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Journal of volcanology
and geothermal research

Journal of Volcanology and Geothermal Research xx (2004) xxx–xxx

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Volcanic ash-leachates: a review and recommendations for sampling methods

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Received 5 August 2004; received in revised form 8 November 2004; accepted 15 November 2004

Abstract

Tephra in plumes can scavenge and thereby rapidly deposit volatiles including sulphur, halogen and metal species. These may then be leached (e.g. by rainfall), potentially releasing heavy loadings to soils and water bodies. Several eruptions have resulted in contamination of pasture, sometimes with serious impacts on livestock. Water quality has also been an issue in some areas affected by tephra fall. This work synthesises the literature on volcanic ash-leachates and considers the controls on volatile adsorption. General trends emerge for basaltic, intermediate and silicic tephra, as well as for variable particle size and transport distance. The applications of ash-leachate data to plume-gas geochemistry, calculation of volatile budgets and environmental impact assessment are evaluated. Comparisons for different eruptions are hampered by disparities in leachate analysis techniques. A standardised methodology is therefore proposed to facilitate future health impact assessment and volcanological interpretation of results from different sites.

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Keywords: adsorption; leaching; volatiles; volcanic ash

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1. Introduction

The principal gases released during volcanic activity are water, carbon dioxide, sulphur dioxide, hydrogen, hydrogen sulphide, carbon monoxide and hydrogen chloride. Many volatile metal elements are also released (e.g. [Allard et al., 2000](#)). These sulphur and halogen gases and metals are subsequently removed from the atmosphere by processes of chemical reaction, dry and wet deposition, and by adsorption onto the surface of fine tephra particles (ash). Here we consider the consequences of adsorption of volatiles onto ash in volcanic plumes and how these adsorbed species can be measured. The processes by which volatile scavenging occur are not well understood and we review the current understanding of the controlling factors.

Volatiles scavenged by ash particles reach the ground more rapidly than they would by dry deposition, because of the faster deposition velocities of the ash. Upon deposition, the adsorbed materials can be dispersed into the environment, where they have the potential to injure vegetation, livestock and people. The rate of their dispersal depends on the affinity of the materials to the ash, the nature of the surface of the ash, the substrate on which the ash is deposited (e.g. deposition straight onto a plant leaf will have a much faster impact than deposition onto a previous layer of ash) and the presence of water, either as standing water, surface run-off or rainfall.

One of the first investigators to consider soluble material on volcanic ash was [Lacroix \(1907\)](#), but it was more than 60 years before the first comprehensive consideration of the source of the soluble materials was made by [Taylor and Stoiber \(1973\)](#). They demonstrated that the materials leached from pristine ash by water were greatly enriched compared to those from pre-washed ash, which suggested that the origin of the materials was not glass in the ash. Additionally,

they calculated that the volume of rock needed to supply the leached concentrations for a completely ash-glass source would have been far larger than that used. They concluded that the predominant source for the leached materials had to be plume gases that had deposited on particle surfaces. The findings from this and subsequent work (in particular [Rose, 1977](#)) showed that analysis of materials adsorbed on ash by leaching with a known solution provides information on the plume volatile composition, as well as what the environmental impacts of their deposition might be.

Here we consider only the short-term leaching of materials adsorbed onto the surface of pristine (non-weathered) ash. Other studies have considered the longer-term implications of tephra leaching where the glass starts to weather ([Dahlgren et al., 1999](#); [Gislason and Oelkers, 2003](#); [Oelkers and Gislason, 2001](#)). Such weathering can be rapid at high temperatures or acidities, but the concentrations of materials released do not pose as great a hazard to the environment as those from adsorption. Some material “weathered” by the leach solution may be found in ash-leachates, in addition to the materials adsorbed in the plume, but comparison of leach contents to the tephra composition can help discriminate between the material sources. Using this approach, [Delmelle et al. \(2000\)](#) found that leached Mg, Ca, Na and K had originated from the ash particle, and not the plume. Conversely, some material adsorbed in the plume may react with the surface of the ash and become insoluble or too strongly bonded to be removed by rapid leaching. Analysis of ash before and after leaching ([Delmelle et al., 2000](#)) indicates that adsorbed F might be one of the materials less affected by leaching and hence may be systematically underestimated in leachate solutions.

Not all volcanic emissions are adsorbed by ash so the overall composition of the gas phase cannot be

approximated from the leachate data (Varekamp et al., 1982). The main elements to demonstrate significant surface enrichment on ash compared to its bulk composition are sulphur, as sulphate (SO_4^{2-}), chlorine (Cl) and fluorine (F) (Delmelle et al., 2000) (most metals occur at minor or trace levels). Their principal sources are the magmatic gases sulphur dioxide, hydrogen chloride and hydrogen fluoride. These elements are of relevance to both plume studies and human health-hazard assessment. Indeed, ash-leachate studies on deposited ash are used as a proxy for volcanic plume composition to complement, or substitute for, other measurement techniques that traditionally look at Cl and S ratios. The ratios of S, Cl and F are used here to demonstrate the trends between different volcanoes and their eruptions. Data are plotted following the scheme elaborated by Giggenschbach (1996). The data are presented as ratios to enable comparison between volcanoes where actual concentrations may vary by orders of magnitude. Other elements detected in leachate solutions may be derived from the ash itself (see above) and so do not provide such good grounds for between-volcano comparison.

Previous work on ash-leachates has shown that volatile concentrations in the leachate vary according to eruption parameters (e.g. Armienta et al., 2002; Rose et al., 1973), sample location (e.g. Oskarsson, 1980; Rubin et al., 1994) and analysis method (e.g. Risacher and Alonso, 2001; Smith et al., 1982). Giggenschbach (1996) suggested that SO_4^{2-} , Cl and F leachate values were internally consistent for individual eruptions (and demonstrated a degree of regional clustering for Central America), but that large variations observed between volcanoes could not be explained without further data. Some of the main variables influencing leachate composition are considered in detail below, together with a review of previous ash-leachate work. This reveals that ash-leachate studies have been conducted to investigate a variety of volcanological questions, including the processes of adsorption and the impacts of leaching of deposited ash. It also shows that a wide range of analysis techniques have been used, such that comparison between results, even for the same eruption or volcano, is not always justifiable. To enable future comparison between ash-leachate studies, we propose here a preliminary standard method-

ology for sample preparation and analysis. This recommended method was initially drawn up for the International Volcanic Health Hazard Network (IVHHN), a commission of the International Association for Volcanology and Chemistry of the Earth's Interior (IAVCEI) and is awaiting ratification. It is recognised that this method requires further development and vetting based on rigorous sample testing, but until that stage a common methodology would aid in cross-examination of data from different locations.

2. Controls on adsorption

During an eruption, magma and gases are expelled from the volcanic vent into the atmosphere. Within the vent, the erupting material changes from a predominantly liquid magma-phase to one of gas phase at the fragmentation level. Interaction between gas-phase materials and ash can occur from this fragmentation level to potentially hundreds of kilometres downwind in the eruption plume, the scale of which depends on the type and magnitude of the eruption. The main controls on subsequent adsorption of volatile elements onto tephra are:

- (1) Magma type and tephra composition;
- (2) Mode of eruption;
- (3) Gas-pyroclast dispersion immediately following fragmentation;
- (4) Concentration of the plume;
- (5) Ratio of particles to gas;
- (6) Particle size-fractions;
- (7) Particle surface area, porosity and texture;
- (8) The temperature/chemical history of the particle trajectory through the plume;
- (9) Environmental conditions, including wind and humidity;
- (10) Extent of hydrothermal interaction at the volcano.

Some of these are discussed in more detail in the sections below.

Adsorption may occur by gas-to-particle interactions or liquid-to-particle interactions. Scanning electron microscope (SEM) and transmission electron micrographs images of airborne ash collected in volcanic plumes show a liquid coating to many

particles, which is interpreted to be sulphuric acid (Cadle et al., 1979; Casadevall et al., 1984; Rose et al., 1980). (Once condensed onto particles, sulphuric acid rarely evaporates because its saturation vapour pressure is so low (Jacobson, 2002).) SEM images and profiling of deposited ash also show the presence of surface particles (Rose et al., 1973), salts (Rose, 1977; Rose et al., 1980) and soluble fluorine (Oskarsson, 1980) on ash surfaces. In the fluorine study, no F was detected in vesicles inside particles and no etching of vesicle walls was seen, showing that all fluorine compounds were adsorbed onto the surface of the ash (Oskarsson, 1980). Reports of mildly corrosive effects of ash on contact with metals (e.g. Fruchter et al., 1980) and vegetation (e.g. Le Guern et al., 1980) provide evidence that ash can have an acidic coating whilst transported.

Water plays a role in adsorption, but it is unlikely that it is the primary control. Calculations of volatile budgets have shown that ~10–20% of HCl (Rose, 1977) and ~30–40% of S (Rose, 1977; Varekamp et al., 1982) emitted may be scavenged. If water were the controlling factor, the higher solubility of HCl over SO₂ would suggest that the percentage of HCl scavenged should be much greater than that of S. Numerical modelling experiments (Textor et al., 2003) have shown that the majority of water vapour in the plume forms ice at heights from 3 to 4 km, which would limit gas solution. Additionally, any water on sedimenting tephra re-evaporates before reaching the surface boundary layer (Tabazadeh and Turco, 1993; Textor et al., 2003) so gases dissolved in this water layer will not reach the ground. Instead, the species may form soluble salts on the ash surface. Ca²⁺, Na⁺, Mg²⁺, SO₄²⁻ and Cl⁻ are the predominant species released on first exposure of volcanic ash to water (Delmelle et al., 2000; Smith et al., 1983) and ratios of Na⁺ to Cl⁻ and Ca²⁺ to SO₄²⁻ show that in many cases the abundance of these anions and respective cations is approximately 1:1 (de Hoog et al., 2001; Rose, 1977; Rose et al., 1973; Smith et al., 1983). This provides evidence for the presence of these elements on the ash as the salts NaCl and CaSO₄. SEM observations on Galunggung ash confirmed that the 1:1 relationship seen between S and Ca in water leachate was due to the presence of anhydrite (CaSO₄) and gypsum (hydrated CaSO₄) on the ash (de Hoog et al., 2001). Molar ratios on Mt. St. Helens ash also

suggested the presence of the soluble salts KCl and MgSO₄ (Taylor and Lichte, 1980). Highly soluble F may be contained within CaSiF₆ and NaF salts (Cronin and Sharp, 2002) and experiments with HF (Oskarsson, 1980) have shown that CaSiF₆ is the major fluoride compound formed on the ash surface. Smith et al. (1983) proposed that these salts condense as microscopic crystals in the high-temperature core of the eruption column before being adsorbed by ash particles (see Section 2.4). Alternatively, Delmelle et al. (2000) concluded that the origin of the cations was the ash itself, suggesting reaction of the gases with the ash surface.

