

1 **Ash leachates from some recent eruptions of Mount**
2 **Etna (Italy) and Popocatépetl (Mexico) volcanoes and**
3 **their impact on amphibian living freshwater organisms**

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14

15 **Abstract**

16 Leaching experiments were carried out on fresh ash samples from Popocatépetl 2012,
17 Etna 2011 and 2012 eruptions, in order to investigate the release of compounds in both
18 double-deionised and lake (Lake Ohrid, FYR of Macedonia) waters. The experiments
19 were carried out using different grain sizes and variable time of stirring (from 30
20 minutes to 7 days). Results were discussed in the light of changing pH and release of
21 compounds for the different leachates. In particular, Etna samples induced alkalisation
22 and Popocatépetl samples induced acidification of the corresponding leachates. The
23 release of different elements does not show correlation with time of stirring, with the
24 measured maximum concentrations reached in the first hours of washing. General
25 inverse correlation with grain size was observed only for Na⁺, K⁺, Cl⁻, Ca²⁺, Mg²⁺,
26 SO₄²⁻, and Mn²⁺, while the other analysed elements show complex, scattering
27 relationship with grain size.

28 Geochemical modelling highlights leachates saturation only for F and Si, with
29 Popocatépetl samples sometimes showing saturation in Fe.

30 The analysed leachates are classified as undrinkable for humans on the basis of
31 European laws, due to excess in F⁻, Mn²⁺, Fe, and SO₄²⁻ (the latter only for Popocatépetl
32 samples).

33 Finally, the Etna 2012 and Popocatépetl leachates were used for toxicity experiments on
34 living biota (*Xenopus laevis*). They are mild toxic, and no significant differences exist
35 between the toxic profiles of the two leachates. In particular, no significant embryo
36 mortality was observed, while even at high dilutions the leachates produced more than
37 20% of malformed larvae.

38

39 **1. Introduction**

40 Volcanic ash is the most widely distributed product of explosive volcanic eruptions, and
41 areas hundreds of kilometres from an erupting volcano could receive ash falls (Ruggieri
42 et al., 2010; Sulpizio et al., 2014). Even minor quantities of deposited ash represent a
43 major hazard for the modern technical society and the environment (Blong, 1984;
44 Johnston and Houghton, 2000). Deposition of fresh volcanic ash can disrupt power lines
45 (Wardman et al., 2012), transport networks and water supplies (Martin et al., 2009;
46 Wilson et al., 2012), or induce pH variations and pollution in soils and surface water,
47 which have a serious impact on vegetation, animals and people (Ayrís and Delmelle,
48 2012).

49 In particular, deposition of volcanic ash into aqueous environments leads to dissolution
50 of adsorbed salts and aerosols, increasing the bioavailability of both key nutrients and
51 pollutants. This is because acids, metal salts and adsorbed gases on tephra (airborne
52 volcanic particulate matter) surfaces are highly soluble, dissolving rapidly on contact
53 with water (Frogner et al., 2001). These soluble surface accumulations have been
54 termed ‘ash-leachates’ by previous investigators (e.g. Witham et al., 2005) and we use
55 this term hereafter. Ash-leachate chemistry and volume can vary considerably,
56 depending on different gas solubility and degree of magma degassing prior or during the
57 eruption (Oppenheimer, 2003). These processes are largely governed by the
58 composition of the source magma (Armiénta et al., 2002), but additional factors are also
59 important, like the tephra particle size, the gas/ash ratio, and the time the ash remains in
60 the volcanic cloud (Óskarsson, 1980; Witham et al., 2005).

61 Over 55 soluble components have been reported in volcanic ash leachates, with the
62 anions Cl^- , SO_4^{2-} and F^- and the cations Ca^{2+} , Na^+ and Mg^{2+} generally occurring at the
63 highest concentrations (Witham et al., 2005).

64 The rapid release of nutrients and metals following the mixing of unhydrated ash or
65 aerosols with surface waters has been the focus of field studies (Gíslason et al., 2002;
66 Uematsu, 2004; Flaathen and Gíslason, 2007; Jones and Gíslason, 2008) and

67 experimental studies (Frogner et al., 2001; Duggen et al., 2007). The effects of ash fall
68 on natural waters and water supplies have focused mainly on the consequences of
69 increased levels of turbidity (ash suspended in water), acidity and fluoride content
70 (Collins, 1978; Óskarsson, 1980; Weniger and Blaser, 1983; Cronin and Sharp, 2002;
71 Stewart et al., 2006; Smithsonian Institution, 1997). On the other hand, contamination of
72 drinkable water is a major concern for public health, due to the potential for outbreaks
73 of waterborne infectious diseases due to the inhibition of disinfection at high levels of
74 turbidity. Moreover, elevated concentrations of fluoride increase the risks of dental and
75 skeletal fluorosis (Stewart et al., 2006).

76 Impacts of ash on environment have been reported subsequently to a number of historic
77 eruptions. During the 1783–84 eruption of Laki (Iceland) 50% of the livestock in
78 Iceland perished, many probably as a result of fluorine poisoning (Thorarinsson, 1969;
79 Grattan and Charman, 1994; Steingrímsson and Kunz, 1998). After the 1947–48
80 eruption of Hekla in Iceland, some rivers and streams showed temporarily elevated
81 fluoride concentrations (up to 9.5 mg/l; Stefánsson and Sigurjónsson, 1957). The ash
82 from 1969 Ruapehu eruptions contaminated water supplies, with pH values ranging
83 from 4.4 to 6.0 (Collins, 1978; Stewart et al., 2006). Similar pH values in receiving
84 waters following volcanic ash deposition have been reported in many other studies
85 (Wilcox and Coats, 1959; Cronin and Sharp, 2002; Smithsonian Institution, 1997). The
86 ash from 2012 Mt. Tongariro eruption (New Zealand) had higher concentrations of F^- ,
87 Al^{3+} , Ca^{2+} and SO_4^{2-} and had generated significant agricultural problems, including
88 livestock deaths (Cronin et al., 2014).

89 Several recent eruptions have had high quantities of fluorine adsorbed on the tephra,
90 including: Hekla, Iceland in 1970, 1991, and 2000 (Frogner et al., 2001; Gudmundsson
91 and Óskarsson, 1992; Thorarinsson and Sigvaldason, 1972), Lonquimay, Chile in 1989–
92 1990 (Araya et al., 1990; Araya et al., 1993) and Ruapehu, New Zealand in, 1995–1996
93 (Shanks, 1997; Cronin et al., 2003).

94 Other than fluoride release and acidity, little attention has been paid to contamination of
95 water supplies by other soluble components of ash. There are some reports of elevated
96 levels of iron, sulphate and chloride (Smithsonian Institution, 1997; 2000; Cronin and
97 Sharp, 2002; Baxter and Ancia, 2002) but little or no discussion of their environmental
98 impact. Evidence for phytoplankton blooms as a result of volcanogenic sedimentation
99 have been observed in lakes (Smith and White, 1985) and in oceans, based on
100 preliminary satellite data (Duggen et al., 2007). Bio-incubation experiments have shown

101 diatoms utilizing nutrients from volcanic ash (Duggen et al., 2007). Mesoscale iron
102 enrichment experiments have shown that Fe addition to low chlorophyll ocean waters
103 can instigate elevated marine primary productivity (Boyd et al., 2000).
104 In order to supply new data useful for understanding the behaviour of release of water
105 contaminants from fresh volcanic ash and their impact on water supplies and living
106 organisms, we collected ash deposits from two recent eruptions of Mount Etna (Italy,
107 August 2011 and April 2012) and from the eruption of May 2012 of Popocatépetl
108 volcano (Mexico). The collected volcanic ash was washed using two different types of
109 water (double de-ionised and natural lake water), and the released compounds analysed
110 for major and trace elements. The results were discussed in the light of international
111 (European drinking water directive, 98/83/EC) drinkable limits for public waters.
112 Since the decline of amphibian populations has been retained a major consequence of
113 the anthropic and naturally occurring environmental changes (Hayes et al., 2010), the
114 ash leachates were also tested for toxicity using the amphibian *Xenopus laevis* as
115 biological model. The bioassays were performed using the standardized Frog Embryo
116 Teratogenesis assay – *Xenopus* (FETAX) (ASTM, 1998), already successfully applied
117 to eco-toxicological investigations for testing single compounds and mixtures (Dawson,
118 1991; Bacchetta et al., 2008), municipal sludge (Chenon et al., 2003), material and
119 sediment extracts (Mantecca et al., 2007; Fort et al., 2001).

120

121 **2. Materials and methods**

122 **2.1 Bulk rock, glass composition and sublimates**

123 The samples used in the experiments are fresh volcanic ash from the eruptions of
124 August 12, 2011 and April 24, 2012 eruptions of Mount Etna (southern Italy), and the
125 eruption of May 2012 of Popocatépetl (Mexico). The samples were placed in
126 polyethylene bags and carried to the laboratory for dry sieving between 63 μm and 1
127 mm at 1 ϕ interval ($\phi = \log_2 d$, where d is the particle diameter).

128 The composition of bulk ash samples was obtained by XRF using a Philips PW1480/10
129 automatic spectrometer (Cr anticathode for major and minor elements, Rh anticathode
130 for Rb, Sr, Y, Zr, Nb and W anticathode for Ce, La, Ba, Ni, Cr, V) at Dipartimento di
131 Scienze della Terra e Geoambientali (University of Bari) following the analytical
132 techniques outlined by Franzini et al. (1975) and Leoni and Saitta (1976). EDS analyses
133 were performed on glass and mineral phases of the different tephra samples embedded
134 in epoxy resin, polished and coated with carbon at the Dipartimento di Scienze della

135 Terra (University of Pisa), using an EDAX-DX micro-analyser mounted on a Philips
136 SEM 515 (operating conditions: 20 kV acceleration voltage, 100 s live time counting,
137 10^{-9} A beam current, ZAF correction). Instrument calibration and performance are
138 described in Marianelli and Sbrana (1998). Back-scattered electrons (BSE) SEM images
139 of sublimate compounds on ash surfaces were obtained with a 50XVP LEO Scanning
140 Electron Microscope at the Dipartimento di Scienze della Terra e Geoambientali
141 (University of Bari).

142

143 **2.2 Leachates analyses**

144 Two types of water were used for washing the ash samples: double de-ionised (mQ)
145 water, and Lake Ohrid (Macedonia) water. Lake water was filtered immediately after
146 sampling through 0.2 μm Millipore membranes (cellulose acetate).

147 Leaching experiments were performed on 2 g of sieved ash, which was added in
148 previously washed plastic cuvettes containing 20 ml of mQ water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) or
149 lake water. The washing was performed at ambient temperature ($25\text{-}28^\circ\text{C}$) on a table
150 shaker (stirring at 150 rpm), in order to ensure efficient mixing of the leaching
151 suspension.

152 The stirring duration varied from 30 minutes to 7 days (intermediate steps at some
153 hours, 1 day and 5 days) depending on the amount of available ash. The grain-sizes that
154 were used varied from 1 mm to 0.063 mm.

155 The samples were centrifuged for 10 minutes at 3500 rpm and filtrated immediately.

156 The pH of the leachates was measured using a glass electrode (ORION), sensitive of the
157 activity of H^+ ions, coupled with an Ion Analyser EA920 (instrumental error less than
158 0.5 pH units, reproducibility of the data better than 5%).

159 The ammonia and ammonium concentration was measured using a specific electrode
160 (ORION) coupled with an Ion Analyser EA920, following the procedure recommended
161 in Clesceri et al. (1998). The additions method (Harvey, 2000) was used for this
162 analysis. NH_4Cl standards were prepared starting from 1000 γ/ml obtaining the standard
163 NH_4Cl 100 γ/ml and the standard NH_4Cl 10 γ/ml (reproducibility of the data better than
164 10%). The analysis provides the sum of NH_3 and NH_4^+ in the solution, whose partition
165 (Table 1) is pH dependent:

166

$$167 \quad \alpha = \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K}{10^{-\text{pH}}} \frac{\gamma_{\text{NH}_4^+}}{\gamma_{\text{NH}_3}}$$

168

169 where in square brackets are the concentrations of the two chemical species, γ indicating
170 the activity coefficients, and K is the thermodynamic constant (pK=9.24). NH_3 and
171 NH_4^+ concentrations can be therefore calculated using:

172

$$173 \quad [\text{NH}_4^+] = \frac{C}{\alpha+1}; [\text{NH}_3] = \frac{C\alpha}{\alpha+1}$$

174

175 Composition of major elements (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , F^-) of ash leachates
176 was determined by ion chromatography (IC). Trace elements were measured using an
177 inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optimal
178 2000 DV instrument. Operating conditions were: power 1400 W, plasma argon flow
179 rate 15 Lmin⁻¹, nebulizer argon flow rate 0.55 Lmin⁻¹, and sample flow rate 2 mLmin⁻¹.
180 1.

181 A Dionex-model 100 with AS4A ION CAP anion exchange column and chemical
182 suppression of eluent conductivity technique were used to analyse anions (F^- , Cl^- , SO_4^{2-}),
183 while the analysis of cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), was performed using a Model 600
184 Dionex with ION PAC CS12A and chemical suppression of eluent conductivity
185 technique. The reproducibility of the data is better than 4% for both anions and cations.
186 The calibration curves for each element were prepared using calibration standards, and
187 repeated for the analysed elements every 10 samples. The samples were diluted by a
188 factor of 1:10.

189 The calibration curve for trace elements was carried out using calibration standards
190 prepared diluting a stock solution (1000 ppm) with deionised water. Recovery
191 experiments were carried out by adding measured volumes of aqueous standard
192 solutions of each metal to measured volumes of an acidified deionised water samples.
193 Calibration curves were repeated for the analysed elements every 14 samples.

