Research

Dry Deposition and Heavy Acid Loading in the Vicinity of Masaya Volcano, a Major Sulfur and Chlorine Source in Nicaragua

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Certain volcanoes constitute the world's largest sources of SO_2, HCl, and HF emissions and contribute significantly to regional acid deposition. However, the impact of volcanic acid emissions to nearby ecosystems remain poorly documented. In this paper, the spatial pattern of acid dry depositions was monitored within 44 km of Masaya Volcano, Nicaragua, with a network of sulfation plates. Measured SO_2 deposition rates were $<2-791$ mg m^{-2} day^{-1}. The plates also collected the dry deposition of HCl at rates of $<1-297$ mg m^{-2} day^{-1}. A similar deposition velocity V_d (gas transfer) of 1.6 ± 0.8 cm/s was calculated for SO_2 and HCl above the plate surfaces. Quantities of SO_2 and HCl deposited daily within the area surveyed amounted to 1.5×10^8 g and 5.7×10^7 g, respectively, which correspond to about 10% of the total SO_2 and HCl released by the volcano. These depositions may generate an equivalent hydrogen flux ranging from <1 to 30 mg m^{-2} day^{-1}. Our results demonstrate that volcano emissions can dramatically affect acid deposition downwind and in turn cause extreme acid loading of the local ecosystems. This study opens exciting prospects for investigating the sensivity of volcanic ash soils to acid inputs.

Introduction

Recognition that sulfur releases from metal smelters and coal-power plants are a major contributor to atmospheric acid

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deposition is long standing (*1*). Natural analogues of these anthropogenic emitters are certain volcanoes, which persistently eject sulfur gases, mainly in the form of SO_2, at rates of $0.1-100$ kg s^{-1} into the atmosphere (*2*). Recent studies indicate that this natural source contributes significantly to regional sulfur deposition in Asia (*3*). Surprisingly, little is known about acid deposition in the vicinity of a volcanic emitter. Abatement strategies for industrial sulfur gas releases are not readily applicable to degassing volcanoes, and as a result, local environments can be subjected to harmful fumes for many years. Furthermore, volcanic emissions also contain substantial amounts of halogen gases, mainly HCl and HF, that may enhance acid deposition.

Although there is historical evidence for disruption to ecosystems in areas exposed to volcanic degassing (*4−6*), the problem of acid deposition in volcanic areas has been poorly investigated. The few studies available (e.g., refs *7* and *8*) only report on the intermittent and local influence of volcanic emissions emanations on rainwater chemistry. The cumulative amounts of acid precursors dry-deposited onto the land following several months of sustained fumigation is of special interest mainly because dry deposition is an important means by which air pollutants can be transferred to terrestrial environments. Its quantification is essential to determining critical loads to ecosystems.

Acquiring meaningful long-term dry deposition estimates is difficult (*9*). The variable used to estimate deposition rates is the dry deposition velocity V_d, whose product with concentration at a specified height yields the mass flux density. Since V_d varies with the type of surface, wind speed, atmospheric stability, and possibly other factors, it is seldom measured directly. Rather, a V_d value is modeled or assumed in order to calculate dry deposition. In this context, monitoring of a volcanic area, usually associated with complex topography with a various surface types (forest, agricultural fields, water surfaces, and vegetation-free surfaces), is particularly challenging. Surrogate surfaces may provide a meaningful alternative to measuring cumulative acid dry deposition. Among these surfaces, sulfation plates (*10*), which consist of lead dioxide-treated plastic, have been used successfully to monitor SO_2 deposition downwind of industrial point sources (*11−13*). It is a simple and cost-effective technique that provides spatial and temporal information on dry deposition. Unfortunately, artificial surfaces cannot adequately account for the complexity of natural surfaces, and the method may only yield crude estimates of deposition. Nevertheless, these may bound within acceptable limits if the V_d of the air pollutant of interest can be determined and subsequently compared with expected V_d values for natural surfaces.

Here, we present the results of a study conducted in proximity of Masaya Volcano, a major volcanic source in south central Nicaragua. The primary objectives are (i) to measure the acid dry deposition pattern around the volcano using sulfation plates and (ii) to evaluate the removal efficiency of the volcano acid emissions by the process of dry deposition. This project is part of a program aimed at understanding the impact of volcanic activity on the environment.

