

Examining the ecological impacts of persistent volcanic degassing at Masaya, Nicaragua, using multi-temporal MODIS NDVI and ground-based data

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Masaya volcano is located within the most densely populated area in Nicaragua and has been in a persistent state of passive degassing since entering its current phase in 1993. The volcanic emissions are predominantly blown in a west to southwest direction by regular trade winds during the dry season, which runs approximately from December through April. Continued long-term exposure to these volcanic emissions is known to result in a range of human and environmental impacts.

At Masaya changes in the sulphur dioxide gas flux have most frequently been documented during the dry season using field campaigns of FLYSPEC measurements and/or diffusion tubes. Dry deposition of volcanic sulphur, chloride and fluoride has been determined using sulphation plates. Previous satellite-based assessments of vegetation have mostly been limited to two-date change detection but compositional analyses of soils and plants show uptake into the local ecosystems. Although proximity and spatial distribution are known to influence vegetation response, little is known about the impact on vegetation of temporal variations in gas flux and/or direction, particularly during the wet season, from May to November.

Therefore this study presents a time-series of more than 200 Moderate Resolution Imaging Spectrometer (MODIS) Normalised Difference Vegetation Index (NDVI) 250 m 16 day composite data from 2002-2012. Results from the satellite-based data are compared and contrasted with the available ground-based measurements of gas flux and deposition alongside vegetation surveys of species richness and abundance, as well as plant morphological responses.

Incorporating this increased understanding of the annual and long-term vegetation responses to the volcanic plume will inform risk reductions strategies related to human health, land use and agricultural productivity.

Environmental implications of persistent degassing: Evidence from Masaya volcano, Nicaragua

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Understanding the effects of persistent gas emission is of great importance for human toxicology and agricultural productivity as volcanic contaminants that enter the food chain via uptake by plants can pose a serious ecological threat. In this study the active system at Masaya volcano (Nicaragua) is investigated in order to assess the environmental impacts caused by its continuous degassing.

Contaminant deposition in the plume-affected area was assessed by the quantification of sulphate deposition and heavy metal concentrations in the soils (Fe, Cr, Cu, Mn, Ni, Zn, Se, As and Hg). The organic carbon contents and pH of the soil samples were also determined. Vegetation samples of *Dalechampia scandens* (Euphorbiaceae) and *Tillandsia recurvata* (Bromeliaceae) were also analysed for heavy metals, and their potential as biomonitors of volcanic pollutants assessed.

The data demonstrate that organic carbon and pH play important roles in the accumulation of heavy metals by influencing the cation exchange capacity and bioavailability of the soil (White, 2006). High levels of organic carbon were associated with a greater accumulation of metals, while the effect of pH was more closely linked to specific metals. Heavy metal concentrations were highest in the agricultural soils, with some elements such as Cu and Mn exceeding soil guideline values (Environment Agency, 2009). The transfer of soil contaminants into *D. scandens* is closely linked to soil properties but the plant also appears to be greatly affected by the atmospheric conditions. The growth distribution of *T. recurvata* is linked to the concentration of contaminants, and suggests a level of resistance that allows the plant to grow until a certain contamination threshold has been reached. This may allow us to recognise concentrations of contaminants associated with its presence.

Because Masaya volcano is continuing its current degassing cycle, the further accumulation of heavy metals may significantly impact soil quality, soil-plant transfer and agricultural productivity in the region. Further monitoring of the effects of volcanic emissions on the local environment is therefore required in order to help minimise the adverse effects of this plume.

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High-resolution size distributions and emission fluxes of trace elements from Masaya volcano, Nicaragua

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Active volcanoes are significant natural sources of trace elements to the atmosphere yet the processes of emission and the impacts of deposition into terrestrial and aquatic environments remain poorly understood. The varying contributions of volatile degassing and magma ejection (i.e., spattering, spraying, extrusion and fragmentation) to the emission of trace elements from Masaya volcano (Nicaragua) are investigated through measurement of high-resolution trace element size distributions using cascade impactors in 2009 and 2010. The volatile elements (e.g., As, Cd, Tl, Cu, Pb, Zn) are strongly correlated across the size distribution and exist in the plume primarily as fine sulfate (0.6 μm diameter) with lesser amounts transported as coarse sulfates (3.5 μm diameter) and coarse chlorides (11 μm diameter). These results suggest that trace elements released from the magma as chlorides react rapidly with H_2SO_4 in the plume to form sulfates. In contrast, the non-volatile elements (e.g., alkali earth and rare earth) exist primarily as particles in the 1-10 μm range and show no correlation with sulfate, chloride or the volatile elements, suggesting that they are emitted primarily by magma ejection. Trace element emission fluxes from Masaya in 2010 were estimated using filter pack measurements, with emissions of Cu, Zn, As, Tl, Rb and Cd each in excess of 10 kg d^{-1} . These emission fluxes are similar to those measured in 2000-2001 suggesting notable decadal stability in the emission of trace elements from Masaya.

