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# Composition, distribution and neutralization of "acid rain" derived from Masaya volcano, Nicaragua

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ABSTRACT

Acid rain (pH 2.5–5.0) from the volcanic plume of Masaya Caldera, Nicaragua, is composed of HCl and $H_2SO_4$ in systematically varying proportions. The dominance of HCl in volcanic acid rain makes it distinctly different from anthropogenic acid rain. The pH of volcanic acid rain is largely controlled by its HCl concentration. Volcanic acids are locally damaging, killing vegetation with the conspicuous exception of the shrubs *Malanthora* and *Lantana*. These shrubs have the ability to rapidly and completely neutralize acid rain by releasing $K^+$ at their leaf surfaces. The mechanism by which these plants sustain their acid neutralizing capacity is evidently by pumping acidity into the soil in exchange for $K^+$ from soil exchange surfaces. In effect the *Malanthora* shrub layer is acting as a short-term acid sink for incident acid rain. However, the final acid sink in this system is the base exchange reservoir of the local soils.

## 1. Introduction

The Santiago vent of Volcan Masaya (Fig. 1) has been erupting copious amounts of gas since 1979. The current activity represents only the latest episode in a series of such eruptions, and has exceeded 1,000 tons per day discharge of $SO_2$. These gas eruptions have a historical recurrence interval of some 25 years and the eruption episodes last several years (McBirney, 1956). The Masaya crater is located in the NE tradewind belt, so that the volcanic gas plume persistently streams from NE to SW (Fig. 1). The plume thus occupies a rather well-defined corridor, under which "acid rain" impinges on the landscape. In addition to acid rain, the highland area, Llano Pacaya (Fig. 1), is also exposed to direct volcanic gas fumigation. Llano Pacaya is considerably higher than the Santiago vent, so that the plume's trajectory is forced physically against and over the highland itself. Damaged and dead vegetation is most conspicuous on the slopes leading up to the Llano Pacaya rim. Upwind and downwind from the Llano Pacaya highland, the plume is almost always aloft and acid rain is the only effect manifested by the volcanic plume. Except for the immediate plume sector, the Llano Pacaya rim is characterized by a diversified cloud forest. In contrast, in the sector affected by the volcanic gases and acid rain, only the weedy composites *Malanthora*, *Nivia* and *Lantana spp.* grow in profusion. The original trees and other vegetation in this zone have been killed by the present volcanic gas fumigation and/or acid rain. As will be shown here, these shrubs have a notable ability to survive and prosper under the present hostile chemical conditions. In this report we shall describe and discuss the chemistry of the acid rain under the volcanic plume of Santiago, and how this acid rian is neutralized by the existing ecosystem, including the rôle of *Malanthora* and *Lantana*.

## 2. Methods

During the summers of 1980, 1981 and 1982, we sampled variously the acid rain, throughfall and soil water at several points under the volcanic plume (Fig. 1). Rain and throughfall were

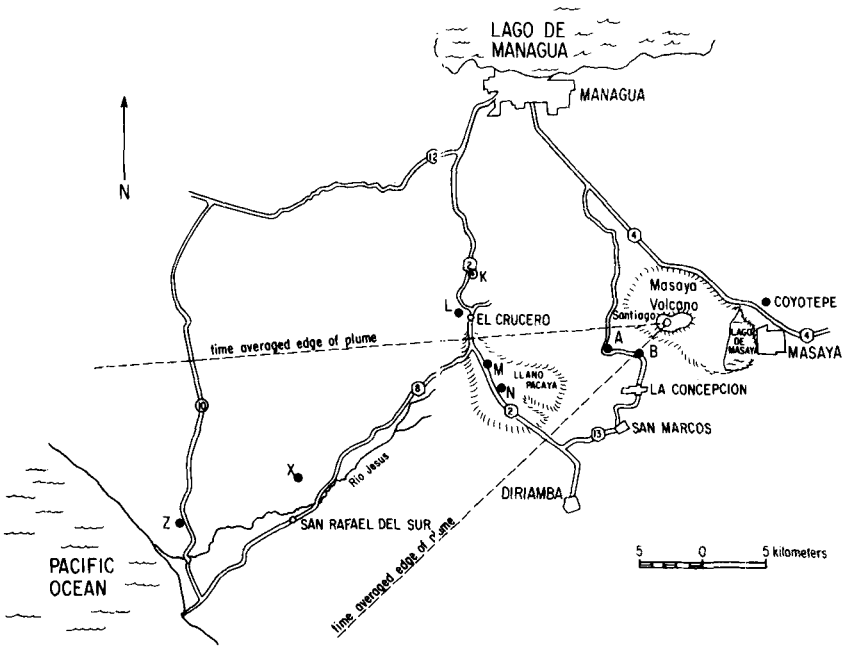


*Fig. 1.* Location of Masaya Volcano, the volcanic plume from Santiago vent, and the water sampling sites.

collected by means of an open funnel of the type described by Likens, et al. (1977). Sampling was done mostly in August when it rains reliably every day in the study area, and at this time rain, throughfall and soil water samples were collected daily. During September–December, 1981, weekly composite samples of rain were collected. pH of rain and soil samples were measured in the field. Polypropylene screened throughfall funnels were set exclusively under *Malanthora* except at control site K, where only unaffected cloud forest vegetation occurs.

Rain collection sites were distributed along the axis of the plume, and one station, Coyotepe, was established immediately upwind from Santiago (Fig. 1). Porous cup alundum lysimeters were emplaced in A, B, C, and R horizons at site B and M, and as controls at sites L and K.