Experimental Section

Area Description. Masaya Volcano is a basaltic edifice undergoing recurrent degassing since 1852 (*4, 14*). The irregular topography around the volcano (Figure 1A) results
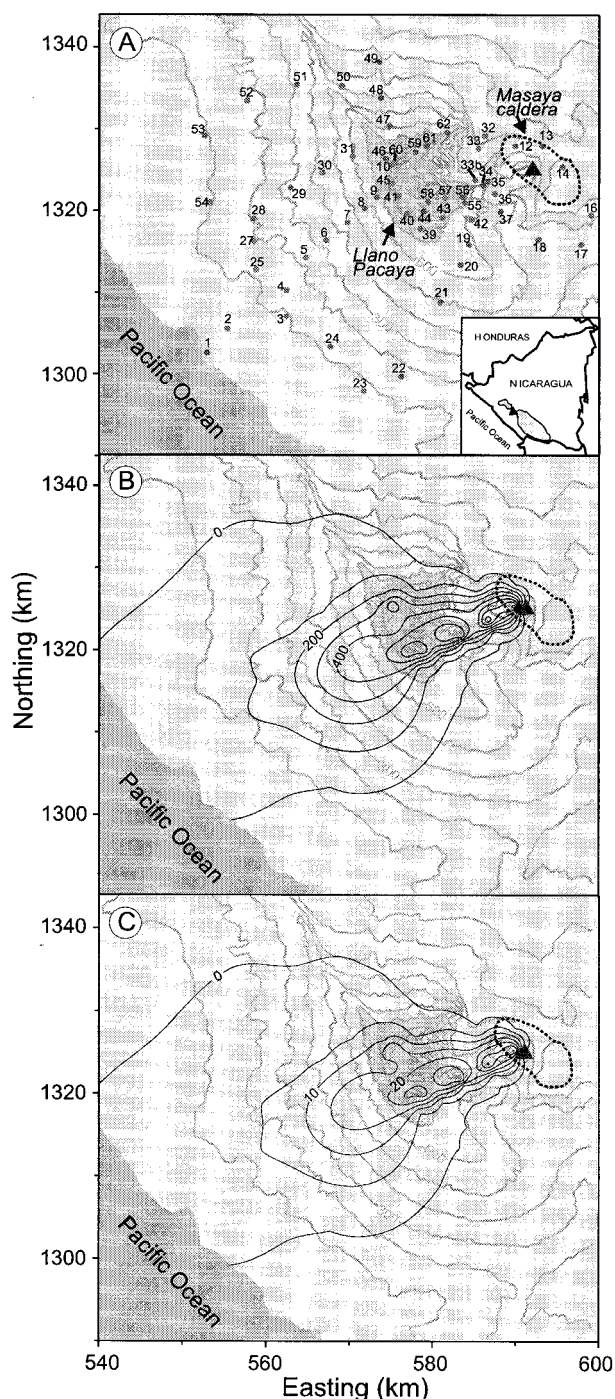
FIGURE 1. (A) Map of the study area in the vicinity of Masaya Volcano, Nicaragua, with the locations of the main topographic features and sites monitored over the period February–March 1999. Heights in meters. Shaded area is the Llano Pacaya Ridge. The dotted ellipse sketches the Caldera Rim, and the black triangle represents the degassing vent. (B) Sulfation rate (mg of SO$_2$ m^{-2} day^{-1}) contour map based on measurements made during the study period. (C) Spatial pattern of calculated hydrogen deposition fluxes (mg of H$^+$ m^{-2} day^{-1}) for the study period.

from the combined effects of past eruptions, which produced a caldera and thick pyroclastic deposits, and erosional processes. In contrast to many volcanoes, Masaya has a comparatively subdued topographic expression. With a height of 560 m above sea level, the emission source is actually lower than the second prominent topographic feature of the region, the Llano Pacaya, located approximately 15 km to

the west. This ridge has an elevation of 700–920 m and is flanked by numerous steep valleys and gorges. West of the Llano Pacaya, the land slopes toward the Pacific Coast (44 km from the volcano).

The present gas crisis at Masaya started in mid-1993. Monitoring of this activity in 1999 revealed that the volcano is emitting approximately 19 kg s^{-1} of SO$_2$, 7 kg s^{-1} of HCl, and 1 kg s^{-1} of HF into the atmosphere and that these emissions are carried westward by the prevailing trade winds (15). The Masaya Volcano is currently one of the world's strongest sources of SO$_2$ and also contributes substantial amounts of halogens to the atmosphere. Historical accounts (e.g., ref 4) reported on the blighting effects of the volcanic fumes on the vegetation along the Llano Pacaya ridge, while the influence on rain chemistry of the Masaya plume also was demonstrated (8).

