

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**

4  
5 **M. D'Addabbo<sup>1</sup>, R. Sulpizio<sup>1,2</sup>, M. Guidi<sup>3</sup>, G. Capitani<sup>4</sup>, P. Mantecca<sup>4</sup>, G.**  
6 **Zanchetta<sup>5</sup>**

7

8 [1] (Dipartimento di Scienze della Terra e Geoambientali, via Orabona 4, 70125, Bari, Italy)

9 [2] (IDPA-CNR, via M. Bianco 9, Milan, Italy)

10 [3] (IGG-CNR, via Moruzzi 1, Pisa, Italy)

11 [4] (Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Piazza  
12 della Scienza 1, 20126, Milano, Italy)

13 [5] (Dipartimento di Scienze della Terra, via S. Maria 53, 56126, Pisa, Italy)

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 (Ohrid lake, 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 alkalinisation  
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  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  
26  $\text{SO}_4^{2-}$ , and  $\text{Mn}^{2+}$ , 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  $\text{F}^-$ ,  $\text{Mn}^{2+}$ , Fe, and  $\text{SO}_4^{2-}$  (the latter only for Popocatépetl  
32 samples).

mac 7/11/15 21:43

**Eliminato:** Italian

34 Finally, the Etna 2012 and Popocatépetl leachates were used for toxicity experiments on  
35 living biota (*Xenopus laevis*). They are mild toxic, and no significant differences exist  
36 between the toxic profiles of the two leachates. In particular, no significant embryo  
37 mortality was observed, while even at high dilutions the leachates produced more than  
38 20% of malformed larvae.

39

#### 40 **1. Introduction**

41 Volcanic ash is the most widely distributed product of explosive volcanic eruptions, and  
42 areas hundreds of kilometres from an erupting volcano could receive ash falls (Ruggieri  
43 et al., 2010; Sulpizio et al., 2014). Even minor quantities of deposited ash represent a  
44 major hazard for the modern technical society and the environment (Blong, 1984;  
45 Johnston and Houghton, 2000). Deposition of fresh volcanic ash can disrupt power lines  
46 (Wardman et al., 2012), transport networks and water supplies (Martin et al., 2009;  
47 Wilson et al., 2012), or induce pH variations and pollution in soils and surface water,  
48 which have a serious impact on vegetation, animals and people (Ayris and Delmelle,  
49 2012).

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

62 Over 55 soluble components have been reported in volcanic ash leachates, with the  
63 anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{F}^-$  and the cations  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  generally occurring at the  
64 highest concentrations (Witham et al., 2005).

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

Myriam 14/10/15 11:24

Eliminato: i

Myriam 14/10/15 11:24

Eliminato: i

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

79 Impacts of ash on environment have been reported subsequently to a number of historic  
80 eruptions. During the 1783–84 eruption of Laki (Iceland) 50% of the livestock in  
81 Iceland perished, many probably as a result of fluorine poisoning (Thorarinsson, 1969;  
82 Grattan and Charman, 1994; Steingrímsson and Kunz, 1998). After the 1947–48  
83 eruption of Hekla in Iceland, some rivers and streams showed temporarily elevated  
84 fluoride concentrations (up to 9.5 mg/l; Stefánsson and Sigurjónsson, 1957). The ash  
85 from 1969 Ruapehu eruptions contaminated water supplies, with pH values ranging  
86 from 4.4 to 6.0 (Collins, 1978; Stewart et al., 2006). Similar pH values in receiving  
87 waters following volcanic ash deposition have been reported in many other studies

88 (Wilcox and Coats, 1959; Cronin and Sharp, 2002; Smithsonian Institution, 1997). [The](#)  
89 [ash from 2012 Mt. Tongariro eruption \(New Zealand\) had higher concentrations of F<sup>-</sup>,](#)  
90 [Al<sup>3+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> and had generated significant agricultural problems, including](#)  
91 [livestock deaths](#) (Cronin et al., 2014).