Two types of problems have been recognized with porous cup lysimeters; both have been addressed in this study. First, lysimeter collection has been shown to alter soil solution chemistry through leaching of base cations from the lysimeter and adsorption of ions (particularly $PO_4^{-3}$) by the lysimeter (Shuford et al., 1977; Morrison, 1982; Grover and Lamborn, 1970). This study has utilized the suggestions proffered by these authors. Furthermore, the degree of contamination observed by these authors is very small with respect to the concentrations and concentration changes observed in this study. Nevertheless, the ionic strengths observed in our soil waters are similar to those in the above-mentioned study.

The second problem involves the fact that the percolation rate in the soil may differ from that measured by the lysimeter (Van der Ploeg and Beese, 1977). This potential difference is only significant for this study when measuring fluxes to calculate soil leaching and uptake rates. Only $Cl^-$ was so studied. Chloride is a very conservative element in this environment (Gebhardt and Coleman, 1974a). It was assumed to travel with percolating waters without any adsorption or uptake. Thus, its increasing concentration in the soil with depth was used to gauge increases in ionic strength with depth caused by evapotranspiration. Only measurements using similar dimensioned lysimeters were used; they were equilibrated for one year, then used sparingly (to prevent clogging). There is minimal variation in soil matrix texture with depth at the lysimeter sites. Thus, the differences between lysimeter

behaviors with depth can be neglected when comparing ion fluxes at various depths, using a relative scale.

In 1981, all samples were chemically analyzed using the methods described by Likens et al. (1977). A selected list of our water chemistry data is given in Tables 1, 2, and 3 for rain, throughfall and soil water, respectively. A complete tabulation of our chemical data is given in Johnson and Parnell (1983) and is available on request. All 1982 samples were analyzed as in 1981, with the following exceptions: anions were measured using ion chromatography, and total aluminium, iron, and silica were measured by DC plasma atomic emission spectroscopy. Good agreement has been found between autoanalyzer (1981 methods) and ion chromatography (1982 methods) for inorganic anions (C. Cronan, pers. comm.). Exchangeable base saturation procedures follow Adams and Evans (1962) and weight % of amorphous aluminosilicates was determined by procedures from Hodges and Zelasny (1980).

In Fig. 2 we show a test of the accuracy of our overall chemical methods, comparing our observed pH values with those predicted from the total chemical analyses. The plot shows a regression slope of one and a correlation of +0.987 (Fig. 2). Charge balances were completed for every rain and soil solution sample and came within an average of $\pm 1.4\%$.

## 3. Precipitation chemistry

In this study, we observed rain pHs ranging from 2.47 to 6.38, 4 orders of magnitude of

Table 1. *Rain chemistry*

| | $Cl^-$ | $SO_4^{-2}$ | $NO_3^-$ | $NH_4^+$ | $Na^+$ | $Mg^{+2}$ | $Ca^{+2}$ | $K^+$ | $SiO_2$ | pH |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | |
| Coyotepe | | | | | | | | | | |
| 24 Aug. 81 | 0.16 | 0.7 | 0.12 | 0.04 | 0.05 | 0.01 | 0.11 | 0.05 | 0.0 | 5.00 |
| 25 Aug. 81 | 9.15 | 1.9 | 0.00 | 0.02 | 0.12 | 0.72 | 0.55 | 0.14 | 0.9 | 3.50 |
| 1 Oct. 81 | 0.77 | 0.6 | 0.07 | 0.14 | 0.38 | 0.08 | 0.23 | 0.33 | 0.4 | 5.53 |
| Site A | | | | | | | | | | |
| 24 Aug. 81 | 1.94 | 3.0 | 0.17 | 0.12 | 0.06 | 0.02 | 0.05 | 0.08 | 0.1 | 3.90 |
| 25 Aug. 81 | 0.22 | 0.4 | 0.17 | 0.01 | 0.02 | 0.01 | 0.06 | 0.07 | 0.0 | 5.10 |
| 24 Oct. (1:25) | 0.23 | 0.3 | 0.00 | 0.03 | 0.12 | 0.03 | 0.10 | 0.06 | 0.1 | 6.20 |
| 24 Oct. (4:15) | 30.0 | 9.1 | 0.07 | 0.01 | 0.73 | 0.18 | 0.51 | 0.62 | 1.9 | 2.90 |
| Site M | | | | | | | | | | |
| 24 Aug. 81 | 0.22 | 0.9 | 0.09 | 0.04 | 0.02 | 0.01 | 0.02 | 0.01 | 0.0 | 4.51 |
| 25 Aug. 81 | 0.07 | 0.4 | 0.00 | 0.02 | 0.03 | 0.02 | 0.37 | 0.02 | 0.0 | 6.38 |
| | | | | *Malanthora* throughflow chemistry | | | | | | |
| Site A | | | | | | | | | | |
| 24 Aug. 81 | 11.1 | 12.0 | 0.00 | 0.11 | 0.35 | 2.3 | 7.24 | 8.9 | 10.0 | 6.48 |
| Site M | | | | | | | | | | |
| 24 Aug. 81 | 2.90 | 8.7 | 0.20 | 0.24 | 0.11 | 0.86 | 2.78 | 7.8 | 8.0 | 6.31 |
| 25 Aug. 81 | 3.02 | 3.2 | 0.17 | 0.13 | 0.07 | 0.64 | 1.72 | 5.2 | 6.5 | 6.59 |
| Site Z | | | | | | | | | | |
| 24 Aug. 81 | 11.2 | 7.6 | 0.04 | 0.19 | 1.39 | 1.64 | 5.42 | 6.3 | 9.0 | 6.45 |
| 25 Aug. 81 | 3.78 | 2.2 | 0.10 | 0.28 | 0.32 | 0.87 | 2.41 | 21.0 | 6.0 | 6.38 |
| | | | | Lysimeter chemistry | | | | | | |
| Site M (25 cm) | | | | | | | | | | |
| 24 Aug. 81 | 86.3 | 11.3 | 142 | 0.03 | 4.0 | 9.9 | 55.8 | 51 | — | 5.63 |
| 26 Aug. 81 (64 cm) | 65.5 | 10.9 | 125 | 0.09 | 2.5 | 8.4 | 46.8 | 47 | — | 5.99 |
| 24 Aug. 81 | 72.5 | 45.0 | 350 | — | 14.0 | 21.1 | 92.4 | 49 | — | 5.25 |
| 26 Aug. 81 (150 cm) | 62.0 | 41.0 | 292 | 0.02 | 13.0 | 19.2 | 76.6 | 52 | — | 6.00 |
| 24 Aug. 81 | 35.8 | 52.0 | 91 | 0.07 | 16.0 | 10.4 | 37.2 | 10.6 | — | 5.50 |
| 26 Aug. 81 | 37.5 | 57.0 | 94 | 0.05 | 16.0 | 11.1 | 38.1 | 9.9 | — | 6.32 |

