Precipitation Chemistry and Nutrient Loading by Precipitation in a Tropical Watershed

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Bulk precipitation samples were taken weekly on the shore of Lake Valencia, Venezuela, over a period of 2 years. All samples were analyzed for total particulates, particulate carbon, hydrogen, nitrogen, and phosphorus, major soluble cations and anions, and soluble nitrogen, phosphorus, and carbon compounds. Total insoluble particulate material reaching the watershed averages 139 kg/ha/yr, of which about 25% is organic and 75% inorganic. The total loading rate of insoluble particulates is dramatically higher during the 100-day dry season than during the remaining portion of the year. The dry season increase in total insoluble particulates is entirely attributable to the inorganic fraction, however, as the particulate carbon and nitrogen loading actually decreases during the dry season. Total loading rates for soluble constituents are generally within the upper range of values reported in the literature for the temperate zone. In terms of equivalents the order of total annual loading rates for soluble cations is Na⁺ > Mg²⁺ > Ca²⁺ > H⁺ > NH₄⁺ > K⁺. For soluble anions the order of loading is HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻ > PO₄³⁻. Organic nitrogen and organic phosphorus account for major portions of the total nitrogen and phosphorus loading. Soluble silicon loading is quite low. The loading rates of all soluble components on a weekly basis are much higher during the wet season than during the dry season except for soluble inorganic phosphorus, which shows evidence of association with the inorganic particulate fraction that begins to peak during the dry season. There are striking seasonal peaks in the loading rates for almost all precipitation components. Except for soluble inorganic phosphorus and insoluble particulates, which begin to peak well before rains start, the peaks occur very abruptly with the first rains. At this time, as much as 15% of the total annual loading may occur in a flush lasting 1 or 2 weeks. Removal of nitrogen oxides is particularly dramatic and can lead to the development of very acid rainfall at this time (pH < 4.0). Considerable combustion of vegetation occurs toward the end of the dry season and appears to contribute significantly to the buildup of large atmospheric burdens of materials that are removed during the first few rains. A components of variance analysis shows that within the wet season the total amount of rainfall in a given week is the most important variable explaining week-to-week variation in loading rates. After the first week or two of flushing there is some continued seasonal decline in loading of some components, but the trend is weak. The amount of insoluble particulate material in a given week during the rainy season accounts for negligible amounts of variance in loading of solutes except for calcium and phosphate, which show suggestive associations with particulates. The radical seasonal changes in loading rates, the flushing effect just at the beginning of the wet season, and the role of combustion in seasonally augmenting loading rates are all factors of possible general importance in the tropics wherever extended dry seasons occur.

INTRODUCTION

Precipitation is a major source of nutrients and ions for both terrestrial and aquatic systems [Hutchinson, 1954; Gormham, 1958; Likens et al., 1977]. This subject has been little studied in the tropics. Important published studies covering a significant time span include those of Jordan et al. [1972] for Puerto Rico, B. L. Haines (unpublished manuscript, 1979) and Jordan et al. [1979] for the Venezuelan Amazon, Amazoniana [1972] for the Brazilian Amazon, and Visser [1961] for Uganda. All of these studies are very selective in their coverage of chemical components of precipitation. Comprehensive analysis of precipitation at single sites in the tropics appears to be entirely lacking at present. The climates and biological activity patterns at low latitudes may create atmospheric loading regimes considerably different from those of the temperate zone, but the base of information is still too small to permit much generalization.

The present work deals with precipitation chemistry at Lake Valencia, Venezuela. Because the total chemical loading is of primary interest, the analysis deals exclusively with bulk precipitation, which is the composite of wet and dry precipitation [Whitehead and Fehr, 1964]. Collections were made continuously over a 2-year period beginning in early 1976 and were analyzed for a wide variety of substances at weekly intervals.

WATERSHED DESCRIPTION

The Lake Valencia watershed lies in the Aragua Valley of northern Venezuela (Figure 1). Watershed elevations range from 404 m, the current level of Lake Valencia, to slightly over 1800 m at the peak of the coastal mountain chain to the north. The area of the watershed is approximately 3000 km². Its natural vegetation is tropical deciduous forest at the lower elevations and rain or cloud forest at the higher elevations, although the watershed has for the most part been deforested. The average annual rainfall at lake level is 700–800 mm/yr, which is very unevenly divided between a dry season and a rainy season.

Sugar cane and some other row crops are extensively cultivated in the lowland areas of the Aragua Valley. The mountainous sides of the watershed are little used for agriculture and are minimally used for pasture because of the predominance of tough grasses. The watershed has a relatively high population density (~400 individuals/km²) centered on the cities of Maracay and Valencia near the lake (Figure 1). The valley is a light industrial as well as agricultural center. There is considerable automobile traffic in the two major cities and on the perimeter road that follows the lake shore-
line. Major air pollution from point sources is not obvious, although extensive burning of the vegetation during the dry season releases large amounts of smoke that markedly reduce visibility at that time of year. Winds blow predominantly from the east, but reconstruction of true wind trajectories would be difficult because of the complicating effects of surrounding mountains.