Charge balance calculations for water leachates show, in general, a charge excess of <10% (de Hoog et al., 2001; Fruchter et al., 1980; Taylor and Lichte, 1980). This indicates a low probability of large quantities of unaccountable anions (e.g. from carbonate–bicarbonate). Examples where an excess of cations occurs are probably due to increased sample acidity, possibly due to the presence of an aqueous layer of H₂SO₄.

Similarity of S/Cl ratios measured in leachates and in the plume gas phase (measured by open path infrared spectroscopy) at Soufrière Hills volcano, Montserrat (Edmonds, 2001) suggest that S and Cl are adsorbed to a similar extent onto the ash, and that SO₂ and not H₂SO₄ is being adsorbed. Measurements of gaseous and aerosol HF and HCl in volcanic plumes (Lazrus et al., 1979) suggest similar removal rates by adsorption for these gases also, although scavenged HCl may be subsequently lost from the ash surface by volatilisation. These findings are important in that they validate the use of leachates as a proxy for plume gas ratios.

Pre-eruption interaction of lithic ejecta with hydrothermal fluids, for example during phases of lava dome degassing, may inflate leachate concentrations of certain elements, but comparison of leachates from juvenile and lithic ash should help resolve any uncertainty.

The time-scale of adsorption is an important consideration. Ash deposited very close to volcanoes has been seen to have high concentrations of adsorbed volatiles (e.g. Soufrière Hills, Edmonds et al., 2003 and Avacha, Ivanov et al., 1996). In these instances, the time between eruption of the ash and its deposition is very short—a matter of minutes—,

meaning that adsorption processes must act efficiently over this period. Dilution of plumes after initial eruption is rapid and concentrations may drop by a factor of 10^5 in a period of few hours (Casadevall et al., 1984). The rate of gas–particle interaction would be expected to decrease correspondingly with dilution, reducing the chance of adsorption as time progresses. Preliminary laboratory studies of gaseous sulphur dioxide adsorption by Gu et al. (1999) showed that for a range of temperatures (-70 °C to 20 °C) the adsorption process reached equilibrium within 24 h. Continued dilution of an eruption plume with time would probably prevent equilibrium in reality, however. Gu et al. (1999) did not consider the higher temperatures that would be experienced by the ash and gas in the initial phases of their eruption, and more adsorption experiments are required for high temperatures. The role of plume temperature in adsorption is discussed in more detail in Section 2.4, but it is important to note that residence times of ash in the hottest parts of the plume will be relatively brief. Tephra also cools very rapidly, with greater rates for smaller particles, so any temperature-related processes would be expected to have only a short time-interval over which to act. All of these factors suggest that adsorption is a rapid process predominating in the young plume.

2.1. Magma type and tectonic setting

Magma type influences the composition of the volcanic gas phase. At the simplest level, andesite and rhyolite S, Cl and F contents are quite similar, but basalt S content is higher by a factor of about 10, and Cl and F content is much lower (Giggenbach, 1996). Beyond these generalisations, variability within magma types is considerable, reflecting differences in gas solubilities and degrees of magma degassing (Oppenheimer, 2003). This variability leads to not only different gas emissions, but also different adsorption and deposition characteristics. The magma source is probably also the main control on metal contents in ash-leachates (Armentia et al., 2002).

Variation in adsorbed SO_4^{2-} , Cl and F with tephra composition is shown in Fig. 1(a). This demonstrates that SO_4^{2-} , Cl and F ratios for the principal magma types broadly differ. Andesite and dacite tend to have

low relative F contents, with andesite having the greatest relative S content of all the compositions. Dacite has a greater relative Cl content than andesite and basalt-andesites generally have a much higher proportion of F. Basalt leachates exhibit a wide scatter.

Inspection of Fig. 1(b) shows several volcanoes with particularly high relative amounts of fluorine, notably in Iceland and Melanesia. Leachates from New Zealand volcanoes appear dominated by sulphur, whilst the Central American volcanoes studied indicate low F contents, but variable Cl/S ratios. This depiction of ash-leachate values by location reflects the many factors governing adsorption and reveals that Giggenbach's (1996) clustering of data by region was over-simplified.

2.2. Eruption style

The hazard posed by ash-leachates depends on the eruption type, which influences the volumes of ash and volatiles produced and their dispersion. The following generalisations can be made about the primary eruption styles:

- (1) *Plinian* and *vulcanian* eruptions deposit ash over a large area in a short time, resulting in rapid ash accumulation. The area affected by ashfall is strongly controlled by eruption magnitude and wind conditions and can exceed 10^4 km² for magnitude 5 eruptions (as defined by Pyle, 1999). For rarer magnitude 7 eruptions, the area covered by a tephra depth of at least 1 cm can exceed 10^6 km². Gases and tephra are well mixed in these eruption columns, even though the eruption duration is relatively short. Impacts from the ash may not be noticed until the eruption has ended and may last much longer than the period of activity. Ash aggregation is common in plinian ashfall due to several processes including electrostatic forces (e.g. Gilbert et al., 1991), tropospheric water, etc., resulting in more rapid deposition close to the vent. Separation of the ash plume from the gas plume has been observed in some cases (Rose et al., 2000). If this occurs, the contact time between the gas and silicate particulate components is decreased, potentially limiting scavenging.

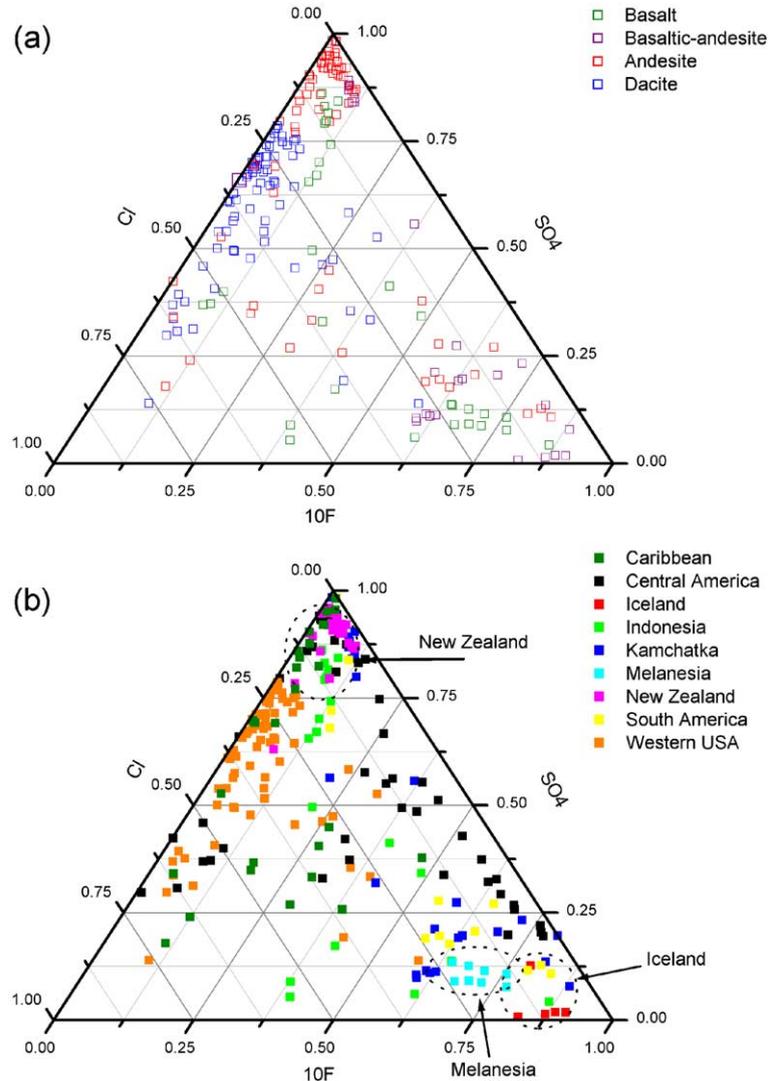


Fig. 1. Ternary diagrams of relative SO_4^{2-} , Cl and F ($\times 10$) adsorbed mass concentrations from ash-leachate analysis for (a) ash composition (where known); (b) by location. Data are presented for the volcanoes in Fig. 2. A colour version of this figure is available online.

(2) *Hawaiian* and *strombolian* eruptions disperse ash less widely than *plinian* eruptions and there is less opportunity for interaction between the ash and gases in the smaller plumes. Clast sizes may also be larger limiting the total surface area of the tephra within the plume. The hazard associated with ash leaching increases in proportion to the size and duration of the eruption, as more ash is erupted. Changes in wind direction during the course of the eruption will extend the area impacted,

though obviously limit the accumulation of tephra (and hence adsorbed volatiles) in any one place.

(3) *Phreatomagmatic* eruptions can cause particle clustering due to increased water content, and thus may have enhanced deposition closer to the source and decreased deposition at distance, reducing the distal hazard. Volatilisation of hydrothermal or lake waters during eruption may increase the reserve of material which can be adsorbed, for example by the availability of

sulphur, sulphates, chlorides, etc., in precipitates or in solution.

The eruption style will influence the concentrations of gases and particles in the plume, the size distribution of tephra, the ratio of particles to gases and the transport time of ash in the plume (although not necessarily ash surface texture, [Delmelle et al., 2004](#)). These, in turn, will control the degree of interaction between ash and volatiles, and, hence, adsorption.