Sampling Sites. The study was conducted during four weeks in February–March 1999. In the dry season (December–May), there are steady easterly trade winds that blow accross Masaya Caldera. Fifty-five monitoring stations were installed within 44 km downwind of the volcano, while four background stations were established to the east, upwind of the source (Figure 1A). The sampling units were placed 1.5–2.5 m above the ground and in open areas as much as possible. Inverting the samplers prevented contamination from wet deposition. The exposure times varied from 21 to 27 days.

Sulfation Plates and Diffusion Tubes. The sulfation plates were made after Huey (10) by coating Petri dishes with an adhesive lead dioxide paste. These work on the principle that atmospheric SO$_2$ reacts with lead dioxide to form insoluble lead sulfate. The device is exposed to ambient air for a specified period and provides reliable SO$_2$ absorption (or sulfation) rates on the plate surface (11, 16). In conjunction with the sulfation plate, a commercially available (AEA Technology, U.K.) diffusion tube was used for the simultaneous determination of atmospheric SO$_2$ concentration. The diffusion tube contains a potassium hydroxide-impregnated absorbing medium at one end and a porous poly(tetrafluoroethylene) membrane at the other end to prevent wind-driven shortening of the diffusion path (17).

Analytical Methods. After being exposed, the lead dioxide was systematically transferred from the sulfation plates and treated with potassium carbonate (10). The extract solution was analyzed for sulfate (SO$_4^{2-}$) content by ion chromatography. The mean value of 10 blanks was 98 ± 40 μg of SO$_4^{2-}$ per plate. Analysis of the exposed plates also revealed the presence of chloride (Cl$^-$), but this anion could not be detected on the blank plates. The unforeseen detection of Cl$^-$ is believed to reflect the dry deposition of HCl gas onto the plate surface (see below). The absorption rates or sulfation (mg of SO$_2$ m^{-2} day^{-1}) and chloridation (mg of HCl m^{-2} day^{-1}) rates were determined from the sulfation plate area (0.00181 m^2) and the duration of exposure. A practical detection limit for the sulfation rate was assumed to be three times the standard deviation of our mean blank, while the instrumental detection limit for Cl$^-$ was used to provide a detection limit of the chloridation rate. This corresponds to a 30-day exposure of the sulfation plate to a sulfation rate of 1.5 mg of SO$_2$ m^{-2} day^{-1} and a chloridation rate of 0.5 mg of HCl m^{-2} day^{-1}. The mean relative deviation of the method obtained by exposing 12 sampler pairs was 2.1% and 2.5% for SO$_2$ and HCl absorptions, respectively. Chemical analysis of the diffusion tubes was conducted at AEA Technology, where the absorbent medium was removed and absorbed SO$_2$ was extracted as SO$_4^{2-}$ with a hydrogen peroxide solution (17). Sample solutions were also analyzed by ion chromatography. The mean value of nine travel blanks was 0.18 ± 0.09 μg of SO$_4^{2-}$ per tube. The detection limit (i.e., three times the standard deviation of the blank) of the method corresponds

to an exposure of the tube to approximately 5 μg of SO_2 m^3 for 30 days. Exposing 11 diffusion tube pairs at sites assessed the precision of these measurements. The mean relative deviation was 5.5%.

Results and Discussion

Sulfation and Chloridation Rates. The sulfation plate data indicated low rates of sulfation (<2 mg of SO_2 m^{-2} day^{-1}) at sites upwind of Masaya Volcano. In contrast, sulfation rate values ranging from <2 to 791 mg of SO_2 m^{-2} day^{-1} occurred downwind at sites exposed to the acid emissions. For comparison, maximum sulfation rates measured by the same method downwind of industrial sulfur point sources are in the range 10−100 mg of SO_2 m^{-2} day^{-1} (*12, 13, 16*). The areal distribution of the sulfation rates around the volcano is best described from the contour map constructed by kriging and shown in Figure 1B. Clearly, this suggests a strong influence from Masaya's emissions on the dry deposition pattern of SO_2. Sulfation rates above background values were detected over an area of about 1250 km^2, which corresponds to an average dispersion by the trade winds of the SO_2-containing plume over a 40° sector. The sulfation rate contour map reveals a general decrease in sulfation rates with distance from the volcano, simply reflecting bulk dilution of the SO_2 emissions during transport. The highest sulfation rates were found on the outer caldera rim slope, within 6 km of the emission source. Field observations suggest that the steep caldera wall encircling the degassing crater of Masaya to the west is a direct obstacle for the plume emissions. We suspect that secondary turbulences forming on the leeward side of the caldera rim promote downflow of the airborne pollutants, thus enhancing dry deposition.