METHODS

Bulk precipitation samples were collected with a large Plexiglas funnel (collecting area, 0.23 m²) mounted 3 m from the ground surface. The use of such a large collector, described by Lewis and Grant [1978], is essential if the nutrient loading is to be quantified on a weekly basis. The collector was situated on a small hill very near the lakeshore at an elevation of 415 m (Figure 1). The area 25 m around the collector was cleared of tall vegetation (>1 m). There were no roads or agricultural activities within 1 km of the collector. Activities within a 5-km radius included a highway and some vegetable and cane farming. The nearest village was 10 km distant. Eighty percent of the area in a 5-km radius was lake surface or undisturbed deciduous forest.

Samples were collected every week. Rain funneled into a nylon screen of 1-mm mesh and then through a coiled piece of rubber tubing, which served as a vapor barrier, into a clear borosilicate bottle enclosed in a dark bag. When the sample was collected, the surface of the collector was rinsed with 500 ml of distilled water to remove dry fallout that had collected since the last rainfall. The rinse was collected separately from the accumulated rain, and the two were mixed together after determination of the pH and alkalinity. When there was no rain in the bottle, the pH and alkalinity of the rinse water were measured.

All time-sensitive analyses were completed on the day of sample collection. Particulate and dissolved components were separated by filtration through clean glass fiber paper (Whatman GF/C, effective pore size ~2 μm). The filters, which had been preweighed, were dried at 105°C and reweighed to give the dry weight of particulate material. Subsamples were then taken for carbon-hydrogen-nitrogen (CHN) analysis using a CHN analyzer on duplicate or triplicate subsamples of the original particulate material. Another portion of the filter was used in a determination of insoluble particulate phosphorus by sulfuric acid digestion with selenium and heat sufficient to clear the sample. The digest was analyzed by the phosphate technique of Murphy and Riley [1962]. A test of the efficiency of this method with rock and tissue standards showed that the digestion efficiency exceeded 95%.

The dissolved fraction was processed as follows. Cations were determined by atomic absorption, sulfate was determined by a barium chloride precipitation method [Golterman, 1969], and bicarbonate was determined by acid titration to a pH of 4.4. Silicates were determined by a molybdate method [Armstrong and Butler, 1962]. Nitrate was determined by cadmium-copper reduction of the sample followed by formation of an azo dye [Bendschneider and Robinson, 1952; Wood et al.,
1967]. Ammonia was determined by a modified phenol-hypochlorite technique [Solorzano, 1969; Koroleff, 1976], and soluble reactive phosphorus was obtained by an ascorbic acid method [Murphy and Riley, 1962]. Dissolved organic carbon was computed from absorbance according to the equation of Lewis and Canfield [1977], and dissolved organic nitrogen and phosphorus were obtained by ultraviolet combustion of the sample [Manny et al., 1971] followed by reanalysis for nitrogen and phosphorus constituents.

Chloride analysis was done by a mercuric thiocyanate method [U.S. Environmental Protection Agency, 1979] at longer intervals (monthly) than the other analyses. The data on chloride will thus be sufficient to permit computation of total annual loading but not detailed enough to show patterns through time.

Since the samples were collected at only one site, spatial heterogeneity of loading rates may be of some concern. Variance in loading rates on a particular week is of two types: error variance and spatial variance. Error variance includes variance due to collection technique at a particular site and analytical variance. Since errors are subject to control by the investigator, it is assumed here that they are not a major cause for concern, especially in view of the very large number of analyses which are averaged to produce the annual loading rate figures.

Spatial variance, which may be considerable, is of two types: fixed and ephemeral [cf. Lewis, 1978]. Ephemeral spatial variance on a particular week is caused by random patchiness in bulk precipitation over the watershed. Fixed spatial variance, on the other hand, is due to patchiness in the average loading rates at different sites. A point source of pollution may generate fixed spatial variance, whereas the ephemeral component of spatial variance is more likely to be due to random variation in the amount of rainfall or other weather variables.

Little is known about the relative importance of fixed and ephemeral components of spatial variance in various kinds of watersheds. It is highly likely, however, that the ephemeral component will be dominant in explaining total spatial variance. This is particularly true if the sampling interval is short, as is the present study. The fixed component may prove to be of interest where point sources of pollution are present, however.

Fixed and ephemeral patchiness have been studied in a Rocky Mountain watershed by collection methods identical to those used in the present study [Grant and Lewis, 1980]. The ephemeral component of variance was dominant; the fixed component was essentially nonexistent. In a given week, two

| TABLE 1. Average Chemical Composition of Insoluble Particulate Material in Bulk Precipitation Reaching the Aragua Valley, Venezuela |
|-----------------|------------------|----------------|----------------|
| Fraction        | Amount, kg/ha/yr| Percentage of Total Particle Weight | Relative Variability, CV, % ((S/Â·X) Â· 100) |  
| Total           | 139              | 100.0          | 97             |  
| Total organic   | 39               | 28.0           |                |  
| Total inorganic | 100              | 72.0           |                |  
| C               | 19.6             | 14.1           | 53             |  
| H               | 3.25             | 2.33           | 47             |  
| N               | 2.35             | 1.70           | 67             |  
| P               | 1.18             | 0.85           | 102            |  

Determinations are weekly for 100 weeks.

