Protocol for analysis of volcanic ash samples for assessment of hazards from leachable elements

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Report Contents

1.0 INTRODUCTION

Volcanic eruptions can produce a wide range of hazards. Although phenomena such as pyroclastic density currents and surges, sector collapses, lahars and ballistic blocks are the most destructive and dangerous, volcanic ash is by far the most widely distributed eruption product[1] and the most likely to be encountered by the public. Following an eruption, the public, civil authorities and agricultural producers will often have major concerns about the effects of volcanic ash on human and animal health, drinking water supplies, crops, soils and surface runoff. Freshly-erupted ash contains a range of potentially toxic soluble elements, which may be released either rapidly or more slowly upon contact with water or body fluids.

As part of the immediate emergency response, there should be rapid dissemination of information about the physical and chemical properties of the ash and its hazardous potential. However, there is a wide range of tests that can be carried out and chemical components that can be tested for, which can lead to confusion about whether a health threat exists or not. The purpose of this protocol is to recommend clear, standard and reliable methods for the rapid assessment of hazards from leachable elements, each applicable to specific purposes. The four applications considered here are:

- A 'general purpose' water leach, relevant to assessing impacts on drinking water supplies, livestock drinking water and fish hatcheries, and availability of soluble elements for plant uptake;
- Assessing ingestion hazards to livestock;
- Assessing ingestion hazards to humans; and
- Assessing inhalation hazards to humans.

The adoption of standardised methods will improve and facilitate the comparability of results among different studies and enable the ongoing development of a global database of leachate information relevant for informing improved volcanic health hazards assessment.

The methods should be used in association with other tests to assess ash hazard. For example, a protocol for assessing the respiratory health hazard of volcanic ash is available on the website of the International Volcanic Health Hazard Network (www.ivhhn.org) and will now incorporate the leachate methods recommended here.

This protocol was the outcome of a two-day workshop held at the Institute of Hazard, Risk and Resilience, Durham University, UK, on June 14-15, 2011, attended by the authors. A 2005 review of ash-leachate studies (Witham et al., 2005), which made preliminary recommendations on standard methods for characterising ash leachates, was used as the starting point for discussions at this workshop. Written submissions to the workshop were also provided by Dr Maria Aurora Armienta, of the Universidad Nacional Autonoma de Mexico (UNAM), Mexico; Dr Niels Oskarsson, University of Iceland, Iceland; and Dr Claire Witham of the UK Met Office. These contributors also reviewed a draft version of this protocol. Further review comments were provided by Dr Tom Casadevall and Dr

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[1] Volcanic gases can also be widely dispersed. Guidelines with information on health hazards of volcanic gases are available on the IVHHN website: http://www.ivhhn.org/images/pdf/gas_guidelines.pdf

Christina Neal of the United States Geological Survey. Finally, the protocol was reviewed by Dr Janet Slate, USGS Bureau Approving Official.

2.0 GENERIC METHODOLOGY APPLICABLE TO ALL LEACHATE STUDIES

See accompanying flow chart (Figure 1) for the specific procedures for intended purposes. Acronyms used are defined in Section 7.0.

2.1 Ash collection, storage and preparation

2.1.1 Ash collection

- Collect ash in clean plastic trays where possible. Where no trays are available, try to collect from a relatively flat, clean, dry, hard surface such as uncovered steps or a flat roof. Avoid locations where other surface dust or salts are likely to have accumulated. Be aware of the possibility of contamination from surfaces sampled from (for example, copper, chromium and arsenic from tanalised fence posts or zinc from galvanised roofing materials). Always record the surface each sample is collected from.
- See USGS AVO web site (http://avo.alaska.edu/ashfall.php) or IVHHN website (www.ivhhn.org) for comprehensive advice on ash collection methods.
- If you are able to collect a measured area sample, record the thickness of the ashfall, the dimensions of the area the sample is collected from and the weight of the sample.
- If the ash deposit appears heterogeneous (with respect to characteristics such as grain size, colour etc), and if it is logistically possible, we highly recommend collecting multiple samples from a single site, then compositing and homogenizing subsamples to reduce variability. Collection of comparable subsamples can be accomplished using a plastic container (e.g., Tupperware[2]) of known dimensions as a template (see Hoefen et al. 2009, http://pubs.usgs.gov/of/2009/1038/) to ensure each subsample is collected over the same size area.
- Try to collect ash in a pristine condition (dry, not rained on), if possible. Always record the state of the sample, particularly whether or not it has been wetted prior to collection.
- For IVHHN recommendations on information to be recorded, see: http://www.ivhhn.org/uploads/en/IVHHN_Ash_Collection_Procedures.pdf

2.1.2 Ash storage

- Store ash in Ziploc[2] plastic bags, airtight plastic containers or lab-grade HDPE tubs. If not available, use clear plastic bags/containers. Avoid the use of glass containers for storage because of the potential for interaction between ash constituents and glass.
- Report if condensation of water is observed within the sample container.
- If possible, store samples in a desiccator to prevent absorption of moisture from the atmosphere.

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[2] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

- Try to avoid long periods of storage before analysis (to reduce the impacts of ongoing surface acid reaction with volcanic glass).