Mechanism of high concentration events of sulfur dioxide at the surface around Sakurajima Volcano

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One hour data of SO₂ and SPM (Suspended Particulate Matter) at 20 surface stations in Kagoshima Prefecture for eleven years since 2001 were analysed, together with dispersion images of Sakurajima plumes obtained by automatic long-term recordings at the sites 10-15 km away from the source at different directions supplemented by occasional satellite data and meteorological information.

Yearly variation of high concentration events of SO₂ and SPM reflected the eruptive activities of Minamidake crater at the summit, which gradually decreased in this century, and Showa crater at the eastern shoulder of the mountain, which started in 2006 and has become very active since 2009. Temporal variation of the events depends strongly on the direction and distance of a site from two nearby sources, and the meteorological condition which may change within few hours. The advection of SO₂ and SPM from the volcano can be inferred from plume images, as the volcanic gas tends to behave together with the plume.

When the upper wind is strong enough, exceeding 10 m/sec at 925 hPa which is close to the summit height, the plume tends to be blown down to the foot of the mountain and then rises somewhat following the pattern of mountain-lee wave. If there is a station at the foot in a narrow area downstream from the source, one may find high concentration of SO₂ exceeding 100 ppb and associated SPM in many cases. In the narrow area downwind of the plume, relatively high concentration events may often be seen at a distance 20-40 km from the source.

When there is a calm wind, the plume rises a few hundred meters or more from the crater, and the concentrations of SO₂ and SPM at the surface stay rather low. The situation is similar in the case of a big eruption with heavy ash-fall, which are mostly coarse-grained near the volcano. However, high SO₂ concentrations at the ground may also happen in light winds when convective mixing on sunny days brings the SO₂ (and SPM) back to the ground level at the downstream.

In some cases, SPM is almost lacking in a plume classified as white one with little ash components. On the other hand, an overall increase of SPM was sometimes found at almost all stations owing to the drift of Asian dust or polluted air from Chinese continent.

The enigma of reactive nitrogen in volcanic emissions

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Nitrogen fixation has been reported at numerous active volcanoes. Where it occurs, it should enhance nitrogen bioavailability in the local environment and reactive nitrogen chemistry in the troposphere. Measurements of reactive nitrogen species in volcanic emissions are highly variable, in part due to an incomplete assessment of a diverse speciation (e.g., NO, NO₂, HNO₃, NO₃⁻ and NO₂HO₂), but suggest typical molar ratios of NO_y/H₂O = 10⁻⁵. These high levels of reactive nitrogen species may be explained by equilibrium in high temperature (>1000 C) mixtures of magmatic and atmospheric gases. However, using a kinetic model for a simplified magmatic and atmospheric gas mixture (i.e., the C-O-N-H-Ar system), we show that the rate of thermal nitrogen fixation is too slow for equilibrium to be attained in transient mixtures forming at volcanic vents. Other mechanisms for high NO_y/H₂O should therefore be considered including the catalysis of nitrogen fixation by metal salts. Our results also suggest that H₂ and CO should oxidise extremely rapidly (<10⁻³ s at 1100 C) at volcanic vents, conflicting with recent measurements indicating the stability of these reduced species. We therefore propose that high temperature oxidation at volcanic vents is a sporadic process due to variability in the mixture lifetime (with time and across the mixing front between magmatic and atmospheric gases). This variability would result in minimal losses of H₂ and CO while still allowing oxidised trace species (e.g., NO, OH, Br, Cl) to form in significant concentrations and thus influence the chemical evolution of the volcanic plume at ambient temperatures.