| TABLE 2. Loading Rates for Various Soluble Components of Bulk Precipitation in the Lake Valencia Watershed as Determined From Weekly Samples Over 100 Weeks |
|-------------------------------|-----------------|-----------------|-----------------|
| Input                         | Input           | Variability, CV, % ((S/Â·X) Â· 100) |  
| Kg/ha/yr                      | Eq/ha/yr        |                              |  
| Ca++                         | 8.60            | 430                          | 84              |  
| Mg++                         | 5.47            | 450                          | 100             |  
| Na+                          | 16.6            | 721                          | 111             |  
| K+                           | 4.28            | 109                          | 127             |  
| H+                           | 0.32            | 322                          | 451             |  
| HCO₃⁻                        | 50.0            | 820                          | 110             |  
| SO₄²⁻                        | 16.3            | 338                          | 100             |  
| Cl⁻                          | 19.2            | 540                          |                |  
| PO₄³⁻                        | 0.30            | 29                           | 121             |  
| NO₃⁻                        | 1.28            | 91                           | 142             |  
| NO₂⁻                        | 0.050           | 4                            | 121             |  
| NH₄⁺                        | 2.43            | 173                          | 168             |  
| DOC                          | 13.4            |                              | 109             |  
| DON                          | 1.33            |                              | 136             |  
| DOP                          | 0.196           |                              | 180             |  
| Si                           | 1.106           |                              | 122             |  

DOC, DON, and DOP are dissolved organic carbon, nitrogen, and phosphorus. * Estimate based on a smaller number of samples (monthly).

stations 1 km apart and slightly different in elevation produced on the average a deviation of about 30% with respect to their common mean for a variety of chemical constituents. Over a period of several weeks, however, and particularly in seasonal or annual averages, the loading rates for stations at different locations in the same watershed were virtually identical.

The present analysis is based on the assumption that fixed spatial variance is negligible. If this is the case, then a series of samples taken sequentially at one station through time provide statistically meaningful replication in both time and space. The statistical validity of 100 weekly samples taken at one station is essentially identical to that of 50 samples taken on alternate weeks at two different stations over the same period or less frequently over a network of stations. If the samples are spread through space rather than through time, there will be greater resolution on individual collection dates, but the trend between collection dates will not be as well resolved. The reverse is true if the samples are spread extensively through time but not through space. The present collection method, which is time-intensive, precludes exact quantification of total watershed loading on any given week because of ephemeral spatial variance. The emphasis is instead placed on seasonal averages, annual averages, and trends, which are well resolved by the time-intensive sampling.

RESULTS

Table 1 summarizes the percentage chemical composition of insoluble particulate material in bulk precipitation and the associated loading rates. On the assumption that approximately 50% of the dry weight of organic material is carbon [Winberg, 1971], particulates are also broken down into total organic and total inorganic fractions. About three quarters of the particulate material is inorganic, and the other quarter is organic. Table 1 shows that phosphorus is the most variable of the two analyzed fractions of particulate material.

Table 2 summarizes loading rates for soluble materials. Anions total 83% of cations, indicating acceptable internal analytical consistency. The failure of an exact cation-anion match
loading and the accompanying changes in percentages of carbon, nitrogen and phosphorus in the particulate component. Important features of Figure 3 include (1) major seasonal change in total particulate loading and (2) major seasonal change in relative chemical composition of particulates.

Figure 4 summarizes the weekly loading rates for major metal cations. Pronounced seasonal patterns are evident. During the dry season the loading rates tend to be low. There is an abrupt increase in weekly loading rate for all four cations just at the start of the rainy season, followed by a quick decline, after which little trend is evident for the rest of the rainy season. Even after the early decline, wet season loading rates are higher than those of the dry season.

Figure 5 shows the seasonal changes in major anions and silicic acid. Bicarbonate shows low during dry season loading and higher during wet season loading. The wet season loading rates are not so uniformly high for bicarbonate as they are for the major metal cations, however. Also, the loading patterns for bicarbonate differ from those of major metal cations in that bicarbonate is attributed to the limited amount of chloride data and possible slight underestimates of sulfate, for which the analytical methods are marginally satisfactory.

Cation abundance by equivalents is Na⁺ > Mg²⁺ > Ca²⁺ > H⁺ > NH₄⁺ > K⁺. Anion abundance by equivalents is HCO₃⁻ > Cl⁻ > SO₄²⁻ > NO₃⁻ > PO₄³⁻. There is a reasonable match of average chloride and sodium loading on an equivalent basis, but this is misleading. The match of the two ions is not at all good on a week-to-week basis, indicating different sources for a significant proportion of these ions.

Total loading rate for dissolved organic carbon is very close in magnitude to particulate carbon loading (Table 1). Dissolved carbon compounds in the bulk precipitation have a nitrogen content not greatly different from that of organic matter derived from organisms (e.g., 12:1 by weight for phytoplankton [Parsons et al., 1977]), whereas dissolved organic phosphorus is present in considerably smaller amounts in relation to C and N than one might expect in living organisms. For phosphorus the order of relative abundance of fractions is particulate > soluble inorganic > soluble organic. For nitrogen the order is soluble inorganic > particulate > soluble organic.

The dissolved silicon loading rate is low. Dissolved silicon may be in part produced by artificial weathering [cf. Likens et al., 1977; Lewis and Grant, 1978]. The contact between inorganic particulates and accumulated rainfall in the collection vessel over the course of a week may lead to the solution of measurable amounts of silicon, as does the slow reaction of rainwater with the borosilicate collection vessel. The estimated dissolved silicon loading rate should thus be considered only as an upper bound for true soluble silicon loading.