Table 2. *Neutralization of acid rain by Malanthora*

| Site | Date | pH rain | pH thru | Base added* (μeq) | $K^+$ rain (μeq) | $K^+$ thru (μeq) |
|---|---|---|---|---|---|---|
| A | 24 Aug. 81 | 3.90 | 6.48 | 310 | 2.8 | 228 |
| M | 24 Aug. 81 | 4.51 | 6.31 | 193 | 0.3 | 199 |
| M | 25 Aug. 81 | 6.38 | 6.59 | 126 | 0.5 | 133 |
| Z | 24 Aug. 81 | 6.30 | 6.38 | 163 | 4.9 | 161 |
| Z | 25 Aug. 81 | 5.89 | 6.45 | 136 | 0.8 | 133 |

* The amount of base which has been added to incident rain to transform it into *Malanthora* throughflow. Calculated as the difference between the ionic chemistry of throughflow and rain, i.e., base added $= (\Sigma(+) - \Sigma(-))$ throughflow minus $(\Sigma(+) - \Sigma(-))$ rain, where $\Sigma(+)$ is the sum of all strong bases and aluminium, while $\Sigma(-)$ is the sum of all strong acids, $Cl^-$, $SO_4^{2-}$ and $NO_3^-$. $H^+$ and carbonate alkalinity are not included in these calculations.

Table 3. *Potassium and nitrate changes during throughflow and soil percolation*

| | pH | $K^+$ (μeq) $l^{-1}$ | $NO_3^-$ (μeq) $l^{-1}$ |
|---|---|---|---|
| *Site A* | | | |
| (mean data 23–26 Aug.) | | | |
| rain | 3.09 | 30.0 | 6.4 |
| throughflow | 6.48 | 228 | 0 |
| soil—25 cm | 5.18 | 330 | 30 8 |
| *Site M* | | | |
| (mean data 21–26 Aug.) | | | |
| rain | 3.86 | 1.3 | 0.9 |
| throughflow | 6.55 | 580 | 1 .5 |
| soil—25 cm | 5.77 | 1381 | 17 6 |
| soil—64 cm | 5.36 | 1163 | 40 4 |
| soil—150 cm | 5.81 | 592 | 13 6 |

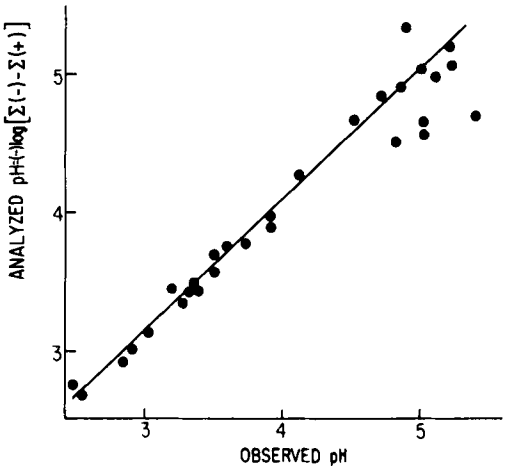


*Fig. 2.* Plot of observed acid rain pH versus that predicted from analysed chemical data (Table 1). No species of carbonate ions are included in the data plotted. Data base is only partly recorded in Table 1; the complete rain chemistry data set is given in Johnson and Parnell (1983).

acidity. Without exception the high pHs occurred upwind of the volcanic vent while the lower pHs were found close-in to the vent, downwind. On a given day, the acidity of the rain under the plume diminished rapidly with distance away from the vent. For example, during a single collection period on 18–19 August 1980, days with normal NE winds, the pHs of rain at sites A, N, X and Y (Fig. 1) were 2.60, 3.45, 3.78, and 3.97, respectively. This sequence of decreasing acidity downwind, for the same storm event period, most likely reflects the dilution and spreading of volcanic gas as a function of downwind distance. At a given station under the plume, the pH of rain tended to be independent of rainfall amount through the course of individual events, over at least two orders of magnitude of rain amount. This observation suggests that the volcanic acids in the plume are replenished as fast as they are removed by rain.

