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Surface Reactivity of Etna Volcanic Ash and evaluation of Health Risks

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Surface Reactivity of Etna Volcanic Ash and evaluation of Health Risks[1]

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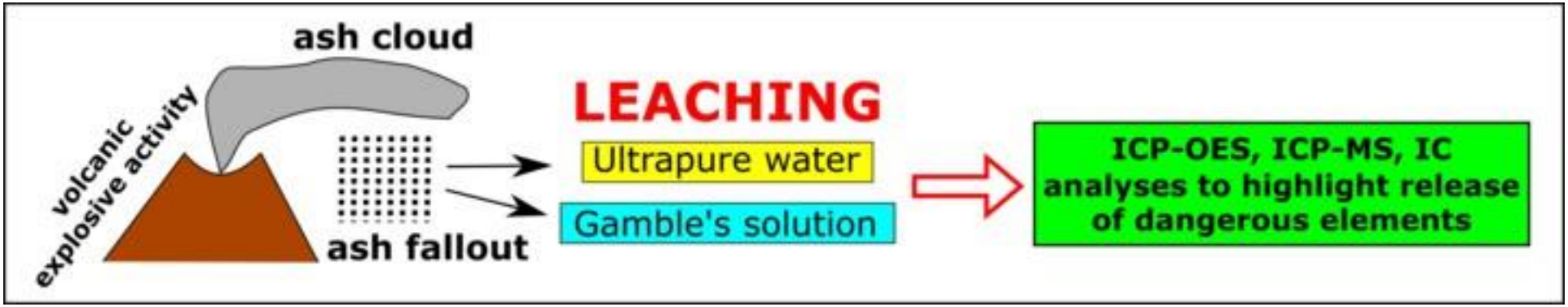
*Graphical Abstract



*Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

- Volcanic ashes emitted during explosive eruptions may have effects on human health
- Surface reactivity of ashes from Mount Etna activity was characterized
- Interaction with human organism was simulated by leaching experiments
- Most of the released elements are well below the Italian legal limits
- Few elements (B, Cd, Ni and As) are released in higher level than permitted

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ABSTRACT

This work is a part of a research project conducted in order to characterize the volcanic ash from Mount Etna, focusing in particular on the surface reactivity of ashes and possible consequence for

human health. In this framework, a sampling campaign began on 16 March, 2013, taking advantage of the intense volcanic activity on Etna. The interaction between volcanic ash and human organism was simulated treating two classes of representative Etnean particles with ultrapure water (grainsize of 850 um) and Gamble's solution mimic lug fluids (grainsize < 38 μm) with the aim to evaluate the risk due to gastric and respiratory exposure to volcanic particles. The leachates were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Ionic Chromatography (CI) in order to highlight possible dangerous elements released in water solutions according to USGS protocol. Analyses of Gamble's solution highlighted a release of elements smaller than in watery solutions and always below the thresholds established by the Italian law. On the contrary, analyses of watery solutions evidenced, for some elements (B, Cd, Ni and As), levels higher than permitted by Italian law. Considering the effects of these elements on human health, further investigations are necessary and currently carried out in order to better constrain the release process and the specific effects on human organism.

1. Introduction

Volcanic hazard has always been considered a subject of great social and scientific interest since that about 455 million people (9% of the total world population in 1990), lived within 100 km of an active volcano during Holocene (Small and Newmann, 2001). In most cases, the attention was focused on catastrophic eruptions characterized by lahars or pyroclastic density currents. However, volcanic ash falls are certainly of considerable importance due to the great distances that they can reach, sometimes covering wide areas (Blong, 1996).

The first modern studies on the possible effects of volcanic ash on human health date back at the beginning of the Eighties following the catastrophic 1980 eruption of Mount St. Helens (Sarna-Wojcicki et al. 1981a,b; Waitt et al., 1981; Beck et al. 1982; Baxter et al, 1983). Afterward, this research was extended to others volcanoes worldwide such as Mt. Sakurajima, Japan (Yano et al.,

1985; 1987), Rabaul volcano, Papua New Guinea (Le Blond et al., 2010), Southern Andes (Ruggieri et al., 2011) and the Vesuvius (Horwell et al., 2010). In these works, an evaluation of the health hazards, particularly with regards to respiratory effects, has been carried out; in addition, environmental aspects regarding the ash-water interaction and surface reactivity have been considered (Horwell et al., 2003, 2010; Ruggieri et al., 2010, 2011; Bagnato et al., 2011). Particularly, short-term respiratory effects including exacerbation of existing asthma and bronchitis, as well as acute respiratory symptoms have been reported after volcanic eruptions (Baxter et al., 1983; Horwell and Baxter, 2006). Furthermore, a possible relationship between ambient air pollutant concentrations and birth outcomes has been suggested and a study conducted among residents of Montevideo, Uruguay, during the eruption of the Puyehue volcano, found evidence that exposure to high levels of PM10 during the third trimester of pregnancy may have increased preterm births (Balsa et al., 2016). However, most of the early studies on this topic were focused on the effects of crystalline silica present in the volcanic ashes (Horwell and Baxter 2006) and thus priority was given to the study of high-silicic deposits. In this context, the chemical effects of the volcanic ash with basic composition (SiO_2 < 52 wt.%) are poorly investigated.

On the whole, the aforementioned studies evidenced the need of a multidisciplinary analysis protocol in order to verify the effect and the toxicity of volcanic ashes and to support epidemiological analyses on effects that eruptions can have on human health (Damby, 2012). Furthermore, some authors evidenced the difficulty in evaluating the long-term risk determined by pathologies such as silicosis, pneumoconiosis, and chronic obstructive pulmonary disease in populations subject to prolonged exposure (Horwell and Baxter, 2006).

The difficulties on the study of the effects of volcanic ashes on human health are due to the complexity of the interaction between ash particles and organisms, which are influenced by many factors such as from the inorganic matter: the grain size, the bulk and surface mineralogical and chemical composition and the physical properties while from the organism side. In this scenario, an important

topic regards the risk linked to the volcanic ashes chemical release on fluids of toxic elements (Stewart et al., 2013).

Mount Etna volcano (Sicily, Italy), with an elevation of 3340 m a.s.l. is the highest and most active volcano in Europe. In the last decade, beginning from 2011, its activity has considerably increased compared to previous years (Gambino et al. 2016; Corsaro et al., 2017; Ferlito et al., 2017; Pompilio et al. 2017; Giacomoni et al. 2018; Viccaro et al., 2019). In particular, more than 20 eruptive events occurred in 2013 (De Beni et al. 2015; Calvari et al., 2018; Freret-Lorgeril et al., 2018). These eruptions are frequently characterized by a robust or predominant explosive activity (paroxysms) causing consistent ash emission, whose impact on human activities proved to be very strong.

Worth of note is the scarcity of studies (Censi et al., 2011; Montana et al., 2012) concerning the mobility of chemical elements of Mt. Etna volcanic ashes with water or other fluids. Moreover, Barsotti et al. (2010) performed a quantitative hazard assessment to determine the potential impacts of volcanic tephra fall on human health and infrastructure in the Mt. Etna slopes using a numerical modeling. Fano et al. (2010) conducted an epidemiologic study on acute health effects on the nearby population.

The present study was conducted in the framework of a multidisciplinary project using an integrated approach of nutritional and molecular epidemiology, mineralogical and chemical pollutant characterization and in vitro assays, to evaluate the risk of DNA methylation due to air pollution taking into account lifestyles and demographic and socioeconomic factors, in healthy women living in the metropolitan area of Catania, Italy (Barchitta et al. 2017; 2018).