194 Reproducibility of the data is better than 3%.

195

196 **2.3 FETAX test**

197 Ash leachates from Etna 2012 and Popocatépetl in mQ water were used for laboratory
198 analysis on living biota. The methodology of the FETAX assay and the experimental
199 design imply that adult *Xenopus laevis* were maintained in aquaria with de-chlorinated

200 tap water at a $22^{\circ}\text{C} \pm 2$, alternating 12h light/dark cycles and fed a semi synthetic diet
201 (Mucedola S.r.l., Settimo Milanese, Italy) three times a week.

202 For a single bioassay, three males and three females received a 300 IU human chorionic
203 gonadotrophin (HCG) via injection in the dorsal lymph sac to induce mating. Breeding
204 tanks were filled with FETAX solution (composition in mg/l was 625 NaCl, 96
205 NaHCO_3 , 30 KCl, 15 CaCl_2 , 60 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and 70 MgSO_4 , pH 7.5-8.5) and aerated
206 before introducing a couple. Amplexus normally ensued within 2h to 6h and the
207 deposition of fertilized eggs took place from 9h to 12h later. After breeding, the adults
208 were removed and the embryos were collected in 60 mm glass Petri dishes. Abnormally
209 cleaved embryos and necrotic eggs were removed.

210 Normally cleaved embryos at midblastula stage (stage 8), 5h post-fertilization (hpf)
211 (Niewkoop and Faber 1956) were selected for testing and then placed in 6 cm glass
212 Petri dishes, each Petri containing 10 ml of control or test solutions. Test solutions were
213 generated by diluting the Etna and Popo mQ leachates in FETAX solution, to obtain the
214 final dilutions of 1:5, 1:10, 1:50, and 1:100.

215 For each female the plates were duplicated or triplicated when well-cleaved embryos
216 were available. All the Petri were incubated in a thermostatic chamber at $23 \pm 0.5^{\circ}\text{C}$
217 until the end of the test, 96 hpf. At this moment mortality and malformation data were
218 generated as endpoints of the assay.

219 The number of dead embryos versus their total number at the beginning of the test led to
220 the mortality percentages and the number of malformed larvae versus the total number
221 of surviving ones gave the malformed larva percentages.

222

223 **3. Results**

224

225 **3.1. Ash composition and surface analysis**

226 The bulk rock composition, the glass/mineral phases and the sublimated composition of
227 the collected samples were analysed by XRF and SEM-EDS techniques. The bulk
228 composition (Table S1) of Etna samples plot in the hawaiite field, while the
229 Popocatépetl sample can be classified as andesite (Fig. 1).

230 The EDS analyses on glass of Etna samples (Table S2) show an almost homogeneous,
231 more evolved composition (mugearites) with respect to the parental bulk analyses (Fig.
232 1). The Popocatépetl glass analyses gather on a trend from andesite to rhyolite (Fig. 1).

233 As from SEM-BSE images of polished samples, both Etna and Popocatépetl samples
234 are porphyritic, with phenocrystals and groundmass microcrystals (Fig. 2). The
235 mineralogical assemblage of Etna samples comprises Mg-rich olivine clinopyroxene,
236 plagioclase, and oxides (Table S3). In particular, the clinopyroxene is diopside in both
237 2011 and 2012 samples (Fig. 3a). Plagioclase in the sample from the 2011 eruption has
238 an almost homogeneous bytownite composition (Fig. 3b), while in the sample from the
239 2012 eruption shows a compositional range between bytownite and labradorite (Fig.
240 3b).

241 The mineralogical assemblage of Popocatépetl comprises ortho- and clino-pyroxenes,
242 plagioclase and oxides (Tables 3). Orthopyroxenes are enstatite (Fig. 3a), while
243 clinopyroxenes are augites (Fig. 3a). Plagioclase shows a small compositional range
244 within the labradorite field (Fig. 3b).

245 SEM-BSE images are shown in Figure 4. The sublimates recognized on ash surfaces of
246 Etna 2011 (Figs. 4a and 4b) and Etna 2012 samples are mainly sodium chloride (NaCl,
247 halite) and calcium di-fluoride (CaF₂, fluorite) (Figs. 4c and 4d). Popocatépetl samples
248 show abundant sublimate compounds, including sodium chloride, calcium sulphate
249 (gypsum, CaSO₄·2H₂O or anhydrite CaSO₄), iron sulphide (pyrite FeS₂ or greigite
250 Fe^{II}Fe^{III}₂S₄) and native S (Figs. 4e and 4f).

251

252 **3.2. Ash leachates**

253 Leaching experiments (Tables 1 and 2) were performed using 2 g of sieved ash, which
254 was added with 20 ml of mQ or lake water.

255

256 **3.2.1 pH variation**

257 The pH of ash leachates ranges from ca. 4 (Popocatépetl 63 µm) to ca. 6.50 (Etna 2011
258 0.5 mm; Fig. 5). The pH variation is very limited when plotted versus different times of
259 stirring within each sample, for both mQ and lake waters (Fig. 5). This indicates that
260 most of the pH variations are acquired within the first 30 minutes of stirring.

261 As a general behaviour, the Popocatépetl leachates induce acidification in the solution,
262 diminishing the pH values of 0.24±0.18 (lake water; Table 2) and 0.57±0.30 (mQ water;
263 Table 1) pH units (Fig. 5). The Etna samples show opposite behaviour, i.e. induce slight
264 (0.34±0.11 pH units for lake water; Table 2) to moderate (1.34±0.2 pH units for mQ
265 water; Table 1) alkalization (Fig. 5). In both cases is evident the buffering effect of lake

266 water on pH variations, which also show a slight dependence to decreasing grain size of
267 leached ash (Fig. 5).

268

269 **3.2.2 NH₃-NH₄⁺ concentration**

270 The analysed samples show a very limited amount of ammonia (NH₃) concentration
271 with respect to the ammonium (NH₄⁺) one. This is mainly due to the range of pH of the
272 produced leachates, which, in any case produced different amounts of NH₃-NH₄⁺ when
273 using mQ or lake water (Fig. 6). In particular, the ammonia-ammonium concentration in
274 mQ water is negligible for Etna samples, while it increases for Popocatépetl samples. In
275 lake water, the Popocatépetl samples release NH₃-NH₄⁺ almost constantly (variation
276 within 1 mg/l), while the Etna samples either do not release NH₃-NH₄⁺ (samples Etna
277 2011) or have scattered release of NH₃-NH₄⁺ with time (samples Etna 2012; Fig. 6).
278 When effective, also the release of NH₃-NH₄⁺ shows correlation with decreasing grain
279 size (Fig. 6).

280

281 **3.2.3 Anions**

282 Figure 7 shows the variations of F⁻, Cl⁻, and SO₄²⁻ concentrations for different grain
283 sizes versus time of leaching. The general patterns show small variation of
284 concentration versus time for all anions, indicating their release occurring in the first 30
285 minutes. It makes exception the SO₄²⁻ in mQ water, which reaches a constant release
286 after 60 minutes.

287 The concentration of Cl⁻ is below 10 mg/l for most of the samples in both mQ and lake
288 water, with the exception of Popocatépetl ash with grain size of 63 μm and some
289 scattered anomalous values (Fig. 7).

290 Irrespective of water used, the release of SO₄²⁻ is negligible in Etna samples, while it is
291 the most significant in Popocatépetl samples. For the latter, the concentration of SO₄²⁻
292 significantly increases with diminishing grain size and moderately increases with
293 leaching time (Fig. 7).

294 The concentration pattern of F⁻ is more complex than those of the other anions, with
295 different release in the two types of leaching water. In particular, the 2011 Etna samples
296 produce the greatest concentrations in both water types, although higher in mQ water
297 (Fig. 7). The 2012 Etna samples show lower concentrations, and in lake water they are
298 below 10 mg/l. The Popocatépetl samples have concentration of few mg/l (below 10
299 mg/l), and a slight correlation with decreasing grain size in mQ water (Fig. 7). In both

300 types of waters, all the samples show a general slight correlation with increasing
301 leaching time.

302

303 **3.2.4 Major cations**

304 Figure 8 shows the variations of Na^+ , K^+ , Mg^{2+} and Ca^{2+} concentration for different
305 grain sizes versus time of leaching. The general patterns show small variation of
306 concentration versus time for all cations indicating their release occurring generally in
307 the first 30-60 minutes, while the Popocatépetl samples reach the highest concentration
308 after 3-5 days in lake waters. The concentration of Na^+ is below 20 mg/l in Etna
309 samples in both mQ and lake water, and it is between 30 and 60 mg/l in Popocatépetl
310 samples. The concentration of K^+ is below 7 mg/l for most of the samples in both mQ
311 and lake water, with the exception of Etna 2012-1mm sample in mQ water (Fig. 8). It is
312 worth noting that the concentration of Na^+ and K^+ for the Etna 2012 samples in lake
313 water leachate is close or below the concentration these cations have in pure lake water
314 (Fig. 8).

315 Irrespective of the water type used, the release of Ca^{2+} and Mg^{2+} is negligible for Etna
316 samples, while it is the most relevant in Popocatépetl samples (Fig. 8). Their
317 concentration increases at diminishing grain size except for lake water after 24 hours
318 (Fig. 8).

319

320 **3.2.5 Trace elements**

321 Figure 9 shows the variations of B, Si, Fe_{Tot} , Mn^{2+} and As^{3+} concentration for different
322 grain sizes versus time of leaching. The general patterns show irregular variation of
323 concentration versus time for all the trace elements. B concentration shows a scattered
324 distribution versus time of leaching in mQ water, although a fair anti-correlation is
325 visible for 3 out of 4 Etna samples (Fig. 9). It is below the lake water concentration for
326 almost all the analysed samples (Fig. 9). The concentration of Si is scattered in both mQ
327 and lake water leachates, although a fair increase in concentration is visible with time of
328 leaching for both Etna and Popocatépetl samples (Fig. 9).

329 Irrespective of water typology used, the release of Fe_{Tot} and Mn^{2+} is lower in Etna
330 samples than in Popocatépetl ones, showing a scattered distribution with some very high
331 peaks (Fig. 9).

332

333 **3.3. Biological impact of leachates**

334 The results from the FETAX test clearly show that the leachates from Etna and
335 Popocatépetl ash are very poorly embryo toxic. At the dilutions used, no significant
336 increase in embryo mortality was indeed observed (Fig. 10 a, b). The percentages of
337 malformed larvae at the end of the test progressively increased with decreasing dilutions
338 in the groups exposed to Etna leachates (Fig. 10a), while a non-linear increase was
339 observed in those exposed to Popocatépetl leachates (Fig. 10b). The maximum values of
340 about 40% malformed larvae were registered at the highest concentrations of leachates.
341 These results do not evidence significant differences in the effects induced by Etna and
342 Popocatépetl leachates, although it is worth noting the higher scores obtained in larvae
343 exposed to Etna leachates at low concentrations (1:100 and 1:50), with respect to the
344 Popocatépetl ones.

345

346 **4. Discussion**

347

348 **4.1 General remarks**

349 The data presented in the preceding sections illustrate the complexity that accompanies
350 the leaching of compounds from fresh volcanic ash. Analysing the figures and the tables
351 presented, it emerges clearly how the physical and chemical processes occurring during
352 the simple washing of fresh volcanic ash interact with the surrounding aqueous
353 environment. It follows that to extract simple laws of compound release at different
354 boundary conditions is not straightforward, having to face with dynamic processes that
355 changes in function of the progressive variation of the experimental geochemical
356 environment.

357 In the following, we analyse the data taking into account the major variables potentially
358 influencing the experimental results. Finally, the potential toxicity of ash leachates will
359 be discussed in the light of potable water pollution and alteration of life cycle of living
360 biota (tadpoles embryos, *Xenopus laevis*).

361

362 **4.2 Origin of leached elements**

363 The mQ water is almost pure water, thus it does not contains any other element or
364 compound that could react with the leaching material. Therefore, it is better suitable for
365 the analysis of leached compounds from volcanic ash than lake water, whose dissolved
366 elements and molecules can react with leached elements and alter their original
367 assemblage.

368 The sublimates on ash surfaces of Etna 2011 (Figs. 4a and 4b) include mainly (Na,K)Cl
369 (sodium/potassium chloride), (Ca,Mg)F₂ (calcium/magnesium fluoride), and (Ca,
370 Mg)SO₄ (calcium/magnesium sulphate). The formation of leachates from solubilization
371 of these superficial salts is also confirmed by the stoichiometry of mQ water analysis,
372 where the relative abundance of these elements is almost completely balanced. Only
373 few residual fractions of Ca²⁺, Mg²⁺ and F⁻ scattered in the different grain-size fractions
374 remain unbalanced (Table S4). The concentration of all the elements is below their
375 respective solubility limit, except than Si²⁺ and F⁻ (Table S5). It means that all the salts
376 from the ash surface passed into the leachates, with the exception of Si and F ones,
377 which may have been remained partially not dissolved. The slight excess of Mg²⁺ and
378 Ca²⁺ in most of the Etna 2011 samples (Table S4) might indicate the presence of
379 carbonates in the leachates, since CO₃²⁻ was not analysed. When considering the
380 stoichiometry of the leachates, it emerges that F⁻ compounds are the most dissolved in
381 Etna 2011 samples, along with variable amount of SO₄²⁻ and minor Cl⁻ compounds
382 (Table S4).

383 The Etna 2012 sample shows very similar stoichiometry of leachates to Etna 2011, with
384 fractional remnants of unbalanced elements that comprise K⁺, Ca²⁺, and Mg²⁺ (Table
385 S4). Mg concentration is close to the maximum solubility limit, and dissolved F
386 compounds dominate the leachates (Table S4).