Ash-leachate composition for a given eruption sequence will vary with changes in eruption style. [Figs. 2 and 3](#) show that one volcano can produce a wide spread of leachate values. Data from Popocatepetl, Mexico, collected during 1996, demonstrate this well ([Fig. 2](#)) and have been used to distinguish the magmatic or phreatomagmatic character of eruptions ([Armienta et al., 1998](#)). Leachate data for Soufrière Hills Volcano, Montserrat ([Fig. 3](#)) clearly distinguish between periods of dome growth and stagnation. The mass of material scavenged can also change during activity. [Rose et al. \(1973\)](#) found that SO_4^{2-} and Cl

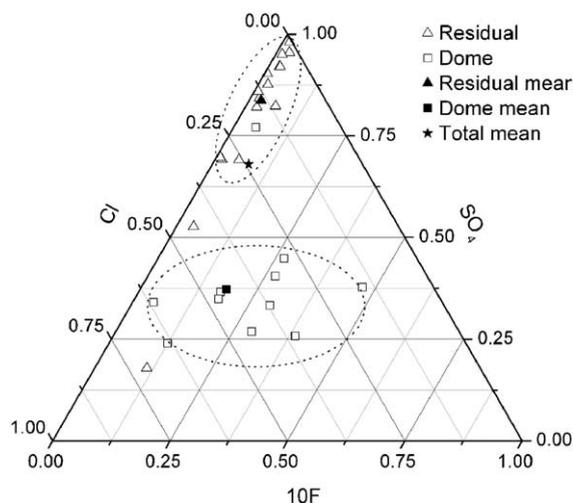


Fig. 3. Data for Soufrière Hills, Montserrat demonstrating the clear change in leachate composition between dome growth and residual activity (after [Edmonds, 2001](#)). Mean values for the two periods are very different to the overall mean.

contents on ash from Fuego and Cerro Negro were an order of magnitude higher during latter stages of the eruptions than at the start. This is most likely due to

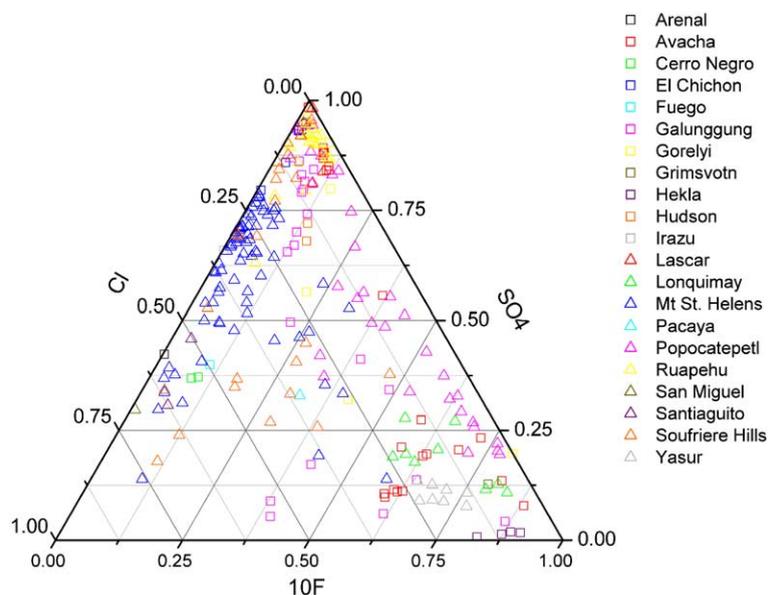


Fig. 2. Relative masses of adsorbed Cl, SO_4^{2-} and F ($\times 10$) by volcano. Data sources are the same as for [Fig. 1](#) ([Armienta et al., 2002](#); [Armienta et al., 1998](#); [Christenson, 2000](#); [Cronin et al., 1998](#); [Cronin et al., 1997](#); [de Hoog et al., 2001](#); [Edmonds, 2001](#); [Fruchter et al., 1980](#); [Gronvold and Oskarsson, 2002](#); [Ivanov et al., 1996](#); [Kirsanov and Yu Ozerov, 1984](#); [Nehring and Johnston, 1981](#); [Oskarsson, 1980](#); [Risacher and Alonso, 2001](#); [Rose et al., 1978](#); [Rose et al., 1973](#); [Rubin et al., 1994](#); [Smith et al., 1983](#); [Stoiber et al., 1980](#); [Stoiber et al., 1981](#); [Taylor and Lichte, 1980](#); [Taylor and Stoiber, 1973](#); [Varekamp et al., 1982](#); [Varekamp et al., 1984](#)). Data for Lonquimay and Yasur are approximate based on the graph of W. Gigenbach in SEAN 14:07 ([Smithsonian Institution, 1989](#)). A colour version of this figure is available online.

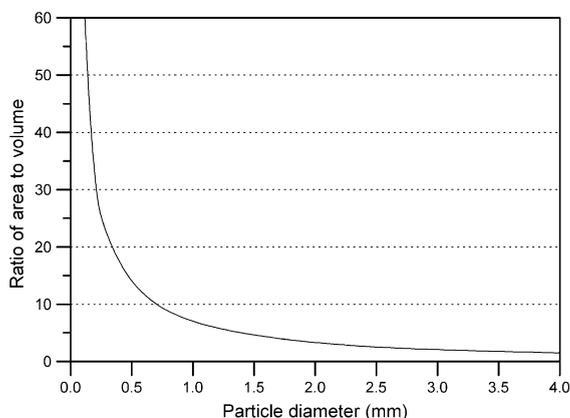


Fig. 4. Increase in area-to-volume ratio as particle size decreases (modelled as a perfect sphere, ratios for tephra will be larger).

increased gas emission, rather than any change in adsorption process.

From the lower percentages of the total emissions of hydrogen chloride adsorbed onto ash compared to sulphur, it appears that adsorption is not occurring solely via a water layer and that another mechanism must operate. However, data from Galunggung (de Hoog et al., 2001) suggest that during phreatomagmatic activity the amount of HCl scavenged as a percentage of the total volatile budget is much higher. This is most likely due to an increased role of water in the scavenging process. Data from Ruapehu (Cronin et al., 2003) suggest that tephra from hydrothermal systems may continue to leach F for some time after deposition, presumably as it is retained in different compounds such as CaF_2 , AlF_3 and $\text{Ca}_5(\text{PO}_4)_3\text{F}$, instead of the more soluble ones formed on “dry” magmatic tephra.

The ternary diagrams in Figs. 1 and 2 do not contain any information on parameters such as particle size, distance from the vent, etc., which may all be influencing the ratios. These are important factors, which we now consider.

2.3. Particle size

The concentration of deposited species depends upon the size-fraction of the tephra. Adsorption (inferred from leachate concentrations) is much greater for smaller particles (Fruchter et al., 1980; Oskarsson, 1980; Rose et al., 1973; Rubin et al., 1994). The proportion of smaller particles increases as

travel distance in the plume increases due to the deposition of larger clasts close to the volcano and the decrease in particle terminal velocity with particle size. Particles with smaller diameters tend to have a higher surface area to mass ratio than larger particles (Fig. 4) so are more efficient scavengers of volatiles for the same tephra volume (though vesicularity may provide a high relative surface area in some tephra). This means that as the particle size decreases, the proportion of available volatiles scavenged increases. Consequently, an increase in concentration of scavenged acid species is seen with distance from the vent and at the lateral margins of deposits. Particle shape and surface texture are also important: angularity and vesicularity will increase surface-area:volume ratios of particles. Measurements of surface area using BET gas adsorption techniques (Gislason and Oelkers, 2003; Riley et al., 2003) have shown that the surface area of ash can be almost two orders of magnitude higher than the estimated geometric surface area. This is partly due to surface roughness and the high

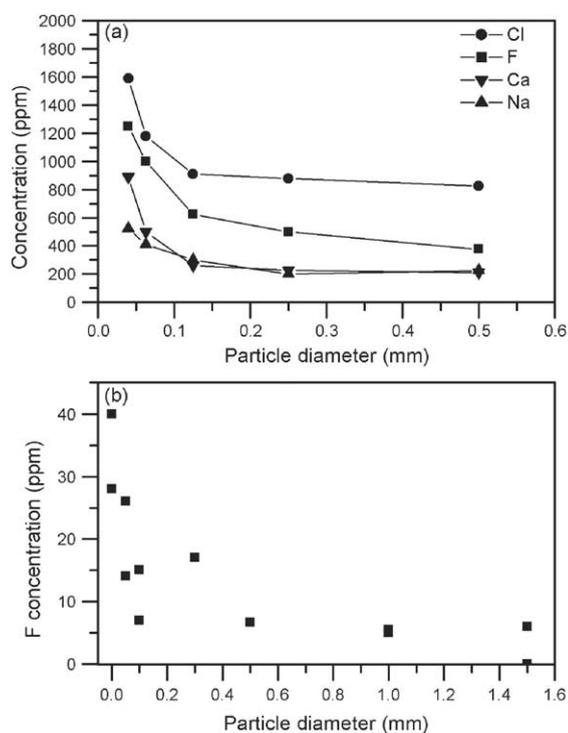


Fig. 5. Effect of particle size on volatile adsorption, determined from ash-leachates (a) Hekla (original data from Oskarsson (1980)), (b) Mt. Hudson (after Rubin et al., 1994).

vesicularity of ash. Consequently, one would anticipate that ash would have a larger surface area/volume ratio than spheres and, hence, that the ash trend curve in Fig. 4 would steepen at larger particle sizes.

Sulphuric acid condenses primarily onto accumulation mode particles (diameters 0.1 to 2 μm) (Jacobson, 2002), due to the larger surface area concentration (surface area per unit volume of air) of the accumulation mode compared to other modes. Concentrations of adsorbed volatiles appear to increase sharply for particle diameters $< \sim 0.1$ μm (Fig. 5). This size is an order of magnitude smaller than the steep increase in area-to-volume ratio seen in Fig. 4. This suggests that the relationship between particle size and adsorption is not solely controlled by the surface area-to-volume ratio.

The size of the particle also influences its transport in the plume and hence its temperature and chemical history (see below). Fine ash is supported in the plume longer than coarser tephra, providing a greater contact time between the ash and the plume-gas during which adsorption can occur (although at great distances, dilution of the plume reduces interaction between the particles and gases/aerosols). The larger particles in the plume also cool more slowly, meaning that

condensation of acids takes place preferentially on the smallest, colder, particles (Oskarsson, 1980). Varekamp et al. (1984) found that distal ashes with abundant tight clusters had high adsorbed-sulphur contents. Coatings of sulphuric acid, as well as condensation of water, may enhance this clustering of fine particles.

Due to the increased adsorption onto fine ash, peak concentrations of leachate species can occur in areas experiencing only a few millimetres of ash deposition. This means that the heaviest loadings on the environment are likely to be found at some distance (tens of kilometres) from the vent. Fig. 6 demonstrates these concepts using data from the 1991 eruption of Mt. Hudson, Chile. The data clearly show an increase in fluoride mass concentration with distance.

The role of particle size in adsorption means that leachate results are influenced by sample location. For instance, at the edges of the plume particle sizes will be finer than those under the centre so will show increased adsorption. Particle size-distribution at any one site will be a function of eruption column dynamics, plume transport (atmospheric diffusion), any coagulation processes, etc. Any calculation of total adsorbed components for an ash blanket from

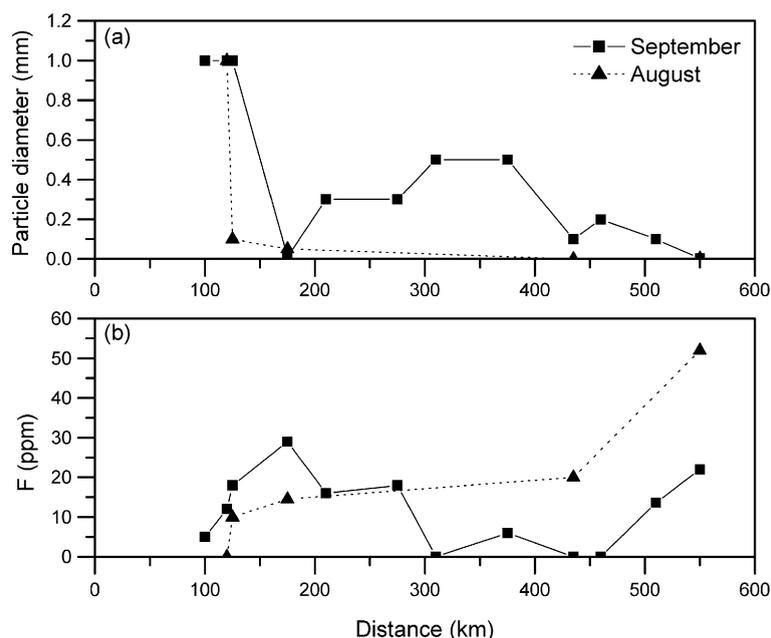


Fig. 6. The relationship between particle size, fluoride mass concentration and distance, as seen after the 1991 eruption of Mt. Hudson, Chile: (a) average size of ash particles with distance from Mt. Hudson; (b) fluoride content of ash-leachate with distance (Rubin et al., 1994).

leachate analysis needs to take account of the variation in particle size with location.