2.1.3 *Sample preparation*

- Weigh samples to obtain total weight of ash per surface area of collection.
- Dry samples at room temperature in an open sample bag or plastic tray (do not use oven or sun). Dry for at least 12 hours to constant weight and re-weigh.
- Homogenize the sample as far as possible, by gently rotating sample container.
- If a sample is to be split, for different analyses, we recommend the 'cone and quarter' method, using a plastic or Teflon-coated knife, unless you have a splitting instrument such as a spinning riffler or Jones splitter.
- **See flow chart (Figure 1) for guidelines on sieve fractions, depending on purpose.**
- If necessary, gently disaggregate clumps with a soft brush or porcelain or agate pestle during sieving.

2.2 Laboratory methods

- Use HDPE equipment if possible, otherwise clean, laboratory grade glassware.
- Rinse equipment with solution to be used for leaching prior to use.
- **See Figure 1 for leaching solution to use, depending on purpose.**
- Weigh subsample. We recommend a minimum sample mass of 0.5 g. Ruggieri et al. (2012) reported that better reproducibility was achieved (during batch leaching trials) using a mass of 1.0 g compared to using 0.1 g. For bulk samples containing substantial proportions of particles >2 mm, it will be difficult to obtain a representative subsample of only one gram, and we recommend using a larger subsample in these cases.
- **See Figure 1 for ratio of ash to leaching solution, depending on purpose.**
- **See Figure 1 for leaching contact time, depending on purpose.**
- Add ash to solution and gently agitate for given time (**see flow chart**). Use a benchtop agitator/shaker or gentle end-over-end shaking to ensure complete contact between the ash and leaching solution.
- Quality assurance and control measures:
    - Always run a blank of the solution being used for leaching.
    - Ideally repeat analyses on multiple samples to determine spatial and temporal variability.
    - Ensure adequate replication (we suggest one in every ten samples).
- All experiments can be carried out at room temperature. However, ingestion and inhalation experiments may benefit from being carried out at 37 °C if possible to better mimic physiological conditions.
- After leaching, centrifuge sample. If a centrifuge is unavailable, leave solution to settle for 10 minutes.
- Take a subsample of leachate for pH and conductivity tests. Ensure that ratios of ash to leaching solution are specified for the interpretation of pH and conductivity data.
- Filter through 0.45 µm filters <u>immediately after centrifugation</u>. Nitrocellulose or nylon filters are preferable and have been demonstrated to be appropriate for volcanic ash and other geological materials. There are some concerns with the potential of acetate

filter materials to release compounds which may interfere with the determination of dissolved fluoride; avoid these if possible.

- Filtration through 0.2 µm filters may be required when using low-capacity ion exchange columns using IC.
- Filter into a rinsed (with filtrate) bottle for anions. For cations, filter into an acid-washed bottle. Preserve samples as appropriate.
- Cation analysis: ICP-MS or ICP-OES. Note that ICP-MS typically has much lower detection limits than ICP-OES. Determinations can also be carried out by AAS.
- Anion analysis: IC or ion-specific electrode (ISE) for fluoride and chloride.
- Present data in mg/kg ash dry weight basis.

3.0 WATER LEACH

Leaching with deionised water is generally accepted as reflecting the dissolution of readily water-soluble compounds adsorbed onto ash particle surfaces. It is important to note that the release of elements into natural waters may differ from their release into deionised water, but after considering the merits of a range of alternative leaching solutions, we concluded that deionised water is the most appropriate solvent due to its wide availability and standard properties.

This ‘general purpose’ water leach is applicable to situations such as predicting compositional changes in roof-fed rainwater tanks and livestock watering troughs, runoff into surface waters and nutrient or toxin availability for immediate uptake by crops.

Ayris and Delmelle (2012) summarised available data on water-extractable elements in ash from a wide range of eruptions, as maximum, minimum, mean and median concentrations. A summary version of this dataset is included in Appendix 1 so that users of this protocol can compare their data with global values.

3.1 Leaching procedure (refer to flowchart)

- Refer to Section 2.2 for general leachate methods.
- Use deionised water as the leaching solution. Note the grade of deionised water used.
- Ratio of ash to leaching solution: we recommend carrying out two complementary tests at ratios of 1:20 and 1:100 (g dry weight ash to mL water)[3]. There may be a trade-off between detection limits and saturation of the leachate solution with respect to secondary mineral phases such as calcium sulphate. Ruggieri et al. (2012) recommend an ash:extractant ratio of 1:10 based on optimisation trials. However, these trials were based on just two ash samples (a pristine sample of ash from the 2008 eruption of Chaitén volcano, Chile, and an ancient volcanic ash deposit from NW Argentina). In our view, this ratio is likely to be too high for the majority of ash samples and is likely to lead to mineral saturation problems, and we note that Chaitén ash leachates were found to be approximately 4-6 times less concentrated in comparison to ash leachates from the 1980 eruption of Mt St Helens (Durant et al., 2011).

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[3] For example, a test extracting 0.5 grams of ash (dry weight) with 50 mL deionised water would be 1:100.