387 The sublimates on ash surfaces of Popocatepetl samples (Figs. 4e and 4f) include
388 mainly (Ca,Mg)SO₄ (calcium/magnesium sulphate), and minor (Na,K)Cl
389 (sodium/potassium chloride). Also in these cases the leachates reflect the dissolution of
390 the salts observed on ash surfaces, as confirmed by stoichiometric calculations (Table
391 S4). It is observable a slight excess of Mg²⁺, Ca²⁺, K⁺ and Na⁺ not balanced by Cl⁻,
392 SO₄²⁻ and F⁻, which might indicate the occurrence of carbonates (not analysed) in the
393 leachates. The concentration of elements in the two samples (0.125 and 0.063 mm)
394 slightly differs (Table S5), with the coarser one that shows saturation with respect to Ca,
395 Si and Fe compounds, and the finer one that shows saturation in fluorite, gypsum,
396 quartz and chalcedony (Table S5). The Mg²⁺ content in mQ leachates from
397 Popocatepetl samples is higher than in Etna samples (Table S4). Taking into account the
398 surface analysis on sublimates, it seems that most of the Mg²⁺ comes from dissolution
399 of Mg-sulphates. This inference is also supported by the strong correlation among Ca²⁺,
400 Mg²⁺ and NH₄⁺ (Fig. 11), which indicate the presence of the ammonium as catalyst for
401 (Ca, Mg) salt dissolution.

402 The composition of leachates in lake water can be quite different from those in mQ
403 water, due to the presence of chemical compounds already present, which can react with
404 elements released from ash surface (Table 2). In order to evaluate the buffering effect of
405 lake water, its chemical composition was subtracted from that of the leachates (Table 3).
406 This allows compare the net release of the different elements using the two water
407 typologies. It is evident comparing data from Tables 1 and 3 how the release of
408 elements from Etna samples is variably lower in lake water than in the mQ one, with
409 loss of some 10% in abundance of F^- , K^+ , Mg^{2+} , Mn^{2+} and especially B, which has a
410 negative net release in lake water (Table 3). This general behaviour is also confirmed by
411 Popocatépetl samples, with the exceptions of a greater release of Mg^{2+} and Ca^{2+} in lake
412 water for the 125 μm fraction (Table 3). Because borates are usually highly soluble, it
413 may suggest the occurrence of adsorption/reaction processes of B with compounds
414 present in lake water.
415 Being the Lake Ohrid water from carbonate springs, the described variations in element
416 abundance between mQ and lake water can be influenced by the presence of carbonates
417 in the latter one. Although carbonates have not been measured directly, their abundance
418 can be calculated using charge balance (Qu et al., 2008; Table 2). However, inspection
419 of HCO_3^- data in Table 2 shows the leachates from both Etna and Popocatépetl samples
420 have indistinguishable contents (in average) with respect to the lake water, with the only
421 exceptions of the Popocatépetl samples with longer time of stirring. This indicates that
422 the net release of Mg^{2+} and Ca^{2+} is limited by the reached solubility limit of most of the
423 leachates (Table S6) in the carbonate-bearing water.

424

425 **4.3 Influence of ash grain size on leachates**

426 It has been suggested that concentration of deposited species on surface particles
427 depends upon the size-fraction of the tephra, and it is higher for smaller particles
428 (Fruchter et al., 1980; Rose et al., 1973; Óskarsson, 1980; Rubin et al., 1994). Particles
429 with smaller diameters have a higher surface area to mass ratio than larger particles so
430 are more efficient scavengers of volatiles for the same tephra volume. This means that
431 as the particle size decreases, the proportion of available volatiles scavenged increases
432 (Witham et al., 2005).

433 In order to investigate the influence of grain size of ash on release of elements, the Etna
434 2011 samples in mQ water are the most suitable, being available leachates from three
435 different grain sizes (Table 1). Analysing the release of elements with different times of

436 stirring, it is evident the inverse correlation with grain size for SO_4^{2-} , Na^+ , K^+ , and Ca^{2+} .
437 The trends for these elements are quite similar for the different times of stirring,
438 indicating a time-independent release for these elements (Fig. 12). A general decrease
439 of release with increasing grain size is visible for Cl^- , although the trends for different
440 times of stirring are not identical (Fig. 12). Release of Mg^{2+} is almost constant for the
441 different grain sizes and for different times of stirring. The release of Mn^{2+} is
442 contrasting. It is inversely related to grain size for time of stirring up to 21,600 s (6 h),
443 while it increases with grain size for times of stirring of 43,200 s (12 h) and 86,400 s
444 (24 h; Fig. 11). B also shows similar pattern, with opposite trends below and above
445 21,600 s (6 h; Fig. 11). These behaviours suggest different kinetics for dissolution of
446 sublimates containing Mn^{2+} and B and precipitation of their salts.
447 The release of F^- shows a unique pattern, with similar values for 0.25 mm and 1 mm
448 grain sizes and lower values for the 0.5 mm grain size (Fig. 12). This behaviour is quite
449 well defined by all the times of stirring, which indicates this is not an aleatory
450 behaviour. Finally, the patterns of Si and Fe are randomly arranged, without any clear
451 correlation of release with grain size and/or timing of stirring (Fig. 12). The different
452 patterns for the various elements of Etna 2011 samples demonstrate how the
453 dependence of element release with grain size is not a general rule. Indeed, a greater
454 release at decreasing grain size holds for alkali and alkaline earth elements together with
455 the sulphate radical SO_4^{2-} , which is a component of most of their original sublimated
456 salts. This is in agreement with already suggested greater capacity of particles with
457 larger surface vs. volume ratio to scavenge elements from the eruptive cloud.
458 The release of B seems to reflect a complex kinetic of adsorption/reaction of B, which
459 can account for the difference in release at different times of stirring (Fig. 12).
460 The scatter release of Fe and Si reflects the random formation of soluble salts of these
461 elements, which are not related to the grain size but more probably to the redox
462 conditions at time of sublimation.
463 Among the most abundant elements, F^- shows a unique pattern, not the explanation is
464 puzzling. It is not related to the active surface of the particles, nor to the composition of
465 the eruptive plume, having all the particles underwent the same eruptive conditions. It
466 may be speculated that some gaseous F might be entrapped in the vesicles that are more
467 abundant in the 1 mm particles than in the 0.25 mm and 0.5 mm, and then may be
468 related to the presence of gaseous F in the vesicles of the coarse ash particles of 1 mm
469 grain size, which can compensate the lower active surface of this grain size.

470 To explore the dependence of element release with grain size for Popocatepetl samples
 471 is less significant, being available only two grain-size fractions. However, as a general
 472 behaviour, the release of elements is significantly greater for the finer grain size (0.063
 473 mm) than for the 0.125 mm fraction (Figs. 7 and 8).

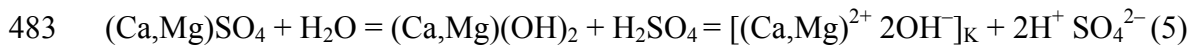
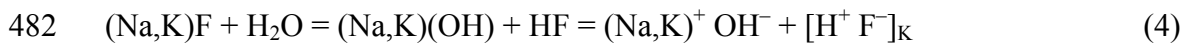
474

475 **4.4 Origin of pH changes**

476 The changes in pH values of leachates with respect to those of mQ and lake water
 477 relates to the release of OH⁻ and H⁺ ions due to hydrolysis reactions of the salts
 478 dissolved from the ash surfaces (§ 6. 1).

479 For Etna samples, the main hydrolysis reactions can be summarized as:

480



485

486 Equation (3) is neutral for pH, producing a strong base and a strong acid that are totally
 487 dissociated in water. Equation (4) produces a strong base and a weak acid, which is only
 488 partially dissociated to supply H⁺ ions. It induces alkalisation of the leachates.

489 Equation (5) produces a strong acid and a weak base, which induce acidification of the
 490 leachates. Equation (6) produces a weak acid and a weak base. Being the equilibrium
 491 constants $K_{\text{HF}} = 6.6 \times 10^{-4}$ and $K_{\text{Ca}(\text{OH})_2} = 5.5 \times 10^{-6}$, the reaction induce slight
 492 alkalisation of the leachates. Being the sublimates on Etna ash dominated by F salts
 493 (Tables 1 and 2), the hydrolysis reactions are dominated by equations (4) and (6). This
 494 explains why the pH of Etna leachates is more alkaline with respect to the mQ water.

495 The alkalisation is less effective when considering leachates in lake water, due to the
 496 presence of dissolved carbonates (Table 2) that buffers the hydrolysis reactions.

497 The same hydrolysis equations hold for the Popocatepetl samples, although they are
 498 dominated by dissociation of (Ca,Mg)SO₄ salts (Tables 1 and 2). This explains why the
 499 Popocatepetl leachates are more acid with respect to the mQ water (Fig. 5). The
 500 correlation of pH value with SO₄²⁻ is also testified by the higher acidification of 0.063
 501 mm leachates with respect to the 0.125 mm ones (Fig. 5; Tables 1 and 2). The pH varies
 502 very little when considering lake water also for Popocatepetl samples, due to the
 503 buffering effect of already dissolved carbonates (Fig. 5; Tables 1 and 2).

504

505 **4.5 Drinkability of water leachates**

506 Drinking water quality is commonly regulated using a two-tier system. Primary
507 standards are legally enforceable limits set for contaminants posing a health risk (Table
508 S7). Secondary standards are non-enforceable guideline values for contaminants which
509 are not known to be a health risk but which make drinking water unacceptable to
510 consumers because of aesthetic factors such as taste, colour or odour (Table S7), or
511 effects on the supply system such as staining or scale deposition (Stewart et al., 2006).
512 Inspection of Etna and Popocatépetl mQ leachates shows that F^- and Mn^{2+} elements are
513 always well above the legal limits for drinkable water (Table 1). Also Fe exceeds the
514 limits in most of the Etna samples and in all the Popocatépetl ones (Table 1). This
515 makes it the water dark in colour, bitter, with metallic taste and can induce dental
516 fluorosis and gastrointestinal disease on consumers. The SO_4^{2-} also exceeds the limits in
517 the Popocatépetl samples, adding salty taste to the water and possible diarrhoea disease
518 to consumers.

519 The inspection of leachates with lake water shows a similar behaviour of mQ water for
520 F^- , which exceeds the legal limits in all the samples. Mn^{2+} is in excess for all the Etna
521 2011 and Popocatépetl samples, but only in two samples of Etna 2012 (Table 2). Fe
522 exceeds the limits for most of the analysed samples, while SO_4^{2-} is in excess in all the
523 Popocatépetl samples (Table 2). Overall, the effects on water and consumers are the
524 same than in mQ water.

525 The inspection of Tables 1, 3 and S4 highlights how the F^- content is the most sensitive
526 element for drinkability of leachates of Etna samples, being its abundance 6 to 14 (mQ
527 water) or 1.5 to 10 (lake water) times the acceptable limit for potability (Tables 1, 3 and
528 S4). The Mn^{2+} and Fe are the most sensitive elements for Popocatépetl samples in mQ
529 water (Tables 1, 3 and S4), with abundances between 10 and 50 times (Mn^{2+}) and 7 to
530 58 times (Fe) the legal limits. Considering lake water, the most sensitive element for
531 Popocatépetl is Mn^{2+} (Tables 1, 3 and S4), being its abundance 3 to 50 times the legal
532 limits for potability.

533 Taking into account the concentration of these elements in Etna and Popocatépetl
534 leachates, it is possible to calculate the minimum weight of ash needed to exceed the
535 legal limits of potability. As an example, for Etna 2011 samples in lake water, only 12
536 kg of ash per m^3 of water are sufficient for making it undrinkable (using F^- as
537 benchmark). It means that, depending on the bulk density of the ash deposit, a thickness

538 of 8 mm/m² (bulk density of 1500 kg/m³) or 6 mm/m² (bulk density of 2000 kg/m³) is
539 sufficient for contaminating the water beyond the potability limits. The same exercise
540 for Popocatépetl samples yields a mean weight of only 8 kg of ash per m³ (using Mn²⁺
541 as benchmark), which corresponds to 5 mm/m² (bulk density of 1500 kg/m³) or 4
542 mm/m² (bulk density of 2000 kg/m³). If applied to Lake Ohrid (water volume of ca. 5.5.
543 km³), the required thickness of tephra deposited over the lake area is 12-15 cm for Etna
544 compositions and 6-8 cm for Popocatépetl ones. Taking into account the thickness of
545 past tephra layers recognised in Lake Ohrid succession (Sulpizio et al., 2010), the only
546 deposit with similar thicknesses is the Campanian Ignimbrite-Y5 (Leicher et al., 2015).
547 It is evident that to contaminate a big water reservoir like Lake Ohrid it is necessary an
548 amount of volcanic ash compatible only with super eruptions. Nevertheless, limited
549 amounts of ash can impinge significantly the availability of a primary resource like
550 drinkable water in many smaller water reservoirs than Lake Ohrid. This is an
551 underestimated volcanic hazard, which can impact large areas and severely affect
552 population if no preventive civil protection actions are taken in advance. Authorities
553 were generally unable to allay public fears because of a lack of supporting information
554 on specific effects of volcanic ash on water supplies, including considerations such as
555 the quantity of ash necessary to produce adverse effects, and the specific nature of
556 contaminants that may pose a health risk to consumers or otherwise compromise the
557 integrity of water supplies. A good example of this hazard is the potential contamination
558 of water reservoirs of southern Italy, which are exposed to ash deposition in case of
559 renewal of explosive activity of Italian volcanoes (Sulpizio et al., 2014).