A significant feature of the acid rain from the Masaya plume is that it is a mixture of HCl and $H_2SO_4$, quite different from anthropogenic acid rain (Likens, et al., 1979). Furthermore, the intensity of acidity in volcanic acid rain is largely produced by HCl; the more acid the rain becomes the more HCl is present (Fig. 3). As noted

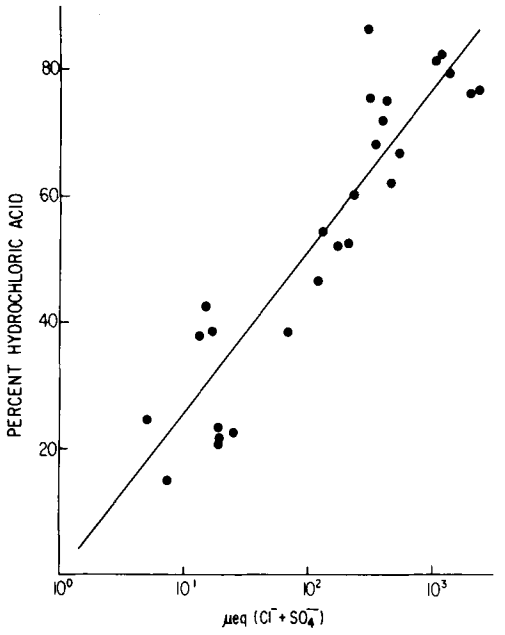


*Fig. 3.* Composition of acid rain from the plume of Santiago. Note that the proportions of HCl in the acid rain increases exponentially with total acidity. Data from Johnson and Parnell (1983).

above, the lowest pHs in volcanic acid rain are found near the volcanic vent. It follows then that the acid rain nearest the vent is characteristically richer in HCl (Table 1, Fig. 3). Carried to its logical extreme, the relationship shown in Fig. 3 implies that as HCl content of the volcanic plume goes to zero, acidity would approach 1 μeq/l of $H_2SO_4$. That is, far downwind from the volcanic vent, acid rain would consist solely of $H_2SO_4$ at a 1 μeq $H^+$/l concentration. Intermediate steps along this trend are indeed observed (sites A, N, X, Z in Table 1).

The variable composition of volcanic acid rain is readily explained by the chloride and sulfur phases existing in the volcanic plume. Chloride is overwhelmingly in the form of HCl gas, while sulfur occurs as $SO_2$ gas and $SO_4^{2-}$ aerosols (Stoiber and Williams, personal comm.). HCl gas is profoundly soluble and will readily be scavanged by water droplets within the plume. On the other hand, $SO_2$ is relatively less water reactive and in fact may oxidize first before becoming hydrolysed (Stoiber and Williams, personal comm.). So, the lifetime of HCl in the volcanic plume should be substantially less than that of $SO_2$, as our data indeed show.

It is noteworthy that the chemistry of rain outside the influence of the volcanic plume is entirely normal (Galloway, et al., 1982) (Table 1). That is, on every observed occasion the rainfall upwind from the Santiago vent showed pHs of 5.0–6.4, a pH range within $CO_2$–$H_2CO_3$ control. During the 24th–26th of August, 1981, hurricane Hilary provided a unique, natural experiment in this regard. Because hurricane Hilary was situated off the Pacific coast of Nicaragua, the normal trade winds were disrupted starting on August 24. Wind direction was variable at first and then by August 25 had completely reversed its normal direction, going from SW to NE. Rainfall chemistry on August 25 shows this change in wind direction in a dramatic fashion. The Coyotepe site, which was normally upwind from the volcano (Fig. 1), became an acid rain site, while sites A, B and M, N became "normal" rain sites (see Table 1). By September 5 the normal tradewind had finally reestablished itself and the usual distribution of acid rain likewise was restored (compare Coyotepe and site A, Table 1).

Similarly, a thunderstorm during October 24, 1981, illustrates the localized acid rain effect (Table 1). At site A, a single storm event at 1:25 pm did not entrain any volcanic gases so that the rain was normal (pH 6.20). Later that day at 4:15 pm the same storm system enveloped the volcanic plume and the incident rain became acid (pH 2.90). Although the examples cited here are only anecdotal in scope, they serve as significant evidence for the high level of localization of acid rain from a volcanic plume.

## 4. Impacted ecosystems

The climate, hydrogeology, and must importantly the vegetation of the Llano Pacaya region mitigate the effects of acid rain on the soil, surface and ground waters of the impacted area (Fig. 1). The watershed to the southwest of Llano Pacaya is occupied by a perennial stream, Rio Jesus. This river is headed and fed by large springs. During August 1980, the pH of both spring and stream water was found to vary between 7.8 and 8.3, which is within the range of

most $CaCO_3$ saturated waters. High ionic conductivity of Rio Jesus waters and its high pH are most likely because of a long residence time in a groundwater reservoir. It is not surprising that Rio Jesus and its associated springs have $HCO_3^-$ as the dominant anion and show no effects at all from the present volcanic activity and incident rain.

The watershed to the northeast of Llano Pacaya drains towards Laguna Masaya; however, no perennial surface streams are present. The water draining into Laguna Masaya is probably groundwater flow. In August 1980, the pH of the lake was >9.0, which may indicate that the lake has had no outlet other than evaporation for some time. The semi-arid climate reinforces this idea. The recent, intense acid rain entering this watershed has not acidified the Laguna Masaya watershed in any tangible way.

In contrast to the chemical stability of surface waters, the terrestrial ecosystems of the Llano Pacaya have historically shown a dramatic response to acidification from volcanic activity at Santiago. As a result of volcanic activity in the early 1950's, substantial coffee acreage became infertile for a period lasting until 1959 (K. Matheson, personal communication). Over the sector of Llano Pacayo presently affected by the volcanic plume, no cultivation occurs and pioneer species such as *Malanthora* and *Lantana* have replaced the cloud forest vegetation destroyed by gas fumigation or acid rain.