- From the results, present the highest value for each element from either test. The 1:20 ratio is used by the USGS because it is the same ratio as commonly used EPA protocols to examine metal mobility from mine wastes and other geological materials. The drawback of this higher ratio (1:20) is that the leachate may reach saturation with calcium fluoride and/or calcium sulphate, thereby underestimating the amount of fluoride and sulphate, respectively, that may be leached. If saturation effects are suspected[4], we recommend re-extracting samples using the same procedure at least once.
- Time in solution: We recommend a contact time of one hour based on studies which indicate rapid initial release rates of ionic species (Jones and Gislason, 2008; Gislason et al. 2011). Very short leaching periods would be unlikely to be workable from a laboratory processing point of view as subsequent steps such as filtration create processing bottlenecks, which could in turn lead to varying contact times. Longer processing times may introduce new problems from re-precipitation of fluoride and other salts (G. Plumlee, pers. comm.).
- Properties of interest: pH, conductivity (prior to filtration), cations by ICP-MS, ICP-OES or AAS, anions by IC or ISE.

3.2 Notes on specific applications of water leach

3.2.1 Roof catchment-based water supplies and open tanks

Volcanic ash deposited on roofs can be washed into rainwater collection tanks, and also deposited directly into open tanks. It should be noted that untreated drinking water (unless derived from a secure groundwater source) cannot be regarded as safe from pathogenic (illness-causing) micro-organisms, and that the absence of a chemical hazard does not imply that it is safe to drink.

Ash leachate composition provides a good indication of final drinking-water composition, as water is commonly consumed untreated and as the deionised water leach provides a reasonable approximation of leaching of ash by rainwater. A simple model to predict concentrations in roof catchment tanks is as follows (adapted from Stewart et al., 2006):

$$\mathbf{C_{water} = C_{ash} * ash\ loading\ in\ kg/m^2 * A/V}$$

where C_{water} is the predicted concentration in tank water in mg/L, C_{ash} is mg soluble element per kg ash from leachate characterisation, ash loading in kg/m^2 is determined from measured area sampling in the field; A is the roof catchment surface area or tank surface area (for open tanks) in m^2, and V is the tank volume in m^3. If ash loading data is unavailable, this term may be substituted with the ash thickness in metres multiplied by a measured or assumed value for ash bulk density in kg/L.

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[4] Cronin et al. (2003) reported that a 24-hour deionised water leach (1:20 ratio), from ash erupted from Mt Ruapehu, New Zealand, resulted in incomplete extraction of water-soluble fluoride, as indicated by re-extractions which released further soluble fluoride in variable quantities ranging from approximately 30% to over 3000% of the original quantity. Re-precipitation may have also been a problem in view of the long contact time.

3.2.2 Treated drinking water supplies

The release of a range of chemical species from volcanic ashfall into surface waters can alter their composition which may in turn affect their suitability as a source of drinking water. The extent to which the composition is altered will depend on the thickness of the ashfall, the soluble salt content of the ash and the volume available for dilution (Stewart et al., 2006). It will also depend on the pre-existing composition of water bodies, with changes more likely to be apparent for very low ionic strength waters.

For treated drinking water supplies, raw water is delivered to a treatment plant. Levels and stages of treatment vary widely, but may include: initial settling to remove suspended solids, the addition of alum or ferric chloride as coagulants, filtration, addition of lime for pH adjustment, chlorine-containing compounds for disinfection and fluoride-containing compounds for dental health.

In our experience, problems arising from contamination of raw water sources with chemical species derived from ashfall are generally minor in comparison with operational problems caused by both waterborne and airborne ash for treatment plants. Nonetheless, as public fears about water supply contamination are commonly reported following a volcanic eruption, we recommend that a full characterisation of the soluble salt content of volcanic ashfall is carried out to identify any anomalously high concentrations of elements, and that these results are communicated to public health authorities (Stewart et al., 2009).

A comparative table of drinking-water standards is provided in Appendix 2. The table lists elements known to be potential toxicants and also those known to affect the aesthetic properties of drinking water (taste, colour, odour, etc.) which may in turn influence drinking-water palatability and acceptability.

3.2.3 Livestock drinking water

Livestock drinking water is commonly provided from shallow uncovered troughs or ponds that may be readily contaminated by volcanic ashfall, because they contain only a small volume.

Good water quality is essential for successful livestock production. Poor quality water may reduce animal productivity, growth and fertility, and in extreme cases animals may die (Cronin et al., 2003). Contaminants in drinking water can also produce residues in animal products such as meat, milk and eggs. Daily water intake varies widely among different types of livestock, and is also influenced by factors such as the climate, diet and the physiological state of the livestock. Daily intake rates can be as high as 85 litres/cow/day for dairy cows in milk (Wilson et al., 2011).

Guideline values regulating the levels of potentially toxic trace elements in livestock drinking water are summarised in Appendix 3. These values are generally intended to be trigger-levels for a management response or further investigation. Toxicological effects are complex and depend on many factors such as the dietary intake of trace elements and metabolic interactions between elements (for instance, an adequate level of dietary calcium tends to suppress the uptake of lead, and zinc-deficient diets aggravate mercury toxicity).

A further issue for livestock drinking water is palatability. Direct effects of an unpalatable water supply are a refusal to consume water, consumption of water at levels inadequate for physiological requirements, or a refusal to consume water followed by a period of excessive consumption if no alternative supply is provided and animals are driven to do so by thirst signals. Indirect health effects can arise because there is a direct relationship between water intake and feed intake, and if water intake is inadequate, animal condition will decline along with production parameters such as milk production, average daily gain and feed conversion ratio. This is known as dehydration-induced hypophagia. Livestock generally find high salinity water unpalatable (Appendix 4).