The aim of this work is the analysis of chemical release from the surface of volcanic ash towards fluids, mainly focussed on the consequences in terms of health and toxicity risk; the particular mechanisms of leaching are not specifically considered in the performed experiments. In recent literature, Barone et al. (2016) showed the important mineralogical and chemical modification of the volcanic glass particles during the last phases of the eruption and the interaction with the volcanic gasses in the plume. The presence of soluble species on the ash grains surface and the chemical

modification of the external layers at nanometric scale suggest a likely interaction with gases and aerosols formed during paroxysmal events, both in the conduits and in the volcanic plume.

The granulometric aspect of the ashes is of fundamental importance in studying the effects on health. In a recent USGS study it was observed that only granules of less than 38 μm can penetrate the lungs and interact with the alveoli (Stewart et al., 2013 and references therein), while larger ashes can be considered as a more general source of risk. As an example, they can release dangerous elements in drinking water or for direct gastric assumption. In line with the aims of the research, the *Protocol for analysis of volcanic ash samples for assessment of hazard from leachable elements* (Stewart et al., 2013) suggests various leaching methods as shown in the flow chart in Fig. 1. For this reason, this study was conducted on two classes of particles, performing Leaching experiments using i) Gamble's solution for particles < 38 μm, in order to mimic a model of interaction between ash and lung and ii) ultrapure water for grains with size of 850 μm, representative of the Etnean ash size.

Risk evaluation is directly linked to the presence of vulnerable elements exposed to a particular danger. In the case of volcanic ash falls, and in particular the dispersal of ash from Etna, it can be seen that they involve not only the whole of Sicily (Fig. S1) but also, when the winds are favourable, the south of Calabria, the surrounding minor islands and, on a few rare occasions, also the northernmost part of the African continent.

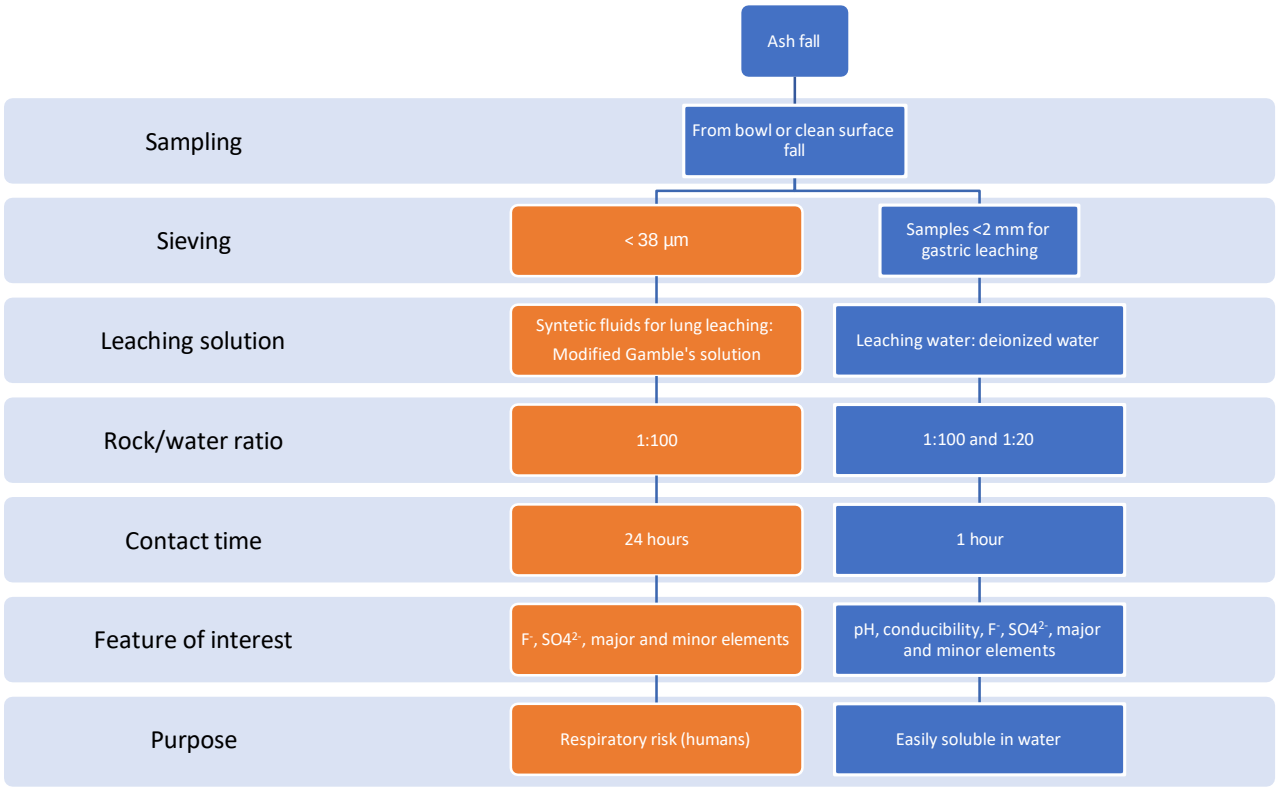

Figure 1. Chart showing the leaching methods applied for volcanic ash.

2. Materials and methods

2.1 Sampling

For the purpose of this work, 9 pyroclastic deposits from paroxysms occurred in April (3 samples) and October-November (6 samples) 2013 were selected. In Table 1 are reported data relating to the sampling sites (place name and geographical coordinates), time and date, traffic and weather conditions. The distribution of the sampling sites is shown Fig. 2. Whole rock chemistry and mineralogical composition of the studied samples are reported in Barone et al. (2016). In brief, ashes from Mount Etna have trachybasaltic composition and are mainly constituted by glass (90-99 wt.%) with few (< 10 wt.%) plagioclase and clinopyroxene crystalline phases. The pyroclastic deposits were

collected, according the IAVCEI (2013) recommendations, after few hours since the deposition, avoiding natural or anthropic contaminations and the contact with water both during the deposition and after the sampling. Furthermore, analysis was carried out shortly from the eruption events. For these reasons, considering the availability of the ICP-MS facilities, the water leaching experiments were realized using the volcanic ashes sampled in the April 2013, while gamble solution leaching were obtained for November 2013 samples. Furthermore, the samples were quartered freezing a portion at -12°C immediately after the collection. This procedure was adopted in order to avoid the dispersion of volatile elements in the period elapsed between sampling and analysis (about 2 months).

Table 1. Site (toponym and geographic coordinates), time and date, sampling method, traffic conditions and weather.