The region downwind of Masaya volcano is blanketed by Holocene and Pleistocene ash fall deposits. These deposits are scoriaceous, locally welded, and frequently contain accretionary lapillae. They are believed to have originated from Masaya volcano and to have buried, to a depth of several meters, the 22,000 year old eruption products of Apoyo caldera (Sussman, 1983). The chemistries of all the Masaya eruption products are remarkably similar, not varying with either time or location (Williams, 1983; Ui, 1972; McBirney, 1956). Thus, a constant geologic substrate exists across the impacted region.

Unlike the ash deposits, the soils do change in age and in character as a function of distance from the volcano. Soils of the Llano Pacaya area surrounding our high elevation sites (Fig. 1) and the Rio Jesus drainage basin downwind are Durandepts, possessing a massive, fractured (Rio Jesus drainage) or unfractured (Pacaya area) duripan. In these soils, percent base saturation (PBS), ordinarily an important parameter in acid neutralization, averages less than 30% (Ministerio de Agriculture y Gonderia, 1971).

The soils which characterize the lower elevations between the Llano Pacaya and the volcano are coarser grained at depth, have thicker A horizons with nearly 100 PBS, and are classified as Mollic Vitrandepts. We have observed that the Mollic Vitrandepts have higher soil slurry pHs throughout their profiles than the Typic or Entic Durandepts. Previous research on Nicaraguan Andepts by Martini and Palencia (1975) suggests PBS is highly correlated to pH, reaching zero between pH 4.0 and 4.5. This observation suggests that the typic Durandept soils of the Llano Pacaya region and Rio Jesus drainage are more sensitive to acidification that the Mollic Vitrandepts which occur east of Llano Pacaya.

## 5. Neutralization mechanism

During the course of our study we observed a striking chemical effect associated with the throughfall of rain from a *Malanthora* herb layer, which grows throughout the plume-impacted area. In August 1980 the pH of this throughfall was measured at 5.5 to 6.53. This contrasts with an incident rain pH of 2.63 to 3.71. The fact that contact with *Malanthora* leaves have caused at least a 100 fold drop in acidity indicates that the vegetation is an important factor in neutralizing acid rain. The hundred-fold neutralization occurs in samples with several mg/l of particulate solids (determined by 0.4 $\mu$m filtration) as well as in samples with no measurable particulate solids. These data suggest that it is the vegetation itself, not impacted dust, which is neutralizing acidity. Furthermore, the base cation to silica ratio in these throughfall samples is far too high to be accounted for by congruent dissolution of amorphous silicate dust.

Complete chemical analyses of the *Malanthora* throughfall are given in Table 1. It is evident by comparing the chemistry of acid rain and throughfall (Table 2) that *Malanthora* leaves have the ability to add strong bases to water, notably $K^+$. There is also an increase in $[Cl^-]$ and $[SO_4^{2-}]$, possibly due to leaching of dry deposition. Evi-

dently, *Malanthora* leaves serve as a base exchanging membrane, with $K^+$ ion leaving the leaf, and $H^+$ ion entering the leaf (Fig. 4). Even when acid rain is not involved (e.g., Table 1, site M, 25 August 81; site Z, 24 and 25 August 1981) $K^+$ is profusely leached from *Malanthora* leaves, at a rate of approximately 130 μeq/l. Furthermore, as the acidity of the rain increases, the rate of $K^+$ leaching increases proportionately. This release of $K^+$ by *Malanthora* evidently mitigates the effects of HCl and $H_4SO_4$, allowing the plant to survive in the midst of a corrosive bath.

The physiologic mechanism of $K^+$ leaching from leaves is not unique to *Malanthora* or to

