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# Development of a simulated lung fluid leaching method to assess the release of potentially toxic elements from volcanic ash



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#### HIGHLIGHTS

## • Investigation of a lung fluid leachate method to assess inhalation hazards of ash

- Element release in leachates is both method-parameter and sample dependent.
- Inclusion of lung surfactant is not necessary when assessing ash leachates.
- Optimal method parameters are extraction up to 24 h at 1:100 ratio.
- Water leach can be used as a conservative estimate of lung bioaccessible elements.

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#### G R A P H I C A L A B S T R A C T



#### ABSTRACT

Freshly erupted volcanic ash contains a range of soluble elements, some of which can generate harmful effects in living cells and are considered potentially toxic elements (PTEs). This work investigates the leaching dynamics of ash-associated PTEs in order to optimize a method for volcanic ash respiratory hazard assessment. Using three pristine (unaffected by precipitation) ash samples, we quantify the release of PTEs (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) and major cations typical of ash leachates (Mg, Na, Ca, K) in multiple simulated lung fluid (SLF) preparations and under varying experimental parameters (contact time and solid to liquid ratio). Data are compared to a standard water leach (WL) to ascertain whether the WL can be used as a simple proxy for SLF leaching. The main findings are: PTE concentrations reach steady-state dissolution by 24 h, and a relatively short contact time (10 min) approximates maximum dissolution; PTE dissolution is comparatively stable at low solid to liquid ratios (1:100 to 1:1000); inclusion of commonly used macromolecules has element-specific effects, and addition of a

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lung surfactant has little impact on extraction efficiency. These observations indicate that a WL can be used to approximate lung bioaccessible PTEs in an eruption response situation. This is a useful step towards standardizing *in vitro* methods to determine the soluble-element hazard from inhaled ash.

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ADDIEVI	ations		
BDL	below detection limit		
DI	deionized water		
DPPC	dipalmitoylphosphatidylcholine		
HR-ICP-MS high resolution inductively coupled plasma			
	spectrometry		
IVHHN	International Volcanic Health Hazard Network		
LOQ	limit of quantification		
PTE	potentially toxic element		
SLF	simulated lung fluid		
S:L	solid (mass) to liquid (volume) ratio		
WL	water leach		

#### 1. Introduction

Some elements present in particulate matter, such as Al, Cd, Fe, Ni, Pb and V, can generate harmful effects in living cells (*e.g.*, oxidative stress) and, therefore, are considered potentially toxic elements (PTEs) (Chen and Lippmann, 2009; Wallenborn et al., 2009). Release of PTEs in the lung environment has been strongly linked with the toxicity of particles and associated adverse health effects (Utembe et al., 2015; Misra et al., 2012). Characterising the presence of these soluble species is thus a primary concern when assessing respiratory health hazards.

Freshly erupted volcanic ash contains a range of soluble compounds that are leached upon contact with water or body fluids. They predominantly consist of mixed sulphate and halide salts, which are emplaced by gas-ash interactions in the volcanic plume and various processes throughout ash transportation and deposition, leading to variable element abundances on ash surfaces (Stewart et al., 2020; Ayris et al., 2015; Witham et al., 2005). The principal method used to quantify species adsorbed onto ash particles is leaching (Stewart et al., 2020). Leachate analyses show that, although an array of cations and anions are readily mobilised, the most abundant soluble elements are usually Ca, Na and K, followed by Al, Mg, Fe and Cu, and the most common minor elements (defined as < 5 mg/kg ash) are Ni and Zn (Ayris and Delmelle, 2012). The release of these elements may result in the contamination of water bodies and soils with potential impacts to human and animal health in ash-affected areas (Stewart et al., 2020; Witham et al., 2005).

As a common hazard assessment strategy, leaching with simulated lung fluid (SLF) is used to investigate the lung bioaccessibility of PTEs for a wide range of inhalable materials (*e.g.*, Martin et al., 2018; Dean et al., 2017; Wiseman and Zereini, 2014; Wolf et al., 2011; Plumlee and Morman, 2011; Gray et al., 2010; Colombo et al., 2008; Twining et al., 2005). SLFs are solutions that comprise a mixture of physiologically relevant constituents (electrolytes and organic molecules) representing the conditions in different compartments of the human respiratory system. Acellular *in vitro* studies are easily implemented and can provide a quick and cost-effective alternative to cellular *in vitro* and *in vivo* studies. Although leaching experiments do not reproduce the complex processes that occur in the human body and, thus, the health relevance cannot be directly extrapolated from the results (Boisa et al., 2014; Kastury et al., 2017), they provide a first-order understanding of the release of PTEs in the lung environment.

The most commonly used SLF is known as Gamble's solution. It is a near-neutral (pH 7.4) solution consisting of cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) and anions (HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>) at concentrations representative of those measured in lung lining fluid (Gamble, 1967), with acetate  $(H_3C_2O_2^-)$  and citrate  $(H_5C_6O_7^{3-})$  substituting for macromolecules such as proteins and lipids, despite having different biochemical functionalities. There are now varying formulations of the original Gamble's solution, though modifications are often presented without a clear explanation (Kastury et al., 2017). These modified solutions include organic compounds that are representative of anions and functional groups in the lung lining fluid (e.g., albumin, mucin, citrate, glycine, cysteine, glutathione, lactate, pyruvate, etc.), which can act as chelating agents towards specific metals or metalloids of interest and may promote dissolution of otherwise insoluble compounds (Caboche et al., 2011: Pelfrêne et al., 2017), as well as lung surfactants (e.g., dipalmitoylphosphatidylcholine; DPPC), which can increase wettability of particles, improve contact between leachant and metals, and prevent aggregation (Caboche et al., 2011; Pelfrêne et al., 2017). Such modifications add to the complexity of the solution and hinder comparison among studies, particularly because the impacts of these modifications on overall leaching dynamics are not understood.