2.4. Temperature and chemical history

Rose (1977) hypothesised that the variety of initial and fallout trajectories followed by tephra in the plume would produce variable scavenging. This idea was developed by Oskarsson (1980) who proposed that the reactions in a plinian eruption column could be divided into three temperature-dependent zones: the “salt formation zone”, the “surface adsorption zone” and the “condensation zone” (Fig. 7). In the salt formation zone, a small fraction of the degassing volatiles forms aerosol salt particles at magmatic temperatures. This zone probably extends down to the fragmentation level. Subsequent interaction of this salt aerosol with an aqueous layer on a particle may result in adsorption. Smith et al. (1983) proposed that the formation of salts in the high-temperature core of the eruption column and their subsequent condensation as microscopic crystals was the main source of the salts seen adsorbed on ash particles, but experiments by Oskarsson (1980) and Delmelle et al. (2000) suggest that gases are also

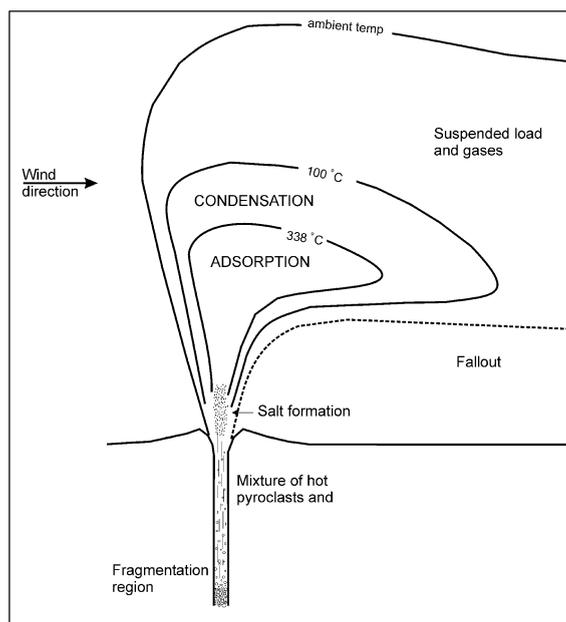


Fig. 7. Three temperature-dependent zones within a Plinian eruption column (after Oskarsson, 1980).

adsorbed directly onto the ash. Oskarsson’s experiments using a HF-H₂O gas mixture showed that adsorption of HF onto ash is temperature dependent and occurs at temperatures below 600 °C; adsorption increases as temperature decreases. Oskarsson (1980) proposed that this process was similar for the other main volatile species and concluded that the maximum rate of adsorption of volatiles onto the surface of tephra occurs at intermediate temperatures in the plume (~300–700 °C) in a surface adsorption zone. The particles that reside in this adsorption zone of the eruption column therefore have the greatest opportunity for volatile scavenging. The presence of metals in the hot zones of the plume may also catalyse reactions and enhance adsorption.

The condensation zone of the plume is characterised by temperatures below 338 °C. In this zone, sulphuric and halogen acids condense and form aerosol, which may later be adsorbed onto particles. Condensation of acids and water also occurs directly onto particle surfaces, increasing volatile scavenging from the plume. Beyond this zone, gas adsorption experiments at temperatures spanning those of the upper troposphere and lower stratosphere (Gu et al., 1999) indicate that at 20 °C SO₂ adsorption is similar to the Langmuir relationship and occurs as a monolayer coating onto the ash. At –70 °C, adsorption is nearly linear, suggesting that the amount of SO₂ adsorbed is proportional to the concentration in solution.

2.5. Environmental conditions

Coagulation, deposition and dispersion of ash are partly controlled by wind and humidity in the vicinity of the volcano. Those areas downwind of the volcano in the prevailing wind regime are most at hazard from ashfall and the leaching of any adsorbed materials. This hazard increases with eruption duration and also with distance, as the greater travel-time of the plume allows increased interaction between plume constituents, further oxidation of SO₂ to SO₄²⁻ (Martin et al., 1986) and greater time for adsorption processes to act. Higher wind speeds extend the range of the hazard by transporting the fine tephra further.

Increased humidity promotes the role of water in adsorption and coating of particles with an aqueous layer may facilitate the adsorption of volatile species. Humidity is thought to have had a strong influence on

the distribution of adsorbed sulphur on ash from the recent eruptions of Popocatepetl (Armienta et al., 2002). Particularly high sulphate concentrations were recorded in leachates from ash of the 17 October 1998 eruption, which occurred towards the end of the rainy season when average air humidity values were enhanced. This increase in adsorption was explained by enhanced growth of sulphuric acid droplets in higher humidity conditions, which increased the probability of contact with ash particles (Armienta et al., 2002). The presence of orographic clouds around a degassing vent may also result in the coating of ash particles with water and enhance scavenging.

3. Ash-leachate studies

The current method for quantifying volatiles adsorbed onto ash in volcanic plumes is to leach samples of deposited ash with known solutions and analyse the leachate for ions and elements. To date, over 55 articles reporting original volcanic ash-leachate data for 27 volcanoes have been published. These are summarised in Table 1 along with the methods of analysis used in each study. Only those where the method was explicitly given are included in the table. The articles are listed by region of the volcano(es) considered. The wide range of techniques used prevents categorisation by method. Each table entry contains information on the literature source, eruption (volcano and year), the purpose of the leachate study, the particle size fraction used (if any), the solute used, solute/ash ratio (ml g^{-1}), type of agitation used and the time, resting time for the mixture, ions measured in the leachate and the analysis techniques used. Where authors have used more than one analysis method in their study these have been given as separate entries in the database. The remaining studies not included in the table (including Budnikov, 1990; Deger, 1931, 1932; Hinkley and Smith, 1982; Kirsanov and Yu Ozerov, 1984; Rose et al., 1978, 1982; Rubin et al., 1994; Stoiber et al., 1980, 1981), report ash-leachate analysis results, but exclude details of the methodology. We are aware of some further leachate work, particularly from Japan, but have been unable to obtain the relevant sources to include in the database.

A review of the literature (Table 1) shows that leachate studies have been conducted in the past for four main reasons:

- (1) To be used as a proxy for volcanic-plume gas concentrations;
- (2) Investigation of environmental impacts (including effects on soil, crops, algae, ocean water, snow and human health);
- (3) Investigation of the chemistry and processes of adsorption;
- (4) To determine the origins of the adsorbed material.

The first two reasons are the most common. Additional applications of leachate data include their inclusion in calculations of volatile budgets (see Section 6.3), use in predicting zones of high environmental loading following an eruption, and investigation of agricultural detriment or value of the leached elements (e.g. Bornemisza and Morales, 1969). The eruptions of Mt. St. Helens in 1980 provided the source of the most studies conducted for an individual volcano, and many of the different applications and impacts of leachates were examined.

Over 55 soluble components have been detected in ash-leachate studies, of which the most commonly analysed are Cl, Ca, Na, SO_4^{2-} , Mg and F. These are also the elements with the highest concentrations in volcanic-ash water leachates. The comparison of concentrations reported in studies is hindered, however, due to differences in the analysis methods used. This is true for work on the same volcano as well as between volcanoes.

4. Ash-leachate analysis techniques

The concentrations of the different chemical components measured in ash-leachate studies depend not only on the adsorption processes and mechanisms discussed above, but also on:

- (1) Sample location: distance from the vent (Ivanov et al., 1996; Rose, 1977; Rubin et al., 1994; Smith et al., 1983) and relation to the wind direction;

Table 1
Summary of previous works analysing volcanic ash-leachates

Reference	Region and eruption	Purpose	Particle size fraction	Solute	Solute/ash ratio (ml g ⁻¹)	Agitation type	Agitation time	Resting time	Ions measured	Analysis method
<i>Caribbean</i>										
Edmonds et al. (2003)	Soufrière Hills, 1996–2001	Comparison to plume gas measurements		deionised water	5	agitated	1 h	6–8 h	Cl, SO ₄ ²⁻	Ion chromatography
Horwell et al. (2003)	Soufrière Hills, 1997–2001	Health impacts	<4 µm	distilled water, NaCl, 1% nitric acid and/or NaOH	400	–	–	4 weeks	Fe	ICP-AES
<i>Central America</i>										
Armienta et al. (1998)	Popocatepetl, 1994–1996	Plume proxy		deionised water	25	agitated then centrifuged	2 h then 15 min	–	Ca, Cd, Cl, Co, Cu, F, K, Mg, Mn, Na, Pb, SO ₄ ²⁻ , Sb, Ti, Tl, Zn	ICP-MS, potentiometry, flame emission and ion chromatography
Armienta et al. (1998)	Popocatepetl, 1994–1996	Plume proxy		deionised water	2	agitated	1 h	6–8 h then repeated	Ca, Cd, Cl, Co, Cu, F, K, Mg, Mn, Na, Pb, SO ₄ ²⁻ , Sb, Ti, Tl, Zn	ICP-MS, potentiometry, flame emission and ion chromatography
Armienta et al. (2002)	Popocatepetl, 1996–1998	Controls on materials on the ash		deionised water	25	agitated then centrifuged	2 h then 15 min	–	As, Cl, Co, Cr, Cu, F, Mg, Mn, Mo, Ni, Pb, SO ₄ ²⁻ , Se, Ti, Tl, V, Zn	ICP-MS, potentiometry and ion chromatography
Bornemisza and Morales (1969)	Irazu, 1963–1964	Environmental impacts (soil)		water	37.5 cm ³ to 1360 g	–	–	column	Al, Ca, K, Mg, NH ₄ , NO ₃ , PO ₄ , SO ₄ ²⁻	Various chemical tests including titration and flame photometry
Murata et al. (1966)	Irazu, 1963–1964	Study of constituents and impact on vegetation		distilled water	5				Cl, SO ₃ ⁻ , SO ₄ ²⁻	
Rose et al. (1973)	Cerro Negro, 1971 and Fuego, 1971	Calculation of emissions and also examination of adsorption process	–	water	2	agitated	1 h	6–8 h then leach repeated	Ca, Cl, F, K, Mg, Na, SO ₄ ²⁻	Atomic absorption spectrophotometer, ion selective electrodes and turbidimetric method
Rose et al. (1978)	Fuego, 1974	Plume proxy		water					Ba, Ca, Cl, Cu, K, Mg, Mn, Na, S, Se, Zn	
Smith et al. (1982)	Fuego, 1973 and 1974; Pacaya, 1974; Santiaguito, 1967, 1975 and 1976	Environmental impacts	850–106 µm and <106 µm after crushing	distilled deionised water	4	rocker shaker	1 h	overnight	Al, B, Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Li, Mg, Mn, Mo, Na, Pb, Si, Sr, U, V, Zn	ICP-OES, ion electrode, some others