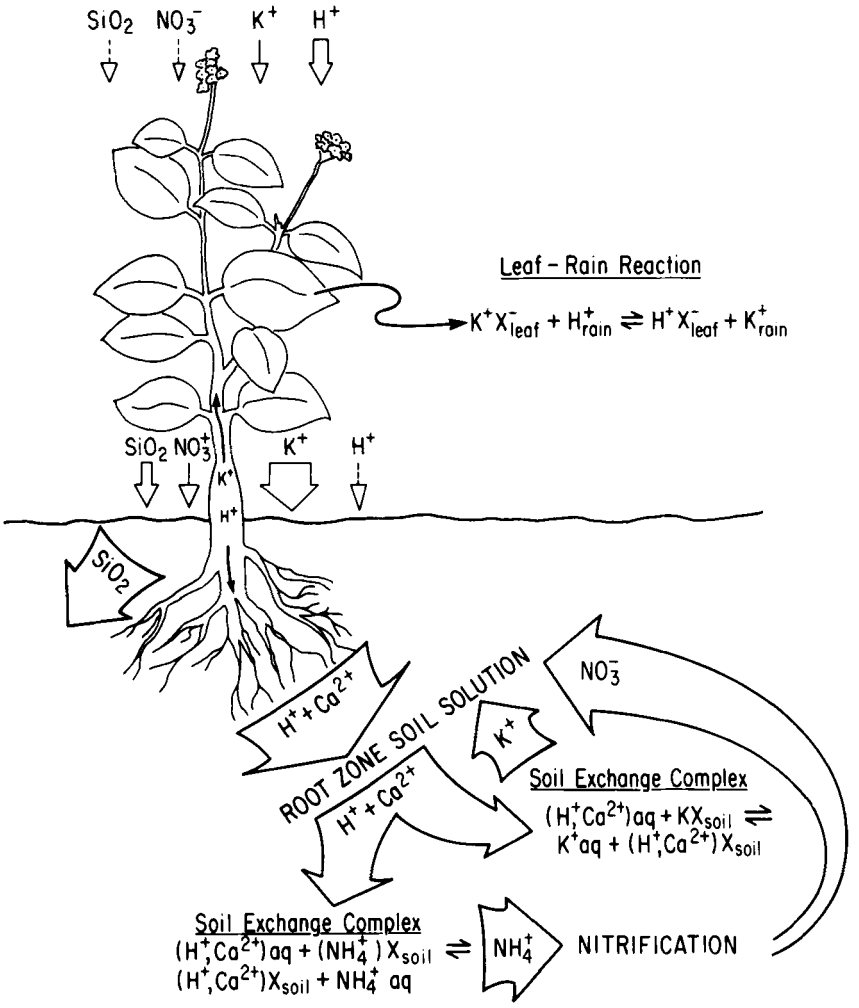


*Fig. 4.* Qualitative model of $K^+$ and $H^+$ cycling among *Malanthora* or *Lantana*, precipitation, throughfall and soil water. $X^-$ symbolizes the cation exchange surfaces in the soil or leaf surface. Quantitative data that support this model are given in Tables 1–3. The arrow shaft thicknesses are proportional to the concentration of each ion. A dashed line is used where concentrations are less than 1 μeq/l, a solid line where less than 10 μeq/l. The low amount of $SiO_2$ and the low ratio of $SiO_2$ to base cations in the throughfall suggests that dissolution of silicate minerals is an insignificant part of the neutralization process. Instead, leaching of base cations, particularly $K^+$, from the leaves' surfaces is responsible for the neutralization of the acid rain. The source of these base cations is the root zone of the soil, where acidity added by the plant mobilizes $K^+$ for uptake by the plant, and $NH_4^+$, which is nitrified.

chemically stressed systems. It has been noted previously that $K^+$ and $Ca^{2+}$ have the highest leachabilities of any cations, both in temperate and tropical ecosystems (Crozat, 1978; Lawson and Winchester, 1979; Whittaker, et al., 1979). These authors report that the cycling of some $K^+$ from the soil, through the plant, and its loss by leaching from leaf surfaces is commonplace.

The other half of the cycle—just how the roots obtain $K^+$ from the soil—is also suggested by our chemical data. The site of acidification as shown by our soil water data is clearly the root system of *Malanthora* (Table 3). Acidity in the soil reaches its maximum in the root zone (25 to 65 cm). Note further that in addition to $H^+$, remarkable amounts of $NO_3^-$ also appear at this level in the soil (Table 3). Plant roots, including those of *Malanthora*, extract $K^+$ (and other bases) from soil exchange sites by releasing $H^+$ and acid anions to the soil. Uribe and Lüttge (1984) describe this mechanism as a hydrogen ion pump. Thus, while *Malanthora* leaves act as an acid-sink (Table 2), *Malanthora* roots simultaneously act as an acid source (Table 3). We show in Fig. 4 a representation of these chemical pathways and reactions. The chemical changes we have observed in this process involve several orders of magnitude of change in $K^+$ and $NO_3^-$ concentration (Tables 2, 3). These changes are therefore real, systematic effects, not just an artifact of our analytical techniques.

The exact mechanism by which *Malanthora* acidifies the soil is not known. It cannot be the direct addition of $HNO_3$ as the plant would soon become deficient in nitrogen. We therefore speculate that the source of the nitrogen is from the soil, specifically exchangeable $NH_4^+$. We note that the sum of exchangeable acidity ($H^+$ plus total dissolved Al) plus the exchangeable cations $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$ is less than three quarters of the cation exchange capacity value of the acidified soils. Thus, we infer that $NH_4^+$ may comprise a significant portion of the total exchange complex. If this is the case, then acidification of the soil by *Malanthora*, say by organic acids, would drive off $NH_4^+$ from soil exchange sites (Fig. 4). The $NH_4^+$ thus freed would readily and rapidly oxidize to $NO_3^-$, a common nitrification reaction in soils. This scenario is, of course, only speculation and we cannot preclude other possibilities. The only certainty here is that $K^+$ and $NO_3^-$ are intimately involved in *Malanthora's* ability to survive in a hostile, acid rain environment (Tables 2, 3).

An alternative explanation for the elevated $NO_3^-$ levels, flushing of the soil after a dry season, is easily dismissed. The samples with highest $[NO_3^-]$ were taken in the middle of the rainy season (which extended from June through September). In addition, Gebhardt and Coleman (1974a, b) have shown that the other dominant ion in these solutions, $Cl^-$, could not displace $NO_3^-$ from anion exchange sites into solutions. Also there is insufficient $SO_4^{2-}$ to displace this much $NO_3^-$.

The abundance of $Ca^{2+}$ in the soil solution (Table 1, Fig. 4) should be expected in Durandept soils. $Ca^{2+}$ dominates the exchangeable bases of these soils, comprising typically 45–87% of the PBS. Our data provide no evidence for the presence of $Ca^{2+}$-organic complexes in the soil, such as the Ca-oxalate reported by Graustein, et al. (1977). Our ionic charge balance for soil solutions are virtually complete, allowing few equivalents for $Ca^{2+}$-organic ions.