The viability of an SLF method to assess volcanic ash has not yet been specifically tested. In contrast to the highly polluted geological materials that are usually of interest for lung bioaccessibility studies (e.g., mine waste, soils, urban dust; Kastury et al., 2017; Plumlee and Morman, 2011), volcanic ash contains very low concentrations of readily soluble PTEs (Stewart et al., 2020), particularly where speciation is a primary concern for toxicity (As, Cd, Cr, Hg, Pb, Se). However, ash has an abundance of generally non-toxic elements like Ca, Na, S and Cl (Ayris and Delmelle, 2012). Since some of these ions are already present in SLF in substantial quantities, as either components of the SLF recipe or as impurities in the reagents, this can cause signal reduction or poor precision during measurements (*i.e.*, high background values). This can then cause difficulties in determining concentrations leached from the ash. especially for minor elements, including PTEs, because of the necessity of making large dilutions of the sample matrix. Thus, there is a clear need to test different parameters of a SLF method for volcanic ash to establish their influence on apparent PTE bioaccessibility.

There is no consensus on leaching parameters (such as extraction time and solid to liquid ratio (S:L)) appropriate for the inhalation pathway on which to base a method for ash (Kastury et al., 2017). Recommendations for an SLF leachate method applied to volcanic ash were an outcome of expert discussions hosted by the International Volcanic Health Hazard Network (IVHHN) (Stewart et al., 2013), but the method was not fully tested. Therefore, these recommendations were not included in the IVHHN protocol for the rapid assessment of hazards from leachable elements in ashfall (Stewart et al., 2020). This was mainly because testing of the 2013 protocol faced the aforementioned difficulties associated with measurement of low PTE concentrations from ash in typical SLF solutions. Additionally, there was the concern that an SLF method may not be readily available for eruption response work because of the number and expense of analytical-grade reagents required for SLF preparation. Rapid analysis and dissemination of results is the kev intention of this method, which sits within a broader IVHHN protocol to rapidly assess health-relevant physicochemical and toxicological characteristics of volcanic ash (available at www. ivhhn.org). This leachate protocol currently includes a generalpurpose deionized (DI) water leach (WL) that is appropriate for assessing the impacts of ashfall on water resources, such as drinking water supplies, and a 'simple gastric' leach that is intended to estimate the bioaccessible fraction of PTEs in the event of ash ingestion by humans or livestock (Stewart et al., 2020). An SLF method was not yet developed to a point where inclusion would provide timely data during an eruption response.

To date, only three studies have addressed leaching of volcanic ash in SLF. In the first, Damby (2012) investigated which minerals dissolve and the types of secondary minerals that might precipitate in the lung following inhalation of volcanic ash using samples from five different volcanoes (Colima, Merapi, Mount St. Helens, Santiaguito and Unzen). After a four-week incubation of samples in SLF at 37 °C, a loss in mass, attributed to glass dissolution, was noted among all samples, but no new mineral precipitation was observed using X-ray diffraction. In the second study, Tomašek et al. (2019) leached synthetic ash laden with sulphate salts in water and determined that the majority of salts dissolved within 10 min. Using the resulting water-leach concentrations, saturation in SLF was simulated by reaction-path modelling. The SLF was undersaturated in sulphate salts (CaSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>), suggesting that no new phases were being formed and the predominant salt deposits found on ash surfaces would dissolve in lung fluid, likely prior to cellular uptake. In a recent study, Barone et al. (2020) quantified the soluble element burden of volcanic ash samples from Etna volcano in water and SLF according to the initial recommendations by Stewart et al. (2013).

The primary objective of this study is to develop a robust in vitro method to assess the release of PTEs from ash in the lung environment to evaluate the hazard of volcanic eruptions to public health. Given the scarcity of past ash leaching studies on which to base such a method, and the general lack of studies reporting comparative efficiencies of existing SLF approaches, this work establishes the effect of different SLF compositions and extraction parameters (ash to leachant ratio and extraction time) on the efficiency of leaching PTEs. This is a critical first step in the development of a standardised method for health hazard assessment and inclusion with other, existing IVHHN ash analysis protocols as the lung lining fluid is the first interface that inhaled materials come into contact with in the airways. A second objective of this work is to compare element leaching efficiency in SLF and DI water (i.e., IVHHN's general-purpose WL). Toxicology studies of particulate matter indicate that water-soluble elements may be associated with toxic effects in the lungs (Oller et al., 2009; Costa and Dreher, 1997), and that their release into water may differ from their release into an SLF (Caboche et al., 2011; Pelfrêne et al., 2017). Hence, the present experiments were designed to ascertain whether WL could be used as a proxy for SLF leaching of volcanic ash. DI water is the most common leachant for ash studies (Stewart et al., 2020) due to its wide availability. Its use for rapid respiratory hazard assessment would bolster data comparability with previous assessments, and eliminate the need to perform multiple leachate analyses on a sample, which are often difficult to obtain in sufficient amounts.

#### 2. Materials and methods

#### 2.1. Volcanic ash samples

For this study, three ash samples from recent volcanic eruptions were selected (Table 1). The samples were collected fresh (unaffected by precipitation or surface weathering) from ashfall deposits according to IVHHN ash collection recommendations (Stewart et al., 2020) and stored in self-sealing plastic bags. The SLF leaching experiments (*Section 2.3*) were carried out in batch conditions on bulk volcanic ash, which had not been oven dried. Each sample was homogenized by gently rotating in a sealed container before taking a sub-sample for leaching experiments.