Other noticeable heterogeneities in the spatial pattern of sulfation rates occur at more distal sites as shown by the presence of additional maxima (>500 mg of SO_2 m^{-2} day^{-1}) ~15 km from the volcano. This seems to relate to a rise in terrain associated with the Llano Pacaya ridge. The southeast margin of the ridge also was affected by a strong lateral gradient in sulfation rates. All together, these features reveal the chronic fumigation of the Llano Pacaya area, including the highlands and steep valleys. The low height of the degassing crater relative to the land downwind often causes the plume to be at ground level for several kilometers, a phenomenon that increases dry deposition. The intensity of fumigation will likely depend on the existence of a low-level capping temperature inversion that impedes plume rise. These peculiar conditions may add to ephemeral but intense morning fumigation events, which are associated with increased vertical mixing of air as heating of the surface after sunrise dissipates the nocturnal inversion. The sulfation rate measurements at Masaya indicate that topography exerts a strong control on plume dispersion and subsequent deposition.

Hydrogen chloride is the dominant chlorine compound of high-temperature volcanic gases (*18*). It is a highly reactive species that may be readily captured by the lead dioxide coating of the sulfation plates, possibly to form lead chloride. Therefore, we suspect that the detection of Cl$^-$ on the plates exposed downwind of Masaya indicates capture of volcanic HCl. The measured chloridation rates show a strong linear correlation ($r = 0.98$) with the sulfation rates (Figure 2), which suggests minimal interference between SO_2 and HCl during collection. Chloridation rates were below the detection limit (<1 mg of HCl m^{-2} day^{-1}) at background sites. However, chloridation rates ranged from <1 to 297 mg of HCl m^{-2} day^{-1} at sites affected by the gas emissions. Over the period of study, these rates were 2−3 times lower than the sulfation rates, but patterns of sulfation and chloridation are identical.

Dry Deposition of SO_2 and HCl. The sulfation and chloridation rates determined within 44 km of Masaya
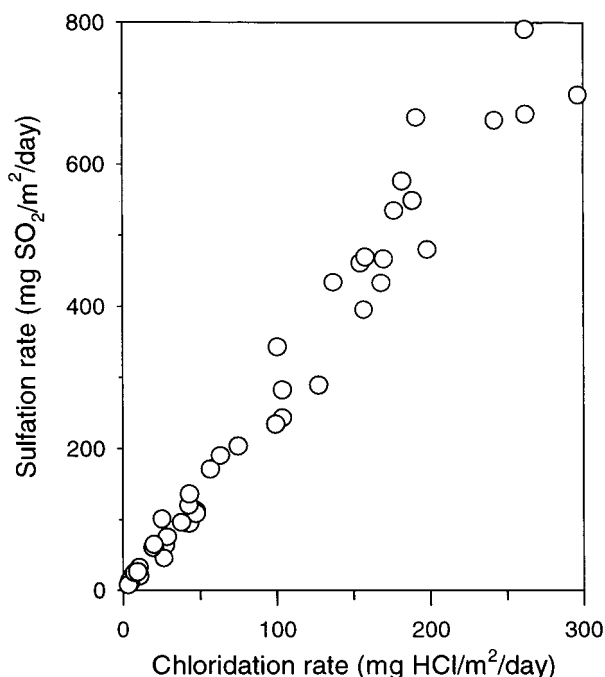

FIGURE 2. Scatter plot of sulfation and chloridation rates measured with sulfation plates in February−March 1999.