SITE	DATE	COORDINATES	TIME	ID	SAMPLING METHOD	TRAFFIC	WEATHER
					Fall-out	High volume pump	
Fiandaca (Pennisi)	12/04/13	37°38'19.75"N 15° 7'59.74"E	10:00	Fi 1A	X	X	Absent
Fiandaca (Pennisi)	12/04/13	37°38'19.75"N 15° 7'59.74"E	15:44	Fi 2A	X	X	Absent
Belpasso	18/04/13	37°36'5.24"N 14°58'57.74"E	16:17	Bel 3A	X	X	Absent
Sant'Alfio	17/11/13	37° 45' 05,88" N 15° 05' 36,95"E	03:00	S. Alf. I	X	-	Absent
Milo	17/11/13	37° 46' 20,20" N 15° 04' 45,59"E	04:00	Mil. I	X	-	Absent
Fiumefreddo	23/11/13	37° 48' 16,22" N15° 11' 55,92"E	10:00	Fium. I	X	-	Absent
Citelli Basso	28/11/13	37° 47' 4,34" N15° 3' 36,93"E	01:00	Cit. Bas. I	X	-	Absent
Santa Venerina	28/11/13	37° 41' 04,28" N 15°08'35,10"E	11:00	SVen	X	-	Absent
Santa Tecla	28/11/13	37°38'09,52" N 15°10'33,62" E	12:00	STec	X	-	Absent

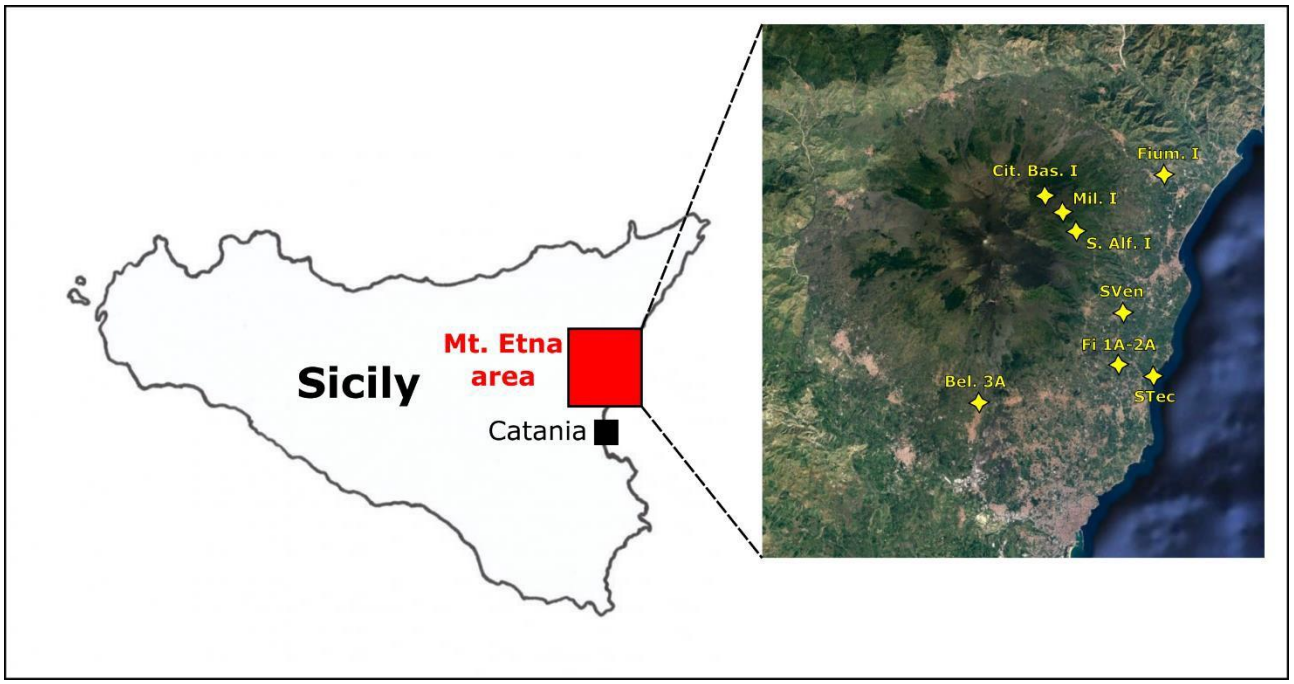

Figure 2 – Sampling location on Mount Etna area (from Google Maps).

2.2 Ultrapure water Leaching experiments

The leaching experiments were carried out according to the literature recommendation (Witham et al., 2005; Stewart et al. 2013) on < 850 μm grain size fraction of each sample. The reagents were solubilised in ultrapure water which has standard characteristics that makes it possible to compare tests performed on different samples. It also highlights the solution of the compounds that are easily released from the ash surfaces. Nevertheless, it should be remembered that the release of elements in natural water can be different from that observed in deionized water (USGS Prot.). Deionised water as leachant has a widespread use because it allows a rapid screening of the potentially hazardous species easily leached from the ashes (Witham et al. 2005; Ruggieri et al 2010, 2011, 2012 a,b; and references therein).

To enter into details, as regards the rock-deionised water ratio to be used, the literature provides different values. In particular, Stewart et al. (2013) suggest a ratio of 1:100 to 1:20 (g/mL) while

166 Ruggeri et al. (2012a and references therein) propose 1:50, after a series of experiments including
167 other ratios. As far as contact times are concerned, these are fixed at 1 hour and 24 hours. These
168 parameters were determined on the basis of laboratory studies (Jones and Gislason, 2008; Gislason
169 et al 2011). However, high solid liquid ratios and/or high contact times are not advised since they can
170 lead to saturation and precipitation phenomena (for example fluoride and salts in general, Stewart et
171 al., 2013) causing a loss of information regarding the quantity of elements in solution.
172 In this scenario, grain size, rock-water ratio and contact times are all parameters that are observed
173 and determined according to the leaching solution used and the aims of the research. Given that this
174 research project aims to identify the health risks brought by gastric assumption of volcanic ash, in
175 line with the protocol we used ultrapure water for short period leaching tests.
176 The leach solution used for this study is Millipore ultrapure water and the ash/water ratio is 1:25
177 g/mL. Each ash sample has been agitated for 90 min using a shaker. During the leaching experiments,
178 the variation of pH was measured. At the end the mixture was filtered using 0.45μm surfactant-free
179 cellulose acetate membrane filters (Millipore©). The solutions were analyzed by inductively coupled
180 plasma optical emission spectrometry (ICP-OES, Optima 3100×, PerkinElmer), and by inductively
181 coupled plasma mass spectrometry (ICP-MS, Elan 6000, PerkinElmer) following the methodology
182 developed by Fernandez-Turiel et al., (2000) and adapted at Centres Científics i Tecnològics of the
183 Barcelona University (Ruggieri et al. 2010, 2011, 2012a,b). Ca, Mg, Na, K, Si, S, B, P, Fe, and Sr
184 were analised by ICP-OES and Cl, Ag, Al, As, Au, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er,
185 Eu, Ga, Gd, Ge, Hf, Hg, Ho, I, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Pt, Rb, Sb, Se, Sm, Sn, Ta,
186 Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr. by ICP-MS.
187
188 *2.3 Leaching test with Gamble's solution*
189
190 Gamble's solution is used because of its ability to mimic pulmonary fluid from a chemical-physical
191 point of view, allowing a model of ash-lung interaction, which otherwise would be difficult to study

192 and to be reproduced in the laboratory. In fact, lungs may act as a route to introduce elements into the
193 circulation and deliver them to the appropriate site elsewhere in the body (Marques et al., 2011). The
194 use of simulated biological fluids can give a better understanding of the release mechanisms and
195 possible *in vivo* behavior of a product; it also enhances the predictive capability of the leaching tests.
196 The leaching method recommended by the protocol is similar to that used for many years for
197 evaluating the pulmonary bio-solubility and bio-durability of materials, including asbestos and ash
198 from fires (Plumlee and Norman, 2011).
199 In this work, the solution used for leaching the investigated volcanic ash samples consisted in a
200 modified Gamble's solution, from which some organic compounds were eliminated, because this
201 solution is very similar to pulmonary fluids and has an almost neutral pH. The modified Gamble's
202 solution used in this work was prepared according to the procedure shown in Table S1 and have pH
203 = 7.88, alkalinity (200 µl – HCl N/100) = 2080 mg/l and conductivity = 12.400 µS/cm. According to
204 the protocol, leaching experiments were conducted at room temperature (22 ± 0.5 °C) and ambient
205 partial pressure of carbon dioxide, P_{CO_2}. Gamble's solution composition ensures conditions close to
206 equilibrium with respect with minerals and gives it with a low reactivity. Alkalinity is due to
207 bicarbonates and phosphate and leaching of metals from mineral surfaces is slightly favoured by
208 organic ligands (citrate and glycine). We predicted saturation state with respect to minerals of our
209 solutions by using PHREEQC (using the database PHREEQC Interactive 3.1.6-
210 9191\database\llnl.dat). The highest saturation index (SI is the logarithm, ln, of the ratio among ionic
211 activity product and the solubility constant) was obtained after interaction with Etna dust grains (see
212 results section) and confirmed equilibrium with minerals (calcite SI of 1.1, aragonite SI of 0.95,
213 gibbsite SI of 1.7).
214 The quantities of elements released by ash dissolved in Gamble's solution were determined by ICP-
215 MS and ICP-OES analyses, carried out in line with the USGS protocol. Calcium, Mg, Na, K, S and
216 Si analyses were performed using an ICP-OES ARL FISONS Spectrometer Model 3520 while an
217 ICP-MS Perkin Elmer Spectrometer Model DRC-e was used for the trace metals determination.