Smith et al. (1982)	Fuego, 1973 and 1974; Pacaya, 1974; Santiaguito, 1967, 1975 and 1976	Environmental impacts	850–106 μm and <106 μm after crushing	HCl solution pH 3.5–4	4	rocker shaker	1 h	overnight	Al, B, Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Li, Mg, Mn, Mo, Na, Pb, Si, Sr, U, V, Zn	ICP-OES, ion electrode, some others
Smith et al. (1982)	Fuego, 1973 and 1974; Pacaya, 1974; Santiaguito, 1967, 1975 and 1976	Environmental impacts	850–106 μm and <106 μm after crushing	carbonate–bicarbonate pH 9.9	4	in oven at 80 °C	1 week		Al, B, Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Li, Mg, Mn, Mo, Na, Pb, Si, Sr, U, V, Zn	ICP-OES, ion electrode, some others
Taylor and Stoiber (1973)	Central American volcanoes 1963–1970	Origins of materials on the ash	several	water	2	agitated	1 h	6–8 h then repeated	Br, Ca, Cl, Co, Cr, Cu, F, K, Li, Mg, Mn, Na, Ni, SO_4^- , Zn	Atomic absorption, turbidometric method and ion exchange electrode
Varekamp et al. (1984)	El Chichon, 1982	Plume proxy		double-distilled water	2.5 and 143				As, Br, Ca, Ce, Cl, Cr, Co, Cu, F, Fe, K, Na, Sb, SO_4^- , Zn	INA and ion chromatography
<i>Europe</i> Cimino and Toscano (1998)	Etna, 1996	Impact of ash on atmospheric/rainwater composition	0.1–0.3 mm	distilled water	10, 33.3, 500, 2000	stirred	3 min–3 h	–	Ca, Cu, Fe, K, Mg, Mn, Na, SO_4^- , Zn	Atomic absorption spectrophotometer and ion chromatography
<i>Iceland</i> Frogner et al. (2001)	Hekla, 2000	Ocean fertilising potential	44–74 μm	deionised water; artificial and natural seawater		–	–	flow-through reactor	Cl, Co, Cu, Fe, F, Mn, Ni, PO_4 , SO_4^- , Si, Zn	ICP, spectrophotometry and ion chromatography
Oskarsson (1980)	Hekla, 1970	Time to leach all F and its quantity		distilled water	50	shaken	0–300 min	–	Ca, Cl, F, Na	
Oskarsson (1980)	Hekla, 1970	Time to leach all F and its quantity		distilled water	50	shaken	1 h	–	Ca, Cl, F, K, Mg, Na, SO_4^-	
Oskarsson (1980)	Hekla, 1970	Time to leach all F and its quantity		distilled water	4	shaken	1 h	–	Al, Ca, Cl, F, H, K, Mg, Na, SiO_2 , SO_4^-	
<i>Indonesia</i> de Hoog et al. (2001)	Galunggung, 1982	Controls on materials and plume proxy		deionised water	80	shaken	4 h	–	Al, Ca, Cl, F, Fe, Mg, Mn, Na, S, Si	ICP-AES and ion-selective electrode

(continued on next page)

Table 1 (continued)

Reference	Region and eruption	Purpose	Particle size fraction	Solute	Solute/ash ratio (ml g ⁻¹)	Agitation type	Agitation time	Resting time	Ions measured	Analysis method
<i>Indonesia</i> de Hoog et al. (2001)	Galunggung, 1982	Controls on materials and plume proxy		0.01 M nitric acid	80	shaken	4 h	–	Al, Ba, Ca, Cl, Cu, F, Fe, K, Mg, Mn, Na, P, S, Si, Y, Zn	ICP-AES and ion-selective electrode
<i>Japan</i> Kawaratani and Fujita (1990)	Sakurajima, 1985–1986			distilled water		–	–	24 h	Al, Ca, Cl, F, Fe, K, Mg, NH ₄ , NO ₃ , Na, SO ₄ ²⁻ , Si	ICP, atomic absorption spectrometry, indophenol method and ion chromatography
Nogami et al. (2000)	Akita-Yakeyama, 1997	Plume proxy		pure water	14				Cl, S	Ion chromatography
<i>Kamchatka</i> Ivanov et al. (1996) Tovarova (1958)	Avacha, 1991 Bezymianny, 1955–1956	Plume proxy Transportation of mineral matter on surface	<1 mm	twice distilled water	4			48 h	CO ₂ , Ca, Cl, H ₂ S, HCO ₃ , K, Mg, NH ₃ , Na, R ₂ O ₃ , SO ₄ , SiO ₂	
<i>Melanesia</i> Cronin and Sharp (2002)	Yasur and Ambrym, 1999	Health impacts		water	20	shaking	16 h	–	Al, As, B, Cd, Cl, Co, Cr, Cu, F, Fe, Li, Mn, Mo, Ni, Pb, SO ₄ ²⁻ , Sb, Sn, V, Zn	ICP-MS and ion chromatography
<i>New Zealand</i> Christenson (2000)	Ruapehu, 1995–1996	Adsorbed material and sulphur budget		distilled-deionised water, then heated to 60 °C	~10	ultrasonic bath	15 min	overnight	Al, Br, Ca, Cl, F, Fe, K, Li, Mg, Na, NO ₃ , SO ₄ ²⁻	Ion chromatography, ICP-AES
Cronin et al. (1998)	Ruapehu, 1995 and 1996	Effects on soil fertility		water	40	shaken	24 h	–	Al, As, B, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sn, Sr, Zn	ICP-AAS
Cronin et al. (1997)	Ruapehu, 1995	Effects on soil fertility		water	40	shaken	24 h	–	Al, As, B, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sn, Sr, Zn	ICP-AAS and ICP-MS
Cronin et al. (2003)	Ruapehu, 1995 and 1996	Impacts on cattle		water	20	shaken	24 h	–	F	Ion chromatography or ion selective electrode

<i>South America</i> Giggenbach, (Smithsonian Institution, 1989)	Lonquimay, 1989	Plume proxy		distilled water					Al, Br, Ca, Cl, F, Li, K, Mg, NO ₃ , SO ₄ ²⁻ , Si and trace constituents	
Risacher and Alonso (2001)	Lascar, 1993	Origins of materials on the ash		near neutral deionised water	10	shaken	15, 30, 60, 120, 300, 600 min		B, Br, Ca, Cl, F, I, K, Li, Mg, Na, NO ₃ , PO ₄ , Si, SO ₄ ²⁻	Atomic absorption spectrometry, colorimetry and ion chromatography
Risacher and Alonso (2001)	Lascar, 1993	Origins of materials on the ash		near neutral deionised water	10	stirred	15, 30, 60, 120, 240, 480 min		B, Br, Ca, Cl, F, I, K, Li, Mg, Na, NO ₃ , PO ₄ , Si, SO ₄ ²⁻	Atomic absorption spectrometry, colorimetry and ion chromatography
Viramonte (Smithsonian Institution, 1987)	Lascar, 1986			distilled water	10	stirred	5 min		Ca, Cl, K, Mg, Na, SO ₄ ²⁻	
Viramonte (Smithsonian Institution, 1987)	Lascar, 1986			0.1 M HCl	10	stirred	15 min		Ca, Cl, K, Mg, Na, SO ₄ ²⁻	
Williams et al. (1986)	Nevado del Ruiz, 1985	Plume proxy		deionised distilled water			1 h		Cl, SO ₄ ²⁻	Ion chromatography
<i>Western USA</i> Dahlgren et al. (1999)	Mt. St. Helens, 1980	Chemical weathering of tephra				–	long period study	–	Al, Ca, Cl, Fe, K, Mg, Na, NO ₃ , PO ₄ , Si, SO ₄ ²⁻	ICP and ion chromatography
Fruchter et al. (1980)	Mt. St. Helens, 1980	Potential health impact	all, <75 µm and >75 µm	water	1	stirred	10 min	1 h	Cl, NO ₃ , SO ₄ ²⁻	
Fruchter et al. (1980)	Mt. St. Helens, 1980	Potential health impact	all, <75 µm and >75 µm	water	10	stirred	10 min	1 h	Al, As, B, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, Ni, Mo, NH ₄ , NO ₃ , Na, Pb, SO ₄ ²⁻ , Si, V, Zn Ca, Cl, K, Mg, Na, SO ₄ ²⁻	Ion chromatography and plasma emission spectroscopy
Gough et al. (1981)	Mt. St. Helens, 1980	Effects on crops	<2 mm							ICP-OES
Hinkley et al. (1980) (methods in Dethier et al., 1981)	Mt. St. Helens, 1980	Leach composition and comparison to soils		water	~0.6 initially	–	–	4 h in column (repeated)	B, Ba, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, V, Zn	
McKnight et al. (1981a)	Mt. St. Helens, 1980	Impact on algae		simulated lake water		–	–	9 h in column	Ba, Ca, Cd, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Sr, Zn	ICP-ES
McKnight et al. (1981b)	Mt. St. Helens, 1980	Impact on algae		WC medium	1.25	–	–	14 h in column	Ba, Ca, Cd, Cl, Co, Cu, F, Fe, K, Li, Mg, Mn, Mo, N, Na, P, SO ₄ ²⁻ , Sr, Zn	ICP-ES

(continued on next page)

Table 1 (continued)