3.2.4 Fish hatcheries

Volcanic eruptions are major natural disturbances, and extensive deposition of ash can lead to significant ecological changes in aquatic environments (Miserendino et al., 2012). This can in turn compromise the high standard of water quality necessary for fish hatcheries and other forms of aquaculture. In general, documented reports of volcanic eruption impacts on fish populations (both wild and farmed) suggest that impacts are predominantly due to the physical effects of suspended ash rather than the release of soluble components from ash surfaces. For salmonids, effects of an increased suspended particulate burden are threefold: effects on behaviour such as foraging and homing (Whitman et al., 1982); changes to habitat such as smothering of gravel-sized substrate used to lay and incubate eggs; and physiological stresses, including abrasive effects of ash upon sensitive life stages such as yolk sac larvae (Boehlert, 1984).

We are unaware of any reports of impacts on fish populations attributable specifically to the release of toxicants (including acidity) from volcanic ashfall. Nonetheless, we recommend that a full characterisation of the soluble salt content of volcanic ashfall is carried out to identify any anomalously high concentrations. For example, Frogner Kockum et al. (2006) noted that ash from the 2000 Hekla eruption, Iceland, produced an acidic leachate with very high aluminium and fluoride concentrations upon contact with deionised water, and proposed that this ash could therefore produce toxic effects in freshwater systems due to the persistence of soluble aluminofluoride complexes (AlF_x^{+3-x}).

3.2.5 Availability of soluble elements for immediate uptake by plants

Leachable elements can provide immediate stimuli to plant growth. For example, SO_4^{2-} has been shown to boost pasture growth following ashfall (Cronin et al., 1998). This fertilising effect extends to cations such as K^+ and Mg^{2+}, depending on the composition of tephra. In some feed crops such as brassicas, boosting of S concentrations in the plant can generate a toxic effect in grazing animals, or exacerbate existing copper deficiencies (Cronin et al., 1997; 1998). Boosted trace-elemental compositions in pastures or feed crops can also generate potentially toxic conditions (e.g., high Se). In addition, compounds toxic to plants that may cause a drop in pasture production are typically related to depressions in soil-water pH levels and the increased solubility of Al-OH complexes. Fluoride, which can be toxic to animals, is not normally taken up by normal pasture or feed plants, unless under certain pH conditions and as Al-F complexes (Cronin et al., 2000). Ayris and Delmelle (2012) note that the entry of fluoride into soils is normally accompanied by its strong retention, although it may be more poorly held in coarse, clay and Fe-Al oxide poor soils. Plants may also vary in their ability to take up F. Plants of the *Camellia* family (e.g., tea) are known for their ability to readily take up F to high levels.

4.0 GASTRIC LEACH

The gastric leach estimates hazards from leachable elements in fresh volcanic ash that is ingested (eaten) by leaching ash with a solution that mimics conditions in the stomach. Children may deliberately or accidentally ingest ash that adheres to their hands. In general, adults are unlikely to ingest significant quantities of ash, although in heavily ashy environments, both adults and children may accidentally ingest substantial quantities of inhaled ash particles that are cleared from the respiratory tract. Livestock may ingest significant quantities of ash along with their food, with close-grazing animals such as sheep being particularly susceptible. This process has led to cases of livestock poisoning and death with even thin (<2 mm) ashfalls under high feed-stress conditions (Cronin et al., 2003).

For volcanic ash, fluoride is generally the most important toxicant to evaluate for gastric bioaccessibility (Armienta et al., 2011). As shown by ash from the 1995-1996 Ruapehu eruptions, water leach tests did not indicate excessive quantities of water-soluble fluoride yet several thousand sheep died from fluorosis following the eruptions (Cronin et al., 2003). These authors concluded that the phreatomagmatic nature of some of the eruptions led to the formation of calcium and aluminium fluoride and phosphate adsorbed phases which are sparingly soluble in water but much more soluble in the digestive system of grazing animals. The gastric leach test helps understand if such forms of fluoride may be present in ash samples.

Gastric leach tests are regularly applied to samples of contaminated soils, mine wastes and other materials to estimate the fraction of metal toxicants that will be solubilised in acid stomach compartments and available for uptake in the circulatory system (this is termed the bioaccessible fraction). Although the amounts of metals present in most volcanic ash samples are typically well below levels that can be found in mine wastes or contaminated soils, the results of the gastric leach test applied to ash samples may provide insights into potential metal uptake pathways for various ash-exposed species with acid stomach compartments.

The amounts of potential toxicants in ash that can be taken up via inadvertent ingestion may be estimated more quantitatively by multiplying the bioaccessible fraction of the toxicant in the ash by the amount present in the ash and by plausible intake rates. For inadvertent ingestion of soil (or in this case, ash) there are published estimates of daily ingestion rates of children and adults, ranging from approximately 10 mg/day in clean conditions to approximately 500 mg/day in very dusty or ashy conditions. These intake amounts can be added to estimated intakes from other sources such as drinking water and food, and compared against maximum daily recommended intake rates available for selected toxicants such as fluoride (e.g., CDC, 2001).