Moreover, F, Cl and NH_4 contents were determined by ionic chromatography (IC) using a DIONEX cromatograph model ICS 3000. The analyses were carried out on 9 leached solutions, after appropriate dilutions. Precision, calculated as (SD/measured average value) × 100 and accuracy, calculated as ((measured average value - certified value)/certified value) × 100, for each analisys were determined using reference material solutions. The Certified Reference Material EP-L-3 (by SCP-Science, Canada) and the Standard Reference Material Nist 1643-e were used in the ICP-MS analyses, while the Certified Reference Material EP-H-3 (by SCP-Science, Canada) were used in the ICP-OES analyses. All accuracy values were included into ± 3%, while the precision values were generally minor to 3 %; only Li and B precision values were close to 10%.

2.4 BET analyses

Lastly, the specific surface of the ash particles was determined by BET adsorption analyses using a Sorptmatic 1990 System (Fisons Instruments) on samples having a grain size < 38 μm (Mil I dry and Fium I) at the University of Cagliari. The analyses were performed at 37 °C for 720 minutes and at 150°C for 720 minutes. Before the analysis, samples were vacuum dried at 200 °C for 16 hours.
The total surface area was measured using the Brunauer, Emmet and Teller (BET) gas adsorption method. Measurements were performed using a Sorptmatic 1990 System (Fisons Instruments) to determine the adsorption-desorption isotherms at 77 K. Before the analyses, the samples were heated under vacuum at 150°C for 16 hours at a rate of 1 K/min.

3. Result and discussion

3.1 Leachate composition with Ultrapure water

In order to assess the release of chemical species of ashes in aqueous environments, extractions were carried out on <850 µm fraction of four samples. The pH variation of suspension (1g of ash : 25ml of ultrapure water) has been measured for 2 hours. All the samples have similar behavior shown as average in Fig. S2. Immediately after the beginning of the experiment the original pH (5.9) drops to 4.9, then it rises up to 5.79 after 30 minutes following a logarithmic trend. Successively the pH slightly increases up to 5.88 at the end of the experiment. This behavior suggests fast dissolution of highly soluble acidic compounds followed by progressive leaching of alkaline species promoted by the acidity of the medium (Cimino and Toscano, 1998).

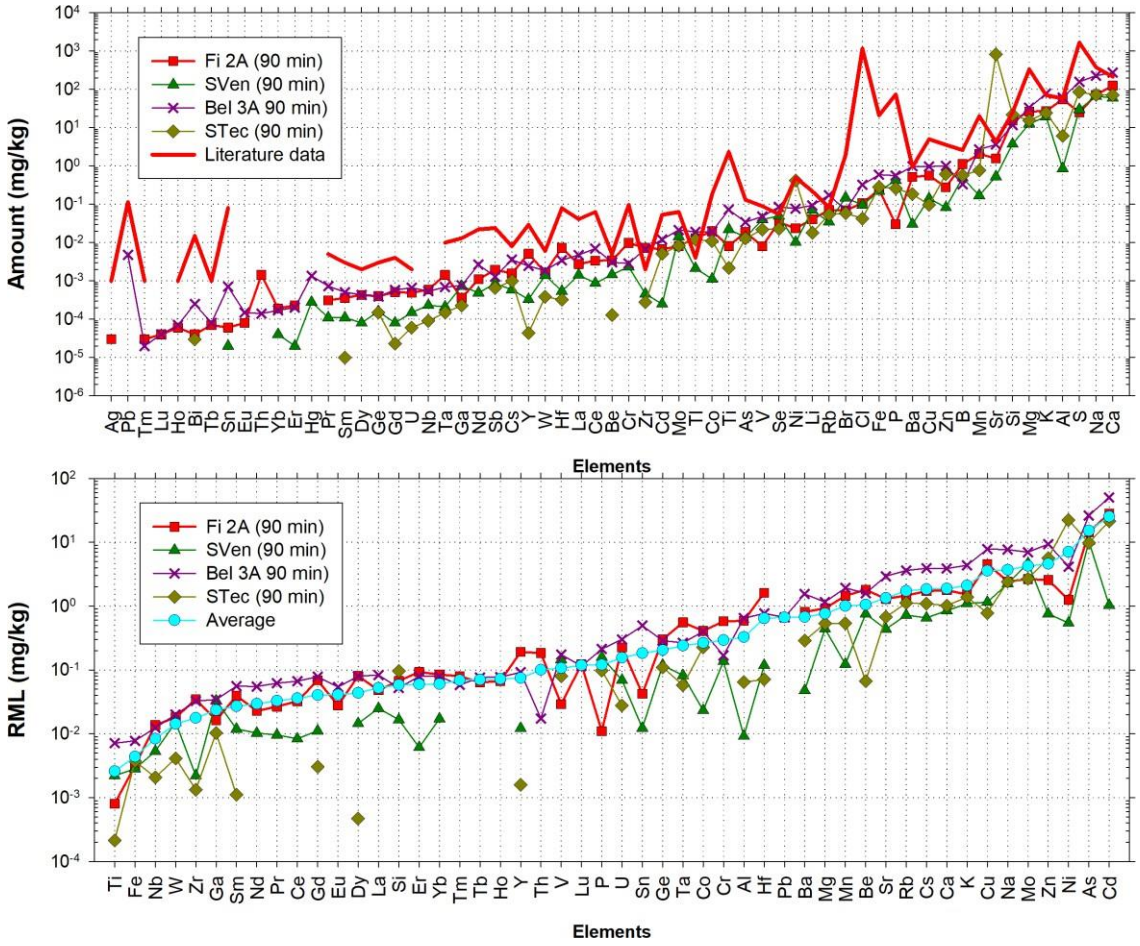

Figure 3. Spider diagram showing the quantities of trace elements in the analysed samples obtained by leaching with ultrapure water (top) and relative mass leached factors (RML) from leaching with ultrapure water (bottom).