92 Several recent eruptions have had high quantities of fluorine adsorbed on the tephra,  
93 including: Hekla, Iceland in 1970, 1991, and 2000 (Frogner et al., 2001; Gudmundsson  
94 and Oskarsson, 1992; Thorarinsson and Sigvaldason, 1972), Lonquimay, Chile in 1989–  
95 1900 (Araya et al., 1990; Araya et al., 1993) and Ruapehu, New Zealand in, 1995–1996  
96 (Shanks, 1997; Cronin et al., 2003).

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

mac 6/11/15 22:32
<b>Formattato:</b> Apice
mac 6/11/15 22:32
<b>Formattato:</b> Apice
mac 6/11/15 22:33
<b>Formattato:</b> Apice
mac 6/11/15 22:33
<b>Formattato:</b> Apice
Myriam 14/10/15 10:59
<b>Formattato:</b> Inglese (Regno Unito)

104 diatoms utilizing nutrients from volcanic ash (Duggen et al., 2007). Mesoscale iron  
105 enrichment experiments have shown that Fe addition to low chlorophyll ocean waters  
106 can instigate elevated marine primary productivity (Boyd et al., 2000).  
107 In order to supply new data useful for understanding the behaviour of release of water  
108 contaminants from fresh volcanic ash and their impact on water supplies and living  
109 organisms, we collected ash deposits from two recent eruptions of Mount Etna (Italy,  
110 August 2011 and April 2012) and from the eruption of May 2012 of Popocatépetl  
111 volcano (Mexico). The collected volcanic ash was washed using two different types of  
112 water (double de-ionised and natural lake water), and the released compounds analysed  
113 for major and trace elements. The results were discussed in the light of international  
114 ([European drinking water directive, 98/83/EC](#)) drinkable limits for public waters.

mac 7/11/15 21:43  
**Eliminato:** and Italian

115 Since the decline of amphibian populations has been retained a major consequence of  
116 the anthropic and naturally occurring environmental changes (Hayes et al., 2010), the  
117 ash leachates were also tested for toxicity using the amphibian *Xenopus laevis* as  
118 biological model. The bioassays were performed using the standardized Frog Embryo  
119 Teratogenesis assay – *Xenopus* (FETAX) (ASTM, 1998), already successfully applied  
120 to eco-toxicological investigations for testing single compounds and mixtures (Dawson,  
121 1991; Bacchetta et al., 2008), municipal sludge (Chenon et al., 2003), material and  
122 sediment extracts (Manteca et al., 2007; Fort et al., 2001).

123

## 124 **2. Materials and methods**

### 125 **2.1 Bulk rock, glass composition and sublimates**

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

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

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

146

## 147 **2.2 Leachates analyses**

148 Two types of water were used for washing the ash samples: double de-ionised (mQ)  
149 water, and Lake Ohrid (Macedonia) water. Lake water was filtered immediately after  
150 sampling through 0.2  $\mu\text{m}$  Millipore membranes (cellulose acetate).

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

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

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

160 The pH of the leachates was measured using a glass electrode (ORION), sensitive of the  
161 activity of  $\text{H}^+$  ions, coupled with an Ion Analyzer EA920 (instrumental error less than  
162 0.5 pH units, reproducibility of the data better than 5%).

163 The ammonia and ammonium concentration was measured using a specific electrode  
164 (ORION) coupled with an Ion Analyzer EA920, following the procedure recommended  
165 in Clesceri et al. (1998). The additions method (Harvey, 2000) was used for this  
166 analysis.  $\text{NH}_4\text{Cl}$  standards were prepared starting from 1000  $\gamma/\text{ml}$  obtaining the standard  
167  $\text{NH}_4\text{Cl}$  100  $\gamma/\text{ml}$  and the standard  $\text{NH}_4\text{Cl}$  10  $\gamma/\text{ml}$  (reproducibility of the data better than  
168 10%). The analysis provides the sum of  $\text{NH}_3$  e  $\text{NH}_4^+$  in the solution, whose partition  
169 (Table 1) is pH dependent:

170

$$171 \alpha = \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K}{10^{-\text{pH}}} \frac{\gamma_{\text{NH}4+}}{\gamma_{\text{NH}3}}$$

mac 6/11/15 14:47
<b>Formattato:</b> Interlinea: 1,5 righe
mac 6/11/15 14:47
<b>Eliminato:</b> ..
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito), Pedice
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito), Pedice
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito), Apice
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 14:46
<b>Formattato:</b> Inglese (Regno Unito)
Unknown
<b>Codice campo modificato</b>

173

174 where in square brackets are the concentrations of the two chemical species,  $\gamma$  indicate  
 175 the activity coefficients, and  $K$  is the thermodynamic constant ( $pK=9.24$ ).  $NH_3$  e  $NH_4^+$   
 176 concentrations can be therefore calculated using:

177

$$[NH_4^+] = \frac{C}{\alpha + 1} ; [NH_3] = \frac{C * \alpha}{\alpha + 1}$$

179

180 Composition of major elements ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $F^-$ ) of ash leachates  
 181 was determined by ion chromatography (IC). Trace elements were measured using an  
 182 inductively coupled plasma optical emission spectrometry (ICP-OES) using an Optimal  
 183 2000 DV instrument. Operating conditions were: power 1400 W, plasma argon flow  
 184 rate 15  $L\text{min}^{-1}$ , nebulizer argon flow rate 0.55  $L\text{min}^{-1}$ , and sample flow rate 2  $mL\text{min}^{-1}$ .

185

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

194 The calibration curve for trace elements was carried out using calibration standards  
 195 prepared diluting a stock solution (1000 ppm) with deionised water. Recovery  
 196 experiments were carried out by adding measured volumes of aqueous standard  
 197 solutions of each metal to measured volumes of an acidified deionised water samples.  
 198 Calibration curves were repeated for the analysed elements every 14 samples.  
 199 Reproducibility of the data is better than 3%.

200

### 201 2.3 FETAX test

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

mac 6/11/15 15:54
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 15:54
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 15:56
<b>Formattato:</b> Interlinea: 1,5 righe
mac 6/11/15 15:54
<b>Formattato:</b> Tipo di carattere:Symbol, Corsivo, Inglese (Regno Unito)
mac 6/11/15 15:54
<b>Formattato:</b> Inglese (Regno Unito)
mac 6/11/15 15:55
<b>Formattato:</b> Pedice
mac 6/11/15 15:55
<b>Formattato:</b> Pedice
mac 6/11/15 15:55
<b>Formattato:</b> Apice
mac 6/11/15 15:54
<b>Formattato:</b> Inglese (Regno Unito)
Unknown
<b>Codice campo modificato</b>
Unknown
<b>Codice campo modificato</b>
mac 6/11/15 16:00
<b>Formattato:</b> Italiano
Myriam 14/10/15 11:20
<b>Eliminato:</b> $l\text{min}$
Myriam 14/10/15 11:20
<b>Eliminato:</b> $l\text{min}$
Myriam 14/10/15 11:20
<b>Eliminato:</b> $l\text{min}$

208 tap water at a 22°C ± 2, alternating 12h light/dark cycles and fed a semi synthetic diet  
209 (Mucedola S.r.l., Settimo Milanese, Italy) three times a week.  
210 For a single bioassay, three males and three females received a 300 IU human chorionic  
211 gonadotrophin (HCG) via injection in the dorsal lymph sac to induce mating. Breeding  
212 tanks were filled with FETAX solution (composition in mg/L was 625 NaCl, 96  
213 NaHCO<sub>3</sub>, 30 KCl, 15 CaCl<sub>2</sub>, 60 CaSO<sub>4</sub>-2H<sub>2</sub>O, and 70 MgSO<sub>4</sub>, pH 7.5-8.5) and aerated  
214 before introducing a couple. Amplexus normally ensued within 2h to 6h and the  
215 deposition of fertilized eggs took place from 9h to 12h later. After breeding, the adults  
216 were removed and the embryos were collected in 60 mm glass Petri dishes. Abnormally  
217 cleaved embryos and necrotic eggs were removed.  
218 Normally cleaved embryos at midblastula stage (stage 8), 5h post-fertilization (hpf)  
219 (Nieuwkoop and Faber 1956) were selected for testing and then placed in 6 cm glass  
220 Petri dishes, each Petri containing 10 ml of control or test solutions. Test solutions were  
221 generated by diluting the Etna and Popo mQ leachates in FETAX solution, to obtain the  
222 final dilutions of 1:5, 1:10, 1:50, 1:100.  
223 For each female the plates were duplicated or triplicated when well-cleaved embryos  
224 were available. All the Petri were incubated in a thermostatic chamber at 23±0.5 °C  
225 until the end of the test, 96 hpf. At this moment mortality and malformation data were  
226 generated as endpoints of the assay.  
227 The number of dead embryos versus their total number at the beginning of the test led to  
228 the mortality percentages and the number of malformed larvae versus the total number  
229 of surviving ones gave the malformed larva percentages.  
230