Reference	Region and eruption	Purpose	Particle size fraction	Solute	Solute/ash ratio (ml g ⁻¹)	Agitation type	Agitation time	Resting time	Ions measured	Analysis method
<i>Western USA</i>										
McKnight et al. (1981b)	Mt. St. Helens, 1980	Impact on algae		WC medium	0.87	–	–	12 h in column	Ba, Ca, Cd, Cl, Co, Cu, F, Fe, K, Li, Mg, Mn, Mo, N, Na, P, SO ₄ ²⁻ , Sr, Zn	ICP-ES
Nehring and Johnston (1981)	Mt. St. Helens, 1980	Plume proxy		triply distilled water	2.5	stirred	1 h	briefly	Al, As, B, Ba, Be, Bi, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, SO ₄ , Sb, Se, Si, Sr, Ti, Tl, V, Zn, Zr	Spectrophotometer, specific ion electrode
Smith et al. (1983)	Mt. St. Helens, 1980	Environmental impacts		distilled deionised water	4	rocker-shaker	1 h	overnight	Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Li, Mg, Mn, Mo, Na, Pb, SiO ₂ , SO ₄ ²⁻ , Sr, U, V, Zn	ICP-OES, ion chromatography and fissure track
Smith et al. (1983)	Mt. St. Helens, 1980	Environmental impacts		HCl pH 3.5–4	4	rocker-shaker	1 h	overnight	Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Li, Mg, Mn, Mo, Na, Pb, SiO ₂ , SO ₄ ²⁻ , Sr, V, Zn	ICP-OES, ion chromatography and fissure track
Smith et al. (1983)	Mt. St. Helens, 1980	Environmental impacts		carbonate–bicarbonate pH 9.9	4	in oven at 80 °C	1 week		Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Li, Mg, Mn, Mo, Na, Pb, SiO ₂ , Sr, U, V, Zn	ICP-OES, ion electrodes and fissure track
Taylor and Lichte (1980)	Mt. St. Helens, 1980	Environmental impacts		deionised water	~0.6 initially	–	–	4 h in column (repeated 3 times)	As, B, Ba, Be, Ca, Cd, Cl, Co, Cu, F, Fe, Hg, K, Li, Mg, Mn, Mo, NH ₄ , NO ₃ , Na, Pb, SO ₄ ²⁻ , Se, SiO ₂ , Sr, V, Zn	ICP-ES, atomic absorption spectrometry, ion chromatography, ultraviolet absorption spectrometry and ion selective electrode
<i>Other</i>										
Delmelle et al. (2000)	Various unknown	Comparison of leached to unleached ash	<100 μm	water					Ca, Cl, F, K, Mg, Na, S	Ion chromatography, atomic emission spectroscopy

Dashes indicate where sampling stages are known to have been omitted.

- (2) The pH of the solution used as the leach (Smith et al., 1983) and the type of acid used, if any;
- (3) The ash/leach-solution ratio (Armienta et al., 1998; Varekamp et al., 1984);
- (4) The time that the ash is left in contact with the leach solution (Ivanov et al., 1996; Risacher and Alonso, 2001);
- (5) The ash grain-size fraction used (Oskarsson, 1980; Risacher and Alonso, 2001);
- (6) Whether samples were ground before leaching, exposing greater vesicle surface area;
- (7) The contribution of dry deposition following the ash deposition;
- (8) Any rainfall or increase in humidity (such as fog) following deposition;
- (9) The time to analysis following sample collection (leached concentrations of soluble metals decrease with time, G. Plumlee, pers. comm.).

For example, smaller particle size-fractions usually give higher elemental concentrations than larger particles and acid leach treatments generally remove much larger amounts of material from ash (Hinkley and Smith, 1982) than water leaches (although evidence suggests that much of this may be from glass). Detected leach concentrations of certain elements may also depend on the presence of other species under certain pH conditions, e.g. Al may reduce F (e.g. Manoharan et al., 1996). All of these factors, except for the conditions following deposition, can be controlled by methodology.

Measurements of scavenged volatiles using the ash-leachate technique are hindered if rain has fallen during or following ash deposition, as this naturally leaches much of the adsorbed material into the environment. For this reason, only pristine ash should be used in leachate studies. Unfortunately, volcanic clouds can provide a rich source of cloud condensation nuclei and atmospheric convection and often initiate rainfall. Redistribution of ash by wind subsequent to deposition will also complicate leachate results, so samples should be collected as soon as possible. Where the focus of the investigation is on environmental impacts, this natural ash redistribution may not be so critical, and composite samples could actually provide a good representation of the cumulative effect on the environment (Taylor and Lichte, 1980). Rose et al. (1973) showed that ash-leachate

concentrations can vary down through the entire thickness of an ash deposit, reflecting changes in column dynamics, magmatic volatile concentrations, atmospheric transport, etc., with time. Samples collected from the near surface of the deposit may therefore under or over estimate the mass of material scavenged, depending on the dominant tephra layer, if concentrations are extrapolated to the whole thickness. Samples collected from different stratigraphic positions in the deposit will provide a more accurate estimate and can be used to evaluate variability in volatile scavenging as a function, for instance, of eruption intensity.

Table 1 demonstrates the wide variety of analysis techniques used in previous studies. The main inconsistencies in methodology are:

- (1) Choice of particle-size fraction;
- (2) Grinding of samples;
- (3) Use of water or acid solutions;
- (4) Ash-to-water ratio. These vary by over one order of magnitude from 1:2 to 1:80;
- (5) Contact times, which vary from 3 min to 24 h;
- (6) Sample agitation. Some authors agitate the ash-solute mixture continually, others for a period and some not at all. Agitation times vary from 3 min to 24 h;
- (7) Different ion analysis techniques;
- (8) Different units of reporting for concentrations, including mg/kg ash, ppm mass, ppm volume, mg l^{-1} and $\mu\text{eq l}^{-1}$.

Samples or ash-leach solutions have even been heated in some studies. The use of such a wide-range of methods introduces error to direct numerical comparisons between surveys and suggests that a common leachate methodology would be beneficial for future work in this area. Element ratios and ternary diagrams (e.g. Figs. 1 and 2) provide a means for comparing relative leachate concentrations and, particularly, gas composition between volcanoes and different stages in individual volcanic activity where different methods have been used, but they are of limited value for environmental and health applications, which require actual concentrations. Two points that plot in the same position on a ternary diagram may differ by orders of magnitude in their concentrations and this is of great impor-

tance for assessing potential impacts. The depiction of relative values is also problematic for the other leachate applications, since species are likely to behave differentially under the various treatments. For example, the acidity of the solute used can influence the resultant leachate concentrations: the amount of adsorbed F may be underestimated with water leaching due to its apparent presence on ash in both soluble and insoluble form (Delmelle et al., 2000). Comparison of results from leaching Galunggung ash with water and 0.01 M HNO₃ (de Hoog et al., 2001) showed that greater quantities of Cl and F were leached by acid solutions, whilst S values were similar to those in water. Ca was also greatly enhanced in the acid leach. Similar findings for Mt. St. Helens ash led Hinkley and Smith (1987) to attribute this increase in Ca to cation exchange of H⁺ with Ca in the tephra. Correlation between increases in F and P also seen in the Galunggung acid leach led de Hoog et al. (2001) to suggest that this might be due to the dissolution of fluoroapatite salts (Ca₅(PO₄)₃F) in the acid.

The form, and hence solubility, of materials on the ash may be influenced by the eruption style. Cronin et al. (2003) found that not all of the “readily available” F on Ruapehu ash was adequately estimated by a single water extraction and that a second repeated extraction (using a ratio of 1:20) released 70–270% of the original quantity of F. This is in contrast to results from Hekla (Oskarsson, 1980) and Vanuatu volcanoes (Cronin and Sharp, 2002) that showed that most F was released immediately in water. The difference may be due to the hydrothermal influence on the Ruapehu eruption and the formation of less soluble salts. Leachates from juvenile and resurgent material may also give different results (e.g. Kirsanov and Yu Ozerov, 1984), due to pre-eruption interactions between vent materials and fumarolic or hydrothermal products.

5. Recommendations

Differences in analysis techniques, in particular ash/water ratio, have the potential to influence strongly leachate element concentrations. Although ratios of elements and ions derived from differing analysis techniques may be similar, concentrations

may differ widely. The need for a single method is, therefore, greatest in those applications, such as environmental and health impacts, where information on the concentrations is required. Use of a consistent method in these applications will enable rapid comparison of results with leachate values recorded for other volcanic eruptions, and their subsequent impacts (if any), to determine whether a hazard is posed. The use of one technique for leachate surveys at the same volcano over time and by different workers will also aid comparison of results and facilitate construction of base-line data sets. In all applications, it is important that the ash/water ratio is high enough to prevent saturation of the solution.

To facilitate comparison between the results of leachate studies, we suggest, in collaboration with the IVHHN, that the following method should be used in addition to other variations in method that individual workers might like to implement. (Further explanation of the recommended method is provided below.) We invite all contributions of further data, or previously reported measurements that we have overlooked, for inclusion in the ash-leachate database (<http://www.ivhhn.org>).

- (1) Use polyethylene equipment at all stages of the analysis;
- (2) Ash should be pristine (i.e. not subjected to rainfall or deposited through cloud or fog). The times since eruption and sample collection should also be noted;
- (3) The leach solution should be distilled deionised water;
- (4) Non-ground ash from all particle size fractions at the sample site should be used in the leach;
- (5) An ash (g) to water (ml) ratio of 1:25 should be used;
- (6) Agitate ash-leach mixtures for 90 min (ideally by shaking) in a sealed container;
- (7) Filter mixture using 0.45 µm surfactant-free cellulose acetate membrane filters (commonly used filters are those manufactured by Millipore and Whatman). Centrifuging samples prior to filtration will enable faster filtration and easier ash sample recovery. For analysis of mercury, addition of a preservative to a separate filtered split is required to prevent volatilisation or sorption onto container walls;

- (8) Analyse filtered leach samples using available equipment, such as an ion chromatographs, ICP spectrometers, or ion selective electrodes, with appropriate standard solutions as calibration;
- (9) Dry and weigh each ash sample and determine its particle size distribution (for small, 1–2 g, leached samples, sieving a larger mass of a bulk sample will prevent large sieve losses);
- (10) Ideally, repeat the analysis with similar ash samples to obtain a mean for that sample site;
- (11) Present results in mg/kg ash, and give the distance from the vent, the particle size distribution and the number of samples analysed.

For other techniques used, the full method, particularly the ash to solute ratio, should be stated.

It is important to note that this recommended method is not based on an exhaustive study to find optimal conditions, but rather on the most widely used methodologies. We have suggested a deionised water leach, due to its frequent past use, availability, ease of use in the field, and comparability to drinking water. A mildly acidic leach is more representative of rainwater, particularly in the vicinity of an active eruption, so a repeated analysis of the ash with an acid solution would also be insightful. Acid concentrations used in previous work have varied from 0.1 to 0.0001 M (pH 1–4) and the leaches have been composed of either nitric acid (HNO₃) or hydrochloric acid (HCl). To facilitate analysis of adsorbed Cl⁻, we recommend the use of nitric acid at a standard solution of 0.001 M (pH 3). This level of acidity is in keeping with measured rainwater pH at Montserrat (Edmonds et al., 2003) and elsewhere (Table 2). To examine the leaching effects of rainwater in detail, knowledge of the

composition of rainwater in the region of interest could be used to make up a suitable proxy solution.