256 On average, in the chemical composition of the leachate alkaline, earth-alkaline elements (Ca> Na >
257 K ~ Mg) and Al are the most abundant cations. Regarding anions, S is much more abundant than Cl;
258 additionally, the S/Cl ratio (average = 758) is considerable higher than the Mt. Etna gas composition
259 (average = 2.4, Aiuppa, 2009) in contrast to what generally observed in many volcanoes (de Hoog et
260 al., 2001; Witham et al., 2005). Finally, cations largely exceed measured anions (S and Cl) indicating
261 a large quantity of not measured anions (e.g. F and C) or volatilization of anions.
262
263 The concentrations of all the measured elements have been compared with a compilation of data
264 collected from leachate obtained on products of worldwide volcanoes (Ayris and Delmelle, 2012a,b).
265 In Fig. 3 spider diagram the elements are reported in order of abundance of the median values of the
266 dataset. The data from the present work generally follow the literature trend. Results are comparable
267 for Be, Zr, Tl, Se, Ni, Rb, Ba, Sr, K, Al, Na and Ca, whereas the other elements contents are lower
268 when compared to literature data; in some cases (P, Fe and Cl) the difference is of four orders of
269 magnitude (Fig. 3).
270
271
272 The leachate raw composition obtained from the volcanic ash depends on a series of factors: the
273 chemical composition of the magma involved represent a broad range of variation in the initial
274 availability of each element concerned; the ratio of glass/crystal in the ash is an important variable,
275 since some elements can concentrate in some relatively insoluble mineral phases (i.e. if P is present
276 - and therefore highly concentrated - in apatite, P is a highly immobile element even under prolonged
277 leaching periods); last but not least, the broad chemical composition of the eruptive column directly
278 originate differences in soluble salt epitaxies generated on ash surface inside the eruptive column; the
279 surface/volume ratio of the particles is directly related to the grain morphology and consequently on
280 the surface availability of the particle acting as crystallization interface. In this sense is especially
281 useful to compare ash leachates of chemically contrasted eruptions (see f.i. Ruggieri et al., 2011)

The concentration of selected leachate elements from the dataset of the present study was also compared with the drinking water standards for U, Hg, Cr, Cd, Mo, As, Se, Ni, Cl, Fe, Ba, Cu, Zn, B, Mn, Al, Na (Stewart et al. 2006). In Fig. 4 are reported the range of maximum concentration values established by USA, New Zeland, Japan and World Health Organization and the range of the determined values from the investigated Mount Etna samples. With the exception of Cr, Mo, Cl, Cu and Zn the concentrations of all the elements present in the leachate with ultrapure water from Mount Etna ashes exceed the drinking water standards of one or more of the aforementioned countries/organization. This is particularly evident for Ni in sample STec, Mn in Bel 3A, and Al in Fi 2A and Bel 3A, where their values are tens to hundreds time higher than the established standards (see Tab. 2 and data from Stewart et al., 2006).

Table 2. Concentration of dissolved elements released during leaching experiment expressed as µgr/kgt for elements measured with ICP-MS and as mg/kg for elements (marked with *) measured with ICP-OES. In italic for each samples the RLM are reported of the elements for which is known the concentration of tephras emitted during the 2012 and 2013 eruptions (Behncke et al. 2014; Bonaccorso et al. 2014).

µgr/kg *mgr/kg	**Fi A**		**SVen**		**Bel 3A**		**STec**	
Li	40.59	-	69.75	-	93.64	-	18.040	-
Be	3.45	*1.805*	1.45	*0.757*	3.04	*1.590*	0.128	*0.067*
B*	1.12	-	0.49	-	0.33	-	0.57	-
Na*	72.22	*2.437*	66.68	*2.250*	228.09	*7.696*	71.53	*2.413*
Mg*	26.45	*0.922*	12.66	*0.442*	33.23	*1.159*	15.36	*0.536*
Al	55.02	*0.589*	0.86	*0.009*	60.47	*0.647*	6.04	*0.065*
Si*	15.24	*0.068*	3.74	*0.017*	11.79	*0.052*	21.66	*0.096*
P*	0.03	*0.011*	0.42	*0.159*	0.56	*0.212*	0.26	*0.098*
S*	24.95	-	29.85	-	156.78	-	85.17	-
Cl	107.72	-	94.86	-	323.09	-	42.610	-
K*	27.02	*1.522*	19.54	*1.101*	77.33	*4.358*	24.48	*1.380*
Ca*	124.69	*1.777*	59.51	*0.848*	272.52	*3.883*	71.62	*1.020*
Ti	8.12	*0.001*	22.22	*0.002*	72.04	*0.007*	2.168	*0.000*
V	7.99	*0.029*	39.85	*0.145*	47.85	*0.174*	21.945	*0.080*
Cr	9.81	*0.577*	2.33	*0.137*	2.86	*0.168*	< d.l.	-
Fe*	0.24	*0.003*	0.22	*0.003*	0.59	*0.008*	0.28	*0.004*
Mn	2.06	*1.449*	0.17	*0.124*	2.73	*1.923*	0.77	*0.539*
Co	19.67	*0.409*	1.12	*0.023*	19.31	*0.401*	10.848	*0.225*
Ni	23.54	*1.257*	10.19	*0.544*	77.37	*4.132*	417.813	*22.313*
Cu	562.04	*4.572*	141.98	*1.155*	961.48	*7.822*	96.230	*0.783*
Zn	278.49	*2.570*	82.20	*0.759*	1010.47	*9.326*	614.098	*5.668*
Ga	0.36	*0.016*	0.73	*0.033*	0.76	*0.034*	0.228	*0.010*
Ge	0.40	*0.300*	0.16	*0.119*	0.39	*0.287*	0.148	*0.110*
As	18.83	*14.394*	13.51	*10.325*	34.28	*26.210*	12.810	*9.794*
Se	33.99	-	49.67	-	85.88	-	22.975	-
Br	68.95	-	148.53	-	70.48	-	58.578	-
Rb	70.48	*1.465*	34.81	*0.724*	173.40	*3.605*	53.793	*1.118*
Sr*	1.58	*1.298*	0.53	*0.437*	3.58	*2.945*	821.216	*0.675*
Y	5.12	*0.192*	0.33	*0.012*	2.45	*0.092*	0.043	*0.002*

Zr	7.23	*0.035*	0.46	*0.002*	6.79	*0.033*	0.278	*0.001*
Nb	0.59	*0.014*	0.23	*0.005*	0.54	*0.012*	0.090	*0.002*
Mo	8.09	*2.648*	14.38	*4.704*	21.40	*7.003*	8.168	*2.672*
Ag	0.03	-	< d.l.	-	< d.l.	-	< d.l.	-
Cd	6.71	*28.212*	0.25	*1.030*	11.99	*50.410*	5.113	*21.504*
Sn	0.06	*0.042*	0.02	*0.012*	0.70	*0.494*	< d.l.	-
Sb	1.95	-	0.85	-	1.29	-	0.653	-
Cs	1.56	*1.721*	0.59	*0.655*	3.54	*3.914*	0.993	*1.097*
Ba	516.42	*0.814*	30.40	*0.048*	979.23	*1.544*	183.668	*0.290*
La	2.74	*0.048*	1.43	*0.025*	4.74	*0.083*	< d.l.	-
Ce	3.38	*0.032*	0.87	*0.008*	6.96	*0.067*	< d.l.	-
Pr	0.31	*0.027*	0.11	*0.010*	0.73	*0.062*	< d.l.	-
Nd	1.10	*0.023*	0.49	*0.010*	2.64	*0.055*	< d.l.	-
Sm	0.36	*0.039*	0.11	*0.012*	0.51	*0.056*	0.010	*0.001*
Eu	0.08	*0.028*	< d.l.	-	0.15	*0.054*	< d.l.	-
Gd	0.51	*0.069*	0.08	*0.011*	0.58	*0.078*	0.023	*0.003*
Tb	0.07	*0.064*	< d.l.	-	0.08	*0.077*	< d.l.	-
Dy	0.43	*0.080*	0.08	*0.015*	0.43	*0.080*	< d.l.	*0.000*
Ho	0.06	*0.067*	< d.l.	-	0.07	*0.077*	< d.l.	-
Er	0.23	*0.093*	0.02	*0.006*	0.20	*0.080*	< d.l.	-
Tm	0.03	*0.080*	< d.l.	-	0.02	*0.058*	< d.l.	-
Yb	0.19	*0.085*	0.04	*0.017*	0.17	*0.079*	< d.l.	-
Lu	0.04	*0.123*	< d.l.	-	0.04	*0.115*	< d.l.	-
Hf	7.28	*1.617*	0.54	*0.119*	3.46	*0.769*	0.320	*0.071*
Ta	1.43	*0.557*	0.21	*0.082*	0.68	*0.266*	0.148	*0.058*
W	1.67	*0.018*	1.40	*0.015*	1.85	*0.020*	0.383	*0.004*
Hg	< d.l.	-	0.28	-	1.35	-	< d.l.	-
Tl	12.93	-	2.12	-	18.96	-	12.010	-
Pb	< d.l.	-	< d.l.	-	4.74	*0.666*	< d.l.	-
Bi	0.04	-	< d.l.	-	0.25	-	0.030	-
Th	1.43	*0.184*	< d.l.	-	0.14	*0.017*	< d.l.	-
U	0.49	*0.225*	0.15	*0.069*	0.66	*0.303*	0.060	*0.028*