4.1 Leaching procedure (refer to flowchart)

- Size fractions[5]: past studies have chosen different sieve fractions to assess animal (<2 mm) and human (<250 µm) ingestion because animals are thought to ingest the whole ash

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[5] There is precedent for using the <2 mm fraction for livestock ingestion but current research is underway to assess whether the use of different size fractions alters the content of leachable elements. This protocol may be updated as a result. A study of metal bioaccessibility in soils found little difference in both total and

sample along with their food whereas children are more likely to ingest finer size fractions adhering to their hands.

- Leaching solution: we recommend an acid leach to assess hazards of ingestion of ash by livestock and humans. We have chosen a pH of 1.5 as this is the lowest pH that is found in the gut. We recommend using HCl as this is the dominant acid in the stomach.
- Ratio of ash to leaching solution: there are two ratios in regular use for ingestion experiments. A ratio of 1:100 is used by the EPA and by the Institute of Food Research, UK; whereas the ratio 1:40 is used by the BGS, following the BARGE method. We recommend using a 1:100 ratio to avoid saturation effects, although for some ash compositions a 1:40 ratio may be more suitable.
- Time in solution: we recommend 1 hour based on EPA standards and previous literature.
- Temperature: experiments at York University show that carrying out gastric leaches for fluoride determination at room temperature are comparable to those at 37 °C.
- Analysis: The USGS does not measure anions for gastric leaches (other than fluoride). Fluoride can be measured by IC but care needs to be taken when the sample matrix contains high levels of chloride present from the leaching acid. In newer instruments, the strength of the eluent can be adjusted during the run allowing better separation of species eluted.
- At low pH values, the formation of aluminium and iron fluoride complexes in solution may interfere with the measurement of the free fluoride anion by IC. This is why the use of the ISE methods is preferred for determining fluoride in gastric leach solutions. This method generally requires the use of an ionic strength adjuster (ISA) which can contain a pH adjuster and a decomplexing agent, such as a TISAB (total ionic strength adjustment buffer). Based on the dissolved iron and aluminium concentrations and pH of the gastric solution, the analyst should assess which ISA composition is best suited for measuring fluoride.

5.0 SIMULATED LUNG FLUID LEACH

This leaching procedure is intended to assess the potential respiratory inhalation hazards posed by short-term leaching of toxicants from fine fractions of ash that enter the lungs. It can also be used to estimate longer-term dissolution rates of more biodurable minerals in volcanic ash in the lung environment. The leach method we recommend is similar to those that have been used for many years to assess lung biosolubility and biodurability of a wide range of materials from asbestos to radionuclides and wildfire ash (Plumlee and Morman 2011 and references therein). The leach fluid typically used is a modified Gamble's solution, a simulated lung fluid that mimics the near-neutral pH interstitial fluid lining the deep lung. Many different variations of Gamble's solution have been used, each with slight to substantial variations in the types and concentrations of electrolytes and organic constituents used (e.g., organic acids, glycine and surfactants). Plumlee and Morman (2011) present leach results for mine wastes using a serum-based fluid that is substantially more complex than modified Gamble's solution, but gives generally similar results. For the purposes of assessing the respiratory inhalation hazards of volcanic ash, we recommend using modified Gamble's solution

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bioaccessible concentrations between the <250 µm and <2 mm fraction (Morman et al., 2009). Until further volcanic ash-specific tests have been completed these results suggest that the <2 mm fraction may be sufficient for testing bioaccessibility in volcanic ash samples.

which includes the most realistic suite of electrolytes but is relatively simple with respect to additional organic constituents (Table 1).

Table 1 Composition of modified Gamble's solution†

Order of addition	Compound	Concentrations (mg L^{-1})
1	$NaCl$	6400
2	$CaCl_2.2H_2O$	255
3	Na_2HPO_4	150
4	$NaHCO_3$	2700
5	Na_3 citrate.$2H_2O$	160
6	NH_4Cl	118
7	Glycine	190
8	$MgCl_2.6H_2O$	212
9	$Na_2SO_4.10H_2O$	179

† After Caboche et al. (2011) and Davies and Feddah (2003)

5.1 Leaching procedure (refer to flowchart)

- We recommend sieving samples to the more physiologically realistic size range of <38 µm prior to leaching with simulated lung fluid.
- A 1:100 ratio of ash to leaching solution is recommended to keep solids low (as would be the case in the lung) and by analogy with cellular toxicity testing. This ratio is more physiologically realistic and also minimises possible precipitation of mineral phases.
- Extraction time: 24 h is recommended as the residence time of ash in the lungs may be considerable, and as cellular toxicity tests often use this time period.
- Always run a solvent blank for metals and anions as the solvent will be a source of metals.
- We recommend using both ICP-OES and ICP-MS to measure as broad a range of leachate components as possible. Sodium will likely exceed detection of ICP-MS, but not ICP-OES. Sulphate can be measured with IC, ICP-MS or ICP-OES. Fluoride can be determined by IC although further tests are required to assess matrix effects. Additional work is required to optimise fluoride determination on synthetic lung fluid leachates using ion-selective electrodes (ISE).