231 **3. Results**

232 **3.1. Ash composition and surface analysis**

233 The bulk rock composition, the glass/mineral phases and the sublimated composition of  
234 the collected samples were analysed by XRF and SEM-EDS techniques. The bulk  
235 composition (Table S1) of Etna samples plot in the hawaiite field, while the  
236 Popocatépetl sample can be classified as andesite (Fig. 1).  
237 The EDS analyses on glass of Etna samples (Table S2) show an almost homogeneous,  
238 more evolved composition (mugearites) with respect to the parental bulk analyses (Fig.  
239 1). The Popocatépetl glass analyses gather on a trend from andesite to rhyolite (Fig. 1).

241 As from SEM-BSE images of polished samples, both Etna and Popocatépetl samples  
242 are porphyritic, with phenocrystals and groundmass microcrystals (Fig. 2). The  
243 mineralogical assemblage of Etna samples comprises Mg-rich olivine clinopyroxene,  
244 plagioclase, and oxides (Table S3). In particular, the clinopyroxene is diopside in both  
245 2011 and 2012 samples (Fig. 3a). Plagioclase in the sample from the 2011 eruption has  
246 an almost homogeneous bytownite composition (Fig. 3b), while in the sample from the  
247 2012 eruption shows a compositional range between bytownite and labradorite (Fig.  
248 3b).

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

253 SEM-BSE images are shown in Figure 4. The sublimes recognized on ash surfaces of  
254 Etna 2011 (Figs. 4a and 4b) and Etna 2012 samples are mainly sodium chloride (NaCl,  
255 halite) and calcium di-fluoride ( $\text{CaF}_2$ , fluorite) (Figs. 4c and 4d). Popocatépetl samples  
256 show abundant sublimate compounds, including sodium chloride, calcium sulphate  
257 (gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or anhydrite  $\text{CaSO}_4$ ), iron sulphide (pyrite  $\text{FeS}_2$  or grigite  
258  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{S}_4$ ) and native S (Figs. 4e and 4f).

### 260 **3.2. Ash leachates**

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

263

#### 264 **3.2.1 pH variation**

265 The pH of ash leachates ranges from ca. 4 (Popocatépetl 63  $\mu\text{m}$ ) to ca. 6.50 (Etna 2011  
266 0.5 mm; Fig. 5). The pH variation is very limited when plotted versus different times of  
267 stirring within each sample, for both mQ and lake waters (Fig. 5). This indicates that  
268 most of the pH variations are acquired within the first 30 minutes of stirring.

269 As a general behaviour, the Popocatépetl leachates induce acidification in the solution,  
270 diminishing the pH values of  $0.24 \pm 0.18$  (lake water; [Table 2](#)) and  $0.57 \pm 0.30$  (mQ water;  
271 [Table 1](#)) pH units (Fig. 5). The Etna samples show opposite behaviour, i.e. induce slight  
272 ( $0.34 \pm 0.11$  pH units for lake water; [Table 2](#)) to moderate ( $1.34 \pm 0.2$  pH units for mQ  
273 water; [Table 1](#)) alkalization (Fig 5). [In both cases is evident the buffering effect of lake](#)

Myriam 14/10/15 11:33  
**Eliminato:** ..