The hypothesis that acidity is being injected into the root zone by *Malanthora* and that this process is liberating $K^+$ and nitrogen from the soil is further reinforced in Figs. 5, 6. Ion concentrations in these figures have been corrected for the effects of evapotranspiration. This correction was done by assuming $Cl^-$ was conserved as water traveled through the soil (Gebhardt and Coleman, 1974a). Chloride fluxes at any soil depth when standardized by this means are a constant. Thus any increase in $Cl^-$ with depth can be ascribed to evapotranspiration. Details and justification of this standardization method are given in Parnell (1986).

In Fig. 5, left panel, we show that when acid rain (topmost solid symbols) impacts a soil plot (solid symbols from 0–150 cm) $NO_3^-$ concentrations are significantly raised compared to more normal rain conditions (open symbols). In 1981 when acid rain impacted site M (solid circles), $NO_3^-$ concentrations increased more than 6-fold. When more normal rain returned to site M, the $NO_3^-$ concentrations returned to a much lower value (open circles). The data show that $NO_3^-$ is being generated in the soil solutions of site M particularly at depths of 25–65 cm, the zone of maximum rooting. The increase in $[NO_3^-]$ at

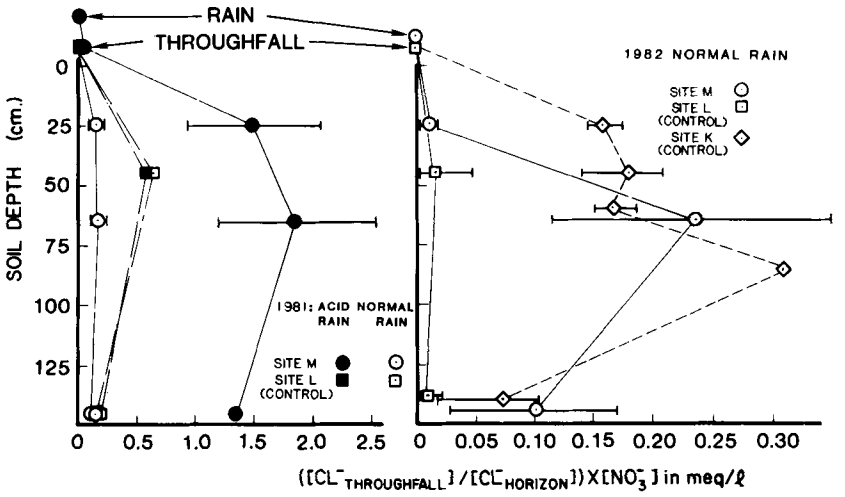


*Fig. 5.* Soil $NO_3^-$ concentration as a function of soil depth. $NO_3^-$ concentration is corrected for evaporation effects by means of a conservative chloride mass balance (Parnell, 1986). On August 24, 1981 (left panel, solid symbols) acid rain fell at site M, but not on control site L. On August 26, 1981 (left panel, open symbols) more normal rain fell at both sites M and L. Note that the nitrate concentration of the soil becomes normal as incident rain pH becomes more normal (left panel). A year later (right panel) these normal nitrate concentrations are again obtained on a day with normal rain (note the change in scale for nitrate concentrations). Bars show the range of values for multiple (3 to 6) samples at the same depth. Symbols without bars represent single data points.

acidified site M is significantly higher than values for a neighboring control site (boxes). The increase in $NO_3^-$ in the soil is evidently a response to the influx of acid rain; $NO_3^-$ concentrations immediately decreases when non-acid rain is restored (left panel, open circles, Fig. 5).

The fact that the rate of $NO_3^-$ influx is a function of acid rain flux is further reflected in the right panel of Fig. 5. During normal rain conditions at site M (open circles), soil $NO_3^-$ concentrations are the same as at control sites (sites L and K). Note the scale differences between the 1981 and 1982 data. It appears then that the natural processes controlling soil $NO_3^-$ are probably the same for all three sites, when ambient precipitation is normal.

The significance of this $NO_3^-$ generation process is reflected in Fig. 6. This plot contrasts the "normal" soil solution $[NO_3^-]$ condition of the control site, against an acid impacted site. As the degree of acidification increases, the amount of $NO_3^-$ released to the soil solution increases. For unacidified conditions, a regression line ($r^2$ = 0.973) suggests a linear relation between $NO_3^-$ and $K^+$. However, when acid anions ($Cl^-$ and $SO_4^{2-}$) are added to the soil through acid rain, the $[NO_3^-]/[K^+]$ ratio changes radically. The increased concentration of $K^+$ (and also $Ca^{2+}$) is the expected electroneutrality response of the soil to increased anionic concentrations. Note, however, that this response is not linear, but exponential. It is clear, therefore, that as soil acidity (or anionic concentration) increases, it becomes increasingly harder for the soil to provide the "excess $K^+$" needed to exchange with $H^+$. Thus, a finite buffer capacity exists in this system. Our experimental data show that it is virtually impossible for the soil exchange sites to release more than 1.6 meq/l $K^+$ to solution (Johnson and Parnell, 1984). This limit is most likely due to a changing $H^+/K^+$ bulk selectivity coefficient for the soil as acidification proceeds. That is, as acid input increases and the *Malanthora* responds by producing acidity in the soil, $K^+$ becomes increasingly hard to extract from exchange surfaces and the amount of $K^+$ that the soil can release or exchange is progressively exhausted.