6.0 RAPID FIELD LEACH TESTS

A simple leach test can be performed in the field using a prepared kit (with sample bottles, filters, field pH and conductivity meters, fluoride ISEA, deionised water, etc.) if information is needed rapidly on potential hazards of fresh ashfall. The USGS Field Leach Test (FLT) (Hageman, 2007), available online at http://pubs.usgs.gov/tm/2007/05D03/), has been used for a number of recent eruptions. Steps in this method are as follows:

- Sieve representative bulk sample to obtain <2 mm fraction;
- Add ash sample to deionised water at ratio of 1:20 ash to water;

- Five minute shaking by hand, 10 minute settling time;
- Remove subsample to record pH and conductivity;
- Filtration through 0.45 µm filter into prepared bottles for analysis;
- A filtered leachate split acidified with several drops of trace metal grade nitric acid is collected for analysis of cations and metals via ICP-MS or ICP-OES;
- An unacifidied, filtered leachate split is collected for analysis of anions by IC;
- Splits can also be collected for other analyses such as dissolved mercury concentration and sulphur isotopic composition of aqueous sulphate.

See Hageman (2007) for complete details of the method.

A field leach test to examine potential gastric bioaccessibility of fluoride in volcanic ash is currently being developed at the USGS. The test uses hydrochloric acid as the leaching solution.

These field methods have been developed for rapid field characterisation of geological materials such as mine wastes. Although difficulties of operating in the field (such as the requisite short agitation time, lack of readily available deionised water, bench space and cleaning equipment, lack of controlled atmospheric conditions) present logistical and interpretational challenges to the user, these tests can nonetheless provide very useful, near real-time information on ash leachate characteristics and eruption processes.

7.0 ACRONYMS

AAS	Atomic absorption spectroscopy
AVO	Alaska Volcano Observatory
BARGE	Bioaccessibility Research Group of Europe
BGS	British Geological Survey
EPA	U.S. Environmental Protection Agency
HDPE	High density polyethylene
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IFR	Institute of Food Research, U.K.
ISE	Ion selective electrode
IVHHN	International Volcanic Health Hazard Network
USGS	United States Geological Survey

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9.0 APPENDICES

Appendix 1 Comparative data for water extractable elements in tephra

Maximum and median concentration (in mg/kg) of water extractable *major* elements in tephra compiled from existing tephra leachate studies (see Ayris and Delmelle, 2012, for complete version)

Element	Concentration (mg/kg ash)		Count[ϕ]
	Maximum	Median	
Ca	23,590	2,140	27
S	17,770	1,662	30
Cl	11,160	1,162	30
Na	2,560	378	28
Mg	4,240	335	27
F	3,140	129	29
P	724	74	12
K	788	71	26
Al	1,164	58	24
Si	390	25	24
Fe	606	21	24
Mn	144	20	22
Cu	95	5	22
N	280	5	11

ϕ Number of volcanoes with ash leachate datasets available for element indicated

Maximum and median concentration (in µg/kg) of water extractable *minor* elements in tephra compiled from existing tephra leachate studies (see Ayris and Delmelle, 2012, for complete version)

Element	Concentration (µg/kg ash)		Count
	Maximum	Median	
Sr	35,048	4,296	14
Zn	53,020	3,575	21
B	7,722	2,606	9
Ti	18,668	2,317	12
Br	13,593	1,931	12
Ba	6,700	943	14
Ni	3,900	499	14
Li	1,880	220	14
Co	1,297	186	16
As	9,325	131	13
All other elements: median <100 µg/kg			

Appendix 2 A comparison of drinking water guidelines (all concentrations in mg/L)

(from Stewart et al., 2006)

		USEPA[1]		WHO[2]	New Zealand[3]		Japan[4]	Potential effects if standard exceeded[5]
		Primary standards (MCLs)	Secondary standards	Health standards	Health MAVs	Aesthetic GVs		
Elements of health significance								
Antimony	Sb	0.006		0.02	0.02			Increase in blood cholesterol; decrease in blood sugar
Arsenic	As	0.01		0.01	0.01		0.01	Skin damage, increased cancer risk
Barium	Ba	2		0.7	0.7			Increase in blood pressure
Boron	B			0.5	1.4		1.0	None stated
Cadmium	Cd	0.005		0.003	0.004		0.01	Kidney damage
Chromium	Cr	0.1		0.05	0.05		0.05	Probable MAV, limited information on health effects
Copper	Cu	2		2	2		1	Liver or kidney damage. NB aesthetic GV 1 mg/L
Fluoride	F	4		1.5	1.5		0.8	Dental and skeletal fluorosis. Range of 0.7-1.0 mg/L recommended for oral health reasons.
Lead	Pb	0.015		0.01	0.01		0.01	Impairs development and learning in children
Molybdenum	Mo			0.07	0.07			None stated
Mercury	Hg	0.002		0.001	0.007		0.0005	Kidney damage
Nickel	Ni			0.02	0.08			None stated
Nitrate	NO_3-N	10		11.3	11.3		10	Can cause methaemoglobinaemia in bottle-fed infants
Selenium	Se	0.05		0.01	0.01		0.01	Liver or kidney damage; damage to circulation and nervous systems
Uranium	U				0.02			Probable MAV
Elements influencing drinking water acceptability (taste, odour, colour etc)								
Acidity	H_3O^+		pH 6.5-8.5			pH 7-8.5	pH 5.8-8.6	Low pH: bitter metallic taste, corrosion High pH: soapy feel, soda taste
Aluminium	Al		0.05-0.2			0.1	0.2	Discolouration, depositions
Chloride	Cl		250			250	200	Taste, corrosion
Copper	Cu		1			1	1	Metallic taste, blue-green staining
Hardness	Ca+Mg					200	300	High hardness causes scale deposition, scum formation. Low hardness (<100) may be more corrosive. Taste threshold varies from 100-300 mg/L.
Iron	Fe		0.3			0.2	0.3	Rusty colour, metallic taste, red staining
Manganese	Mn		0.05			0.04	0.05	Black or brown colour, black staining, bitter metallic taste
Sodium	Na					200	200	Taste threshold
Sulphate	SO_4		250			250		Taste threshold
Zinc	Zn		5			1.5	1	Taste threshold