New insights into the scavenging of fluoride by ash in volcanic eruption plumes

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It is well established that gas-ash interaction in volcanic eruption plumes is the main source of soluble fluoride in ash deposits. The occurrence of fluoride in ash is often a cause of concern as elevated levels of fluoride in the environment may lead to negative environmental and health effects. However, the mineralogy of fluoride compounds on ash surfaces remain not well understood, thus impeding our capacity to assess the hazard posed by fresh or aged ash deposits. We combine the results of leachate, total fluoride and surface-sensitive (X-ray Photoelectron Spectroscopy, Field Emission Scanning Microscopy) analyses performed on ash samples from the 2010 eruption of Eyjafjalokull volcano, Iceland, to provide new insights into the scavenging of fluoride by volcanic ash. We show that soluble fluoride on ash surfaces exists in the forms of simple salts (e.g., sodium fluoride), silicon hexafluorides and/or silicon-fluoride bonds (i.e., Si-F). Calcium fluoride and aluminium fluoride may also occur in some ash samples. There is no evidence for the presence of fluoride in calcium fluorophosphate. Importantly, the eruption style governs the scavenging of fluoride by ash and the mineralogy of the secondary fluoride compounds deposited; magmatic eruptions favour the formation of soluble fluoride on the ash surface, while in phreato-magmatic eruption, fluoride is preferentially removed by the liquid phase of the plume. These results have significant implications for understanding the release of fluoride from and the geochemical reactivity of ash deposits upon exposure to environmental agents.

New insights into volatile adsorption by tephra in volcanic eruptions

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The scavenging of S, Cl and F –bearing volatiles by silicate ash from eruption plumes is a source of diverse physical and chemical effects in volcanic, atmospheric and environmental systems. Retention on ash particles within the plume decreases the volcanic volatile flux to the atmosphere, moderating any perturbation of its chemical or radiative properties. The soluble salts and aqueous acids formed by scavenging may alter ash surface properties, influencing dispersal and fallout by promoting particle aggregation. Upon deposition into the environment, aqueous leaching of the ash surface may result in corrosive damage to vegetation and calcareous biota; algal blooms in lake and ocean surface waters; and changes to soil and sediment pore water chemistry. To determine the severity and significance of these potential effects requires knowledge of the abundance and chemical properties of the salts and acids formed on the ash surface. This necessitates a new, in-depth and quantitative understanding of volatile scavenging mechanisms, expanding upon the simple, conceptual, ‘solid aerosol adhesion – volatile adsorption – acid condensation’ scavenging model proposed by N. Oskarsson in 1980.

Here we present the results of SO₂ and HCl uptake experiments on tephrite, phonolite, dacite and rhyolite glass powders conducted over a range of in-plume temperatures (100–800°C). We identified coupled adsorption-diffusion mechanisms driving SO₂ and HCl scavenging. These volatiles reacted with Ca- and Na-bearing surface sites to form CaSO₄, Na₂SO₄ and NaCl deposits, sustained respectively by near-surface co-diffusion of O²⁻ with Ca²⁺ or Na⁺, and interdiffusion between H⁺ and Na⁺. Our experimental results identify the thermal, temporal and compositional controls acting in the post-fragmentation conduit and eruption plume which regulate the adsorption of SO₂, HCl, and by analogy, HF, on ash surfaces. This constitutes the first significant update to the classical scavenging model of Oskarsson in over thirty years. Using our experimental data, and by reference to plume evolution and conduit flow models, we constructed a predictive model of SO₂ and HCl adsorption by tephra surfaces. We therefore highlight those eruptions where gas-ash interactions may strongly affect ash surface chemistry and the intensity of any induced physical or chemical effects in volcanic, atmospheric or environmental systems.

Geochemical and geocological aspects of volcanic eruptive activity (Klyuchevskaya group of volcanoes, Kamchatka)

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Estimation of concentration of petrogenic elements in seasonal snow cover and glaciers made it possible to introduce a method for estimating geochemical pollution caused by modern volcanism. The snow and ice can be viewed as a reflection of the regional lower atmosphere recording volcanic and anthropogenic pollution impacts on the local atmosphere, water basins and soil.

Glaciochemical data of the volcanic activity in the Klyuchevskaya group of volcanoes were analyzed (eruptions at Sheveluch, Klyuchevskoy, Bezymianny, and Ushkovsky volcanoes). Long-term investigations of single eruptions and core drilling of ice caps at active volcanoes allowed us to use space distribution of soluble and petrogenic elements, which come into natural environment.

It was shown that ion composition of chemical admixtures in snow cover and perennial sequences of firn and ice, along with horizons of buried tephra provide data on volcanogenic pollution, the size and character of ongoing volcanic events.