560

561 **4.6 Effects on living biota**

562 The deposition of volcanic ash on lake systems can impinge significantly the living
563 biota. They can react in different ways, and showing different resilience to the external
564 perturbation, as demonstrated for Lake Ohrid diatoms following the deposition of Y5
565 tephra layer (Jovanovska et al., 2015). In order to evaluate the possible toxicity of
566 released compounds on living biota, the ash leachates (from mQ water) were diluted in
567 FETAX solution to obtain sequential dilutions from 1:5 to 1:100 vol./vol. This was
568 planned to mime natural conditions in which ash leachates are likely progressively
569 diluted in the water basins. Under these experimental conditions both Etna and
570 Popocatépetl leachates results mild toxic to developing *Xenopus laevis* and no
571 significant differences exist between the toxic profiles of the two materials. Anyway,

572 we outline that the higher content in F exhibited by the leachates from Etna may
573 represent a potential teratogenic risk. Indeed, F⁻ is known to be a powerful teratogen, as
574 also demonstrated in *Xenopus laevis* (Goh and Neff, 2003). In this optic, it may be
575 useful to focus on the induced malformations more than on the deaths of embryos. It is
576 evident that for both leachates the number of malformations is greater for low dilutions
577 (Fig. 13), with a good logarithmic fit of the data. This means that even few % of
578 leachates (high dilutions) suddenly increases the malformations above 20%, which only
579 augment of about 10% at higher concentrations (Fig. 13).

580 Also the changing pH did not induce any big differences in teratogenesis. This allows us
581 to consider the experimental results as non-dependent from pH variations.

582 Although promising, these preliminary data on ecotoxicity of Etna and Popocatepetl ash
583 leachates claim for more experimental evidences to fully understand the specific and
584 comparative reactivity of the different leachates in term of teratogenicity.

585

586 **5. Conclusions**

587 Leaching experiments on fresh ash samples from Etna 2011, Etna 2012 and
588 Popocatepetl 2012 eruptions highlights some interesting clues about behaviour of
589 compound release in mQ and lake water. Surface analysis on unwashed ash
590 demonstrates the presence of sublimated salts, and their leaching accounts for the
591 observed composition of leachates in mQ water. The balance of leachates in lake water
592 is more complex, due to the reaction of leached compounds with chemical elements
593 dissolved in the lake water.

594 The hydrolysis reactions of the leached compounds accounts also for the observed pH
595 variations in mQ and lake water, with Etna 2011-2012 samples that induce
596 alkalisation and Popocatepetl samples that induce acidification of the original water
597 samples.

598 Leaching experiments using different times of stirring (from 30 minutes to 7 days)
599 demonstrate the general poor dependence of compound release versus time, with most
600 of the release concentrated in the first hour of washing.

601 Grain size of ash particles has different and sometimes contrasting effects on release of
602 compounds, with general inverse correlation only for Na⁺, K⁺, Cl⁻, Ca²⁺, Mg²⁺, SO₄²⁻,
603 and Mn²⁺.

604 Saturation calculations highlights how Etna samples are always saturated for F and Si in
605 mQ water, while leachates in lake water are saturated in F, Si, and carbonates, reflecting

606 the contribution of elements already present in the used solvent. Popocatépetl samples
607 show general saturation in some Ca, Si, F, and Fe compounds in mQ water, similar to
608 those calculated for lake water.

609 When compared with limits for potability imposed by European laws, it emerges of
610 both mQ and lake leachates from Etna and Popocatépetl samples are classified as not
611 allowed for human drinking due to the excess of F^- , Mn^{2+} , Fe, and SO_4^{2-} (only
612 Popocatépetl samples).

613 Etna 2012 and Popocatépetl leachates were used also for investigating the potential
614 toxicity on living biota (*Xenopus laevis*). Experiments demonstrated they are mild toxic,
615 and no significant differences exist between the toxic profiles of the two leachates. In
616 particular, no significant increase of embryos deaths was observed, while even at high
617 dilutions the leachates produced more than 20% of malformed larvae.

618

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630

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798 Table 1 – Ash leachates in mQ water for the Etna 2011, Etna 2012 and Popocatépetl
 799 samples with different grain sizes and various time of stirring. In bold are reported the
 800 element concentrations that exceed the potability limits. b.d.l. = below detection limit;
 801 n.a. = not assessed.

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Sample	t (10 ³ s)	pH	Δ pH	Anions (mg/l)						Cations (mg/l)					Trace elements (µg/l)					
				NH ₃	NH ₄ ⁺	F	Cl	NO ₃	SO ₄	Na	K	Mg	Ca	B	Si	Mn	Fe	Hg	As	
mQ water		4,96	-	b.d.l	b.d.l	0	1,09	b.d.l	0,57	0,02	b.d.l	b.d.l	b.d.l	0,28	0,26	2	3,5	b.d.l	b.d.l	
E2011-0.25mm	1,8	6,32	1,36	2,80E-05	0,03	21,29	4,66	b.d.l	41,93	16,05	4,85	3,33	12,89	143,31	3594,99	272,50	880,40	n.a.	n.a.	
E2011-0.25mm	3,6	6,15	1,19	1,82E-05	0,02	20,86	4,03	b.d.l	33,86	14,72	4,33	3,13	11,90	89,25	916,47	194,63	158,00	n.a.	2,68	
E2011-0.25mm	10,8	6,32	1,36	1,09E-04	0,10	20,60	4,25	b.d.l	37,98	13,38	4,49	3,23	13,31	67,32	1420,86	233,88	418,00	n.a.	1,8	
E2011-0.25mm	21,6	5,93	0,97	1,51E-05	0,03	19,94	4,00	b.d.l	35,06	14,87	4,29	3,28	12,41	58,14	1403,52	216,00	78,13	n.a.	n.a.	
E2011-0.25mm	43,2	6,29	1,33	1,42E-04	0,14	21,02	4,01	b.d.l	45,52	14,80	5,04	3,96	15,33	53,04	2123,64	280,13	79,00	n.a.	241	
E2011-0.25mm	86,4	6,45	1,49	n.a	n.a	21,38	6,49	1,75	41,14	16,10	5,05	3,94	16,69	48,45	3174,75	n.a.	234,00	n.a.	n.a.	
E2011-0.50 mm	1,8	6,03	1,07	1,83E-05	0,03	15,67	3,32	b.d.l	8,87	6,72	2,55	3,11	9,61	105,06	673,71	133,25	317,75	n.a.	0,92	
E2011-0.50 mm	3,6	6,01	1,05	1,69E-05	0,03	16,64	3,74	b.d.l	9,26	6,32	2,34	3,20	10,00	82,11	668,61	134,88	154,50	n.a.	n.a.	
E2011-0.50 mm	10,8	6,05	1,09	8,29E-06	0,01	16,55	3,95	b.d.l	11,82	7,84	2,88	3,40	9,81	58,14	1151,58	149,75	98,50	n.a.	0,92	
E2011-0.50 mm	21,6	6,14	1,18	2,25E-05	0,03	17,59	3,04	b.d.l	10,20	7,15	2,55	3,57	10,00	430,44	2361,81	164,63	449,50	n.a.	0,51	
E2011-0.50 mm	43,2	6,05	1,09	1,42E-05	0,02	17,19	2,80	b.d.l	9,41	7,20	2,62	3,65	10,32	240,72	1378,02	147,25	16,75	n.a.	n.a.	
E2011-0.50 mm	86,4	6,11	1,15	2,93E-05	0,04	17,36	3,34	b.d.l	9,35	7,52	2,72	3,74	10,41	178,50	2656,14	157,25	307,13	n.a.	n.a.	
E2011-0.50 mm	259,2	6,40	1,44	8,85E-05	0,07	18,03	3,79	b.d.l	10,33	7,91	2,94	4,04	11,81	n.a.	4671,83	n.a.	n.a.	n.a.	n.a.	
E2011-0.50 mm	432	6,48	1,52	8,75E-05	0,06	17,99	3,30	0,52	9,84	8,04	3,02	4,12	11,84	n.a.	5645,58	n.a.	n.a.	n.a.	n.a.	
E2011-0.50 mm	604,8	6,56	1,60	8,25E-05	0,04	17,96	2,80	0,52	9,85	8,18	3,10	4,19	11,88	271,83	6619,33	210,75	166,00	n.a.	n.a.	
E2011-1 mm	1,8	5,76	0,80	n.a	n.a	19,67	2,99	b.d.l	7,17	6,73	1,71	2,16	7,66	435,03	462,57	123,25	22,50	n.a.	0,46	
E2011-1 mm	3,6	5,82	0,86	8,11E-06	0,02	20,29	3,03	b.d.l	7,79	7,94	1,88	2,35	8,43	236,64	3746,97	134,56	736,00	n.a.	n.a.	
E2011-1 mm	10,8	5,95	0,99	1,07E-05	0,02	20,81	2,95	b.d.l	7,09	6,83	1,77	2,42	7,94	176,46	532,44	145,88	121,50	n.a.	0,77	
E2011-1 mm	21,6	5,64	0,88	1,40E-05	0,06	20,84	2,85	b.d.l	7,24	7,39	2,04	2,58	8,47	145,35	1325,49	158,50	468,63	n.a.	0,77	
E2011-1 mm	43,2	5,91	0,95	7,86E-05	0,19	21,19	2,99	b.d.l	7,31	7,55	2,09	2,66	8,79	132,86	2002,26	167,94	313,31	n.a.	0,44	
E2011-1 mm	86,4	6,18	1,22	2,44E-04	0,31	21,54	3,13	b.d.l	7,39	7,72	2,13	2,75	9,11	120,36	2679,03	177,38	158,00	n.a.	0,1	
E2011-1 mm	259,2	6,70	1,74	6,45E-05	0,02	21,32	2,98	b.d.l	6,93	7,62	2,28	3,06	9,40	216,83	#####	212,63	1470,38	n.a.	n.a.	
E2011-1 mm	432	6,70	1,74	8,52E-05	0,02	21,33	3,02	b.d.l	7,44	8,10	2,49	3,23	9,99	n.a.	n.a.	208,38	798,31	n.a.	n.a.	
E2011-1 mm	604,8	6,69	1,73	1,06E-04	0,04	21,35	3,06	b.d.l	7,96	8,58	2,70	3,39	10,57	n.a.	n.a.	204,13	126,25	n.a.	n.a.	
E2012-1 mm	1,8	6,70	1,74	1,66E-04	0,06	9,50	7,14	b.d.l	3,54	6,00	9,00	2,50	8,50	228,48	1048,05	101,25	170,00	n.a.	0,82	
E2012-1 mm	3,6	6,65	1,69	1,70E-03	0,74	9,05	7,56	b.d.l	4,38	6,00	9,50	2,50	9,00	126,99	201,45	n.a.	80,00	n.a.	n.a.	
E2012-1 mm	10,8	6,59	1,63	8,04E-04	0,39	9,50	7,24	b.d.l	n.a	6,25	9,50	2,75	9,75	115,26	361,34	n.a.	42,75	n.a.	n.a.	
E2012-1 mm	21,6	6,54	1,58	9,45E-05	0,05	9,94	6,91	b.d.l	n.a.	6,50	9,50	3,00	10,50	103,53	521,22	92,50	5,50	n.a.	n.d.	
E2012-1 mm	43,2	6,40	1,44	1,39E-04	0,11	10,93	6,66	b.d.l	3,65	5,50	9,00	3,00	10,50	84,66	1646,79	108,75	91,00	n.a.	n.a.	
E2012-1 mm	86,4	6,37	1,41	5,83E-05	0,05	10,56	6,86	b.d.l	3,48	6,00	9,50	3,00	10,00	71,91	1958,91	105,75	44,00	n.a.	0,41	
E2012-1 mm	259,2	6,58	1,62	4,25E-05	0,02	11,45	7,66	b.d.l	3,98	7,50	10,00	3,50	18,50	209,00	3378,33	67,50	286,75	n.a.	n.a.	
E2012-1 mm	432	6,71	1,75	1,09E-04	0,04	11,19	n.a.	b.d.l	n.a.	7,50	10,00	3,75	n.a.	189,50	3816,73	105,13	348,88	n.a.	n.a.	
E2012-1 mm	604,8	6,83	1,87	2,15E-04	0,06	10,93	28,25	b.d.l	44,19	7,50	10,00	4,00	12,00	170,00	4255,13	142,75	411,00	n.a.	n.a.	
Po2012-0.125 mm	1,8	4,52	-0,44	1,59E-05	0,93	3,39	8,45	b.d.l	441,14	28,19	2,34	30,09	85,04	228,67	218,17	774,50	4194,00	n.a.	0,2	
Po2012-0.125 mm	3,6	4,57	-0,39	1,31E-05	0,68	3,42	10,22	b.d.l	466,39	28,31	2,33	28,04	92,23	206,33	297,33	784,00	3873,25	n.a.	0,21	
Po2012-0.125 mm	10,8	4,55	-0,41	1,16E-05	0,63	4,27	6,01	b.d.l	495,46	29,80	3,01	29,97	104,55	214,25	368,75	776,00	3732,25	n.a.	0,56	
Po2012-0.125 mm	21,6	4,54	-0,42	1,36E-05	0,76	4,67	7,12	b.d.l	519,61	30,61	2,91	31,85	109,93	281,54	378,17	926,88	4883,13	n.a.	n.a.	
Po2012-0.125 mm	43,2	4,62	-0,34	1,34E-05	0,62	4,94	6,16	b.d.l	496,57	30,74	3,10	30,44	111,30	348,83	547,83	524,67	2371,67	n.a.	0,62	
Po2012-0.125 mm	86,4	4,7	-0,26	1,82E-05	0,70	3,70	5,27	b.d.l	505,98	29,57	2,83	32,21	111,53	241,83	740,00	794,70	5027,60	n.a.	0,71	
Po2012-0.125 mm	259,2	4,59	-0,37	1,57E-05	0,78	4,35	6,52	b.d.l	528,55	32,60	3,51	32,98	121,35	236,00	1695,00	836,00	3422,83	n.a.	0,1	
Po2012-0.125 mm	432	4,88	-0,10	2,48E-05	0,66	4,25	9,91	b.d.l	511,45	36,65	6,54	31,58	117,61	337,00	#####	861,25	9336,38	n.a.	0,58	
Po2012-0.125 mm	604,8	4,88	-0,08	2,28E-05	0,58	4,33	8,07	b.d.l	531,74	32,75	3,39	32,45	120,76	327,75	2326,75	795,75	2565,75	n.a.	0,67	
Po2012-0.063 mm	1,8	4,01	-0,95	1,01E-05	1,91	3,35	10,1	1,33	492,00	39,64	1,92	43,64	114,31	94,26	446,20	2510,84	6101,33	n.a.	n.a.	
Po2012-0.063 mm	3,6	4,04	-0,92	1,87E-05	3,29	5,29	13,6	2,1	770,00	49,67	2,79	60,53	213,86	84,38	468,46	2916,22	7302,96	n.a.	n.a.	
Po2012-0.063 mm	10,8	4,07	-0,89	2,02E-05	3,32	6,52	14,1	1,63	856,00	55,80	4,47	63,33	234,88	237,00	538,82	1607,35	1808,90	n.a.	n.a.	
Po2012-0.063 mm	21,6	4,05	-0,91	1,85E-05	3,18	7,49	14,1	1,96	854,00	54,06	3,98	60,31	231,09	268,41	775,85	1887,96	1458,51	n.a.	n.a.	
Po2012-0.063 mm	43,2	4,24	-0,72	3,26E-05	3,63	6,58	12,7	1,47	785,00	48,45	7,25	56,71	219,33	78,47	1153,76	2165,58	2483,33	n.a.	n.a.	
Po2012-0.063 mm	86,4	4,13	-0,83	2,44E-05	3,49	7,63	14,3	2,4	899,00	55,50	3,48	65,64	269,38	102,45	2809,21	2635,04	n.a.	n.a.	n.a.	
Po2012-0.063 mm	259,2	4,15	-0,81	2,42E-05	3,31	10,3	13,1	b.d.l	856,00	53,5	4,3									