We recommend using the whole ash sample for the leach, as this prevents contamination that might occur when splitting into size fractions. It also gives the most representative value for the total leachate loadings at each site. Analysis of different particle size fractions may provide more information on transport and adsorption processes, however, and is worth pursuing. To minimise contamination and loss of ions in an extended analysis, the equipment used to separate the size fractions should ideally be synthetic (e.g. silk bolting cloth or acrylic sieves). If unavailable, stainless steel sieves should be used in preference to brass sieves, as these impart less metal contamination.

The recommended ash-to-water ratio is based on frequently used ratios and comparisons between analyses using ratios of 1:143, 1:25 and 1:4 (Armienta et al., 1998; Varekamp et al., 1982). These revealed that, at the higher 1:4 ratio, complete dissolution of SO₄²⁻ is hindered due to supersaturation of the leach with respect to gypsum. Dissolution of fluoride is also hindered by fluorite. To enable complete dissolution a lower ash to water ratio is necessary. Hinkley and Smith (1982) found that most ions were removed in similar amounts by widely varying ash:water ratios, providing evidence for a finite quantity of readily soluble material on the ash that is distinct from the mineral phases and glass. Their results also show that the leaching reaction is strongly directed towards solution in water, indicating that the volume of the water may be less important than the duration of contact.

The recommended agitation time and lack of resting time is a departure from the approach based on the Taylor and Stoiber (1973) method used by most workers. The 90-min combined agitation and contact time was selected based on studies that have examined changing leachate concentrations with time (Frogner et al., 2001; Oskarsson, 1980; Risacher and Alonso, 2001). Analysis by Oskarsson (1980), for example, showed that >77% of maximum concentrations of F, Cl, Na and Ca were leached after 7.5 min of shaking and >90% after 1 h in a total experiment time of 300 min. The lower percentages were seen for F and Na, suggesting that these ions are more strongly bonded to the tephra.

Table 2
The pH of different waters (after Oelkers and Gislason, 2001)

Water body	pH
Rivers	7–8
Seawater	8.2
Unpolluted rainwater	5.6
Acid rain	3
Acid rain in vicinity of erupting volcanoes	2<
Water in organic rich soils	4–7

Similar analysis for Lascar (Risacher and Alonso, 2001) showed that there was a rapid increase in ion concentrations in the first 50–100 min and that subsequent increases in concentration were slight. In experiments with seawater, Frogner et al. (2001) found that most of the adsorbed material had dissolved within 1 h. From these results, the majority of leaching appears to occur rapidly upon contact of the solute and ash. This suggests that the amount of extra information obtained from extended agitation times is slight. Studies of mine-waste leachates have also demonstrated that substantial changes in chemistry and precipitation are possible when samples are left to sit in the leach solution for any length of time following agitation (G. Plumlee, pers. comm.). Risacher and Alonso (2001) also found that the dissolution of volcanic glass became significant at the end of their long time-period leach experiments. These are additional reasons for limiting the agitation time.

For rapid appraisal of leachable ions in the field for the purposes of health-hazard evaluation, agitation can be replaced by quick shaking of the ash–water mixture by hand and the resting time omitted. This leach solution can then be analysed for the most important ions (e.g. F) using ion electrodes. The results will provide a minimum concentration for the leachate loadings and should be followed up by analysis of ash by the complete method.

The wide range of leachate concentrations found for samples at different distances from the eruptive vent (Fig. 6) show that a broad spectrum of samples is needed to fully assess the associated hazard. Samples from a range of locations and distances under the plume ideally should be analysed in any leachate study. Baxter et al. (1986) proposed some simple ash collection techniques, along with an example of an ash-collection reporting form that could be implemented by collaborators or the public to increase the sampling density. Any subsequent analysis or calculation should consider any enrichment of elements that might have occurred on the ash due to non-volcanic processes. This includes adsorption or dry deposition of anthropogenically produced pollutants and metals, and products from vegetation pyrolysis. For environmental and volatile budget assessments, accurate information about the amount of ash present, i.e. the total mass/depth, is also needed.

6. Applications of ash-leachate studies

The range of current applications of ash-leachate studies was summarised in Section 3. Here we consider some of these applications in more detail, in particular, those that concern the fate and impacts of the plume and the adsorbed materials.

6.1. Plume-gas proxy

SO₂ and HCl emissions are frequently measured at volcanoes and their ratio used as an indication of magmatic-hydrothermal processes. These measurements are often made by sampling fumaroles at the vent or, occasionally, using ground based or airborne remote sensing equipment such as ultraviolet or infrared spectrometers. During an eruption, at-vent sampling is prohibited and remote measurements are barely feasible, although have been made by Fourier transform infrared (FTIR) spectroscopy (Burton et al., 2003). Leachates collected from ash deposited during eruptions act as an additional source of information on these gas ratios in the plume (assuming equal adsorption of all gases/elements) and may help to reinforce datasets when other surveillance techniques are prohibited. Information on gas ratios can be used to identify changes in the magmatic system and eruptive activity. This, in turn, can provide information for evaluating the potential hazard of the volcano (Armienta et al., 1998).

Cl/SO₄²⁻ ratios derived from ash-leachates compared to those from plume (e.g. by FTIR) and fumarole measurements over the long-term show similar trends (Edmonds et al., 2003; Ossaka and Ozawa, 1975; Taylor and Stoiber, 1973). This provides strong evidence that variations in the ash-leachate ratios over time principally reflect variations in plume composition and chemistry. Discussion of the reasons for and significance of these changes in plume composition is beyond the scope of this paper.

6.2. Environmental impacts

The elements of most relevance to the environment and to health depend somewhat on the purpose of the investigation, but As, Cl, F, Fe, Hg, Pb, SO₄²⁻ and Se

are particularly important (Table 3). Some elements, including Fe, are important because they increase the surface acidity or reactivity of the ash, which then increases the respiratory hazard associated with the ash (Horwell et al., 2003). Others are important because of potential deterioration in water quality, including change in pH, and impacts on vegetation. Aluminium is included, because, as well as impacting on health, it counters the biological availability of fluoride.

Many adsorbed elements are highly soluble, and rainfall or surface water flow onto freshly deposited ash will readily leach these materials into the environment. The concentration of the leachate itself is highly dependent on the volume of water that comes into contact with the ash. During a rainy season, for example, the volume will be high and, hence, concentrations will be lower. Pulses of high F, Cl and SO_4^{2-} concentration and low pH have been recorded in rivers following deposition of ash during volcanic activity (Klein, 1981; Oskarsson, 1980; Smithsonian Institution, 2000), as have high lake SO_4^{2-} levels (Markhinin, 1988; Weaire and Manly, 1996). The elements Zn, Cu, Cd, Pb and Ba have also been found in leachates at concentrations which could pose short-term hazards to some forms of aquatic life (Smith et al., 1983) and leachate from ash from the 1980 Mt. St. Helens eruption was found to be toxic to blue-green algae (McKnight et al., 1981a).

Drinking water is contaminated by deposition of ash on uncovered water tanks or impounds. Subsequent leaching of adsorbed acids can cause pH levels to fall below acceptable drinking levels (Le Guern et al., 1980) and acidic water can then corrode water supply systems leading to an increase in the concentration of metals and damage to pipes connecting reservoirs and drains. The principal toxic element adsorbed on ash is fluoride (from HF). Drinking water concentrations of F above the guidelines (Table 3) carry an increasing risk of dental fluorosis, and concentrations >10 ppm (volume) lead to skeletal fluorosis (WHO, 1993). At the ash-to-water ratio of 1:25 recommended above, a concentration of F on ash of 37.5 mg/kg is required to exceed the World Health Organisation's (WHO) drinking water guideline level of 1.5 mg l^{-1} . This WHO fluorine guideline value is based on a water consumption estimate of 2 l/adult/day. In hot climates, consumption may be much higher requiring an appropriate modification to the guideline value (Apambire et al., 1997). The use of different ash-to-water ratios by different workers prevents direct comparison to water quality guidelines, because, if we assume total dissolution, the concentration is highly dependent on the water volume. Fig. 8 shows the mass concentrations of F recorded on volcanic ash compared to the minimum mass concentrations required to exceed the guideline level at ash–water ratios of 1:4, 1:25 and 1:80.

Table 3
Volcanic-ash water-leachate concentration ranges for some of the important health-related ions

Ion	Number of studies	Range of concentrations (mg/kg ash)	Calculated water concentrations (mg l^{-1})	WHO drinking water guideline levels (mg l^{-1})
Al	16	2.4 (Galunggung)–2117 (Gorely)	0.096–84.68	–
As	8	0.01 (Popocatepetl)–<4 (Ruapehu)	0.0004–0.16	0.01
Cl	42	3.8 (Mt. St. Helens)–11,160 (Irazu)	0.152–446.4	250 ^a
F	30	0.1 (Galunggung)–2043 (Avacha)	0.004–81.72	1.5
Fe	22	0.01 (Mt. St. Helens)–91 (Ruapehu)	0.0004–3.64	–
Hg	3	0.0001–0.0087 (Mt. St. Helens only)	4×10^{-6} – 3.48×10^{-4}	0.001
Pb	12	0.001–17.56 (Popocatepetl spans whole range)	4×10^{-5} –0.7024	0.01
SO_4	33	2.4 (Mt. St. Helens)–21,775 (Popocatepetl)	0.096–871	500 ^b
Se	6	0.001 (Mt. St. Helens)–0.64 (Fuego)	4×10^{-5} –0.27	0.01

The calculated water concentrations for each ion are derived using the ash-to-water dilution ratio of 1:25 recommended here. Drinking water quality guidelines (WHO, 1993) for these ions are also provided for reference purposes. Note that the leachate concentrations for different volcanoes are derived using different methods and assume complete sampling of the adsorbed ion mass.

^a No guideline value, but concentrations of this level can give rise to a detectable taste in water.

^b No guideline value, but gastrointestinal effects can result from ingestion of high levels.

