Na and Mg, however, the Hubbard Brook collector yielded higher estimates of deposition than the automatic rain collector over most of the range of depositions recorded. Bogen et al. (1980) found that for various ions the automatic rain collector recorded depositions typically 10 percent lower than other collectors. We make no presumptions as to which collector is the more accurate, but in view of the increased sophistication and interpretation to be gained from the separation of deposition processes, the automatic rain collector seems preferable despite its higher cost. Notwithstanding, the annual weighted average concentrations calculated for the bulk precipitation collector in this study (table 2) are similar to those measured using these collectors in an earlier study in the Santa Ynez Mountains (Schlesinger and Hasey 1980).

NUTRIENT BALANCE IN CHAPARRAL ECOSYSTEMS

In mature chaparral there is a large pool of most nutrients in the soil, but in the case of nitrogen, only a small portion is potentially mineralizable and available for plant uptake (Marion et al., in press). Nevertheless, atmospheric deposition can contribute only a small portion to the annual uptake of nutrients from the

soil in mature chaparral. For example, in *Adenostoma* chaparral in San Diego County, annual uptake of nitrogen is estimated at 3.4 to 8.2 g/m² (Mooney and Rundel 1979, Marion et al., in press). In the Santa Monica Mountains of Los Angeles County, Gray (1981) measured 7.5 g/m²/yr nitrogen uptake from the soil to the aboveground portion of a 22-year-old stand of *Ceanothus megacarpus*. In both cases, the uptake greatly exceeds the estimated total atmospheric deposition of 0.1 to 0.2 g/m²/yr.

If our results are representative of various chaparral areas in southern California, the total atmospheric deposition of nutrients equals or exceeds the annual losses which have been reported in runoff from mature, undisturbed chaparral (e.g., table 3). The thick charcoal-rich varves in the sediments of the Santa Barbara Basin are indicative of the large losses of debris following fires in the chaparral through many millennia (Byrne et al. 1977). DeBano and Conrad (1976, 1978) have measured the losses of nutrients by volatilization in fire and by accelerated runoff after fire for a typical stand of burned chaparral in Santa Barbara County (table 3). The losses greatly exceed the annual inputs from the atmosphere and indicate that more than 60 years may be needed to replenish the nitrogen losses from a single fire. A long replacement time is also indicated for K, based on atmospheric sources; however, substantial quantities of this element are also likely to be replenished by mineral weathering, which is not yet quantified for chaparral ecosystems. Considering chaparral ecosystems on a regional basis, it would be instructive to know the extent to which volatile losses in burned areas result in added deposition in adjacent unburned areas.

There are a number of ways in which these estimates should be improved, including continued regional monitoring and increased study of the importance of nitrogen-fixing processes. To the extent that atmospheric deposition of nutrients is derived from soil dust suspended from the local area, estimates of the atmospheric deposition of ions are greater than the actual input of new quantities of these elements for plant growth. Unfortunately, there is no obvious way to eliminate this overestimate. On the other hand, estimates of deposition derived from open collectors are underestimates to the extent that chaparral shrubs intercept aerosols and fog water from the horizontal airstream (Schlesinger and Hasey 1980).

Atmospheric pollution by oxides of nitrogen which are later deposited as NO₃⁻-N in rainfall may have a stimulating effect on chaparral growth in nutrient-poor sites. Morgan and Liljestrand (1979) reported rainfall concentrations for a variety of sites in the Los Angeles Basin; in the San Gabriel Mountains, concentrations of NH₄⁺-N and NO₃⁻-N in wetfall were 25 and 10 times higher than our values for the Santa Ynez Mountains. The effects of this additional nutrient input, balanced against deleterious effects such as rainfall acidity, have yet to be evaluated.

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