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809 Table 2 - Ash leachates concentrations in lake water and pH values for the Etna 2011,
 810 Etna 2012 and Popocatépetl samples with different grain sizes and various time of
 811 stirring. In bold are reported the element concentrations that exceed the potability limits.
 812 b.d.l. = below detection limit; n.a. = not assessed.

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Sample	t (10 ³ s)	pH	Δ pH	Anions (mg/l)				Cations (mg/l)				Trace elements (µg/l)							
				NH ₃	NH ₄ ⁺	F	Cl	NO ₃	SO ₄	Na	K	Mg	Ca	B	Si	Mn	Fe	Hg	As
mQ water		4,96	-	b.d.l	b.d.l	0	1,09	b.d.l	0,57	0,02	b.d.l	b.d.l	b.d.l	0,28	0,26	2	3,5	b.d.l	b.d.l
E2011-0.25mm	1,8	6,32	1,36	2,80E-05	0,03	21,29	4,66	b.d.l	41,93	16,05	4,85	3,33	12,89	143,31	3594,99	272,50	880,40	n.a.	n.a.
E2011-0.25mm	3,6	6,15	1,19	1,82E-05	0,02	20,86	4,03	b.d.l	33,86	14,72	4,33	3,13	11,90	89,25	916,47	194,63	156,00	n.a.	2,68
E2011-0.25mm	10,8	6,32	1,36	1,09E-04	0,10	20,60	4,25	b.d.l	37,98	13,38	4,49	3,23	13,31	67,32	1420,86	233,88	418,00	n.a.	1,8
E2011-0.25mm	21,6	5,93	0,97	1,51E-05	0,03	19,94	4,00	b.d.l	35,06	14,87	4,29	3,28	12,41	58,14	1403,52	216,00	78,13	n.a.	n.a.
E2011-0.25mm	43,2	6,29	1,33	1,42E-04	0,14	21,02	4,01	b.d.l	45,52	14,80	5,04	3,98	15,33	53,04	2123,64	280,13	79,00	n.a.	241
E2011-0.25mm	86,4	6,45	1,49	n.a	n.a	21,38	6,49	1,75	41,14	16,10	5,05	3,84	16,69	48,45	3174,75	n.a.	234,00	n.a.	n.a.
E2011-0.50 mm	1,8	6,03	1,07	1,83E-05	0,03	15,67	3,32	b.d.l	8,87	6,72	2,55	3,11	9,61	105,06	673,71	133,25	317,75	n.a.	0,92
E2011-0.50 mm	3,6	6,01	1,05	1,69E-05	0,03	16,64	3,74	b.d.l	9,26	6,32	2,34	3,20	10,00	82,11	688,61	134,88	154,50	n.a.	n.a.
E2011-0.50 mm	10,8	6,05	1,09	8,29E-06	0,01	16,55	3,95	b.d.l	11,62	7,84	2,68	3,40	9,81	58,14	1151,58	149,75	98,50	n.a.	0,92
E2011-0.50 mm	21,6	6,14	1,18	2,25E-05	0,03	17,59	3,04	b.d.l	10,20	7,15	2,55	3,57	10,00	430,44	2361,81	164,63	449,50	n.a.	0,51
E2011-0.50 mm	43,2	6,05	1,09	1,42E-05	0,02	17,19	2,90	b.d.l	9,41	7,20	2,82	3,65	10,32	240,72	1378,02	147,25	16,75	n.a.	n.a.
E2011-0.50 mm	86,4	6,11	1,15	2,93E-05	0,04	17,36	3,34	b.d.l	9,35	7,52	2,72	3,74	10,41	178,50	2659,14	157,25	307,13	n.a.	n.a.
E2011-0.50 mm	259,2	6,40	1,44	8,85E-05	0,07	18,03	3,79	b.d.l	10,33	7,91	2,94	4,04	11,81	n.a.	4671,83	n.a.	n.a.	n.a.	n.a.
E2011-0.50 mm	432	6,48	1,52	8,75E-05	0,06	17,99	3,30	0,52	9,84	8,04	3,02	4,12	11,84	n.a.	5645,58	n.a.	n.a.	n.a.	n.a.
E2011-0.50 mm	604,8	6,56	1,60	8,25E-05	0,04	17,96	2,80	0,52	9,35	8,18	3,10	4,19	11,88	271,83	6619,33	210,75	166,00	n.a.	n.a.
E2011-1 mm	1,8	5,76	0,80	n.a	n.a	19,67	2,99	b.d.l	7,17	6,73	1,71	2,16	7,66	435,03	482,57	123,25	22,50	n.a.	0,46
E2011-1 mm	3,6	5,82	0,86	8,11E-06	0,02	20,29	3,03	b.d.l	7,79	7,94	1,88	2,35	8,43	236,64	3746,97	134,56	736,00	n.a.	n.a.
E2011-1 mm	10,8	5,95	0,99	1,07E-05	0,02	20,81	2,95	b.d.l	7,09	6,83	1,77	2,42	7,94	176,46	532,44	145,88	121,50	n.a.	0,77
E2011-1 mm	21,6	5,64	0,68	1,40E-05	0,06	20,84	2,85	b.d.l	7,24	7,39	2,04	2,58	8,47	145,35	1325,49	158,50	468,63	n.a.	0,77
E2011-1 mm	43,2	5,91	0,95	7,88E-05	0,19	21,19	2,99	b.d.l	7,31	7,55	2,09	2,66	8,79	132,86	2002,26	167,94	313,31	n.a.	0,44
E2011-1 mm	86,4	6,18	1,22	2,44E-04	0,31	21,54	3,13	b.d.l	7,39	7,72	2,13	2,75	9,11	120,36	2679,03	177,38	158,00	n.a.	0,1
E2011-1 mm	259,2	6,70	1,74	6,45E-05	0,02	21,32	2,98	b.d.l	6,93	7,62	2,28	3,06	9,40	216,83	#####	212,63	1470,38	n.a.	n.a.
E2011-1 mm	432	6,70	1,74	8,52E-05	0,03	21,33	3,02	b.d.l	7,44	8,10	2,49	3,23	9,99	n.a.	n.a.	208,38	798,31	n.a.	n.a.
E2011-1 mm	604,8	6,69	1,73	1,06E-04	0,04	21,35	3,06	b.d.l	7,96	8,58	2,70	3,39	10,57	n.a.	n.a.	204,13	126,25	n.a.	n.a.
E2012-1 mm	1,8	6,70	1,74	1,66E-04	0,06	9,50	7,14	b.d.l	3,54	6,00	9,00	2,50	8,50	228,48	1048,05	101,25	170,00	n.a.	0,82
E2012-1 mm	3,6	6,65	1,69	1,70E-03	0,74	9,05	7,56	b.d.l	4,38	6,00	9,50	2,50	9,00	126,99	201,45	n.a.	80,00	n.a.	n.a.
E2012-1 mm	10,8	6,50	1,63	8,04E-04	0,39	9,50	7,24	b.d.l	n.a	6,25	9,50	2,75	9,75	115,26	361,34	n.a.	42,75	n.a.	n.a.
E2012-1 mm	21,6	6,54	1,58	9,45E-05	0,05	9,94	6,91	b.d.l	n.a.	6,50	9,50	3,00	10,50	103,53	521,22	92,50	5,50	n.a.	n.d.
E2012-1 mm	43,2	6,40	1,44	1,39E-04	0,11	10,93	6,66	b.d.l	3,85	5,50	9,00	3,00	10,50	84,66	1648,79	108,75	91,00	n.a.	n.a.
E2012-1 mm	86,4	6,37	1,41	5,83E-05	0,05	10,56	6,86	b.d.l	3,48	6,00	9,50	3,00	10,00	71,91	1958,91	105,75	44,00	n.a.	0,41
E2012-1 mm	259,2	6,58	1,62	4,26E-05	0,02	11,45	7,66	b.d.l	3,98	7,50	10,00	3,50	18,50	209,00	3378,33	67,50	286,75	n.a.	n.a.
E2012-1 mm	432	6,71	1,75	1,09E-04	0,04	11,19	n.a.	b.d.l	n.a.	7,50	10,00	3,75	n.a.	189,50	3816,73	105,13	348,88	n.a.	n.a.
E2012-1 mm	604,8	6,83	1,87	2,15E-04	0,06	10,93	28,25	b.d.l	44,19	7,50	10,00	4,00	12,00	170,00	4255,13	142,75	411,00	n.a.	n.a.
Po2012-0.125 mm	1,8	4,52	-0,44	1,59E-05	0,93	3,39	8,45	b.d.l	441,14	28,19	2,34	30,09	85,04	228,67	218,17	774,50	4194,00	n.a.	0,2
Po2012-0.125 mm	3,6	4,57	-0,39	1,31E-05	0,68	3,42	10,22	b.d.l	466,39	28,31	2,33	28,04	92,23	206,33	297,33	784,00	3873,25	n.a.	0,21
Po2012-0.125 mm	10,8	4,55	-0,41	1,16E-05	0,63	4,27	6,01	b.d.l	495,46	29,80	3,01	29,97	104,55	214,25	368,75	776,00	3732,25	n.a.	0,56
Po2012-0.125 mm	21,6	4,54	-0,42	1,36E-05	0,76	4,67	7,12	b.d.l	519,61	30,61	2,91	31,85	109,93	281,54	378,17	926,88	4883,13	n.a.	n.a.
Po2012-0.125 mm	43,2	4,62	-0,34	1,34E-05	0,62	4,94	6,16	b.d.l	496,57	30,74	3,10	30,44	111,30	348,83	747,83	524,67	2371,67	n.a.	0,62
Po2012-0.125 mm	86,4	4,7	-0,26	1,82E-05	0,70	3,70	5,27	b.d.l	505,98	29,57	2,83	32,21	111,53	241,83	580,00	794,70	5027,60	n.a.	0,71
Po2012-0.125 mm	259,2	4,59	-0,37	1,57E-05	0,78	4,35	6,52	b.d.l	528,55	32,60	3,51	32,98	121,35	236,00	1695,00	836,00	3422,83	n.a.	0,1
Po2012-0.125 mm	432	4,86	-0,10	2,48E-05	0,66	4,25	9,91	b.d.l	511,45	36,65	6,54	31,58	117,61	337,00	#####	861,25	9336,38	n.a.	0,56
Po2012-0.125 mm	604,8	4,88	-0,08	2,28E-05	0,58	4,33	8,07	b.d.l	531,74	32,75	3,39	32,45	120,76	327,75	2326,75	795,75	2565,75	n.a.	0,67
Po2012-0.063 mm	1,8	4,01	-0,95	1,01E-05	1,91	3,35	10,1	1,33	492,00	39,64	1,92	43,64	114,31	94,26	446,20	2510,84	6101,53	n.a.	n.a.
Po2012-0.063 mm	3,6	4,04	-0,92	1,87E-05	3,29	5,29	13,6	2,1	770,00	49,67	2,79	60,53	213,86	84,38	468,46	2916,22	7302,96	n.a.	n.a.
Po2012-0.063 mm	10,8	4,07	-0,89	2,02E-05	3,32	6,52	14,1	1,63	856,00	55,80	4,47	63,33	234,98	237,00	538,82	1607,35	1808,90	n.a.	n.a.
Po2012-0.063 mm	21,6	4,05	-0,91	1,85E-05	3,18	7,49	14,1	1,96	854,00	54,06	3,98	60,31	231,09	268,41	775,85	1887,96	1458,51	n.a.	n.a.
Po2012-0.063 mm	43,2	4,24	-0,72	3,26E-05	3,63	6,58	12,7	1,47	785,00	48,45	7,25	56,71	219,33	78,47	1153,76	2165,58	2483,93	n.a.	n.a.
Po2012-0.063 mm	86,4	4,13	-0,83	2,44E-05	3,49	7,63	14,3	2,4	899,00	55,50	3,48	65,64	269,38	102,45	2809,21	2635,04	n.a.	n.a.	n.a.
Po2012-0.063 mm	259,2	4,15	-0,81	2,42E-05	3,31	10,3	13,1	b.d.l	856,00	53,5	4,3	62,8	280	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Po2012-0.063 mm	432	4,18	-0,78	2,70E-05	3,45	10,6	12,8	b.d.l	845,00	56,1	3,5	66,1	275	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

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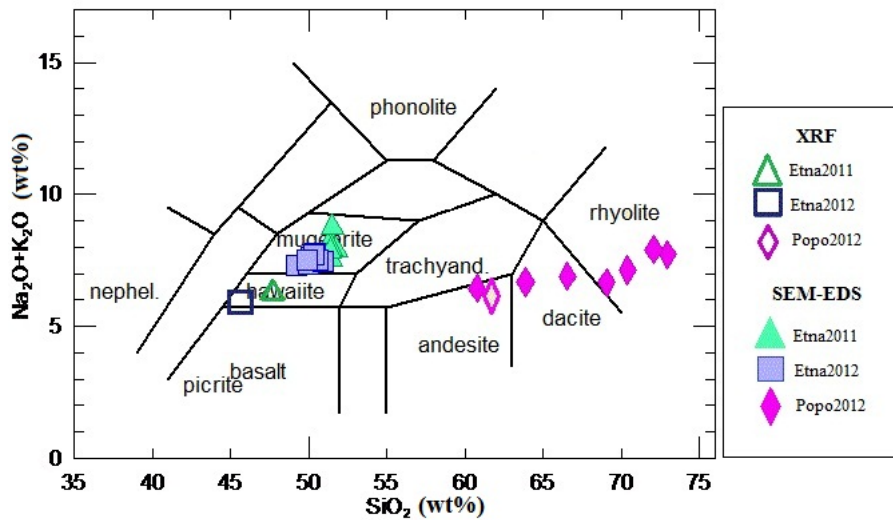
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818

819 Table 3 – Net release of leachates in lake water for the Etna 2011, Etna 2012 and
 820 Popocatepetl samples with different grain sizes and various time of stirring. In *Italic* are
 821 reported the negative release of elements in lake water. b.d.l. = below detection limit;
 822 n.a. = not assessed.