The sample selection was based on available mass to test a number of different leaching parameters, and because samples were previously characterised for their water-leachable element content. All three ash samples have relatively high leachable concentrations. Element concentrations (in mg/kg dry weight ash) were determined previous to this research by WL for 1 h at a solid (mass) to liquid (volume) ratio of 1:100 (Damby et al., 2018; Stewart, C., unpublished) using a standardised protocol by Stewart et al. (2020). These concentrations were normalized to mean concentrations reported in a global dataset on water-extractable elements from volcanic ash (Ayris and Delmelle, 2012) (Fig. 1, Appendix A). All three samples have abundant soluble major elements (>5 mg/L global mean concentration), particularly the ash from Whaakari/White Island volcano. Water-soluble minor elements (<5 mg/L global mean concentration), except for Cu, are present in lower concentrations than global means and some were below detection limits (BDL) in Ambae and Kilauea ash (namely Co in Ambae, Zn in Kīlauea, Cd, Cr, Pb and V in both). These 1 h WL data are compared with the concentrations determined in the present study using the same ash to leachant ratio (1:100) for 24 h WL and SLF at different time points in Section 3.4.

#### 2.2. Selection of leaching parameters

The recommendations for ash leaching in SLF provided by the expert working group convened by IVHHN to standardize the leachate protocols are taken as a starting point for our SLF testing (Stewart et al., 2013). These include an SLF based on Gamble's solution (Table 2), a contact time of 24 h and a 1:100 ash (mass) to leachant (volume) ratio. In the following sections, we summarise the parameter modifications tested in this study.

#### 2.2.1. Leachant

In general, the dissolution rate of elements is dictated by their solubility in different media (*e.g.*, water or SLF) which is predominantly controlled by the pH and composition of the solution (Kastury et al., 2017; Misra et al., 2012). Earlier studies argued that simple leachants, such as water, are not 'physiologically based' and, thus, are not representative of pulmonary exposure (reviewed in Kastury et al. (2017)). It is thought that a WL may underestimate the lung bioaccessibility of metal components due to the absence of organic compounds.

In addition to deionized water, we used four different SLF solutions of a near-neutral pH, all with the same base composition (see Table 2). This range of solution compositions allows determination of the effects of inclusion, or exclusion, of commonly used molecules (glycine, citrate) and a surfactant (DPPC) to deduce whether they are essential components for assessing the ash hazard. For these experiments, the 24 h time-point and 1:100 solid to liquid (S:L) ratio were set as constant.

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#### Table 1

Sample and collection information for the volcanic ash samples used in this study.

Volcano	Country	Eruption date	Magma type	Collection date	Collection location
Ambae	Vanuatu	March 17, 2018	Basalt to trachybasalt <sup>a</sup>	March 17, 2018	Vinangangwe, West Ambae
Kīlauea	USA	May 10-28, 2018	Basalt <sup>b</sup>	May 28, 2018	Kaʻū Desert, Hawaiʻi
Whakaari/White Island	New Zealand	April 27, 2016	Andesite <sup>c</sup>	April 28, 2016	North rim of the crater

<sup>a</sup> Moussallam et al. (2019).

<sup>b</sup> Neal et al. (2019).

<sup>c</sup> Mayer et al. (2015).



**Fig. 1.** Water-extractable major (>5 mg/L) and minor (<5 mg/L) element abundances in analysed ash samples (black circles – Whaakari/White Island, red squares – Ambae, green triangles – Kilauea) normalized to global mean values (Ayris and Delmelle, 2012). Elements not shown were below detection limit (Appendix A). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

#### Table 2

Composition of the simulated lung fluid (SLF) solutions used in this study (see *Section 2.2.1*). Base composition (SLF1) is after Stewart et al. (2013), and modifications are to include lung surfactant (DPPC; SLF2) and to remove citrate (SLF3) or glycine (SLF4). All concentrations are as mg/L.

	SLF1	SLF2	SLF3	SLF4
NaCl	6400	6400	6400	6400
CaCl <sub>2</sub> ·2H <sub>2</sub> O	255	255	255	255
$Na_2HPO_4$	150	150	150	150
NaHCO <sub>3</sub>	2700	2700	2700	2700
NH <sub>4</sub> Cl	118	118	118	118
MgCl <sub>2</sub> .6H <sub>2</sub> O	212	212	212	212
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	179	179	179	179
Na3 citrate 2H2O	160	160	_	160
Glycine	190	190	190	_
DPPC <sup>a</sup> (0.01%)	_	100	-	-

<sup>a</sup> DPPC = dipalmitoylphosphatidylcholine.

#### 2.2.2. Extraction time

To be relevant for inhalation exposures, the sample extraction time *in vitro* should be representative of the residence time of particles in the lung. This is difficult to constrain as particle removal depends on the deposition site within the lungs and clearance mechanisms involved (mucociliary transport, uptake by phagocytic cells, *in situ* dissolution, etc.). These processes operate on the order of hours to days and months (Bailey et al., 2007; Morgan et al., 2004; Gehr et al., 1990). It has also been argued that the shortterm toxic effect of particles that release ions at a fast rate could be identical to those of the dissolved ions (Studer et al., 2010), whereas, for particles that release ions at a slow rate, there is a greater likelihood that the particles will be the cause of the observed adverse effects (Oberdörster, 2000).

The contact times used in previous lung bioaccessibility studies on non-volcanic material vary greatly, ranging from 5 min to 1 year (Kastury et al., 2017), with most studies using  $\leq 24$  h. Reported timeframes in ash-water leachate studies range from 5 min to 2 years (Stewart et al., 2020). A shorter duration timepoint is supported by previous work on volcanic ash leachate studies. Ash leachate studies using water demonstrated that the majority of surface phases were dissolved within the first 10–15 min (Olsson et al., 2013; Duggen et al., 2007), and most sulphate salts were dissolved within 10 min (Tomašek et al., 2019).