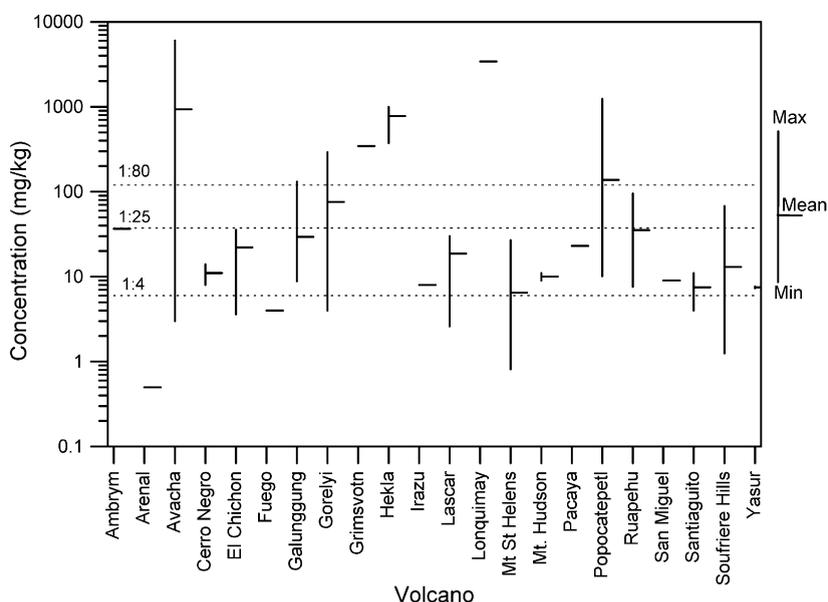


Fig. 8. Soluble fluoride concentrations on volcanic ash (mg/kg), as determined from ash-leachate studies (Armienta et al., 2002; Armienta et al., 1998; Ivanov et al., 1996; Nehring and Johnston, 1981; Oskarsson, 1980; Risacher and Alonso, 2001; Rose et al., 1973; Smith et al., 1983; Stoiber et al., 1980; Stoiber et al., 1981; Taylor and Stoiber, 1973; Varekamp et al., 1982; Varekamp et al., 1984), compared to the minimum mass concentrations required to exceed the WHO drinking water guideline level at ash:water ratios of 1:4, 1:25 and 1:80.

Following detection of increased fluorine levels in leachates from the 12 May 1997 eruption of Popocatepetl, the Mexican National Water Commission started a potable-water monitoring program (Armienta et al., 2002). Levels did not exceed the Mexican standard at any time, but in the area around Popocatepetl the local population are warned in advance to cover water supplies to avoid contamination (M.A. Armienta, pers. comm.). Concerns were also raised over the integrity of water supplies following tephra fall from Soufrière Hills volcano and have prompted regular sampling of water quality on Montserrat. High concentrations of SO_4^{2-} in drinking water can also cause health complaints and sulphate concentrations have been raised (about 8000 ppm) in both acid and water leachates from Nyiragongo (Baxter and Ancia, 2002). Fig. 8 suggests that ash from future eruptions of Avacha, Galunggung, Soufrière Hills and Yasur can have high $\text{F}/\text{SO}_4^{2-}$ levels. These ratio data conceal the concentrations of F, which are more important for impacts, as well as other contributing factors. For example, following the 1970 Hekla eruption, it was the combination of a poor hay crop and fluoride poisoning that caused the deaths of thousands of

plants and crops can cause the appearance of black spots making products unfit for sale (Le Guern et al., 1980). Following the 1980 Mt. St. Helens eruption, for example, leaf necrosis was seen in corn (Kennedy, 1981) and increased levels of S were found in crops (Cook et al., 1981; Gough et al., 1981). Several eruptions have resulted in apparent contamination of pasture by material adsorbed on ash, and morbidity and mortality of livestock from fluorosis were recorded following the recent eruptions of Lonquimay, Hekla and Ruapehu (Cronin et al., 2003; Smithsonian Institution, 1989; Thorarinson and Sigvaldason, 1972). Comparison with data from Mt. Hudson (Fig. 2), where animal deaths were mistakenly attributed to fluorosis, shows that, in general, the former volcanoes have high $\text{F}/\text{SO}_4^{2-}$ ratios. The data also show that ash from Avacha, Galunggung, Soufrière Hills and Yasur can have high $\text{F}/\text{SO}_4^{2-}$ levels. These ratio data conceal the concentrations of F, which are more important for impacts, as well as other contributing factors. For example, following the 1970 Hekla eruption, it was the combination of a poor hay crop and fluoride poisoning that caused the deaths of thousands of

sheep (Thorarinsson and Sigvaldason, 1972). Icelandic livestock are at particular risk from fluorosis following eruption, due to the high magmatic halogen levels that prevail. There is also a risk to animals from excessive S consumption (Cronin et al., 1998; Gregory and Neall, 1996).

The ecological sensitivity to the leachate depends on the type and volume of species deposited and the ability of the environment to buffer this deposition, and leaching of materials adsorbed on ash can be beneficial to the environment. Deposition of ash in New Zealand following activity at Ruapehu in 1995 and 1996, for example, added beneficial amounts of selenium, potassium, magnesium and sulphur to the soil, reducing the need for fertiliser in areas of agriculture (Cronin et al., 1998).

6.3. Calculation of volatile budgets

Knowledge of volcanic volatile budgets is important for constraining both magmatic processes and atmospheric and climatic impacts. The total mass of volatiles released by an eruption is accounted for by syneruptive degassing of the erupted melt (and potentially of unerupted magma), any pre-existing gas phase present in the magma (Gerlach and McGee, 1994; Sharma et al., 2004; Wallace and Gerlach, 1994) and any contribution from hydrothermal systems. Scaillet et al. (2003) and Scaillet and Pichavant (2003) have considered in detail how magmatic volatile budgets for past eruptions can be estimated based on petrological constraints.

Various remote sensing instruments have been used to measure SO₂ emissions during eruptions, including ground-based and airborne ultraviolet and infrared spectroscopy (e.g. Fischer et al., 2002; Oppenheimer et al., 1998; Sutton et al., 2001) and the spaceborne Total Ozone Mapping Spectrometer (TOMS) (e.g. Carn and Bluth, 2003; Guo et al., 2004; Krueger et al., 1995). While these techniques have provided essential data on SO₂ releases, they only measure sulphur as gas phase SO₂. As a consequence, they may not indicate total sulphur releases since they do not measure sulphur already adsorbed on to tephra (or S in sulphate aerosol). To calculate a complete plume volatile budget, data are required on the gas-phase atmospheric volatile mass (e.g. from a source such as TOMS), the aerosol-phase mass, and the total

adsorbed volatile mass, determined from ash-leachate values for different particle sizes and locations. Comparison between the mass of the volatile adsorbed onto tephra and the total volatile mass detected in the atmosphere will give an indication of the importance of adsorption process in regulating injection into the atmosphere.

Calculations by Rose (1977) for Fuego using the petrologic technique for estimating gas release show that ~16% of HCl and ~33% of S emitted were scavenged during this eruption. Varekamp et al. (1984) calculated total sulphur and chlorine budgets for the 1982 eruptions of El Chichon volcano, Mexico and inferred that 30 wt.% of the sulphur originally in the gas phase was adsorbed onto tephra during the eruption. Gerlach and McGee (1994) used TOMS, Correlation Spectrometer and ash-leachate data to determine the total SO₂ release from Mt. St. Helens, 1980–1988, and compared the results to melt inclusion data. Converting their measurements for the 18 May 1980 eruption into a form comparable to the others reveals that ~32% (range=27–41%) of the sulphur emitted that day was scavenged onto tephra. This value is very similar to the Rose (1977) and Varekamp et al. (1982) estimates, but, unlike the other two, does not use the petrologic technique in its calculation. The calculation by de Hoog et al. (2001) that ~35% of sulphur and ~30% chlorine were scavenged from the eruption plumes of Galunggung in 1982–1983 is probably one of the few well-constrained calculations of total volatile budget. Encouragingly, this sulphur value is again very similar to the other estimates. The Cl value is higher than other published values, which they suggest is due to the phreatomagmatic nature of the eruption.

These findings suggest that the “excess sulphur” (in excess of what can be supplied by syneruptive magmatic degassing) identified in numerous eruptions (based on TOMS and other measurements of SO₂) may be typically underestimated by upwards of 40% because the adsorbed component has been neglected. Christenson (2000) included leachate derived estimates of sulphur dioxide in the calculation of the sulphur budget of the 1995–1996 Ruapehu eruption and these values suggest that the minimum degassed magma volume may have been substantially greater than the observed eruption volume.

In addition to gas budgets, leachates can be used to assess the role of volcanic emissions in other global cycles. Taylor and Stoiber (1973) considered that volcanic leachates played an important role in global element cycles, and analysis of leachates of ash and agglomerates deposited during the 1955–1956 eruption of Bezymianny, Kamchatka (Tovarova, 1958) showed that large amounts of soluble material could have been carried out to the ocean. The role of leachates in supplying uranium has also been considered (Smith et al., 1982).

7. Discussion and conclusions

The deposition of volcanic ash with adsorbed volatiles represents a rapid route by which elements and ions such as Cl, Ca, Na, SO_4^{2-} , Mg and F are delivered to the ground. Many elements are highly soluble and rainfall or surface water flow onto freshly deposited ash will readily leach these materials into the environment. Measurements of leachate concentrations from pristine ash are important for assessing plume gas composition and also environmental hazard, and variations in leachate ion ratios may reflect important changes in volcanic activity. The concentrations of materials in the leachate are controlled by: adsorption processes in the volcanic plume, post-deposition influences and the analysis techniques used. Adsorption depends on many factors, including magma type, eruption style, plume temperature and particle size, and these require further investigation. Finer particle sizes appear to experience enhanced adsorption, with the implication that leachate hazards may be high even where ashfall is limited.

There appears to be some similarity in the compositions of leachates derived from volcanoes in the same regions, due to similar magma types. Magmas with a relatively high halogen content pose the greatest hazard to the environment, and volcanoes with high F/ SO_4^{2-} ratios are most likely to have hazardous leachate fluoride concentrations. The greatest risks are to grazing animals through consumption of F coated ash and to humans through contamination of drinking water.

Ash adsorption represents a large volatile sink (up to 40% of some volatiles) often unaccounted for in

calculations of total gas emissions and SO_2 loss rates. This sink is important for the consideration of volatile budgets from explosive eruptions, because atmospheric emissions derived from satellite data may substantially underestimate the true values. Volatile budget calculations and subsequent source apportionments that do not consider the role of ash adsorption should be treated with caution. During eruptive activity, the similarity between leachate-derived gas ratios and those calculated using other techniques allows for leachates to be used as a proxy for plume SO_2 , HCl and HF contents.

The use of different leachate analysis techniques currently prevents good comparison between data. A recommended method has been outlined here with a view to standardising the reporting of leachate results and enhancing their application. This will hopefully prove a valuable addition to volcano monitoring efforts and compilation of data about volcanic emissions and their changes in ratio and mass with activity. Use of the recommended method will be particularly beneficial for environmental and health applications where concentration data are required.

Acknowledgements

We thank S. Cronin and G. Plumlee for their helpful discussion on the recommended method. CW is funded by the UK Natural Environment Research Council (award number NER/S/A/2001/06108). CJH is funded by a Leverhulme Trust Research Interchange Grant, which supports the International Volcanic Health Hazard Network.

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