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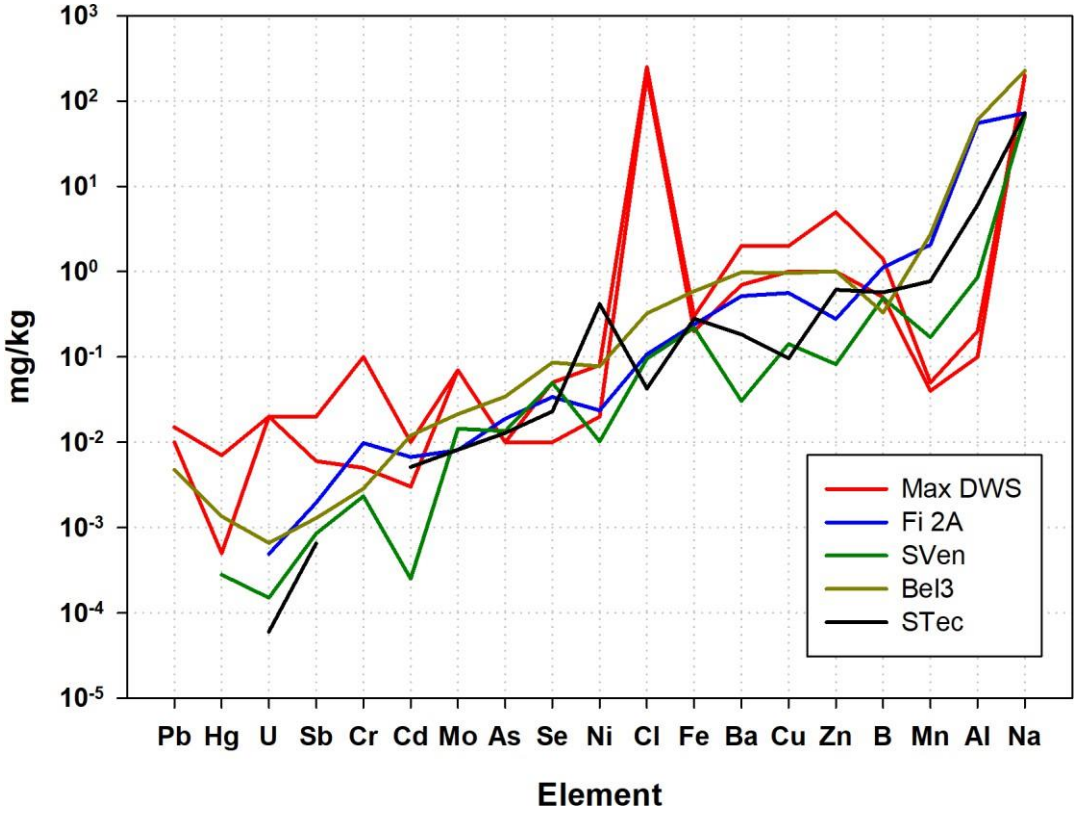

Figure 4. Concentration of selected leachate elements with ultrapure water and range of drinking water standards (DWS) adopted in USA, New Zeland, Japan and World Health Organization from Stewart et al., (2006).

However, the absolute values of elements concentration do not allow us to esteem the mobility of chemical elements in ultrapure water. With this aim, the relative mass leached factors (RML, Ruggieri et al., 2010) was calculated and is reported in Table 2. RMLs are calculated normalizing the fraction of leached element (element/solid by weight) obtained from the batch leaching tests with the total element concentration (element/solid by weight) of the average compositions of tephra emitted by the NSE crater during the 2012 and 2013 eruptions (Behncke et al. 2014; Bonaccorso et al. 2014). RMLs were not determined for Li, B, S, Cl, Se, Br, Ag, Sb, Hg, Tl and Bi because these elements were not analyzed in bulk ashes. The spider diagram of Fig. 3 shows the RLM for all the samples with the elements arranged according to the increasing values of the average composition. On the

basis of the mobility esteemed by the average RML values (see Table 2), the measured elements may be grouped (Ruggieri et al., 2010) in: i) high mobility elements with RML > 5 (Cd, As, in 3 and all 4 studied samples, respectively; Zn in 2 of 4 studied samples); ii) moderate mobility elements with RML between 0.5 and 5 (Mo, Na, Cu and Ni in 3 samples, whereas they behave as high mobility elements in 1 sample; K, Ca, Cs, Rb in all the 4 studied samples; Sr, Be, Mn, Mg in 3 samples, while they show low mobility in 1 sample; Ba, Pb, Hf, Al, Cr, Ta and Th behaves with moderate mobility in 2 or 1 studied samples and show low mobility for the other ones); low mobility elements with RML < 0.5 (all the other elements).

Taking into account the chemistry of the magma, it is useful to compare specifically the Etna samples with those from basic eruptions (around 50 % of silica in bulk composition) like the ones of Copahue, Lonquimay and Llaima volcanoes in the Andes (Ruggieri et al. 2011) instead of the samples and relative leachates of rhyolitic eruptions (around 70 % of silica in bulk composition). Thus, we can remark a similar behavior of Zn and As in the ash leachates of the aforementioned three Andean volcanoes; while in the case of Cd and Pb the behavior in the leachates is just comparable to the one in the case of Copahue and Llaima volcanoes ash.

3.2 Leachate composition with Gamble's solution

The quantity of trace elements discovered using spectrometric and chromatographic analysis are reported in Tables 3, respectively. The spider diagram in Fig. 5 shows the quantity of trace elements in all the analysed samples determined by means of ICP-MS, ICP-OES and IC, listed according to ascending order of weight.

Table 3. Chemical composition of the leachate with Gamble's solution. Major cations, reported in mg/l, were determined in ICP-OES while trace elements, expressed as µg/l, were measured by ICP-MS. Anions, reported in mg/l, were determined by IC.