To determine how extraction varies over a relevant timeframe for volcanic ash in SLF, we tested contact times of 10 min, 1 h, 4 h, 24 h and 48 h, each as a separate experiment. The 24 h time-point was kept as a constant parameter for the S:L ratio and leachant composition tests. This is the time-point at which the measured concentrations of all elements became approximately stable and provides a direct comparison with cellular toxicity tests which commonly use 24 h exposures.

#### 2.2.3. Solid to liquid ratios

The mass of particles that deposits in the lung (*i.e.*, particle loading) following inhalation is variable and largely dependent on ambient particle concentrations, size distribution and personal exposure. To determine *in vitro* S:L ratios relevant for real human exposure, we calculated the potential particle loading following a single ash exposure. We assume 100% particle deposition and a daily inhaled air volume of 25 m<sup>3</sup>, corresponding to a healthy, moderately-active adult (ICRP, 1994), for airborne ash

concentrations of 0.02 and 1 mg/m<sup>3</sup>, reported as minimum and maximum daily averages in the literature (Searl et al., 2002). Using 20 mL as the total volume of lung lining fluid (Macklin, 1955), when ambient concentrations of ash are low (0.02 mg/m<sup>3</sup>) the S:L ratio would correspond to 1:4000, whereas when ambient concentrations are high (1 mg/m<sup>3</sup>) it would be 1:800. In case of an exposure to higher ambient concentrations, which could be experienced during ash clean-up activities (*e.g.*, 10 mg/m<sup>3</sup>) (Searl et al., 2002), the ratio could be even larger and equate to 1:80.

The S:L ratios used in lung bioaccessibility studies to date range from 1:20 to 1:50000, with the majority of studies using ratios <1:100 (Kastury et al., 2017), whereas ash-water leachate studies use ratios from 1:5 to 1:1000 (Stewart et al., 2020). The ratios tested in this study (1:10, 1:20, 1:100, 1:500, 1:1000) reflect this wide range, accounting for experimental/analytical constraints, and include the existing IVHHN recommended ratios for water leach of 1:20 and 1:100 (Stewart et al., 2020). The 1:100 ratio was selected as a constant in the time-series and varying leachant composition tests.

#### *2.2.4. Other method parameters*

Other parameters that may affect extraction and have direct relevance to the respiratory system but were not specifically tested in the framework of this study are temperature and particle size. Whereas most SLF studies incubate particles at 37 °C to replicate body temperature (Kastury et al., 2017), we performed the extractions at room temperature (25 °C) as a system to maintain the elevated temperature and agitate the samples simultaneously was not available. This was justified through preliminary experiments that compared extraction at 25 °C and 37 °C (without agitation) and resulted in little difference in leaching efficiency (*unpublished data*). Therefore, we leached all samples at room temperature to reduce experimental complexity.

Considering that the focus of the current exercise was on the methodological parameters affecting bioaccessibility rather than sample properties, we choose to perform the extractions on bulk (un-sieved) ash samples. Isolation of respirable (sub-4  $\mu$ m) material from bulk ash, in amounts sufficient for leachate analysis, is time-consuming and often impractical. The percentage of sub-4  $\mu$ m particles also varies greatly among samples, depending on the sample collection distance from the vent and the magnitude and explosivity of the eruption, but is typically <17% (Horwell, 2007; Horwell and Baxter, 2006). This is the case for sub-10  $\mu$ m particles as well, which are generally used in lung bioaccessibility assessment studies (Kastury et al., 2017). While it is assumed that analysis of the respirable fraction may be more predictive of real bioaccessibility, and is likely to give higher concentration values than those of bulk extractions due to higher particle surface area, it is not

 Table 3

 Experimental parameters: leachant, extraction time and S:L ratio. Each test was performed in triplicate.

	SLF1	SLF2	SLF3	SLF4	WL <sup>a</sup>
10 min	1:100				
1 h	1:100				
4 h	1:100				
24 h	1:10				
	1:20				
	1:100	1:100	1:100	1:100	1:100
	1:500				
	1:1000				
48 h	1:100				

 $^a~WL=$  water leach, using deionized water (Milli-Q®, resistivity of 18.2 MΩ, pH 7.95  $\pm$  0.05).

always possible to demonstrate the size effect in isolation from other properties (Misra et al., 2012).

#### 2.3. Leaching experiments

Assay parameters evaluated (see Table 3) included composition of the leachant, contact time and ash to leachant (S:L) ratio to determine their influence on the leaching efficiency (Table 3). Each test was performed in triplicate. Depending on the experiment, different amounts of ash were weighed into 50 mL polypropylene centrifuge tubes and corresponding volumes of leachant were added. Samples were then agitated on a platform (horizontal) shaker at 60 rpm at room temperature throughout the extraction duration. Subsequently, samples were centrifuged for 5 min at 3392×g and filtered through 0.45 µm cellulose acetate membrane filters (VWR Chemicals, Belgium) into 15 mL polypropylene tubes using syringe filtration. Leachates were acidified with concentrated nitric acid (HNO<sub>3</sub>) and stored at 4 °C until analysis.

In order to keep the background concentrations low, all reagents used to prepare the SLF (Table 2) were of analytical grade (*AnalaR*® *NORMAPUR*®), purchased from VWR Chemicals (Belgium). The solutions were prepared in deionized water (Milli-Q®, resistivity of 18.2 MΩ). The pH of the solution was adjusted to 7.40  $\pm$  0.05 using concentrated hydrochloric acid (HCl).