Figure 2 summarizes seasonal weather changes which might affect loading rates. It is clear from the figure that the year is sharply divided into two seasons. A dry season spans the period between December and May, when the average wind strength is high and there is virtually no rain, and the rest of the year is marked by calmer weather with at least some rainfall every week.

Figure 3 shows the change through time of total particulate

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**Fig. 2.** Changes in weather on the shoreline of Lake Valencia during the study period.

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**Fig. 3.** Weekly changes in total particulates and the carbon, nitrogen, and phosphorus components of insoluble particulates reaching the Lake Valencia watershed during the study period. Dashed lines separate the seasons. Carbon, nitrogen, and phosphorus are reported as percentages of the total dry weight of insoluble particulates.
loading for the 1–3 weeks following the onset of the rainy season is not always extraordinarily high but rather varies between average and exceptionally low. The peculiar variation in early wet season loading of bicarbonate is explained by the fact that bicarbonate loading is actually a composite variable, reflecting not only the terrestrial sources of carbonates but also the sources of strong mineral acids which can convert bicarbonate to CO₂.

Sulfate shows evidence of a seasonal pattern similar to that of the major metal cations, but the details are less clear, because during 1977, measurements were made only at monthly intervals. There is an anomalous point just prior to the beginning of the wet season in 1978. This point, which is not associated with any measurable rainfall, is not an analytical error, as the accompanying bicarbonate loading is nil and the acidity is very high, indicating the presence of significant amounts of sulfuric acid. The cause of this particular event is not clear.

Nitrate also follows the seasonal pattern of major metal cations but shows an especially exaggerated bunching of high loading rates toward the beginning of the wet season. The peaks are closely related to increased loading rates for the hydrogen ion in both years, especially 1977 (Figure 6). The nitrate is derived from nitrogen oxides converted to nitric acid by rain [Lewis and Weizman, 1980]. The effect of this acid on hydrogen ion loading depends on the amount of bicarbonate available to neutralize the hydrogen ions. In 1977 the amount of nitric acid greatly exceeded the bicarbonate buffer capacity, leading to very low pH. In 1978 the bicarbonate buffer was sufficient to reduce the effect, although there was still an abrupt increase in hydrogen ion loading.

Nitrite loading rates are not graphed, as they follow the pattern of nitrate but are much lower and thus not quantitatively very significant as a source of inorganic nitrogen or as a contributor of anions to the total ionic balance (Table 2).

Silicon, which is actually a very minor anion, is also shown in Figure 5. Silicon would be present principally in the form of undissociated silicic acid at the pH values typical of bulk
Soluble inorganic phosphorus shows a pattern that is very different from that of other soluble substances (Figure 6). Loading rates begin to increase halfway through the dry season from an essentially zero baseline. This continues to the transition between the wet and dry seasons and reaches a peak at the onset of the wet season. High loading rates do not persist but die off to the zero baseline by the time the rainy season is half elapsed.

Dissolved organic carbon shows the same seasonal trends that have been documented for most major anions and cations (Figure 7). Loading rates are high during the wet season and lower during the dry season, and there is a flushing effect just following the onset of the wet season. Dissolved organic nitrogen and phosphorus both show higher loading rates during the wet season than during the dry season, but a flushing effect is not obvious for these.

**DISCUSSION**

**Evaluation of Total Annual Loading Rates**

The results are of interest as an indication of the total annual supply of ions from the atmosphere to the lake and its watershed. For the terrestrial portion of the system, interpretation is not straightforward. It is customary to treat bulk collections as net loading, yet some fraction may be locally cycled inside the watershed, and the terrestrial surface may trap substances much more efficiently than a collector (see overviews by Gorham [1976], Likens et al. [1977], and Lewis and Grant [1978]). These effects tend to cancel each other, but their quantitative importance is not well known. We therefore take the measured loading rates only as a first approximation of the absolute terrestrial loading from the atmosphere. For the lake, evaluation of the data in this context is less equivocal, as there is little reason to suspect that major fractions of

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**Figure 6.** The pH and weekly loading rates of hydrogen ion, ammonia, and molybdate-reactive (soluble) phosphorus over the study period.

**Figure 7.** Loading rates of soluble organic carbon, nitrogen, and phosphorus over the study period.
<table>
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<th>Table 3. Summary of Selected Data on Chemical Loading Rates in Temperate and Tropical Regions (Kilograms per Hectare per Year)</th>
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<tr>
<td></td>
<td>Total Insoluble Particulates</td>
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<tr>
<td></td>
<td>Total Carbon</td>
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<tr>
<td>South America</td>
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<tr>
<td>Lake Valencia</td>
<td>139</td>
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<tr>
<td>Amazon Basin, Brazil</td>
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<tr>
<td>Amazon Basin, Venezuela</td>
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<td>Africa</td>
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<td>New Hampshire forest, Hubbard Brook</td>
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<td>Colorado Mountains, Como Creek</td>
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<tr>
<td>Ontario shield, ELA/</td>
<td>115</td>
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POC is particulate organic carbon; DOC, DOP, and DON are dissolved organic carbon, phosphorus, and nitrogen. ELA is the Experimental Lakes Area.