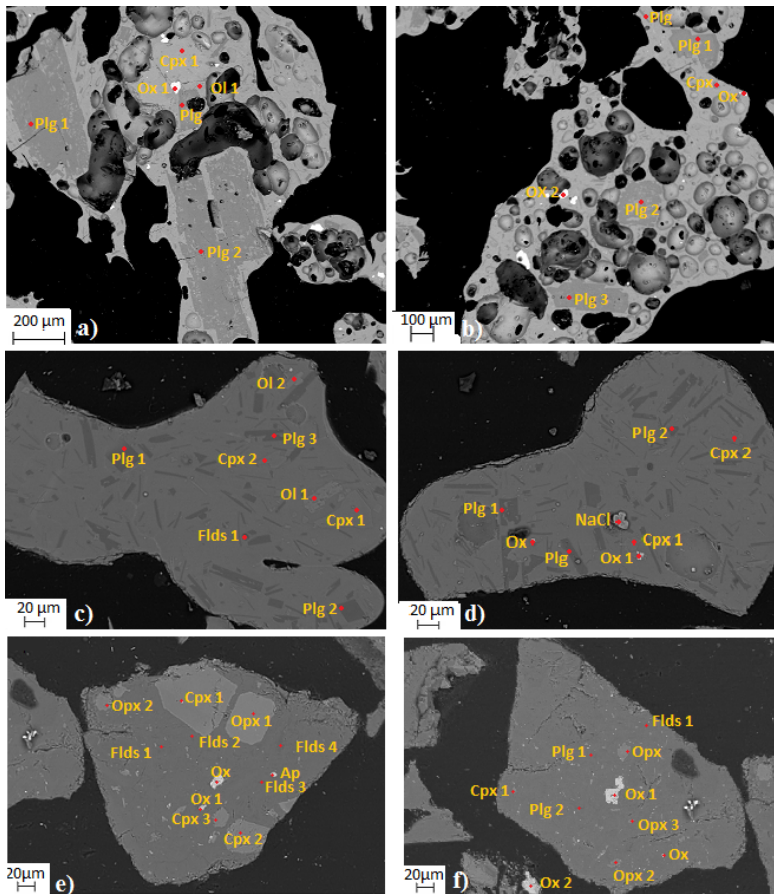
Sample	t (10 ³ s)	Anions (mg/l)				Cations (mg/l)				Trace elements (µg/l)			
		F	Cl	SO ₄	Na	K	Mg	Ca	B	Si	Mn	Fe	As
E12/08/2011-1 mm	1,8	11,88	2,51	6,40	5,76	0,90	1,18	9,79	<i>-240,00</i>	<i>-110,00</i>	104,37	892,63	-0,22
E12/08/2011-1 mm	3,6	11,96	1,00	6,48	7,98	1,29	1,74	13,52	<i>-240,00</i>	10,00	73,85	66,48	-0,28
E12/08/2011-1 mm	10,8	12,90	2,59	6,26	5,62	1,12	1,83	10,79	<i>-240,00</i>	1660,00	94,62	329,88	5,47
E12/08/2011-1 mm	21,6	14,07	2,62	6,55	4,38	0,64	<i>-0,17</i>	5,05	<i>-235,00</i>	1305,00	-1,25	62,88	-0,84
E12/08/2011-1 mm	43,2	13,48	4,07	6,81	4,67	0,49	1,28	5,23	<i>-230,00</i>	950,00	90,62	120,38	-0,04
E12/08/2011-1 mm	86,4	14,07	3,37	6,45	5,48	0,42	0,55	7,68	<i>-120,00</i>	1470,00	96,75	365,38	0,29
E12/08/2011-1 mm	259,2	14,79	2,24	6,53	6,39	1,40	1,98	11,29	<i>-120,00</i>	n.a.	86,00	103,38	0,45
E12/08/2011-1 mm	432	15,24	2,90	5,95	6,96	0,97	1,39	8,93	<i>-120,00</i>	12100,00	124,75	1557,78	-0,33
E12/08/2011-0.5 mm	1,8	11,75	2,50	7,51	5,46	0,95	0,28	7,32	<i>-220,00</i>	3420,00	111,35	436,88	0,22
E12/08/2011-0.5 mm	3,6	11,55	2,33	8,02	5,76	1,01	1,36	8,74	<i>-120,00</i>	7130,00	161,15	3532,78	0,19
E12/08/2011-0.5 mm	10,8	12,78	2,06	8,37	6,42	1,02	1,54	10,71	<i>-210,00</i>	1090,00	95,75	244,75	0,08
E12/08/2011-0.5 mm	21,6	14,75	3,60	10,51	7,72	1,15	2,62	15,39	<i>-130,00</i>	740,00	100,95	54,38	-0,33
E12/08/2011-0.5 mm	43,2	12,80	2,44	8,65	5,76	0,65	0,55	8,38	<i>-60,00</i>	2010,00	92,25	246,50	0,22
E12/08/2011-0.5 mm	86,4	13,57	2,29	8,42	5,92	0,82	0,27	9,00	<i>-130,00</i>	1720,00	118,35	391,18	0,88
E12/08/2011-0.5 mm	259,2	13,76	2,24	8,97	6,58	1,26	1,78	9,82	<i>-230,00</i>	2760,00	99,50	229,50	-0,04
E12/08/2011-0.5 mm	432	15,87	2,93	10,15	9,24	1,46	2,33	13,77	<i>-120,00</i>	12350,00	n.a.	n.a.	0,63
E24/04/2012-1 mm	1,8	2,27	3,12	1,49	0,52	<i>-0,25</i>	0,01	6,66	<i>-130,00</i>	30,00	2,62	22,63	0,11
E24/04/2012-1 mm	3,6	1,31	0,26	<i>-0,28</i>	0,89	<i>-0,92</i>	0,35	7,55	<i>-180,00</i>	80,00	3,75	38,88	-0,12
E24/04/2012-1 mm	10,8	4,12	2,85	0,83	1,61	0,40	0,55	8,64	<i>120,00</i>	910,00	35,62	260,63	0,19
E24/04/2012-1 mm	21,6	2,54	2,81	2,22	2,20	<i>-0,38</i>	<i>-0,16</i>	7,82	<i>-220,00</i>	1750,00	9,15	97,48	0,32
E24/04/2012-1 mm	43,2	4,30	2,44	0,33	0,57	<i>-0,35</i>	0,36	6,73	<i>-210,00</i>	1260,00	37,00	229,88	0,27
E24/04/2012-1 mm	86,4	4,35	2,98	0,81	0,91	<i>-0,33</i>	0,73	8,68	<i>-130,00</i>	1150,00	38,87	443,13	-0,12
E24/04/2012-1 mm	259,2	4,72	3,04	1,04	2,71	<i>-0,51</i>	1,34	9,44	<i>-100,00</i>	n.a.	47,87	663,88	-0,12
E24/04/2012-1 mm	432	9,21	6,66	3,10	3,97	<i>-0,20</i>	<i>-0,01</i>	6,66	<i>-70,00</i>	11410,00	283,65	11476,38	0,32
E24/04/2012-0.5 mm	1,8	2,42	3,14	2,66	0,91	0,59	<i>-0,30</i>	6,86	<i>-110,00</i>	510,00	5,65	189,08	0,19
E24/04/2012-0.5 mm	3,6	1,66	1,12	0,65	0,58	<i>-0,90</i>	0,25	7,01	<i>-160,00</i>	40,00	7,75	38,13	0,51
E24/04/2012-0.5 mm	10,8	0,97	8,67	0,27	<i>-1,78</i>	<i>-1,68</i>	<i>-0,79</i>	3,91	<i>-280,00</i>	430,00	15,37	338,63	0,19
E24/04/2012-0.5 mm	21,6	4,01	8,38	3,24	1,02	0,18	0,44	8,27	<i>-140,00</i>	1150,00	53,00	250,63	9,87
E24/04/2012-0.5 mm	43,2	1,34	<i>-0,07</i>	<i>-0,13</i>	<i>-1,59</i>	<i>-1,19</i>	<i>-0,09</i>	6,97	<i>-210,00</i>	450,00	13,88	141,88	22,42
E24/04/2012-0.5 mm	86,4	0,65	<i>-0,54</i>	<i>-0,79</i>	<i>-0,45</i>	0,01	<i>-0,03</i>	6,18	<i>-220,00</i>	530,00	5,50	67,50	0,19
Popo2012-0.125 mm	1,8	1,87	4,40	491,45	28,81	1,41	34,29	102,90	<i>-381,22</i>	333,45	1347,67	953,42	n.a.
Popo2012-0.125 mm	3,6	2,35	5,67	477,45	30,39	<i>-0,08</i>	36,85	114,52	<i>-327,78</i>	6914,43	1494,58	2,06	n.a.
Popo2012-0.125 mm	10,8	2,01	3,99	557,45	32,24	0,70	37,58	129,73	<i>-391,75</i>	1718,75	137,83	n.a.	n.a.
Popo2012-0.125 mm	21,6	2,19	3,84	486,45	29,92	2,86	34,02	128,70	<i>-407,41</i>	353,98	1092,48	n.a.	n.a.
Popo2012-0.125 mm	43,2	2,27	4,88	565,45	35,50	0,68	40,34	146,00	<i>-401,55</i>	1053,03	1346,64	n.a.	n.a.
Popo2012-0.125 mm	86,4	2,35	4,28	518,45	31,98	3,72	36,55	131,58	<i>-407,78</i>	107,16	415,00	10,65	n.a.
Popo2012-0.125 mm	259,2	2,90	3,74	535,45	58,32	4,51	71,98	242,00	<i>-388,55</i>	384,04	1528,33	43,84	n.a.
Popo2012-0.125 mm	432	2,95	2,30	568,45	44,32	4,62	86,08	289,00	<i>-273,90</i>	10831,68	2435,71	1904,28	n.a.
Popo2012-0.063 mm	1,8	2,62	12,70	755,45	49,86	3,39	62,11	203,52	<i>-369,02</i>	44,35	627,88	39,03	n.a.
Popo2012-0.063 mm	3,6	2,94	13,60	635,45	46,48	0,95	56,18	148,04	<i>-362,76</i>	42,84	262,00	205,51	n.a.
Popo2012-0.063 mm	10,8	3,04	13,60	807,45	49,93	1,74	60,90	206,11	<i>-357,75</i>	469,15	2099,02	62,49	n.a.
Popo2012-0.063 mm	21,6	5,24	27,70	801,45	44,38	2,62	54,63	216,48	<i>-343,98</i>	937,21	2349,63	n.a.	n.a.
Popo2012-0.063 mm	43,2	2,83	12,30	874,45	48,53	1,72	58,78	217,00	n.a.	n.a.	n.a.	n.a.	n.a.
Popo2012-0.063 mm	86,4	2,95	13,20	851,45	44,38	2,62	54,63	216,48	<i>-286,40</i>	1620,70	2683,38	3309,36	n.a.
Popo2012-0.063 mm	259,2	3,59	12,00	834,45	44,02	2,45	53,08	172,00	n.a.	n.a.	n.a.	n.a.	n.a.
Popo2012-0.063 mm	432	3,50	3,72	854,45	40,32	2,02	49,08	160,00	n.a.	n.a.	n.a.	n.a.	n.a.