#### 2.4. Leachate chemical analysis

We analysed a large suite of PTEs (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) and cations that are the main constituents of ash surface coatings (Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>). All element concentrations were measured using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Thermo Finnigan Element II) at the facilities of the Analytical, Environmental and Geochemistry group of the Vrije Universiteit Brussels. Calibration curves of the selected elements were made from dilutions of an acidified multi-element stock solution (ICP-MS Calibration standard 2, VWR Chemicals, Belgium) and single element standards (Certipur® 1000 ppm, Merck, Belgium), with <sup>103</sup>Rh as internal standard. The procedural blanks and experimental samples were diluted 10-fold in 2% HNO<sub>3</sub> solution prior to the analysis. Operational parameters are listed in Appendix B (Tables B1 and B.2). The limits of quantification (LOQs) were calculated as 3-fold standard deviation of the mean elemental concentration measured in the leachates of procedural blanks which underwent the whole extraction procedure (Table 4).

Table 4

Limits of quantification (LOQ) for selected elements in  $\mu$ g/L obtained by HR-ICP-MS in deionized water (DI) and SLF solutions, calculated as three times the SD for the mean of n = 8 procedural blanks for SLF1 and n = 3 for DI, SLF2, SLF3 and SLF4.

_		•				
		DI	SLF1	SLF2	SLF3	SLF4
	Na	100	94831	506282	412779	425928
	Са	5	1340	7445	6320	6451
	Mg	0.7	634	3471	2824	2752
	Κ	1.3	5.4	35	5.1	204
	Al	2.5	31.3	3.4	3.7	14.1
	Fe	1.2	3.3	10.9	2.6	1.2
	Mn	0.06	1.10	0.27	0.12	0.11
	Cu	0.11	0.21	0.11	0.13	0.08
	Cd	0.003	0.008	0.004	0.007	0.009
	Со	0.006	0.005	0.010	0.005	0.002
	Cr	0.23	0.30	0.26	0.27	0.25
	Ni	0.24	0.33	0.28	0.26	0.26
	V	0.006	0.027	0.009	0.004	0.008
	Pb	0.008	0.116	0.027	0.019	0.030
	Zn	0.84	10.77	1.59	1.00	1.32

#### 2.5. Data processing and statistical analysis

Graphical representation and statistical analysis of the data were performed using GraphPad Prism (version 8.3.0; *GraphPad Software*, San Diego, CA). Statistical significance between different experimental parameters was determined using a one-way analysis of variance (ANOVA) with subsequent Tukey's tests. The alpha value was set at 0.05. In the figures, significant differences are denoted by lowercase letters; for all parameters with the same letter, the difference between the means is not statistically significant (p > 0.05), whereas, for parameters with a different letter, the difference is statistically significant (p < 0.05).

#### 3. Results

#### 3.1. Influence of leachant composition on PTE release

The results of ash extraction in four preparations of SLF (SLF1-SLF4) are shown in Fig. 2 (major elements) and Fig. 3 (minor elements). All extractions were for 24 h at 1:100. Across the four SLFs tested, there were notable differences in measured concentrations that were consistent for all ash samples: Al, Fe (Fig. 2) and Cr (Fig. 3) were all found BDL in SLF3; Cu was significantly (p < 0.05) lower in SLF4 (Fig. 3); Mg was significantly (p < 0.05) lower in SLF2, but was otherwise equivalent (p > 0.05) across all leachants (Fig. 2); Ca and K were higher in SLF3 (Fig. 2). The concentration of leached Cd was



**Fig. 2.** Major element concentrations (>5 mg/kg, global mean concentration) in three ash samples (black – Whaakari/White Island, red – Ambae, green – Kilauea) obtained through the extractions in four different simulated lung fluids (24 h, 1:100 S:L). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachants for each ash sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 3.** Minor element concentrations (<5 mg/kg, global mean concentration) in three ash samples (black – Whaakari/White Island, red – Ambae, green – Kilauea) obtained through the extractions in four different simulated lung fluids (24 h, 1:100 S:L). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachants for each ash sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the same (p > 0.05) in all SLFs (Fig. 3). There were no differences in concentrations of K (Fig. 2) and minor elements determined in SLF1 and SLF2 (Fig. 3). While low levels of Pb and Zn were leached in water (Appendix C), their concentrations were BDL in all SLFs. The substantial component of Na in SLF solutions (Table 4) prevents the accurate quantification of Na (Appendix C).

Regarding the extraction behaviour among the three samples, some exceptions could be observed across the different leachants. The concentration of Mn was largely comparable in different SLFs for Whaakari/White Island and Ambae ash but showed significant (p < 0.05) differences in Kīlauea ash (Fig. 2). Although following the

same qualitative pattern for all samples, the concentration of Fe was not statistically different (p > 0.05) across all SLFs for Whaakari/White Island, whereas it was significantly different (p < 0.05) across all SLFs for Ambae and Kīlauea ash (Fig. 2). While concentrations of Cu and Ni were statistically equivalent in SLF1-SLF3 in Ambae and Kīlauea ash, this was not the case in leachates of Whaakari/White Island ash (Fig. 3). Leaching of V was similar for Whaakari/White Island and Kīlauea ash, with lower concentrations in SLF3, in contrast to Ambae ash where the concentrations were equivalent across all SLFs (Fig. 3). Concentrations of Co indicated different magnitudes of leaching across all samples (Fig. 3).