The paper provides results from complex research of a core from a 212-m deep borehole, which was drilled in the glacier at the summit of Ushkovsky Volcano in 1998. Major ion composition as well as pH and ice electroconductivity (EC) vary with depth and time. Both annual and perennial variations in concentration of chemical elements are related to transport of the erupted materials in the atmosphere and sedimentation on the summit of the volcano. Strong variations of ion concentration (from ppb traces to tens for the ppm level) indicates that high values are definitely related to the volcanic eruptions, just like it is shown at depths dated according to the following volcanic eruptions: 35 m for the 1955-1956 Bezymianny eruption; 84 m for the eruption in Hertz crater at Ushkovsky Volcano in spring 1890; 102 m for the 1829 Klyuchevskoy eruption.

Acidic processing enhances iron solubility in volcanic ash: a mechanism for increased iron input and organic carbon production upon ash deposition to the surface ocean.

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Marine primary production, driven by photosynthetic phytoplankton, plays a key role in regulating atmospheric carbon dioxide. However, it is limited by a low concentration of dissolved iron (Fe) in approximately 30% of the surface ocean. Atmospherically deposited volcanic ash is increasingly recognised as an intermittent source of Fe to the marine environment which, over geological timescales, may impact the carbon cycle and ultimately the global climate.

A better understanding of the poorly constrained controls on volcanic ash Fe solubility from magma source to ocean sink is crucial for unravelling the impact of ash on the ocean biogeochemical Fe cycle and thus on primary productivity. Research on mineral dust has highlighted that dust Fe solubility is enhanced by interaction with acids during atmospheric transport. Since volcanic ash particles act as cloud condensation nuclei, the same effect may be expected during atmospheric transport of the ash in volcanic clouds containing sulphuric acid. Thus, studies which have measured Fe release from volcanic ash at near-neutral pH may have underestimated its ocean fertilisation capacity.

We investigate ash Fe release under low pH conditions representative of exposure to volcanic cloud acidity. Seven volcanic ash and five volcanic glass samples, ranging from basalt to rhyolite (48-75 wt.% SiO₂), were exposed to pH 1 sulphuric acid for 336 h in batch reactors. The solution was sampled at regular time intervals and analysed for major element concentrations by optical emission spectroscopy, and for Fe(II)/Fe(III) ratios using the ferrozine method. Changes in sample surface composition were assessed by X-ray photoelectron spectroscopy (XPS), and the surface of selected ash samples was imaged by scanning electron microscopy.

Results indicate that both the glass and mineral phases in ash likely contribute significantly to Fe release at low pH. Element release trends are consistent with silicate leaching and dissolution, and XPS data provide evidence for the formation of a protonated leached surface layer. In contrast to glass, Fe release from ash does not correlate with bulk Fe content. The discrepancy may reflect differences in ash surface reactivity imparted by plume and/or atmospheric processing prior to deposition. Ash from phases I and III of the 2010 Eyjafjallajökull eruption (Iceland) displayed high 1 min Fe release rates (55 and 115 $\mu\text{mol m}^{-2} \text{h}^{-1}$, respectively). The high reactivity of these samples may be due to in-plume processes, namely formation of Fe (oxyhydr)oxide surface deposits during ash oxidation and surface etching by aqueous and gaseous fluoride, respectively. Initial Fe(II)/Fe(III) values in solution suggest oxidation of the surface relative to the bulk of all ash samples. Knowledge of Fe at the ash surface is critical to understanding Fe release from volcanic ash.

Origin of the pumiceous deposits of the Kikai-Akahoya eruption in Yakushima Island, SW Japan

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Numerous wood trunks are involved in pumiceous deposits of the Kikai-Akahoya (K-Ah) eruption along Nagata, Isso and Miyanoura rivers on the northern side of Yakushima Island, 60 km south of Kyushu Island (Geshi, 2009; Okuno et al., 2013). All tree specimens are not charred. It implies that the origin of these deposits is not of pyroclastic flow, and these trees were soaked or floated in the rivers or in the sea when the deposits reached the island. At least two large-scale earthquakes occurred during the eruption (Kobayashi and Naruo, 2002). Geologic evidence of the earthquake is the existence of many clastic dikes which reached some horizons in the K-Ah tephra. The first earthquake occurred shortly before the ignimbrite eruption, and the second one occurred during the ignimbrite eruption. The plausible model is that the first severe earthquake caused many landslides on this mountainous island, and that a lot of trees were transported either by the rivers or in the sea. Tsunamis had to be triggered by those earthquakes, but the largest tsunami occurred apparently after the end of the ignimbrite eruption by the caldera collapse (Kobayashi, 2008). Just after the ignimbrite eruption, the sea surface was widely covered by floating pumice. Therefore, pumiceous deposits must have been formed by the final tsunami, which flowed up along the rivers more than 30 meters a. s. l.