823



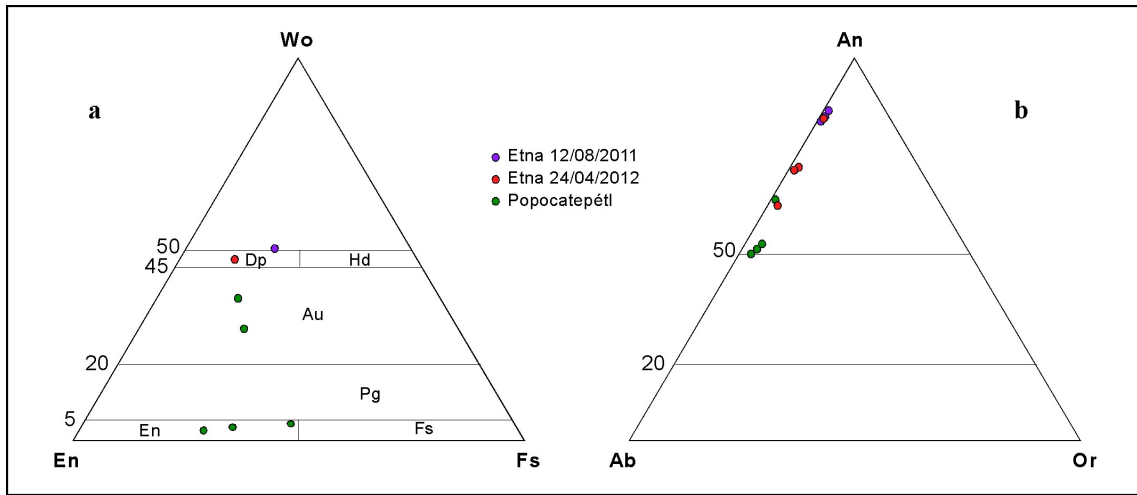
824

825 Figure 1 – Total alkali vs. silica (TAS) diagram for bulk rock and glass analyses of Etna
 826 2011, Etna 2012 and Popocatépetl samples.



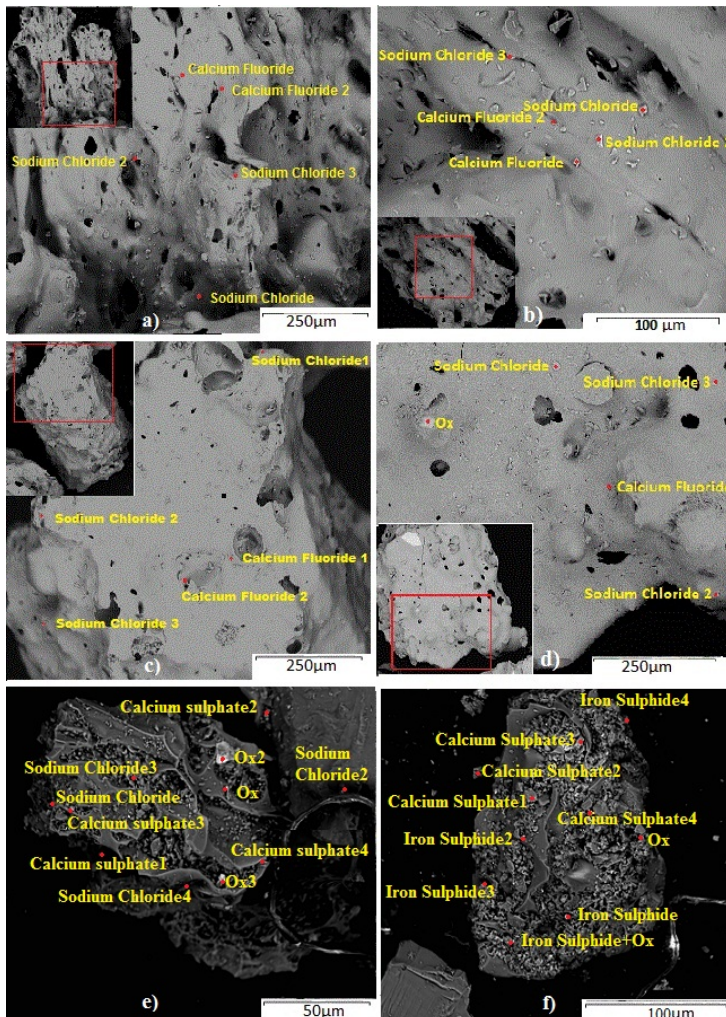
827

828 Figure 2 – BSE-SEM images of polished particles from Etna 2011 (a and b), Etna 2012
 829 (c and d), and Popocatépetl samples (e and f). Cpx = clinopyroxene; Opx =
 830 orthopyroxene; Ox = oxide; Plg = plagioclase; Ol = olivine; Ap = apatite; Flds =
 831 feldspar.



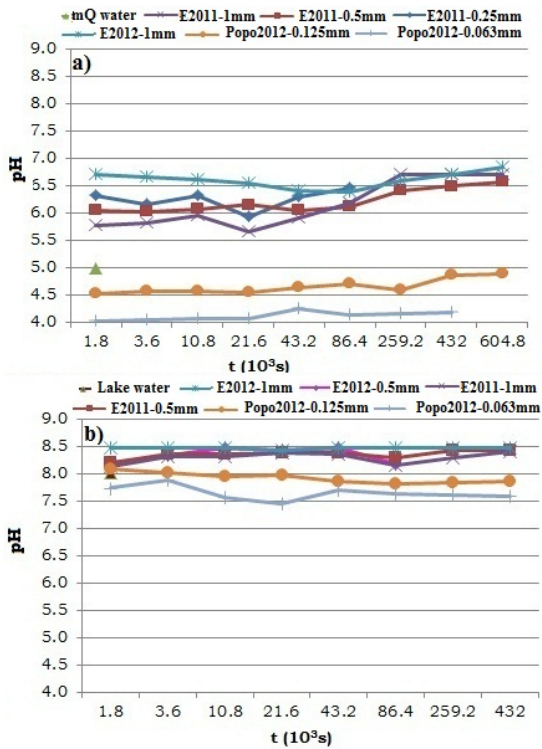
832

833 Figure 3 – Ternary diagrams for the classification of a) pyroxenes and b) feldspars.



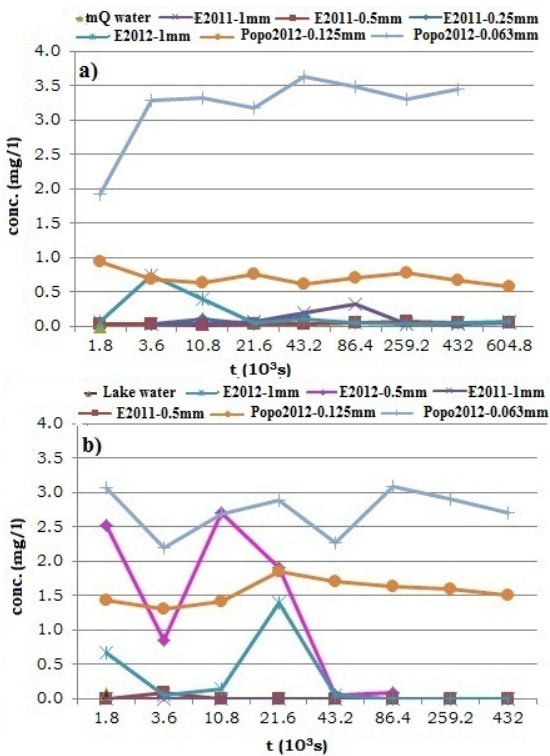
834

835 Figure 4 – SEM-BSE images of fresh ash particles from Etna 2011 (a and b), Etna 2012
 836 (c and d), and Popocatepétl samples (e and f). The inserts in the lower left corner
 837 indicate the investigated area. In yellow are the detected sublimated salts.



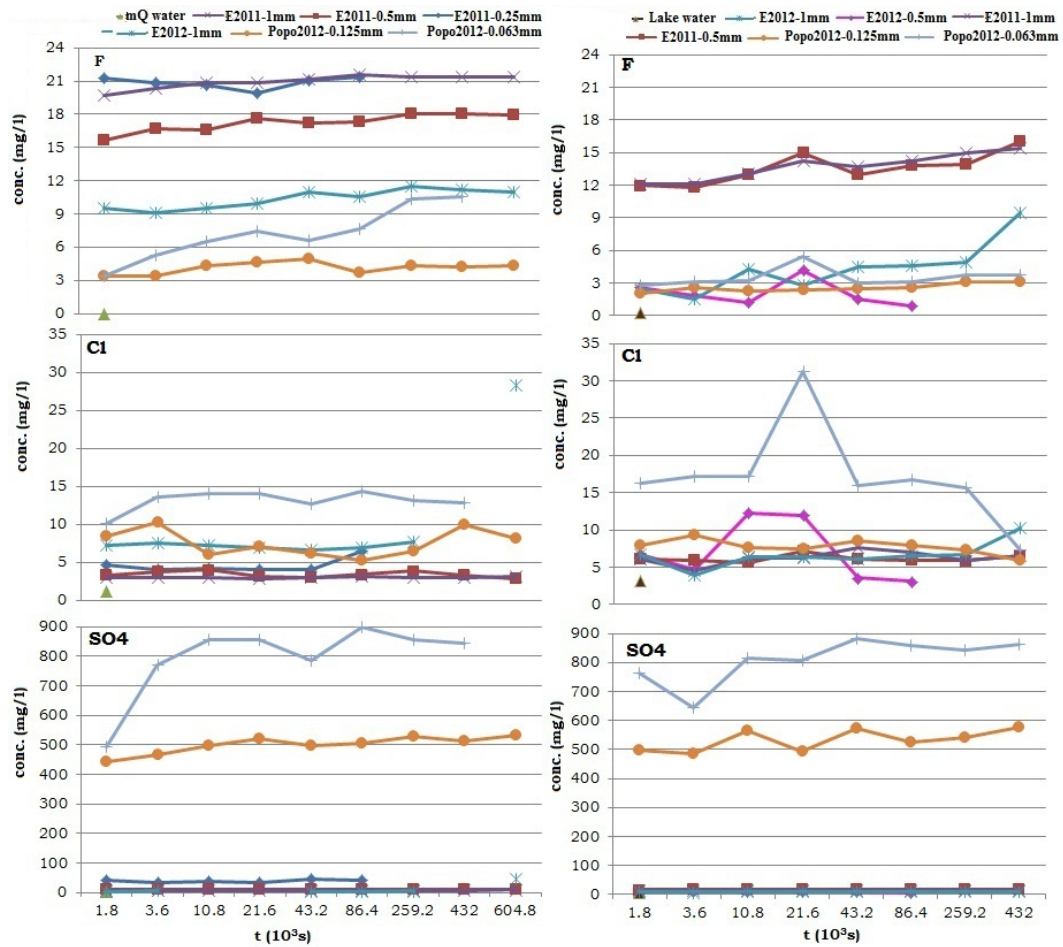
838

839 Figure 5 – a) pH variation of ash leachates in mQ; and, b) pH variation of ash leachates
 840 in lake water. The samples were washed using variable time of stirring and different
 841 grain-size. The pH of mQ and lake water is reported for comparison.



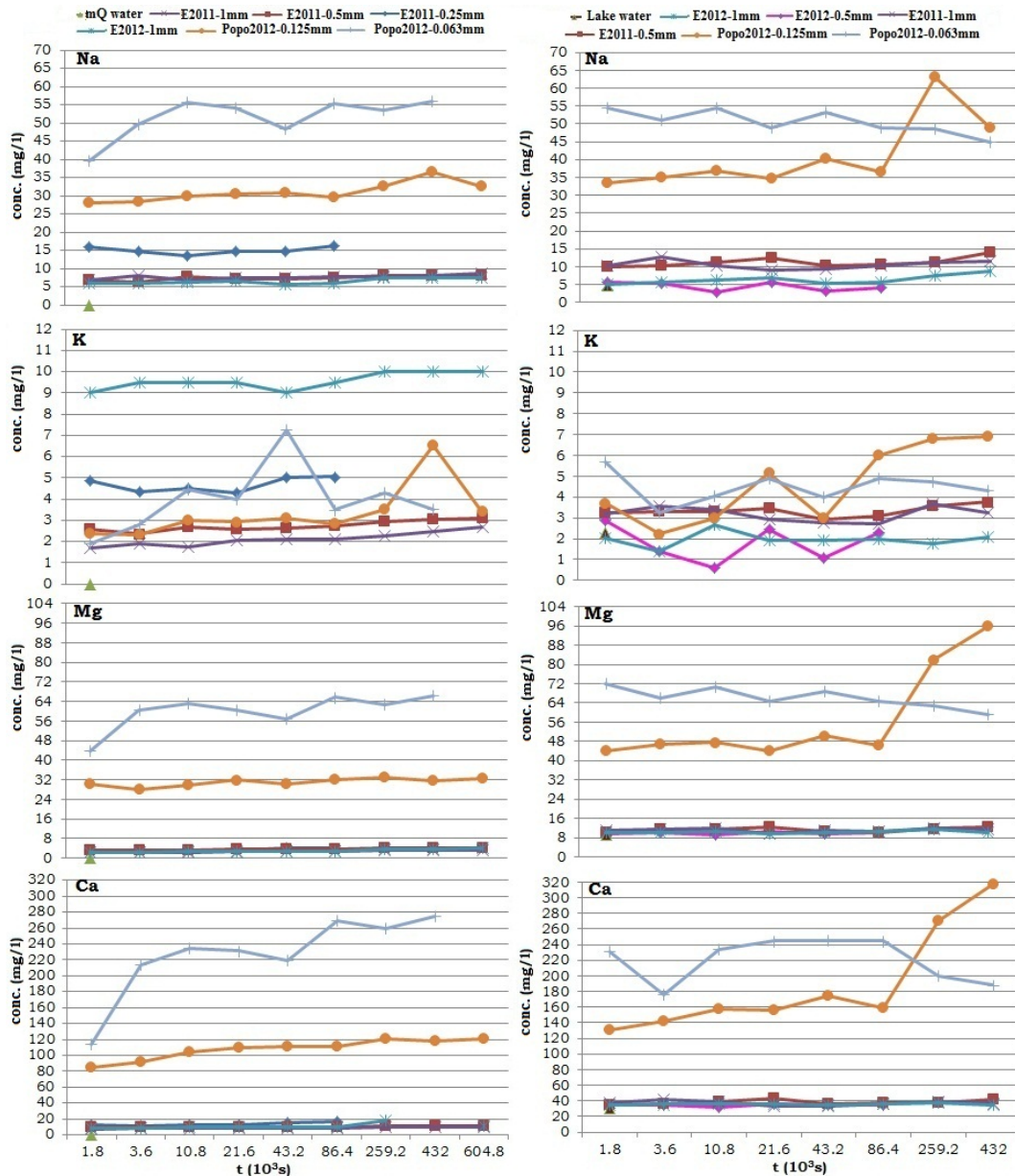
842

843 Figure 6 – $\text{NH}_3\text{-NH}_4^+$ variation of ash leachates in: a) mQ; and, b) lake water for
 844 variable time of stirring and different grain-size. The NH_3 content of mQ and lake water
 845 is reported for comparison.