**Fig. 4.** Major element concentrations (>5 mg/kg, global mean concentration) in three ash samples (Whaakari – black, Ambae – red, Kīlauea – green) obtained through the extractions over varying time-points (for 1:100 S:L in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

#### 3.2. Influence of extraction time on PTE release

Release of PTEs in SLF was tracked over five time intervals, from 10 min to 48 h. Overall, the concentration of individual elements over different time intervals varied among the different samples. Only Mg concentrations remained constant (p > 0.05) across all measured time-points in all samples (Fig. 4). Except for Fe in Ambae ash, the time-series for Al, Fe and Mn were largely consistent with their highest concentrations recorded after the initial 10 min leaching period, after which concentrations decreased by the 4 h time-point and then remained stable, as seen from the little difference (p > 0.05) between concentrations at 4 h, 24 h and 48 h time-points (Fig. 4). This trend was the most prominent for Whaakari/White Island ash leachates and could also be observed for leached Cd, Co, Cr and Ni, whereas their concentrations were

constant over time in Ambae and Kīlauea ash (Fig. 5). Similar behaviour in Whaakari/White Island was exhibited for Cu and V, whereas their concentrations slightly increased by the 48 h timepoint in Ambae and Kīlauea ash (Fig. 5). Leached Ca and K showed a similar qualitative pattern, with a decrease at 1 h compared to the initial concentration at 10 min then followed by an increase over time (Fig. 4).

#### 3.3. Influence of the ash to leachant ratio on PTE release

Five S:L ratios, ranging from 1:10 to 1:1000, were used to assess the influence of ash to leachant ratio on the PTE dissolution from ash in SLF. Among the different tested ratios, concentrations of Mg were found to be stable in all samples (Fig. 6). Concentrations at the two lowest S:L ratios, 1:500 and 1:1000, showed no significant



**Fig. 5.** Minor element concentrations (<5 mg/kg, global mean concentration) in three ash samples (Whaakari – black, Ambae – red, Kīlauea – green) obtained through the extractions over varying time-points (for 1:100 S:L in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

differences (p > 0.05) for Cd, Cr, Cu, Mg, Mn and Ni across all samples, whereas K was lower or BDL in these ratios. As an overall trend, recorded element concentrations increased with decreasing sample loading for Al, Co, Cr, Cu, Fe, Mn and V, and were largely independent of S:L ratios in a range 1:100 to 1:1000 for Ambae and Kīlauea ash, with the exceptions observed in Whakaari/White Island leachates which generally had higher concentrations for these elements. For Whakaari/White Island ash, there was a drop in concentration at 1:20 and/or 1:100 for Al, Co, Fe and Mn. This was the case for Cd as well, which was found to be constant in all S:L ratios for Ambae and Kīlauea samples (Fig. 7). Ni concentrations varied across different samples (Fig. 7).

#### 3.4. Comparison of DI water and SLF leach

A comparison of the concentrations determined in standard WL after 1 h (from Damby et al. (2018) and Stewart, C. (unpublished)) and 24 h, and SLF1 leach for 10 min, 1 h and 24 h (at 1:100 and 1:1000 S/L) is shown in Fig. 8 (major elements) and Fig. 9 (minor elements).

The results demonstrate that most of the water-soluble elements in the analysed ash samples were found in similar or higher concentrations at 24 h than those measured in 1 h WL, with the exception of K and Cr from Whaakari/White Island ash, and Al, Ca, Mn and Fe from Kilauea ash, which were higher in the 1 h WL (Fig. 8).



**Fig. 6.** Major element concentrations (>5 mg/kg, global mean concentration) in three ash samples (Whaakari/White Island – black, Ambae – red, Kilauea – green) obtained through the extractions in varying ash to leachant (S:L) ratios (24 h in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachants for each ash sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The overall trends indicated that the SLF1 leached concentrations of major elements were either comparable to, or significantly (p < 0.05) lower than, those in the 1 h and 24 h WL, with only Mg concentrations being the same across the compared parameters (Fig. 8). The concentrations of minor elements in SLF1 leachates were either comparable to the WL or were higher than the 1 h WL, but lower than the 24 h WL (Fig. 9), except for V, which was significantly (p < 0.05) lower or BDL in the WL.

#### 4. Discussion

## 4.1. Influence of leaching parameters on release of elements from volcanic ash

The results demonstrate the influence of operational conditions on the measured PTE concentrations in SLF. In most cases, changing the parameters had an equivalent effect across all samples, which allowed for an overview of the direct impact of each method parameter.

The effect of specific compounds in the solubilisation of certain



**Fig. 7.** Minor element concentrations (<5 mg/kg, global mean concentration) in three ash samples (Whaakari/White Island – black, Ambae – red, Kilauea – green) obtained through the extractions in varying ash to leachant (S:L) ratios (24 h in SLF1). Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample. Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachants for each ash sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

elements in SLF was clearly demonstrated. The observed differences in the release of PTEs among the four SLF compositions used (Figs. 2 and 3) can likely be attributed to differences in their mobilities and tendencies to form soluble complexes with organic components present in the tested SLF solutions (Table 2). This was shown for glycine, a component of SLF1-SLF3, which likely formed soluble complexes with Cu (Fig. 3). Similarly, Al, Cr and Fe have high affinities for the citrate ion and were not as efficiently released in SLF3 in the absence of citrate (Figs. 2 and 3). Furthermore, there was little difference in leachate concentrations between SLF1 and SLF2, suggesting that inclusion of lung surfactant (DPPC) in SLF imparts limited impact on extraction of PTEs associated with volcanic ash (Fig. 3). The relevance of including DPPC in an SLF has been repeatedly highlighted in the literature (see review by Kastury et al., 2017), mostly due to it being the dominant component of the lung surfactant by mass and its ability to promote dissolution efficiency. While it was shown that DPPC increases the bio-accessibility of certain elements, *e.g.*, Pb, Zn and Sr (Boisa et al., 2014; Caboche et al., 2011; Pelfrêne et al., 2017), it has also been reported that the addition of DPPC results in no significant changes to bioaccessibility (Pelfrêne et al., 2017).