Myriam 14/10/15 11:33  
**Eliminato:** ..  
mac 5/11/15 15:19  
**Eliminato:** 4

mac 5/11/15 15:20  
**Eliminato:** 4

mac 7/11/15 17:26  
**Eliminato:** 0.5  
mac 7/11/15 17:27  
**Eliminato:** to  
mac 7/11/15 17:21  
**Eliminato:** 1  
mac 7/11/15 17:23  
**Eliminato:** within 0.5  
mac 7/11/15 17:17  
**Eliminato:** 1-1.5

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

mac 7/11/15 18:41

**Eliminato:** The pH variations

285

### 286 | **3.2.2 NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> concentration**

287 | The analysed samples show a very limited amount of ammonia (NH<sub>3</sub>) concentration  
288 | with respect to the ammonium (NH<sub>4</sub><sup>+</sup>) one. This is mainly due to the range of pH of the  
289 | produced leachates, which, in any case produced different amounts of NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> when  
290 | using mQ or lake water (Fig. 6). In particular, the ammonia-ammonium concentration in  
291 | mQ water is negligible for Etna samples, while it increases for Popocatépetl samples. In  
292 | lake water, the Popocatépetl samples release NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> almost constantly (variation  
293 | within 1 mg/l), while the Etna samples either do not release NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> (samples Etna  
294 | 2011) or have scattered release of NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> with time (samples Etna 2012; Fig. 6).  
295 | When effective, also the release of NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> shows correlation with decreasing grain  
296 | size (Fig. 6).

297

### 298 | **3.2.3 Anions**

299 | Figure 7 shows the variations of F<sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> concentrations for different grain  
300 | sizes versus time of leaching. The general patterns show small variation of  
301 | concentration versus time for all anions, indicating their release occurring in the first 30  
302 | minutes. It makes exception the SO<sub>4</sub><sup>2-</sup> in mQ water, which reaches a constant release  
303 | after 60 minutes.

304 | The concentration of Cl<sup>-</sup> is below 10 mg/l for most of the samples in both mQ and lake  
305 | water, with the exception of Popocatépetl ash with grain size of 63 µm and some  
306 | scattered anomalous values (Fig. 7).

307 | Irrespective of water used, the release of SO<sub>4</sub><sup>2-</sup> is negligible in Etna samples, while it is  
308 | the most significant in Popocatépetl samples. For the latter, the concentration of SO<sub>4</sub><sup>2-</sup>  
309 | significantly increases with diminishing grain size and moderately increases with  
310 | leaching time (Fig. 7).

311 | The concentration pattern of F<sup>-</sup> is more complex than those of the other anions, with  
312 | different release in the two types of leaching water. In particular, the 2011 Etna samples  
313 | produce the greatest concentrations in both water types, although higher in mQ water  
314 | (Fig. 7). The 2012 Etna samples show lower concentrations, and in lake water they are  
315 | below 10 mg/l. The Popocatépetl samples have concentration of few mg/l (below 10  
316 | mg/l), and a slight correlation with decreasing grain size in mQ water (Fig. 7). In both