Volcano may give reasonable estimates of the actual SO_2 and HCl dry deposition rates, providing that the V_d of SO_2 and HCl above the sulfation plate surfaces mirror the V_d above the ecosystems found in the area. Calculations of the SO_2 V_d associated with the sulfation plates are made using the atmospheric SO_2 concentrations obtained with the diffusion tubes. This yields a V_d of SO_2 for the sulfation plates of the monitoring network varying from 0.5 to 3.8 cm s^{-1}, with a mean of 1.6 ± 0.8 cm s^{-1}. The good linear relationship ($r = 0.92$) between the sulfation rate and the SO_2 concentration values (Figure 3) confirms the validity of our measurements.

The variations in the V_d estimates partly result from the errors affecting the sulfation plate and diffusion tube measurements. However, these should not raise the baseline uncertainty above 10%. Another potential source of V_d fluctuations relates to the sensitivity of the sulfation plates to wind speed. The theoretical model of Liang et al. (*19*) suggests that the absorption rate of SO_2 by sulfation plates is approximately proportional to the square root of the mean wind speed. Thus, exposure of the sulfation plates to similar atmospheric SO_2 levels may yield significantly different V_d values depending on surface wind speed conditions. The peculiar geographical (land and sea) and topographical (hill and valley) configuration of the area monitored certainly produces site-to-site variations in wind speed that may impact the sulfation rates and, in turn, the V_d estimates.

The range of SO_2 V_d values for the sulfation plates also may reflect the occurrence of extreme atmospheric stability or inversion conditions, which lead to intense fumigation of the land. We noted that V_d values tend to be highest on the Llano Pacaya ridge, where plume grounding strongly dictates dry deposition. In this area, the V_d may be aerodynamically controlled, and thus, the sulfation plates probably recorded high sulfation rate episodes even if the replenishment of near-ground SO_2 concentration from aloft was minimal (i.e., low air turbulence). Elsewhere, the samplers could integrate both the low and high deposition events, which typically correlate with the diurnal variability in the turbulent conditions of the planetary boundary layer.

Although an average value of V_d between 0.5 and 0.8 cm s^{-1} is often used for estimating deposition of SO_2 over various
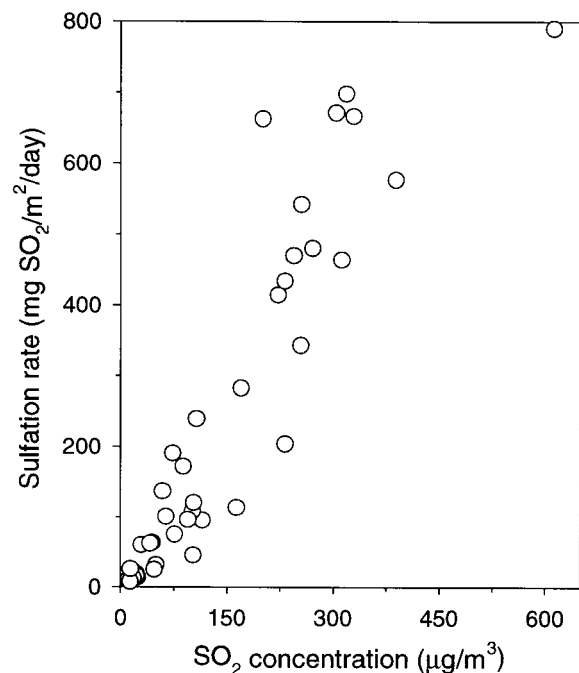
FIGURE 3. Scatter plot of sulfation rates and atmospheric SO_2 concentrations measured with sulfation plates and diffusion tubes, respectively, in February—March 1999.

vegetation and soil surfaces, the value may actually vary from 0.1 to 2.8 cm s^{-1} (20). Some authors (21, 22) suggested that a V_d value of 1.5 cm s^{-1} may actually account for the combined effects of exposed forest soil and vegetation on SO_2 deposition. Recently, Bourque et al. (13) concluded that SO_2 absorption measured by sulfation plates may be a good approximation of SO_2 deposition onto forested lands despite the fact that the surrogate surfaces do not account for a range of effects (e.g., surface wetness, SO_2 saturation, etc.). On the basis of these considerations and on our V_d estimates, we propose the working hypothesis that the pattern of sulfation rates depicted in Figure 1B constitutes a crude but reasonable picture of the actual SO_2 dry deposition distribution at Masaya. The fact that vegetation and soil surface types encountered differ from those found in the Northen Hemisphere for which dry deposition studies usually apply emphasizes the need for extending dry deposition investigations to tropical ecosystems.