The concentrations of PTEs in the leachates in the time-series experiments (Figs. 4 and 5) follow three general trajectories up to 24 h, when most PTE concentrations reach a plateau: increasing,

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**Fig. 8.** Major element concentrations (>5 mg/kg, global mean concentration) in three ash samples obtained through the extractions in water (WL) and SLF1 over varying timepoints. All data are for S:L 1:100, except SLF1 at 24 h denoted with a star (\*), which was extracted at S:L 1:1000. Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample, except for WL at 1 h (n = 1). Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachates for each ash sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

flat, or decreasing. Whereas increasing concentrations can be explained by prolonged release, and a stable concentration explained by rapid dissolution, a decrease in concentration requires sequestering of previously leached elements, which decreases the fraction that remains in the solution over time. This decrease for some elements is possibly a consequence of formation of new, insoluble phases and/or adsorption onto the particles. Such formation of new, insoluble complexes or, alternatively, lack of dissociation of soluble complexes, can be facilitated by the neutral pH of the SLF solution (Pelfrêne et al., 2017; Schaider et al., 2007; Marschner et al., 2006). These processes may also be associated with the differences in PTE extraction in varying S:L ratios. The results indicated that PTE concentrations in SLF1 were largely independent of ratio in the range 1:100 to 1:1000 at 24 h (Figs. 6 and 7), except for Whakaari/White Island ash, where the concentrations were higher in 1:1000 (and 1:500) than 1:100 for some elements (Al, Fe, Cr, Cu, V). It is possible that, in this case, the saturation effect was reduced due to lower particle mass loading in the solution during the extraction.

Overall, it could be seen that some element releases in SLF changed with the different substrate (sample), but the observed leaching behaviours could be summarised as follows:

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**Fig. 9.** Minor element concentrations (<5 mg/kg, global mean concentration) in three ash samples obtained through the extractions in water (WL) and SLF1 over varying timepoints. All data are for S:L 1:100, except SLF1 at 24 h denoted with a star (\*), which was extracted at S:L 1:1000. Data are reported as mg element per kg of ash dry weight and represented as the mean of three replicates for each sample, except for WL at 1 h (n = 1). Error bars are the standard error of the mean. Lowercase letters indicate a significant difference (p < 0.05) between the mean concentrations of leachates for each ash sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

- 1) The concentrations of Mg measured in the SLF leachates were the most stable across the different experiments in all samples;
- 2) The dissolution of Ni in SLF was the least affected by variation in test parameters among analysed PTEs and samples;
- 3) The other elements showed different sensitivities to changes in test parameters and exhibited variability among the three ash samples, with the strongest effects observed for Al, Fe and Mn.

Any sample-specific deviations from these broad effects are likely due to the differences in ash leachable burden (Fig. 1, Table 1),

including the state in which PTEs are bound to the ash particles (Wolf et al., 2011).

#### 4.2. Comparison of SLF and water leach

Our results showed that leachants of similar near-neutral pH with different complexity in their chemical composition affect the release patterns of elements from volcanic ash (Figs. 8 and 9). The solubilisation potential of SLF solutions was particularly noticeable for V, which increased over time in SLF1 and was measured in all

SLF leachates (Fig. 3) yet found in significantly (p < 0.05) lower concentrations (or was BDL) in the WL at 1 h and 24 h (Fig. 9).

Comparison of WL and SLF data demonstrates that the initial release of major elements in SLF1 at 10 min is, to some extent, comparable to that in WL at 1 h (Fig. 8), while minor PTE concentrations are higher in 10 min SLF1 than in 1 h WL, and more similar to those measured in 24 h WL (Fig. 9). In some cases, for the 24 h time-point, it seems that the WL overestimates the amounts extractable in SLF, but this apparent lower leaching efficiency of SLF relative to earlier time-points in SLF1 and WL, in general, is likely a consequence of solution reaching saturation state. This may be explained by progressive dissolution of less soluble surface phases and/or dissolution of the ash grains which, in the case of the WL, does not result in solution saturation, as seen from the differences in PTE concentrations between the 1 h and 24 h WL.

In summary, the results showed that:

- 1) The concentrations of Mg measured in the leachates (WL and SLF) were the most stable in all samples;
- The dissolution of V in SLF was found to be more efficient than in WL regardless of the sample;
- 3) The WL reflects results of the SLF-soluble PTEs for shorter contact times, except for Cu, Co and Ni in some samples.

#### 4.3. SLF analytical challenges

Although we successfully characterised the leaching behaviour of most of the analysed elements in SLF, determining the concentration of Na yielded poor results (Appendix C). These results are probably due to the initial levels of Na in the SLF solutions (Table 2), so the measured concentrations are likely to be less reliable since they are generally similar to those in the blanks: WL concentrations for Na from the 3 samples are 8.1–67.3 mg/L (Appendix C), whereas the limits of quantification for Na are approximately 100–500 mg/L (Table 4). Pb and Zn were BDL in the SLF leachates, even though they were measured in the WL (Fig. 1). The finding of minor elements BDL of the method but present in WL likely results from the solution being too dilute for quantification, or because the concentrations measured in samples are, again, too similar to, or lower than, the blank concentration.

We note, though, that WL concentrations of Pb and Zn were comparatively low in our samples relative to other ash samples (Fig. 1). Therefore, we cannot comment in detail on whether solubilisation of these elements would increase if present in higher concentrations, or whether previously observed increases from other materials were specific to the sample matrix. The mean and median concentrations of soluble elements in ash are generally found at the lower end of their reported ranges (Ayris and Delmelle, 2012), but it is possible that other ash types might exhibit higher PTE concentrations than those analysed here. The range of PTEs investigated in this study are generally the most abundant for ash (Ayris and Delmelle, 2012), and are also commonly analysed in lung bioaccessibility studies (Kastury et al., 2017; Plumlee et al., 2003). Other elements usually present in ash leachates, such as As, Ba, Li, Mo, Se, Si, Sr, were not considered here and their leaching behaviour in SLF is yet to be investigated.