mac 5/11/15 15:20

**Eliminato:** 4

mac 6/11/15 18:30

**Formattato:** Apice

mac 6/11/15 18:30

**Eliminato:**

mac 6/11/15 18:30

**Formattato:** Pedice

mac 6/11/15 22:37

**Eliminato:** Ammonia

mac 6/11/15 18:33

**Formattato:** Tipo di carattere:(Predefinito)  
Times New Roman, Non Grassetto

mac 6/11/15 18:33

**Formattato:** Tipo di carattere:(Predefinito)  
Times New Roman

mac 6/11/15 18:33

**Formattato:** Tipo di carattere:(Predefinito)  
Times New Roman, Non Grassetto

mac 6/11/15 18:32

**Formattato:** Tipo di carattere:Non  
Grassetto

mac 6/11/15 18:33

**Formattato:** Tipo di carattere:(Predefinito)  
Times New Roman, Non Grassetto

mac 6/11/15 18:34

**Eliminato:** in leachates

mac 6/11/15 22:37

**Eliminato:** is

mac 6/11/15 18:37

**Eliminato:** NH<sub>3</sub>

mac 5/11/15 15:20

**Eliminato:** 4

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

330

### 331 | **3.2.4 Major cations**

332 Figure 8 shows the variations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  concentration for different  
333 grain sizes versus time of leaching. The general patterns show small variation of  
334 concentration versus time for all cations indicating their release occurring generally in  
335 the first 30-60 minutes, while the Popocatépetl samples reach the highest concentration  
336 after 3-5 days in lake waters. The concentration of  $\text{Na}^+$  is below 20 mg/l in Etna  
337 samples in both mQ and lake water, and it is between 30 and 60 mg/l in Popocatépetl  
338 samples. The concentration of  $\text{K}^+$  is below 7 mg/l for most of the samples in both mQ  
339 and lake water, with the exception of Etna 2012-1mm sample in mQ water (Fig. 8). It is  
340 worth noting that the concentration of  $\text{Na}^+$  and  $\text{K}^+$  for the Etna 2012 samples in lake  
341 water leachate is close or below the concentration these cations have in pure lake water  
342 (Fig. 8).

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

347

### 348 | **3.2.5 Trace elements**

349 Figure 9 shows the variations of B, Si,  $\text{Fe}_{\text{tot}}$ ,  $\text{Mn}^{2+}$  and  $\text{As}^{3+}$  concentration for different  
350 grain sizes versus time of leaching. The general patterns show irregular variation of  
351 concentration versus time for all the trace elements. B concentration shows a scattered  
352 distribution versus time of leaching in mQ water, although a fair anti-correlation is  
353 visible for 3 out of 4 Etna samples (Fig. 9). It is below the lake water concentration for  
354 almost all the analysed samples (Fig. 9). The concentration of Si is scattered in both mQ  
355 and lake water leachates, although a fair increase in concentration is visible with time of  
356 leaching for both Etna and Popocatépetl samples (Fig. 9).

357 Irrespective of water typology used, the release of  $\text{Fe}_{\text{tot}}$  and  $\text{Mn}^{2+}$  is lower in Etna  
358 samples than in Popocatépetl ones, showing a scattered distribution with some very high  
359 peaks (Fig. 9).

360

### 361 | **3.3. Biological impact of leachates**

mac 5/11/15 15:20

Eliminato: 4

mac 5/11/15 15:20

Eliminato: 4

mac 5/11/15 15:21

Eliminato: 5

365 The results from the FETAX test clearly show that the leachates from Etna and  
366 Popocatépetl ash are very poorly embryotoxic. At the dilutions used, no significant  
367 increase in embryo mortality was indeed observed (Fig. 10 a, b). The percentages of  
368 malformed larvae at the end of the test progressively increased with decreasing dilutions  
369 in the groups exposed to Etna leachates (Fig. 10a), while a non-linear increase was  
370 observed in those exposed to Popocatépetl leachates (Fig. 10b). The maximum values of  
371 about 40% malformed larvae were registered at the highest concentrations of leachates.  
372 These results do not evidence significant differences in the effects induced by Etna and  
373 Popocatépetl leachates, although it is worth noting the higher scores obtained in larvae  
374 exposed to Etna leachates at low concentrations (1:100 and 1:50), with respect to the  
375 Popocatépetl ones.

376

#### 377 | **4. Discussion**

378

##### 379 | **4.1 General remarks**

380 The data presented in the preceding sections illustrate the complexity that accompanies  
381 the leaching of compounds from fresh volcanic ash. Analysing the figures and the tables  
382 presented, it emerges clearly how the physical and chemical processes occurring during  
383 the simple washing of fresh volcanic ash interact with the surrounding aqueous  
384 environment. It follows that to extract simple laws of compound release at different  
385 boundary conditions is not straightforward, having to face with dynamic processes that  
386 changes in function of the progressive variation of the experimental geochemical  
387 environment.