In contrast to SO_2, the dry deposition of HCl has received little attention in the literature. There is a broad agreement that surface resistance to deposition is negligible, which implies that the V_d for HCl under most circumstances is at least as high as for SO_2 (23, 24). Thus, for the sulfation plates, the V_d of HCl may be comparable to the V_d of SO_2. An indirect confirmation of this is obtained from the values of the SO_2/HCl mass ratio of the gas plume and in the dry depositions collected on the sulfation plates. Monitoring of the plume made at the same time at the source with an open-path Fourier transform infrared spectrometer indicated a mean SO_2/HCl ratio value of 2.8—3.0 (25), which is similar to the mean SO_2/HCl ratio value of 2.7 ± 0.5 detected by the sulfation plates. The close agreement between the two ratios supports the idea that SO_2 and HCl in the plume were sampled with comparable deposition velocities by the sulfation plate surfaces, i.e., the mean V_d of HCl for the sulfation plates may be about 1.6 ± 0.8 cm s^{-1}. This value lies within the range of 0.4—17.0 cm s^{-1} for HCl reported for various vegetative surfaces (24). Like SO_2, the working hypothesis is made that the measured chloridation rates provide crude estimates of the HCl dry deposition amounts in the study area.

Removal Efficiency of the Volcanic Emissions and Acid Loading of the Ecosystems. The total dry deposition of SO_2 within 44 km of the Masaya Volcano was computed from the sulfation rate contours (Figure 1B). According to these data, the total daily amount of SO_2 deposited to the land and over a 1250 km^2 area was approximately 1.5×10^8 g. Similarly, we inferred a total HCl dry deposition of 5.7×10^7 g day^{-1}. It follows that the masses of SO_2 and HCl scavenged by the process of dry deposition correspond to less than 10% of the total daily volcanic emissions of SO_2 ($\sim 1.8 \times 10^9$ g) and HCl ($\sim 0.6 \times 10^9$ g). We note similar trends for sulfur budget studies of industrial plumes: the measured or modeled amount of SO_2 deposited to the land as dry deposition is about ~ 2–8% of the total SO_2 emitted into the atmosphere (12, 13).

The significant amounts of SO_2 and HCl deposited over the area affected by the volcano emissions contribute to substantial acid loading. The combined SO_2 and HCl depositions measured within 44 km of Masaya may generate an equivalent total hydrogen (H$^+$) flux ranging approximately from <1 to 30 mg m^{-2} day^{-1}. Moreover, acid loading intensifies in sectors affected by downwash and fumigation. This situation is likely to prevail throughout the dry season (from December to May) and probably recurs each year while the volcano maintains its current level of degassing activity. It follows that the annual hydrogen dry deposition input to the land may vary from ~ 0.1 to 5.9 g m^{-2} yr^{-1}, depending on location (Figure 1C). Acid loading at these rates is 1—10 times the highest acid deposition rates observed worldwide (22). This important finding relies on relatively simple measurements. Nevertheless, its applicability would be uncertain if the actual dry deposition rates of SO_2 and HCl were to depart substantially from those recorded by the sulfation plates, which seems unlikely. Finally, our estimates do not take into account the deposition of HF, a highly reactive species which is emitted at significant rates by the volcano.

Prolonged exposure of the ecosystems around Masaya Volcano to elevated acid inputs may result in acidification and contamination of the soils. Notably, Parnell et al. (26) found a decline in the base-saturation levels of the soils from the Llano Pacaya ridge in response to intermittent acid rains. Soils in the Masaya area are derived from volcanic ash and are Andisols. The ability of such soils to assimilate acid depositions is the subject of ongoing researches aimed at determining critical loads of acidity (27—29). This should be viewed in the broad context of the rapid increase of anthropogenic acid emissions in East Asia (3), where volcanic sources are more important and Andisols are more common than in Europe and North America. A site such as Masaya offers unique conditions to investigate the sensitivity of volcanic ash soils to various acid deposition fluxes. It also enables investigation of the transfer of air pollutants (such as SO_2, HCl, and HF) to ecosystems. The long-term environmental impact of background degassing at persistently active volcanoes may have been overlooked.

Acknowledgments

Supporting Information Available

Table of the SO_2 concentrations, sulfation, and chloridation rates and calculated SO_2 dry deposition velocities and

hydrogen deposition fluxes in the Masaya area (February−March 1999) (1 page). This material is available free of charge via the Internet at http://pubs.acs.org.

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