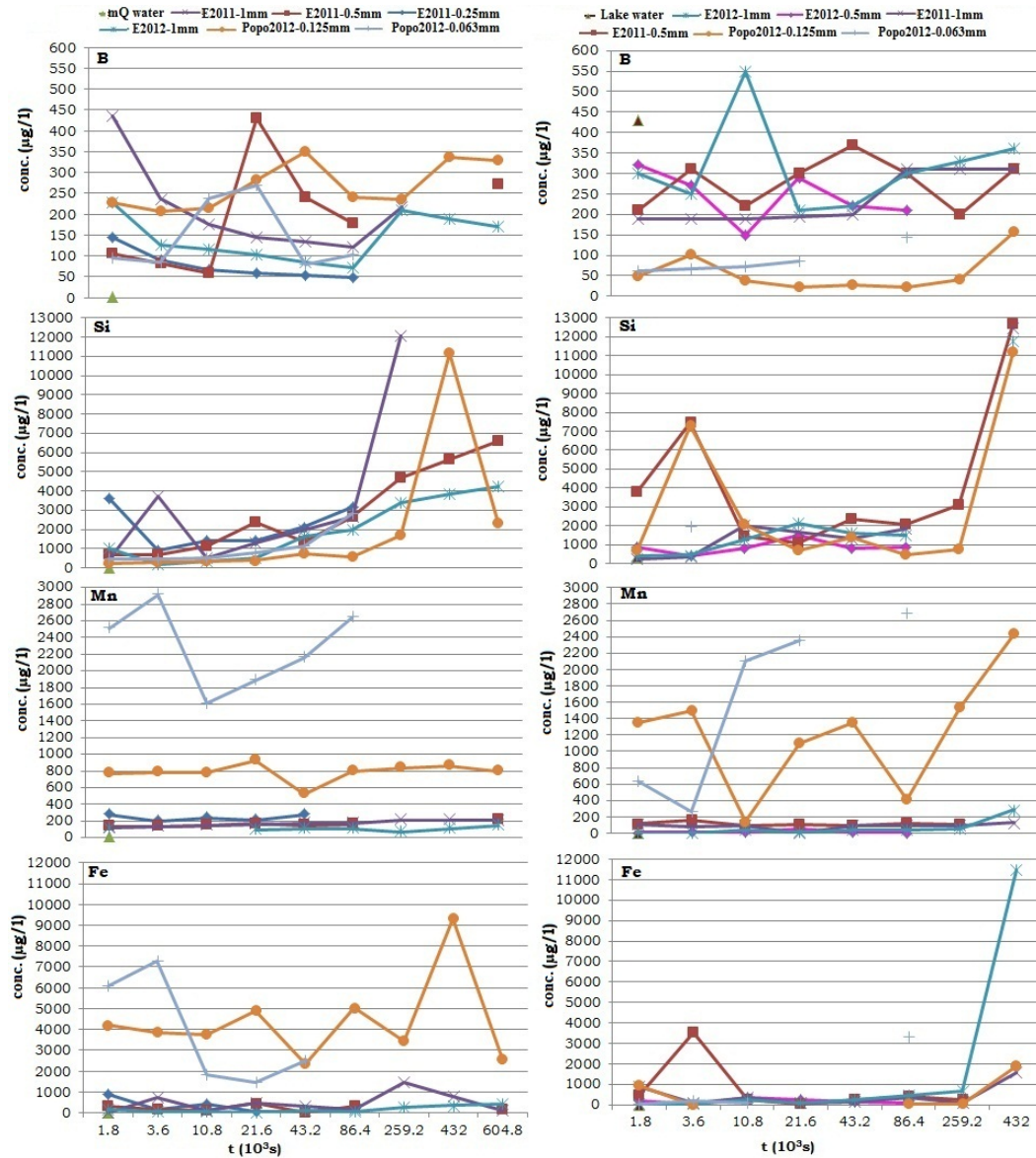
846

847 Figure 7 - Anions (Cl⁻, SO₄²⁻, and F⁻) variation of ash leachates in mQ (left column)
 848 and in lake water (right column) for variable time of stirring and different grain-size.
 849 The different anions contents of mQ and lake water are reported for comparison.



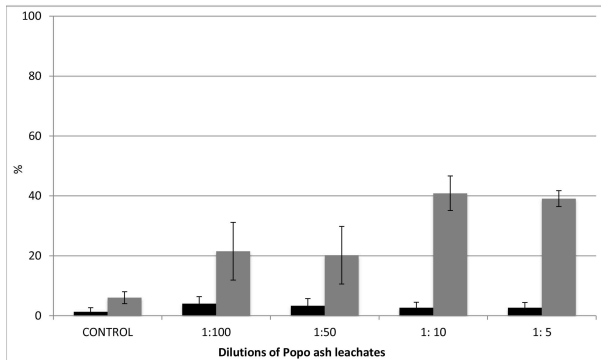
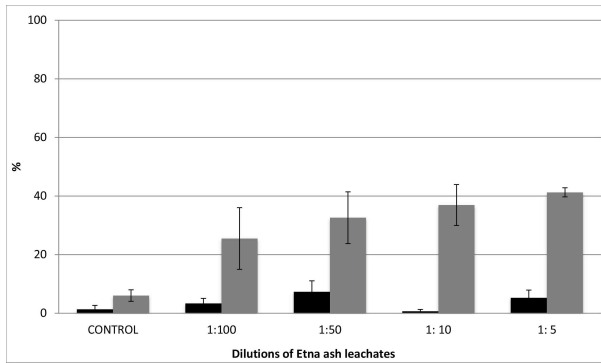
850

851 Figure 8 - Cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) variation of ash leachates in mQ (left
 852 column) and in lake water (right column) for variable time of stirring and different
 853 grain-size. The different cations contents of mQ and lake water are reported for
 854 comparison.



855

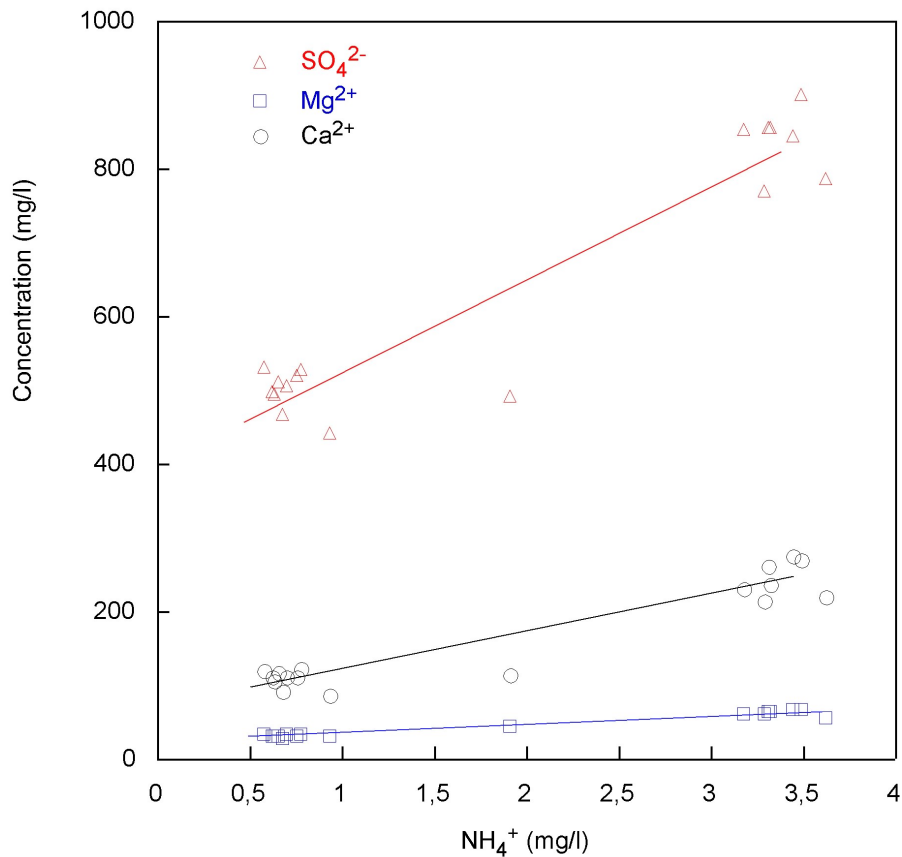
856 Figure 9 – Trace elements (B^- , Si^{2+} , Mn^{2+} , and Fe) variation of ash leachates in mQ (left
 857 column) and in lake water (right column) for variable time of stirring and different
 858 grain-size. The different trace elements contents of mQ and lake water are reported for
 859 comparison.



860

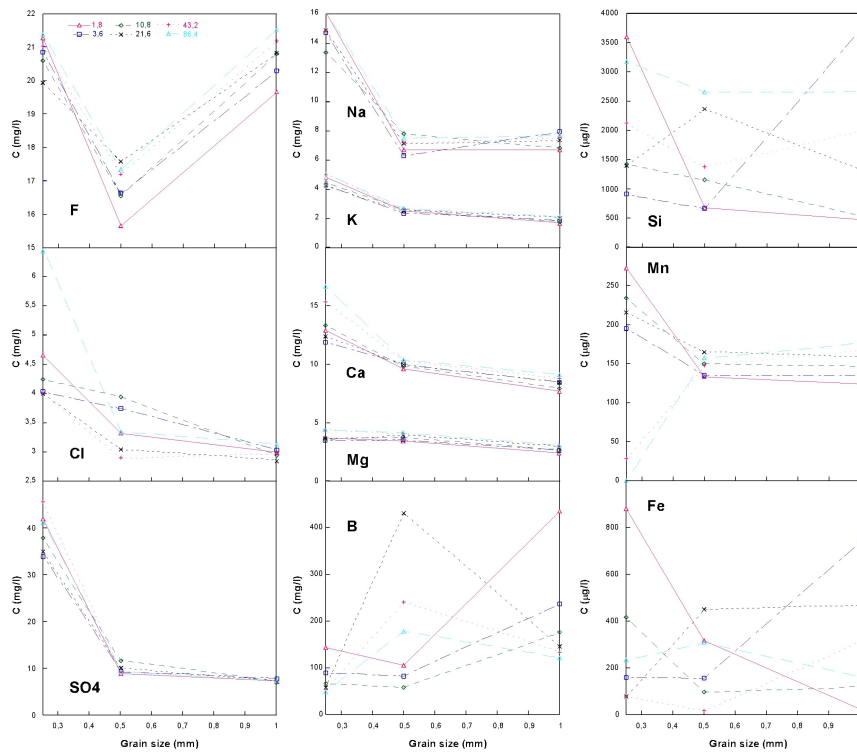
861 Figure 10 – Results of the FETAX test with ash leachates from Etna 2012 (a) and
 862 Popocatepetl (b). Black histograms = mortality %; grey histograms = malformed larvae
 863 %; bars = standard error of the mean.

864



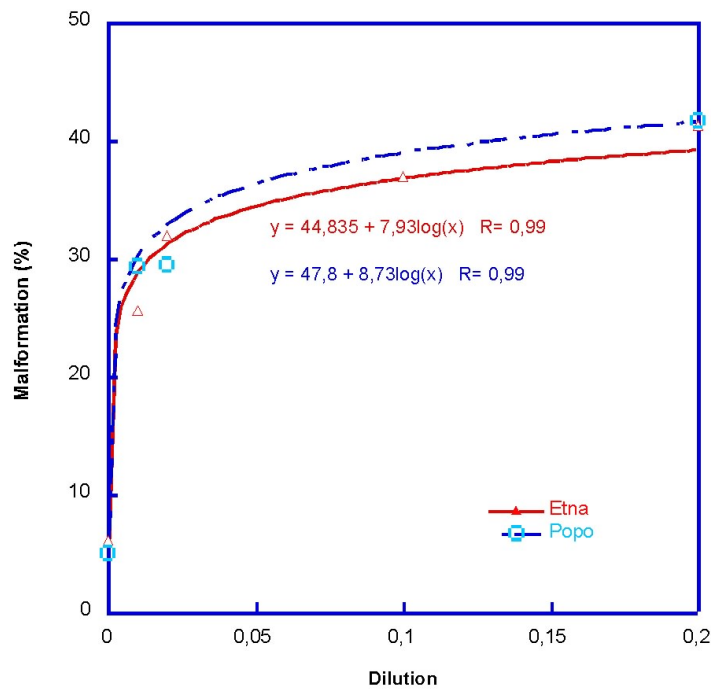
865

866 Figure 11 - Correlation of Ca^{2+} , Mg^{2+} and SO_4^{2-} vs. NH_4^+ for Popocatépetl samples.



867

868 Figure 12 – Dependence of element release to grain-size and times of stirring for Etna
 869 2011 samples. The colours indicate different time of stirring, expressed as seconds \times
 870 10^3 .



871

872 Figure 13 – Malformation of embryos vs. dilution of ash leachates from Etna 2012 and
873 Popocatépetl.