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

392

##### 393 | **4.2 Origin of leached elements**

394 The mQ water is almost pure water, thus it does not contain any other element or  
395 compound that could react with the leaching material. Therefore, it is better suitable for  
396 the analysis of leached compounds from volcanic ash than lake water, whose dissolved  
397 elements and molecules can react with leached elements and alter their original  
398 assemblage.

mac 5/11/15 15:21

**Eliminato: 6**

mac 5/11/15 15:21

**Eliminato: 6**

mac 5/11/15 15:23

**Eliminato: 1**

402 The sublimates on ash surfaces of Etna 2011 (Figs. 4a and 4b) include mainly (Na,K)Cl  
403 (sodium/potassium chloride), (Ca,Mg)F<sub>2</sub> (calcium/magnesium fluoride), and (Ca,  
404 Mg)SO<sub>4</sub> (calcium/magnesium sulphate). The formation of leachates from solubilization  
405 of these superficial salts is also confirmed by the stoichiometry of mQ water analysis,  
406 where the relative abundance of these elements is almost completely balanced. Only  
407 few residual fractions of Ca<sup>2+</sup>, Mg<sup>2+</sup> and F<sup>-</sup> scattered in the different grain-size fractions  
408 remain unbalanced (Table S4). The concentration of all the elements is below their  
409 respective solubility limit, except than Si<sup>2+</sup> and F<sup>-</sup> (Table S5). It means that all the salts  
410 from the ash surface passed into the leachates, with the exception of Si and F ones,  
411 which may have been remained partially not dissolved. The slight excess of Mg<sup>2+</sup> and  
412 Ca<sup>2+</sup> in most of the Etna 2011 samples (Table S4) might indicate the presence of  
413 carbonates in the leachates, since CO<sub>3</sub><sup>2-</sup> was not analysed. When considering the  
414 stoichiometry of the leachates, it emerges that F<sup>-</sup> compounds are the most dissolved in  
415 Etna 2011 samples, along with variable amount of SO<sub>4</sub><sup>2-</sup> and minor Cl<sup>-</sup> compounds  
416 (Table S4).

417 The Etna 2012 sample shows very similar stoichiometry of leachates to Etna 2011, with  
418 fractional remnants of unbalanced elements that comprise K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> (Table  
419 S4). Mg concentration is close to the maximum solubility limit, and dissolved F  
420 compounds dominate the leachates (Table S4).

421 The sublimates on ash surfaces of Popocatépetl samples (Figs. 4e and 4f) include  
422 mainly (Ca,Mg)SO<sub>4</sub> (calcium/magnesium sulphate), and minor (Na,K)Cl  
423 (sodium/potassium chloride). Also in these cases the leachates reflect the dissolution of  
424 the salts observed on ash surfaces, as confirmed by stoichiometric calculations (Table  
425 S4). It is observable a slight excess of Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> not balanced by Cl<sup>-</sup>,  
426 SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>, which might indicate the occurrence of carbonates (not analysed) in the  
427 leachates. The concentration of elements in the two samples (0.125 and 0.063 mm)  
428 slightly differs (Table S5), with the coarser one that shows saturation with respect to Ca,  
429 Si and Fe compounds, and the finer one that shows saturation in fluorite, gypsum,  
430 quartz and chalcedony (Table S5). The Mg<sup>2+</sup> content in mQ leachates from  
431 Popocatépetl samples is higher than in Etna samples (Table S4). Taking into account the  
432 surface analysis on sublimates, it seems that most of the Mg<sup>2+</sup> comes from dissolution  
433 of Mg-sulphates. This inference is also supported by the strong correlation among Ca<sup>2+</sup>,  
434 Mg<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> (Fig. 11), which indicate the presence of the ammonium as catalyst for  
435 (Ca, Mg) salt dissolution.

436 The composition of leachates in lake water can be quite different from those in mQ  
437 water, due to the presence of chemical compounds already present, which can react with  
438 elements released from ash surface (Table 2). In order to evaluate the buffering effect of  
439 lake water, its chemical composition was subtracted from that of the leachates (Table 3).  
440 This allows compare the net release of the different elements using the two water  
441 typologies. It is evident comparing data from Tables 1 and 3 how the release of  
442 elements from Etna samples is variably lower in lake water than in the mQ one, with  
443 loss of some 10% in abundance of F<sup>-</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup> and especially B, which has a  
444 negative net release in lake water (Table 3). This general behaviour is also confirmed by  
445 Popocatépetl samples, with the exceptions of a greater release of Mg<sup>2+</sup> and Ca<sup>2+</sup> in lake  
446 water for the 0.125 µm fraction (Table 3). Because borates are usually highly soluble, it  
447 may suggest the occurrence of adsorption/reaction processes of B with compounds  
448 present in lake water.