° From Amazoniana [1972] except as noted.
°° From Nye and Greenland [1960].
° From Jordan et al. [1979].
°° From Visser [1961] except as noted.
° Average of values from Jones [1960] and Thornton [1965], rainy season only.
° Jones [1960].
°° Likens et al. [1977].
° Based on preliminary unpublished studies (G. E. Likens, personal communication, 1980).
° Grant and Lewis [1979].
°° Schindler et al. [1976].
the chemical components are cycling from lake to atmosphere and back to lake, thus falsely inflating net input. Furthermore, some careful empirical work by Volchok et al. [1970] indicates minimal scavenging ability for water surfaces, so that the collector may approximate actual loading rather well.

It is difficult to put the Lake Valencia annual loading rates into proper context, as the background of information is very poor for the tropics and spotty even for the temperate zone. Table 3 offers selected figures, including some of the most comprehensive data available, on loading rates in tropical and north temperate regions.

Major ion loading for Valencia is generally in the middle to upper range of reported loading rates for other sites in either tropical or temperate localities (Table 3). An interesting exception is documented by the recent work of Jordan et al. [1979], which indicates much higher loading for several major ions in a high-rainfall area of the Venezuelan Amazon than at Lake Valencia or the other areas given in Table 3.

Total nitrogen loading at Lake Valencia is in the middle range of reported values and agrees well with the conclusions that can be drawn from the work of Eriksson [1952], based on widely scattered older literature: ammonia plus nitrate loading in the tropics is generally less than 7 kg/ha/yr as nitrogen. The Valencia data share with the other tropical figures in Table 3 a predominance of ammonia over nitrate. Temperate sites show the opposite tendency. There may exist latitudinal trends in the ratio of ammonia to nitrate in precipitation [see Eriksson, 1952], but this is presently difficult to judge. The data of Junge [1958], in particular, indicate the importance of regional soil types and biotic activity in regulating the total amounts and ratios of inorganic nitrogen compounds.

Lake Valencia is comparatively more extreme in soluble inorganic phosphorous and total phosphorus loading than in nitrogen loading (Table 3). The P:N ratios are 5 times higher for Valencia than for the Canadian Experimental Lakes Area, where phosphorus limitation is pronounced. High values of PO₄ P are also reported by Jordan et al. [1979, Table 5] for the Venezuelan Amazon, but these are so much in excess of the values from Lake Valencia or any other locality as to suggest the influence of major local sources not typical of other areas that have been studied, including Lake Valencia.

Total atmospheric organic carbon transport in the Valencia area is obviously not quantitatively significant by comparison with carbon fixation in either terrestrial or aquatic environments of the watershed (>5000 kg/ha/yr net for Lake Valencia), nor is the total carbon transport by this route particularly high by comparison with other sites that have been studied. The same is true of total insoluble particulates, despite the dry season peak in this component.

In the Lake Valencia watershed the hydrogen ion loading rate (820 eq/ha/yr) is quite high in view of the fact that the bicarbonate loading rate is high (820 eq/ha/yr). This is possible because of the alternation of a season having low hydrogen ion/high bicarbonate loading rates with a season having high hydrogen ion/low bicarbonate loading rates. This marked alternation contrasts with known temperate sites, where the hydrogen ion loading rate is typically more uniform across months [e.g., Likens et al., 1977]. Net hydrogen ion transfer through the air on an annual basis is obviously lower than the extremes would suggest because of the ultimate combination of the hydrogen ion equivalents with the bicarbonate equivalents. Acidity may still be seasonally significant to the biota, of course, in an acute sense [Gorham, 1976].

**Contrasts in Wet and Dry Season Loading Rates**

The relative weekly loading rates for the dry and wet seasons are summarized in Table 4. The dry season rates exceed those of the wet season for only two precipitation components: total particulates and soluble inorganic phosphorus.
For total particulates the dry season loading rates are higher, specifically because of higher amounts of insoluble mineral particles. There is no corresponding increase in the total particulate carbon, hydrogen, nitrogen, or phosphorus loading during the dry season. In fact, there is a substantial dry season decrease in loading for these, indicating that moisture is important either for the generation (e.g., by stimulation of biological activity) or for the removal of airborne organic particulates as distinct from mineral particulates.

Figure 3 would suggest that 30–50% of the particulates is accounted for by organic matter during the wet season, as compared with 10% or less during the dry season. The percentages of carbon and nitrogen are well balanced if both are accounted for by particles of rather ordinary organic matter, but the percentage of phosphorus is considerably higher than one would expect on this basis. Although this might be taken as an indication of an inorganic contribution for particulate phosphorus, there is no supporting evidence that inorganic particulates are generally high in phosphorus. In fact, when the wet season is over, amounts of inorganic particulates begin to rise, but the percentage of phosphorus and total phosphorus transport fall abruptly. High amounts of particulate phosphorus thus definitely do not originate from generalized mineral or soil sources but must be accounted for the special high-phosphorus organic particulates or special inorganic sources that are effective only in the wet season. The mechanism responsible for phosphorus enrichment of particulates in the wet season could obviously be quite important for the transport of phosphorus.

In summary, for the transport of potentially important nutrients (N, P) in insoluble particulate form to the lake the wet season is much more important than the dry season despite large amounts of particulates that are transported during the dry season, as dry season particulates are extremely poor in nitrogen and phosphorus.