Hydrochemical processes and environmental isotope study of groundwaters around Lake Nyos (North-western Cameroon)

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Groundwaters of Nyos catchment situated at the Wum volcanic district in the Western part of the Cameroon Volcanic Line (CVL), have been extensively monitored in summer December 2011 and January 2013 to assess its genetic relationship with lake waters and to identify the main factor controlling its mineralization processes 30 years after the natural disaster which killed about 1700 peoples and more than 3000 cattles (Kling et al., 1989).

The water samples (n= 55) were analyzed on site for temperature, pH, electrical conductivity (EC), oxidation-reduction potential (ORP), alkalinity and Fe²⁺ concentration. The major chemical and stable isotopic compositions were determined in laboratory using ion chromatography and mass spectrometer, respectively.

The results of the chemical analyses indicate that groundwaters is bicarbonate magnesio-calco-alkaline type (HCO₃⁻ » Mg²⁺ > Ca²⁺ > Na⁺ > K⁺) which is almost the same signature as those of epilimnic water of Lake Nyos. In contrast, those of epilimnic water of the lake and soda springs are enriched in HCO₃⁻ and Fe²⁺. This suggests that the shallow water of the lake may constitute the main recharge source of groundwater during summer. The concentrations of major ions in the bottom of the lake are in average 10 times higher than those of groundwaters. This suggests that CO₂-water-rock interaction have a significant role in the hydrochemical processes taking places in the bottom of the lake. Deep waters of the lake with high CO₂ concentration may not influence groundwater in Nyos watershed.

The D/H and 18O/16O ratios of waters from the lake and groundwaters show two general trends. Borehole and lake waters fall on or close to the typical meteoric water line while rivers and streams deviate significantly. These results indicate that groundwaters and lake waters were originated from surface meteoric water and are affected by evaporation in the unsaturated or in the saturated zone.

Complex ash leachate compositions of the 6 August 2012 Mt. Tongariro (Te Maari) eruption, New Zealand, and implications for volcanic health hazard evaluation

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After 115 years of quiescence, Mt. Tongariro erupted suddenly at 2350 hrs (NZ time) on 6 August 2012 from the upper Te Maari Crater. The eruption produced a fine ash of minor volume (0.004 km³) but wide distribution (>1,000 km³), extending over 200 km from source. The threat of further eruptions sparked an investigation of the possible health and agricultural impacts of any future eruptions from this volcano, particularly since the most recent large-scale ash falls in New Zealand, the 1995-1996 Mt. Ruapehu eruptions, had generated significant agricultural problems, including livestock deaths.

Te Maari ash was sampled between 5 and 200 km from the volcano within hours of settling and before rainfall. Analysis of this revealed several unusual features. Using a series of three repeated leaches of the same samples, strong variations in ash properties could be established. Typical single-leaching analyses, most commonly recommended for volcanic ash health impacts, showed highly variable results, in many cases considerably underestimating the potential chemical impact of these tephras. In this case, sample/leachant ratios of 1:20 appeared highly unsuitable for estimating total fluoride and sulphate concentrations and also had limitations for metal analysis. While also limited, leaching experiments using 1:100 ratios provided a more realistic estimate of soluble components.

In addition to method-related variability, total soluble concentrations and leaching behaviour during three sequential runs also varied for ash produced at different times of the eruption and with distance from source. Using the example of fluoride (F), a single leach of the earliest erupted/deposited ash extracted c. 75-90% of the total F removed in three sequential leaches from the same sample. Subsequently erupted ash, deposited only minutes later in an adjacent area due to shifting wind direction, had far less soluble forms of F, with single leaches yielding only c. 30-40% of the total amount extracted over three leaches. Distal ash, collected c. 200 km from source, showed the highest total F concentrations (112 ppm). Similar properties were observed for some cations with the early ash displaying strong correlations of F with aluminium and calcium, while later ash contained significantly lower quantities of aluminium and also released less calcium. The strongly variable leaching behaviour during the course of the eruption appears to reflect changes in soluble components/gas while variation with distance is most likely a function of grain size or an effect of residence time in the plume, i.e. ongoing ash-acid reaction.

The Te Maari data indicate that even if rapid results are required for health hazard assessment, a full understanding of time-dependent leaching behaviour is required before definitive recommendations can be made.