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ID Sample		Blk 15*	Blk 16**	Cit. Bas. I dry*	Mil. I dry <38 m *	Mil. I frozen**	S. Alf. dry **	S. Alf. frozen**	Fium. I< 38 µm *
Ca	mg/l	64,1	62,8	64,3	65,7	63,5	64,4	62,9	65,8
Mg		22	21,1	21,9	22,8	21,4	21,6	21,1	22,3
Na		3260	3230	3180	3250	3150	3090	3050	3130
K		3	3	3	5	3	3	3	4
S		20	19,8	20,9	24,1	19,5	19,5	19,1	24,5
Cl				1770		2310	1980	1610	
NH4					19,3	15,8	12,6	8,3	
F				0,88	9,6	1,6	0,48	1,1	5,9
Si		0,4	0,4	0,6	3,1	0,4	0,4	0,5	1,7
Li	µg/l	<1	<1	<1	7,6	<1	<1	<1	7,6
B		<11	<11	<11	<11	<11	<11	<11	<11
Al		<15	<15	70	150	120	50	110	460
Fe		<55	<55	<55	90	70	100	80	120
Mn		1	1	15	86	11	10	11	38
Ni		2	2	3	12	2	2	2	11
Co		0,16	0,12	0,35	1	0,21	0,2	0,26	0,7
Cu		2	2	25	190	20	19	20	160
Zn		5	3	<3	5	<3	<3	<3	<3
As		<1	<1	<1	3	<1	<1	<1	<1
Sr		30	30	40	130	38	37	39	100
Te		<1	<1	<1	<1	<1	<1	<1	<1
Ba		2	2	8	5	2	1	2	8
Tl		<1	<1	<1	2,7	<1	<1	<1	1,5
Pb		<1	<1	<1	<1	<1	<1	<1	<1
U		<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5

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342 In order to observe any possible enrichment of chemical elements released into the leaching solution
343 with respect to the bulk concentration of the same elements in the analysed ashes, the RML was
344 calculated following the procedure described in section 3.2.

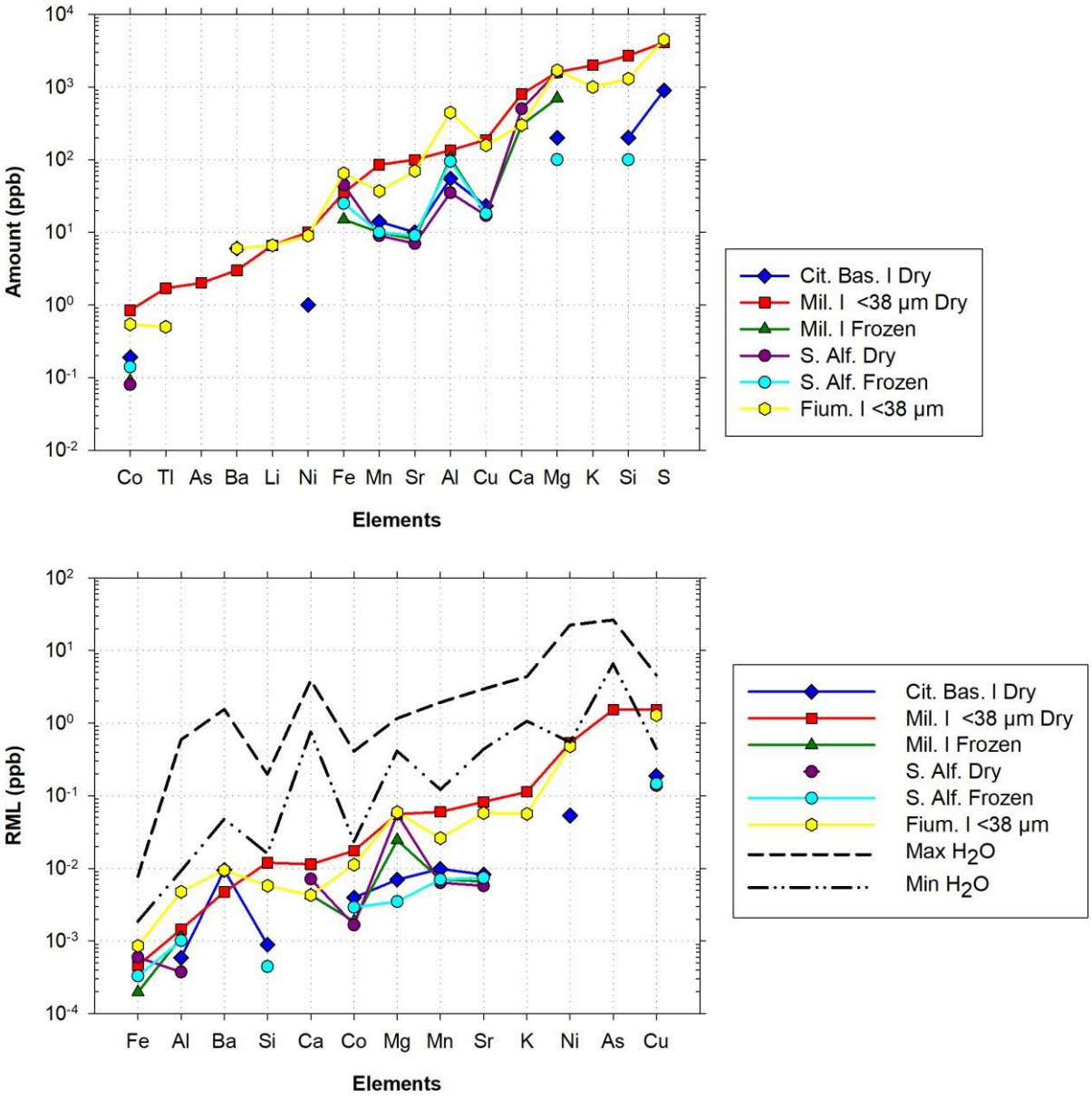

Figure 5. Spider diagram showing the quantities of trace elements in the analysed samples obtained by leaching with Gamble's solution (top) and Comparison of ICP-MS, ICP-OES data of relative mass leached factors (RML).

Given that the bulk concentrations of Li, S and Tl in the analysed ashes were unknown, the RML factors were not determined for these elements. The spider diagram in Fig. 5 shows the RML factor for all the samples listed in order of abundance and compared with the RML of leachate composition with ultrapure water. The results show that the concentrations of elements released in Gamble's solution are lower than or fall between the maximum and minimum values of the concentrations of the same elements released in watery solution.

On the basis of the mobility estimated through the determination of the RML factor, it is possible to observe that:

1) The elements most greatly leached by Gamble's solution are As and Cu, with RML > 1;
2) The elements only moderately leached with 1 < RML >0.05 are Mg, Mn, Sr, K, and Ni;
3) The least leached elements with RML <0.05 are Fe, Al, Ba, Si, Ca and Co.

The results of ionic chromatography, normalized to blank (BLK) analysis are shown in Table 3. From the obtained results, it is possible to see that all the samples contain a quantity of fluoride ranging from 0.48 and 9.6. High amounts of Cl were found in all the samples, in particular in the frozen sample Mil. I, apart from the samples with a grain size < 38 μm (dry Mil. I and Fium. I). Moderate amounts of NH_4 were found in all the samples, except for dry Cit. Bas. I and Fium. I < 38 μm.

3.3 BET surface analyses

The BET results shown in Table S2 provide information regarding the specific surface and the pore volume of the ashes, because they highlighted isotherms which are typical of non-porous systems.