Among the soluble components the wet season loading rates are 2–5 times as high as the dry season loading rates. Exclusions are silicon, which is essentially the same in both seasons; ammonia and dissolved organic carbon, which are 20 times as high in the wet season as in the dry season; and soluble inorganic phosphorus, for which the dry season loading rate actually exceeds the wet season loading rate.

The cation loading patterns are counterintuitive. In view of the very substantial increase in movement of particulate materials during the dry season (Figure 3) one might expect considerable increases in the soluble cation loading rates because of the association of soluble cations with particles derived from terrestrial sources, but this is not the case. Increased transport of mineral material does not facilitate the transport of any soluble component except soluble inorganic phosphorus. The major transport mechanisms for all other ions, including the alkaline earths, which are typically considered to be derived from soils, are not connected with mineral particles and must therefore be attributed to volatile phases, where they occur (N, S), or to aerosols too fine to settle during the dry season. The low dry season loading rates indicate that moisture is essential for effective stripping of all major soluble substances from the atmosphere. Soluble inorganic phosphorus is an interesting exception and is dealt with in connection with seasonal fires.

The high loading rates for most substances during the first 1–3 weeks of rain following the dry season are of special interest. Loading rates for single weeks during this period can be as high as 15% of the total annual loading (Figure 4). The pattern suggests a flushing effect just following the dry season. The occurrence of two episodes of very light rainfall during the dry season of 1977 provides further information about the flushing phenomenon. These very light rains were accompanied by significant increases in the loading rates for all four cations (Figure 4). The increases were not nearly so great, however, as those which occurred two months later with the substantial seasonal increases in rainfall (Figure 4). The data thus suggest that two factors are involved in producing the very highest loading rates: (1) a sufficiently long dry period to set the stage for high removal rates of ions when rainfall does occur, and (2) sufficient rainfall to cause an efficient flushing of the atmosphere.

**Evaluation of Seasonal Fires**

One potentially major factor promoting atmospheric transport during the dry season is combustion of vegetation, which occurs regionally every year on a very large scale. Burning includes both cultivated cane fields and successional vegetation of various kinds, particularly grasses. The association of vegetation burning with dramatically increased hydrogen ion and nitrate loading rates just following the onset of the rainy season has been attributed by Lewis and Weibelzahl [1980] to accumulation of nitrogen oxides released from burning vegetation. The potential role of burning in promoting the atmospheric transport of other substances has not yet been considered, however.

Table 5 provides a basis for judging the relative influence of ash on the seasonal changes in loading rates for various precipitation components. On January 17, 1978, a composite ash sample was collected from freshly burned cane and natural grass vegetation in the watershed. A measured quantity (32 g) of this ash was leached in 2 l of glass-distilled water for 14 hours. The water and associated particulates were then analyzed by the procedures which have already been given for the routine analysis of bulk precipitation. The results are expressed in Table 5 as a percentage of the total weight of ash originally added to the water.

<table>
<thead>
<tr>
<th>TABLE 5. Analysis of Ash From Seasonal Fires in the Lake Valencia Watershed</th>
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<tr>
<td>Ash Composition, %</td>
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<td><strong>Particulates (Insoluble)</strong></td>
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<td>Total</td>
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<td><strong>Solubles</strong></td>
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<td>Ca**+</td>
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<td>Si</td>
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DOC, DON, and DOP are dissolved organic carbon, nitrogen, and phosphorus.
Fig. 8. Photomicrographs (49x) of filters used for (top) lake surface water and (bottom) bulk precipitation of Lake Valencia in January 1978, showing ash on the filter.
The data on ash in Table 5 indicate that approximately two thirds of the ash is insoluble. Of the insoluble fraction, only a small proportion by weight is unreleased carbon and hydrogen; more than half consists of inorganic substances.

One significant feature of the ash is its complete lack of particulate nitrogen, indicating volatile release of nitrogen during combustion. Dry plant tissue would carry approximately 2% nitrogen if the tissues were fresh at collection and probably half this much of the tissues were dead at collection [Whittaker et al., 1979]. Very large losses of nitrogen from litter burned in temperate zone forests are known to occur [Knight, 1964; Wells, 1971; Lewis, 1974], although the mechanism of loss is not entirely clear. Significant amounts of nitrogen oxides are produced under natural combustion conditions [DeBell and Ralston, 1970; Lewis, 1975], and this process may even be significant in the global nitrogen cycle [Cruzen et al., 1979]. Nitrate derived from nitrogen oxides will appear in wet precipitation. In the Lake Valencia watershed it appears that large amounts of nitrogen oxides resulting from vegetation fires build up toward the end of the dry season and are only effectively flushed out after the rains begin. This in turn leads to significant hydrogen ion loading because of the dominating effect of nitric acid on the acid-base balance when the nitrogen oxides are scrubbed out by the first few rains. Some nitrate does appear in the collector during the dry season as well (Table 4), possibly as a result of impaction or association with particles.

Lewis [1975] has shown that soils and litter can release ammonia in significant amounts in response to heating at the time of combustion, even though ammonia is not stable in a hot flame. Thus volatile release of ammonia from fires can be expected as well as nitrogen oxides and may partly account for the very high ammonia pulse at the end of the dry season.