1 The United States Environmental Protection Agency has a two-tier system for the regulation of drinking water quality. The National Primary Drinking Water Standards set Maximum Contaminant Levels (MCLs) that are legally

enforceable, for the protection of public health. The National Secondary Drinking Water Regulations are non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic effects but are not a health risk.

2 The World Health Organisation defines guideline values for a range of chemicals of health significance. No formal guidelines have been set for chemicals affecting the acceptability of drinking water.

3 New Zealand has a two-tier system, as described in the Drinking-Water Standards for New Zealand 2005, revised in 2008. Maximum Acceptable Values (MAVs) have been set for determinands of health significance, whereas Guideline Values (GVs) have been set for aesthetic determinands (similar to acceptability determinands). It should be noted that MAVs are (with some exceptions) designed for a lifetime exposure and thus are not relevant for assessing effects of short term exposures.

4 One set of drinking water quality standards has been established for Japan, by the Ministry of Health, Labour and Welfare.

5 Discussion based on information provided by USEPA.

Appendix 3 A comparison of guideline values for trace elements in livestock drinking water (from Wilson et al., 2009). All concentrations in mg/L.

Parameter	ANZECC[1]	FAO[2]	Canadian[3]	Comments
Aluminium	5	5	5	Relatively non-toxic, but may have neurotoxic effects at high levels
Arsenic	0.5	0.2	0.025	Pigs and poultry are most sensitive and may suffer dehydration and haemorrhagic diarrhea although short term doses are usually tolerated
Beryllium	-	0.1	0.1	Little information available
Boron	5	5	5	Short term exposures are little problem, but long term exposures may cause weight loss and decrease in feed intake
Cadmium	0.01	0.05	0.08	Cd is of concern because it bioaccumulates; high Cd levels may cause teratogenic, mutagenic and carcinogenic effects
Calcium	1000	-	1000	Essential element for bones and teeth; excess Ca can reduce absorption of other nutrients.
Chromium	1	1	0.05	For both Cr(VI) and Cr(III)
Cobalt	1	1	1	Co is an essential micronutrient (component of vitamin B_{12}) but toxic at higher concentrations
Copper	0.4 to 2	0.5	0.5 to 5	There is quite a narrow window between essential and toxic levels of Cu. This varies for different livestock types, hence the ranges of values. Cu toxicity is also dependent on molybdenum and sulphate levels.
Fluoride	2	2	1 to 2	Excessive F intake causes dental and skeletal fluorosis. Intake from feed is also important; the Canadian guidelines recommend using the lower value if feed is high in fluoride
Iron	-	-	-	Some discoloration of meat at 0.1 mg/L in veal calves; also can taint milk at low levels; however guideline values generally not set as iron not considered a health hazard
Lead	0.1	0.1	0.1	Acute lead poisoning is more common (e.g., via contaminated feed) and affects the nervous system; chronic effects include anorexia and emaciation
Magnesium	2000	250-500	-	Mg is essential but high doses cause scouring and diarrhea.
Manganese	-	0.05	-	Deficiency problems are of much more concern than toxicity problems; FAO level is based on human drinking water guideline which is not based on health hazards
Mercury	0.002	0.01	0.003	Hg is of concern as it bioaccumulates and causes severe neurotoxic effects

Molybdenum	0.15	-	0.5	An essential micronutrient toxic at high concentrations; causes diarrhea and loss of appetite
Nickel	1	-	1	Interacts metabolically with iron
Nitrate	400	100	100	Nitrate is readily converted to nitrite, which is much more toxic to animals. Nitrite oxidizes haemoglobin to methaemoglobin which cannot transport oxygen. Symptoms include vomiting, convulsions, cyanosis and death.
Nitrite	30	10	10	
Selenium	0.02	0.05	0.05	Component of enzyme glutathione peroxidase; deficiencies more common than toxicity and feed supplementation is common
Sulphate	1000	-	1000	Sulphur is essential for animal nutrition but high levels cause diarrhea and are unpalatable.
TDS[4]	2000 to 4000	1000	3000	High levels primarily affect the palatability of the water which may lead to indirect health effects (see Section 3.2.3)
Uranium	0.2	-	0.2	Little information available
Vanadium	-	0.1	0.1	Possibly an essential element; interacts metabolically with Cr and Fe; high levels lead to reduced growth
Zinc	20	24	50	Essential micronutrient; many enzymes contain Zn; tolerance generally high