Previous specific surface areas of volcanic ash have been reported in the literature to range from 0.5 to 20 m^2/g using BET analysis (Gislason et al. 2011; Wyegel et al. 2019). The morphology and specific surface of a volcanic ash depend of a number of factors that are here considered. The viscosity of the magma (which in turn depends on the degree of crystallinity and chemical composition) in general favors gas (water, chlorine, sulfur, fluorine etc.) retention. The higher is the degree of crystallinity, the higher becomes the viscosity; crystallinity is the consequence of the cooling history of the magma in a magmatic chamber and/or the magmatic conduct to the surface. The chemical composition ranges from around 40 wt.% of SiO_2 in basaltic magmas up to 75 wt.% in silicic ones. The viscosity is directly proportional to the silica content of the magma and inversely proportional to the water content. In general, higher viscosity and water content is related to a greater specific surface of the ash particles. When considerable amounts of water undergo exsolution and

form vesicles in the volcanic conduct, a high degree of magma fragmentation and thus explosivity is reached in the volcanic eruption, and the ash particles reach a higher specific surface. Since rhyolitic magmas usually contain higher water amounts than basaltic ones, their related ash particles hold greater specific surface. Of course, each eruptive circumstance can lead to different products, and even some moderately explosive basaltic eruption can be characterized by moderate to high vesiculation and higher specific surfaces. Other factors like the presence of external (supergenic) water reaching the magma in the upper part of the eruptive conduct can greatly modify the vesicularity and specific surface of the ashes emitted during basaltic eruptions (see i.e. Gisbert et al., 2009).

Etna values are very close to the lower values analyzed in Gislason et al. (2011; surface area of 0.43 m2/g). The values for Etna ash samples varies from 0.5 and 1 m^2/g. Such low values can be attributed to the chemistry, as pointed out by Wyegel et al. (2019) that found lower values for basaltic ashes. It is worth noting that BET areas measurement are based on gas adsorption and can overestimate the reactive surface with respect to water molecule (Delmelle et al., 2005; Langmann, 2013; Wiegel et al. 2019).

The leached elements were not found always dependent on BET surface area. This suggests that the reactive surface is small and that the porous system is not involved in the ash surface-environment reaction process. The variability of BET total surface area and chemistry of leachate solutions indicate an intrinsic dependence of the sample properties and reactivity on local sampling conditions such as location, actual wind, elapsed time from eruption and so on. Indeed, physical and chemical properties of Etna volcanic ashes and their medical hazard need to be measured in a wide interdisciplinary program of sampling and testing depending also on local conditions. In further experiments, the leachate solutions will be used for cellular toxicity testing.

3.4 Effects of volcanic ash on human health

In general, particulate matter (PM) exposure has a recognized impact on human health, with a wide range of adverse effects (WHO Regional Office for Europe, 2013). Both short- and long-term environmental exposure contribute to disease burden, as demonstrated by increasing mortality risk and years lived with disability (Ostro et al., 2018). In this scenario, several studies reported associations of long-term exposure to PM with diameter under 2.5 μm (PM2.5) or 10 μm (PM10) with all-cause and cause-specific mortality (World Health Organization, 2006). In a recent meta-analysis, PM2.5 was associated with significantly increased risks of all causes of mortality, while PM10 was associated with natural-cause, ischemic heart disease, respiratory and lung cancer mortality (Chen and Hoek, 2020). Globally, fine particulate matter has been associated with a wide range of cancer, including also stomach and colorectal cancer (Grant, 2009; Wong et al., 2015).

PM pollution derives from a wide range of natural and anthropogenic sources. In volcanic areas, eruptions lead to the emission of various pollutants and heavy metals (Komarnisky et al., 2003), which in turn could determine acute or chronic respiratory disorders (Hlodversdottir et al., 2016; Nemery et al., 2001) and, in general, an increased respiratory morbidity and mortality (Longo et al., 2008; Longo et al., 2010). It has been demonstrated that exposure to volcanic ash can exacerbate pre-existing respiratory diseases, such as asthma and bronchitis (Baxter et al., 1981; Baxter et al., 1983), and suppress immune function (Monick et al., 2013). A possible mechanism identified for ash toxicity includes the presence of reactive surface species, that could determine inflammatory reactions in the lungs. However, there is limited epidemiological evidence about the effects of volcanic emissions on human health, probably due to the relatively short timeline of most volcanic eruptions that makes it difficult to assess a long- term cohort study (Gudmundsson, 2011; Hansell and Oppenheimer, 2004). Specifically, PM composition is heterogeneously characterized by the presence of toxic compounds, such as heavy metals, (e.g. arsenic, nickel and cadmium), ions and reactive gases (Tchounwou et al., 2012). For instance, arsenic (As) is associated with several disorders affecting cardiovascular, respiratory, immune and nervous systems (Abdul et al., 2015), while prolonged exposure to nickel (Ni) could produce dermatitis and disorders in the respiratory system (Jaishankar et al., 2014). Short-term effects of cadmium (Cd) involve respiratory inflammation, while long-term exposure could determine injures to liver, lung, immune and nervous systems (Giaginis et al., 2006). Moreover, previous ecological studies demonstrated the association between exposure to heavy metals and diseases of gastrointestinal system (Khazaei et al., 2020). However, evidence about their direct effect on gastric mucosa is still scarce, encouraging further research through pre-clinical and clinical studies.

4. Conclusions

Conclusions

By means of BET adsorption analyses, information was obtained regarding the specific surface and surface porosity of the materials, showing mean specific surfaces of 0.69 m 2 /g with characteristics that are typical of non-porous systems. The Gamble's solution analyses highlighted the release of many elements as shown in Table 3 but at concentrations below the legal limits. Contextually, the results showed that the release of elements in Gamble's solution produced smaller concentrations than in watery solutions. All the elements taken into consideration remained well below the thresholds established by Italian law (legal decree 31/2001 regarding the quality of water destined for human consumption) whereas for watery solutions in milliq water B, Cd, Ni and As showed levels higher than those permitted. Nevertheless, many questions remain unanswered. In particular, research is still on-going focusing on: i) how fallout material interacts with the groundwater and/or the snow, given that Etna is the main aquifer in eastern Sicily, ii) whether breathing fine particles for long periods results in acute and chronic effects on health and, if so, what these effects are, iii) whether the dispersion of ashes in the atmosphere produces effects on marine and terrestrial flora and fauna and the effects caused by deposits on saline water masses and cultivated soils.

Furthermore, environmentally-related health is the result of the totality of environmental exposures including air pollution and socio-economic and lifestyle factors. Epigenetic phenomena, including DNA methylation, a possible mechanism underpinning environment-related health effects, can be potentially modified by these factors, resulting in environmental reprogramming of the genome for exposed individuals and for future generations of offspring (Barchitta et al. 2017; 2018). Although long interspersed nucleotide elements 1 (LINE-1) methylation has been associated with several disorders (Barchitta et al., 2017; Barchitta et al., 2014; Bollati et al., 2009; Carraro et al., 2016; Carreira et al., 2014; Choi et al., 2009; Delgado-Cruzata et al., 2015; Maugeri et al., 2019), evidence about the simultaneously effects of diet and air pollution exposure on DNA methylation is scarce. A recent study conducted by Barchitta and colleagues aimed to evaluate the association of PM10 exposure and adherence to Mediterranean Diet (MD) with LINE-1 methylation in healthy women living in Catania (Barchitta et al., 2018). In line with previous work (Baccarelli et al., 2009; Madrigano et al., 2011; Tarantini et al., 2009), the authors reported that exposure to PM10 is negatively associated with LINE-1 methylation in healthy women, while adherence to MD was associated positively. Notably, these findings underlined how molecular biomarkers might be differentially affected by environmental exposure and lifestyles. Thus, a multidisciplinary approach integrating specific methods and tools, nutritional and molecular epidemiology characterization, mineralogical and chemical analyses and in vitro assays, is necessary to assess the health risk of air

pollutants in a population living in peculiar geological and environmental conditions, due to natural sources of particles from the near Mount Etna volcano. In line with previous considerations, further research is needed to understand molecular mechanisms underlying the effect of volcanic ash on human health, and to evaluate the interaction with other factors characterizing human exposure. The answers to these questions are the object of research currently being carried out, whose results could provide important implications in evaluating risks to the environment and health caused by volcanic ash.

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*conflict of Interest Statement