The acid neutralization process is depleting the exchangeable bases in the soil zone. Fig. 7 shows the range of concentrations and averages of

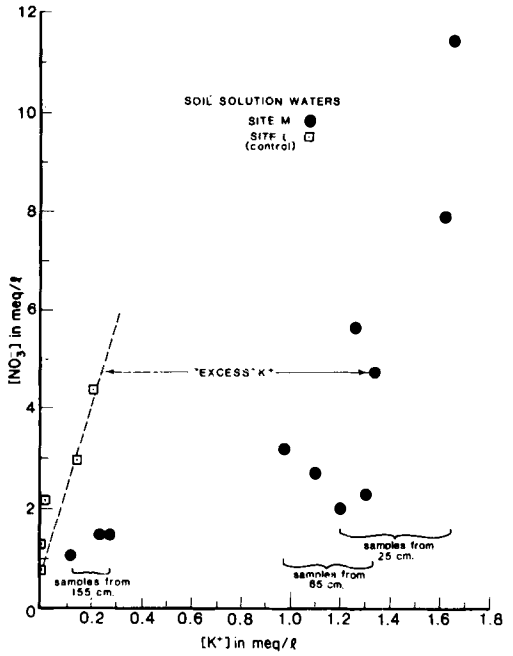


*Fig. 6.* Relationship between soil $K^+$ and soil $NO_3^-$ for both an acid rain plot (site M, solid circles) and a non-acid rain plot (control site L, open boxes). Note that the chemical difference between the two is primarily the excess potassium present in the acid rain impacted plot.

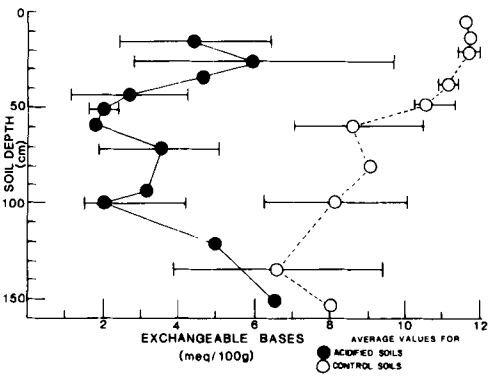


*Fig. 7.* The abundance of exchangeable bases for acidified soils (solid circles and lines) is compared to that for similar, unacidified soils (open circles and dashed line). Circles indicate average values for replicate (3 or 4) analyses of each horizon for 4 acidified soils and 2 control soils. Bars give the absolute range of values for each depth.

exchangeable bases adsorbed in Typic Durandepts for acidified soils (sites A, N, M, LL, X) and unacidified soils (control sites K and L). *Malanthora* occurs at some of the acidified sites and also at one of the control sites, yet no overlap of the data occurs. Thus, vegetative differences alone cannot explain the depletion of exchange sites in soils receiving acid rain. Furthermore, the difference cannot be attributed to a difference in number of possible base exchange sites, because the observed exchangeable acidities (after Page et al. (1982)) for all sites are very similar (Parnell, 1986). In addition, the availability of exchange site material (organic material and amorphous aluminosilicates and sesquioxides) is no greater in the control sites than the acidified sites. Acidified sites M (Km 28) and LL (Km 26) show, if anything, slightly higher concentrations of amorphous aluminum silicates plus aluminum and iron oxyhydroxides in each horizon (Parnell, 1986). Loss on ignition and hydrogen peroxide oxidation data indicate similar values of organic matter content for corresponding horizons at all sites.

In 1982, our data show that the local soils under the volcanic plume already had exhausted about 50% of their normal base exchange capacity (Fig. 7). This perhaps explains why the volcanic activity of Santiago in the early 1950's caused a substantial acreage of coffee plantation to become infertile (K. Matheson, personal communication). We speculate that the affected soils lost their base nutrients as they became acidified in the course of neutralizing volcanic acid rain.

In the shorter-term, however, the effect of the *Malanthora* cover below the Santiago plume is to intercept and chemically neutralize acid rain before it infiltrates the soil. *Malanthora* thus acts as an intermediary between acid rain and the soil, where the final acid-sink really is in this system. Weathering of the volcanic ash represents a long-term source of cations that may partially compensate for these cation losses. It is important to recognize, however, that the neutralization of acid rain would be done by the exchangeable bases in the soil, even in the absence of *Malanthora*. The same chemical principles would apply. As of 1982, the *Malanthora* cover was still thriving under the volcanic plume and its rain of volcanic acids.

## 6. Summary and conclusion

From the above it may be seen that the acidifying effects of the plume from Volcan Santiago makes a richly varied and complicated story. Nevertheless, several firm statements can be made about the present situation:

1. The area impacted by volcanic acid rain is limited and discrete, unlike the widespread contemporary acid rain in Europe and North America.

2. The "acid rain" effect diminished systematically downwind.

3. The intensity of the volcanic acid rain (pH as low as 2.47) is as great or even greater than contemporary anthropogenic acid rain.

4. The composition of the acid rain is HCl and $H_2SO_4$, rather than the $HNO_3$ and $H_2SO_4$ of anthropogenic acid rain.

5. Acid intensity is controlled primarily by HCl.

6. The ground and surface waters of the watersheds affected by the Santiago volcanic plume show no chemical effects (other than increased $[Cl^-]$ and $[SO_4^{2-}]$) at the present time.

7. The shrubs, *Malanthora* and *Lantana* completely neutralize acid rain in their canopies, primarily by releasing $K^+$.

8. Simultaneously with 7 above, the root zone of *Malanthora* is acidified by the release of acidity.

9. The biochemical effect of *Malanthora* involves a tight, efficient recycling of $K^+$ by the plant.

The above conclusions reiterate that the effects of acid rain from the plume of Santiago vent are complex. This form of acid rain is entirely natural and the ecosystem of the affected area shows remarkable adaptations.

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