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1 Australian and New Zealand Environment and Conservation Council (ANZECC) (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality Volume 3: Rationale and Background Information (irrigation and general water uses, stock drinking water, aquaculture and human consumers of aquatic foods). October 2000. http://www.environment.gov.au/water/publications/quality/pubs/nwqms-guidelines-4-vol3.pdf

2 Food and Agriculture Organisation of the United Nations (Ayers and Westcott, 1994)

3 Canadian Environmental Quality Guidelines http://ceqg-rcqe.ccme.ca/

4 Total dissolved solids (salinity); see Appendix 4

Appendix 4 ANZECC guidelines on tolerances of livestock to salinity in drinking water (from Wilson et al., 2009)

Livestock	**Total dissolved solids (mg/L)**		
	No adverse effects expected	*Animals may have initial avoidance but should adapt*	*Loss of production, decline in condition and health*
Beef cattle	<4000	4000-5000	>5000
Dairy cattle	<2400	2400-4000	>4000
Sheep	<4000	4000-10000	>10000
Horses	<4000	4000-6000	>6000
Pigs	<4000	4000-5000	>6000
Poultry	<2000	2000-3000	>3000

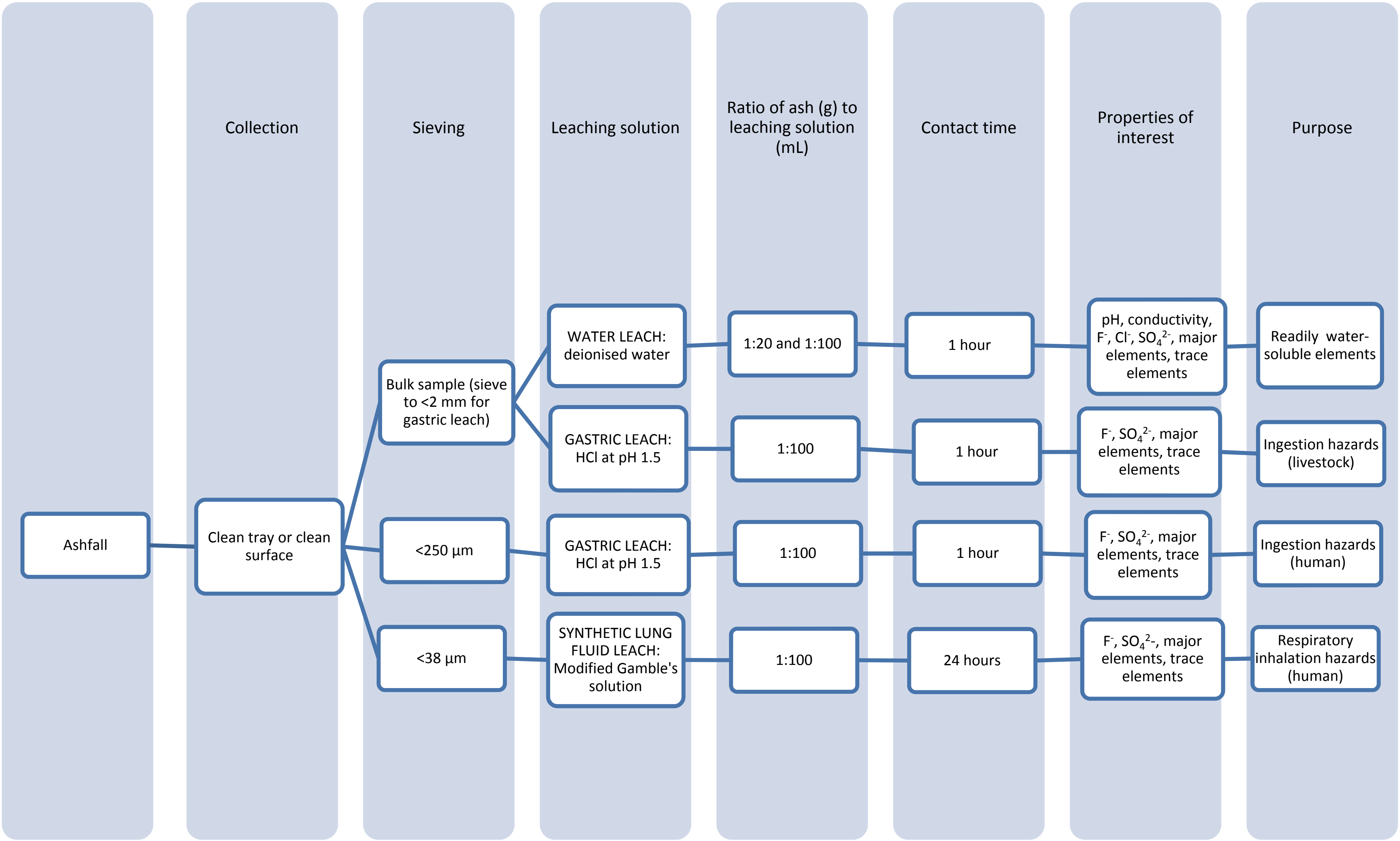

Figure 1 Summary flowchart of ash leachate methods