Considerable amounts of soluble cations, bicarbonate, and sulfate are found in the ash leachate (Table 5). Inorganic soluble phosphorus accounts for only 0.2% of the total weight of ash, but this represents a potentially rich source of phosphorus for precipitation because of the very small amount of phosphorus normally found in precipitation. The relative richness of the ash in soluble phosphorus in fact probably accounts for the unique increase in soluble inorganic phosphorus loading rates during the last half of the dry season and the decline to zero as the wet season progresses. High inorganic soluble phosphorus loading would coincide with the availability of ash, which is only produced in quantity some time after the onset of dry weather.

Soluble organics are present in ash in significant amounts. This is puzzling, as the combustion should lead to loss of most soluble organics. A possible explanation is adsorption by cool ash of volatile organics from smoke in the atmosphere near fires.

Combustion is an accelerator of nutrient cycles. It frees elements from the organic matrix, thus performing the function of decomposition but much more quickly. Fires also facilitate transport of liberated nutrients in several ways. Volatile release of nitrogen oxides, ammonia, and organics is most obvious. In addition, large (>50 μm) ash particles have a sufficiently low specific gravity that they are vulnerable to air transport over long distances. Figure 8 shows evidence of ashfall in a sample from the lake surface (6 km from shore) taken during the dry season (January 11, 1978) and similar evidence from a bulk precipitation sample collected on the same date. Very fine particulates (aerosols) could also account for the transport of significant amounts of a wide variety of substances that are neither volatile nor associated with large particulates of the type which settle readily in the dry season. All of these transport mechanisms are of general interest because of the widespread burning in the tropics (see, for example, Viner [1975] and Craft [1976]).

A sample calculation for potassium illustrates the potential role of ash particle transport in moving soluble but non-volatile materials into the lake. The mean weekly particulate transport during the dry season is 348 mg/m²/week. If the ash component were just one third of this, the ash would account for some 3.3 mg/m²/week of soluble potassium, as compared with a measured loading rate for soluble potassium during the dry season of 3.7 mg/m²/week. Although the weekly percentage of particulates attributable specifically to ash is not known, ash is obviously a potentially important transport mechanism because of its high yield of soluble constituents.

Even though large (>50 μm), iron-rich ash particles are transported regionally during the dry season, the data show that this process is insufficient to raise the dry season loading rates for soluble materials except soluble inorganic phosphorus even up to the level of average wet season loading rates. The extremely high loading rates for almost all substances just at the beginning of the wet season indicate an accumulated atmospheric burden during the dry season in the form of materials which do not come out of the atmosphere in quantity unless substantial moisture is present. Major transport is thus due mainly to volatiles or to extremely fine particulates rather than to large particles subject to rapid settling.

Dependence of Wet Season Loading Rates on Amount of Rainfall

During the wet season the amount of rainfall varies considerably from one week to another. This may explain some of the variance in weekly loading rates. The elapsed time since the previous dry season may also be important in determining the loading rates either by progressive reduction of the atmospheric burden of dissolved and particulate substances or by regional alteration of the entry of materials into the atmosphere from the terrestrial surface through biological or physical/meteorological mechanisms.

The joint effects of the amount of rainfall and the amount of elapsed time since the onset of the rainy season can be tested simultaneously by multiple regression. Loading rate is treated as the dependent variable. The relationship of the dependent variable to (1) amount of rainfall per week and (2) number of days elapsed since the onset of the wet season is then determined. The variables are entered into the multiple regression in hierarchical fashion. The amount of precipitation is always entered first; then residual variation due to time is determined. This order is necessary because there is a slight downward linear trend in the amount of rainfall as the rainy season progresses.

The regressions were done on both a linear and a semilog basis (logarithm of the dependent variable versus linear independent variables). The outcomes of these two approaches are very similar, but the results of the semilog approach are stronger and appear better justified because of its normalization of the loading rate data. The semilog model is thus used here.

Table 4 shows the amount of variance in loading rate during the wet season which can be accounted for by the amount of rainfall. The relationships are all statistically significant (P
<0.05) except for soluble inorganic phosphorus and dissolved organic nitrogen. It is obvious from the foregoing comparison of wet and dry seasons that soluble inorganic phosphorus is not strongly associated with wet precipitation; thus it is reasonable that the loading rates for soluble inorganic phosphorus within the wet season are not dependent upon the amount of rainfall. This is consistent with the interpretation that in contrast to other chemical fractions a large percentage of soluble inorganic phosphorus is associated with ash particles large enough to settle from the air.

The lack of a significant relationship between dissolved organic nitrogen and amount of rainfall is not easily explained. The amount of explained variance for dissolved organic phosphorus, although significant, is low. In contrast, there is a very strong association of dissolved organic carbon and amount of rainfall. Hydrocarbon fractions thus seem to be almost exclusively associated with wet precipitation, whereas organic fractions incorporating nitrogen and phosphorus are more strongly associated with transport mechanisms that are independent of rainfall.

The relation between particulate loading and rainfall is especially interesting, as it indicates a strong contrast between organic and inorganic particulates. Total particulates show a low degree of association with rainfall, but organic components (C, N) show a strong association. This may be explained in terms of the relative settling rates of mineral particles and organic particles. The specific gravity of mineral particles is likely to much higher, and their settling rates therefore may be not so greatly facilitated in a relative sense by wet precipitation. Organic particles are likely to have a much lower specific gravity and thus stay in suspension more readily until they are scrubbed out by wet precipitation.