#### 4.4. Implications for the ash hazard assessment

Based on our experiments, an overview of possible steps towards operationalizing an SLF method for ash leaching is given below:

- 1) Leachant composition. While previous SLF studies have excluded use of phospholipids such as DPPC without justification or explanation, here we clearly show that non-inclusion in a modified Gamble's solution (SLF1, Table 2) is a reasonable SLF modification when determining bioaccessible concentrations of elements from volcanic ash. More profound effects on extraction efficiency were noted for some of the analysed elements in the absence of citrate (SLF3) or glycine (SLF4), confirming the postulation by Stewart et al. (2020) that omission of these key organic compounds could lead to potential underestimation of the real bioaccessibility of PTEs.
- 2) Extraction time. While the release of elements is timedependent, we show that ash-associated PTEs may approximate maximum dissolution in an environment resembling lung lining fluid (Fig. 5) in the first 10 min of leaching. Therefore, even though ash particles may reside in the lung for extended periods of time, our data suggest that a short contact time (up to 4 h) will adequately estimate the upper limit of PTE release, but a longer extraction period (*e.g.*, 24 h) would be necessary for research considering the steady state of bioaccessible PTEs. While still not too time-consuming for an *in vitro* extraction procedure, 24 h extraction would reflect the availability of more slowly soluble compounds. This would also allow comparison with published SLF dissolution data and acute toxicity data (*e.g.*, Tomašek et al., 2019).
- 3) S:L ratio. We show that PTE dissolution in SLF is relatively stable at our lower S:L ratios (1:100 through 1:1000), but at ratios 1:500 and 1:1000 the repeatability is lower (Appendix C) and there is increased risk of introducing potential errors due to small abundances of some elements (*e.g.*, Cd, Cr, Pb, Zn), as a consequence of large sample dilution. Therefore, 1:100 could be adopted as an optimal ratio. This ensures sufficient volume of leachant for the subsequent analysis, while using a minimal amount of ash to produce reliable data. In this way, impracticable scaling up with lower ratios, which require large volumes of SLF, is avoided as well.

Considering the challenges with the method application outlined in this paper, and for the mentioned practical reasons, the SLF leach may be difficult to implement and include on a routine basis within the standardised IVHHN leachates protocol for rapid hazard assessment (Stewart et al., 2020). Our results showed that the WL largely reflects the SLF soluble element concentrations for shorter contact times. This suggests that the general-purpose WL could be considered a suitable analogue for SLF and used as a conservative estimate of soluble elements, for the purposes of rapid respiratory hazard assessment from leachable elements, while acknowledging that some elements may be underreported (e.g., Cu, Ni, V). The WL is much easier to implement in laboratories, thus offering a practical approach to assessing the potential lung bioaccessible PTEs from ash, especially in time-sensitive situations during volcanic crises. Further, previous rapid ash hazard assessments have used a WL (e.g., Damby et al., 2017, 2013; Horwell et al., 2013), so continued use of a WL allows data to be comparable with past case studies. However, given the observed differences between WL and SLF, SLF leach should still be a preferred method for detailed investigations of PTEs of specific concern to respiratory health outside of a response situation.

#### 5. Conclusions

This study aimed to understand the leaching dynamics of PTEs from volcanic ash to inform a choice of parameters for an *in vitro* protocol to estimate the soluble-element hazard from inhaled ash. The release of PTEs was evaluated in varying formulations of SLF and under varying experimental conditions, and compared to a standardised water leach (Stewart et al., 2020). Our findings show that:

- Release of elements in SLF is affected by changes in assay parameters, including S:L ratio, extraction time and solution composition;
- The differences among ash samples are element specific, indicating the role of ash composition in PTE bioaccessibility;
- The addition of lung surfactant (DPPC) is not necessary when assessing bioaccessible concentrations of elements in volcanic ash;
- Some major elements (Ca, Na) are less reliably quantified than minor elements, likely due to their initial, high concentrations in SLF;
- The elements found as the most sensitive to changes in test parameters are Al, Fe and Mn, whereas the least affected were Ni and Mg;
- SLF is more efficient than WL in extracting V, but also Cu and Ni over shorter time periods (≤1 h);
- A WL may be used as a conservative estimate of lung bioaccessibility in a response situation.

This study provides a useful step in the development of a leachate protocol which could form a standard method for volcanic ash respiratory hazard analysis. Future application would allow acquisition of leachate composition data that can be more easily compared to that of other ash characterisation studies, and it will foster the development of a global database of information relevant for informing volcanic health hazard from leachable elements (Stewart et al., 2020).

#### Author contribution

Ines **Tomašek**, Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. David E. **Damby**, Conceptualization, Methodology, Resources, Writing – review & editing. Carol **Stewart**, Conceptualization, Resources, Writing – review & editing. Claire J. **Horwell**, Conceptualization, Writing – review & editing. Geoff **Plumlee**, Conceptualization, Writing – review & editing. Pierre **Delmelle**, Conceptualization, Writing – review & editing. Christopher J. **Ottley**, Conceptualization, Writing – review & editing. Suzette **Morman**, Conceptualization, Writing – review & editing. Sofian **El Yazidi**, Investigation. Philippe **Claeys**, Funding acquisition, Resources, Supervision, Writing – review & editing. Marthieu **Kervyn**, Resources, Supervision, Writing – review & editing. Marc **Elskens**, Resources, Supervision, Writing – review & editing. Mart **Elskens**, Resources, Supervision, Writing – review & editing. Martine **Leermakers**, Methodology, Investigation, Writing – review & editing.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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