Major cations, major anions, and inorganic nitrogen compounds are associated significantly with the amount of wet precipitation. The inorganic nitrogen compounds are taken from a volatile reservoir, which explains their association with wet precipitation. Other major cations and anions, which cannot be gaseous, must be associated with minute aerosols that have insignificant settling rates in the absence of wet precipitation and thus show a strong dependence on wet precipitation for removal from the atmosphere. This contrasts with soluble inorganic phosphorus, which has the opposite tendency and thus appears to be associated with larger particles. These inferences are consistent with inferences drawn from wet season/dry season contrasts.

The flushing effect caused by the first rains at the beginning of the wet season is obvious from the previous graphical presentations of loading rate data (Figures 3–7). The existence of a longer-term flushing effect would not be obvious from simple inspection because of random variation in the amount of wet precipitation but should be evident from the multiple regression analysis. Variance in loading rates attributable to elapsed time after the start of the wet season is shown in Table 4. The amount of variance explained by elapsed time is small, and for many variables the relationship is not significant at all. Thus the primary flushing effect occurs in a matter of 1 or 2 weeks following the onset of the rainy season and extends only weakly into the wet season beyond this. Furthermore, there is no major trend within the wet season in the available pool of atmospheric materials, or this would be manifest as a considerably larger variance component associated with the amount of elapsed time since the beginning of the wet season.

In all cases where the elapsed time is a significant component of variance, however minor, the coefficient in the linear regression equation is negative. That is, the significant relationship always represents a decline through the wet season in the amount of loading with time, after correction for amount of rainfall. For those components showing significant relationships it is possible to calculate the theoretical half-lives for the decline during the wet season by using the time coefficient and the semilog regression model. The half-life λ will be

\[ \lambda = \log (0.5)/\beta, \]

where β is the time coefficient from the semilog regression model (units are day⁻¹). The half-lives computed in this manner vary between 100 and 240 days. These values are so high as to indicate that the mechanism responsible for long-term trends during the wet season is not simple flushing but more probably change in the equilibrium constants affecting the entry and exit of materials with respect to the atmospheric system.

**Relationship of Wet Season Loading Rates to Insoluble Particulate Loading**

Particulate material may be associated with specific soluble fractions because of the adsorption of substances onto surfaces or the inclusion of soluble components in particles. It is possible to test specifically for the role of particulates in accounting for variability in loading rates by extending the multiple regression analysis. The amount of rainfall and the elapsed time since the onset of the rainy season are first entered into the regression equation; then residual variance attributable to the amount of total insoluble particulate material is determined. The results of this analysis appear in Table 4.

Within the wet season, significant variance in the particulate carbon, hydrogen, and nitrogen loading rates is associated with total insoluble particulate material. This is not particularly surprising, as these are all components of insoluble particulate matter. Particulate phosphorus behaves very differently, however. Its lack of association with total particulate matter indicates that the source of particulate phosphorus is quite specific and is not associated with generalized sources which contribute to the major organic and inorganic components of insoluble particulate matter. This reinforces a similar conclusion drawn from the wet season/dry season comparison of particulate phosphorus.

Among the soluble components of bulk precipitation the number of significant relationships with total particulate matter is low. The four major cations do show some significant association, indicating that minor proportions of these soluble substances could be carried on organic or inorganic filterable particles, but the total amount of variance explained by this mechanism is not great. Soluble inorganic phosphorus shows one of the strongest associations with total particulate matter, consistent with the previous conclusion that it is delivered to the watershed specifically in association with ash particles. Calcium is also one of the strongest associations, indicating a particle association for some of the calcium. It should be noted, however, that high particulate loading in the dry season is not accompanied by an increase in calcium loading; thus a general dust or mineral source for the calcium cannot be defended very well. Particles of biological origin seem a more likely source. The other significant associations in the table are so low that they do not warrant discussion.

**Possible Significance of Very Long Distance Transport**

The geographic scope of sources for materials reaching the Lake Valencia watershed in bulk precipitation cannot be specified on the basis of the present data. Sources may be lo-
cal, regional, or global. The possibility of very distant sources, especially in this particular geographic setting, is illustrated by studies of dust fall in the Caribbean [Delany et al., 1967; Prospero, 1979]. Dust originating in African wind storms is transported under some circumstances in large quantities to the Caribbean area and presumably the eastern coast of South America as well. Prospero's information indicates that the southward shift in major air circulation patterns during the north temperate winter would increase dust transport to eastern South America in the winter months. The African dust could contribute to insoluble particulate loading on Lake Valencia during the winter months, which are characterized by substantial loading rates for insoluble particulate materials. At present, no quantitative estimate can be given for such long-distance transport.

Acknowledgments. This work was supported by National Science Foundation grants DEB 7604300 and DEB 7805324 and is part of the joint Venezuelan—North American ecosystem study of Lake Valencia. The author is also indebted to the Fundacion Eugenio Mendoza for logistical support in the field and to F. H. Weibezaehn for discussion and assistance of many kinds. Chemical analytical work was performed by S. Saunders, R. Chadzon, and S. Knight, to whom I am most grateful.

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(Rceived March 5, 1980; revised June 18, 1980; accepted July 2, 1980.)