449 Being the lake Ohrid water from carbonate springs, the described variations in element  
450 abundance between mQ and lake water can be influenced by the presence of carbonates  
451 in the latter one. Although carbonates have not been measured directly, their abundance  
452 can be calculated using charge balance (Qu et al., 2008; Table 2). However, inspection  
453 of HCO<sub>3</sub><sup>-</sup> data in Table 2 shows the leachates from both Etna and Popocatépetl samples  
454 have indistinguishable contents (in average) with respect to the lake water, with the only  
455 exceptions of the Popocatépetl samples with longer time of stirring. This indicates that  
456 the net release of Mg<sup>2+</sup> and Ca<sup>2+</sup> is limited by the reached solubility limit of most of the  
457 leachates (Table S6) in the carbonate-bearing water.

mac 7/11/15 19:55  
**Formatto:** Pedice  
mac 7/11/15 19:55  
**Formatto:** Apice

#### 458 | **4.3 Influence of ash grain size on leachates**

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

466 In order to investigate the influence of grain size of ash on release of elements, the Etna  
467 2011 samples in mQ water are the most suitable, being available leachates from three  
468 different grain sizes (Table 1). Analysing the release of elements with different times of

mac 5/11/15 15:21  
**Eliminato:** 6  
mac 5/11/15 15:23  
**Eliminato:** 2

472 stirring, it is evident the inverse correlation with grain size for  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ .  
473 The trends for these elements are quite similar for the different times of stirring,  
474 indicating a time-independent release for these elements (Fig. 12). A general decrease  
475 of release with increasing grain size is visible for  $\text{Cl}^-$ , although the trends for different  
476 times of stirring are not identical (Fig. 12). Release of  $\text{Mg}^{2+}$  is almost constant for the  
477 different grain sizes and for different times of stirring. The release of  $\text{Mn}^{2+}$  is  
478 contrasting. It is inversely related to grain size for time of stirring up to 21,600 s (6 h),  
479 while it increases with grain size for times of stirring of 43,200 s (12 h) and 86,400 s  
480 (24 h; Fig. 11). B also shows similar pattern, with opposite trends below and above  
481 21,600 s (6 h; Fig. 11). These behaviours suggest different kinetics for dissolution of  
482 sublimates containing  $\text{Mn}^{2+}$  and B and precipitation of their salts.  
483 The release of  $\text{F}^-$  shows a unique pattern, with similar values for 0.25 mm and 1 mm  
484 grain sizes and lower values for the 0.5 mm grain size (Fig. 12). This behaviour is quite  
485 well defined by all the times of stirring, which indicates this is not an aleatory  
486 behaviour. Finally, the patterns of Si and Fe are randomly arranged, without any clear  
487 correlation of release with grain size and/or timing of stirring (Fig. 12). The different  
488 patterns for the various elements of Etna 2011 samples demonstrate how the  
489 dependence of element release with grain size is not a general rule. Indeed, a greater  
490 release at decreasing grain size holds for alkali and alkaline earth elements together with  
491 the sulphate radical  $\text{SO}_4^{2-}$ , which is a component of most of their original sublimated  
492 salts. This is in agreement with already suggested greater capacity of particles with  
493 larger surface vs. volume ratio to scavenge elements from the eruptive cloud.  
494 The release of B seems to reflect a complex kinetic of adsorption/reaction of B, which  
495 can account for the difference in release at different times of stirring (Fig. 12).  
496 The scatter release of Fe and Si reflects the random formation of soluble salts of these  
497 elements, which are not related to the grain size but more probably to the redox  
498 conditions at time of sublimation.  
499 Among the most abundant elements,  $\text{F}^-$  shows a unique pattern, not the explanation is  
500 puzzling. It is not related to the active surface of the particles, nor to the composition of  
501 the eruptive plume, having all the particles underwent the same eruptive conditions. It  
502 may be speculated that some gaseous F might be entrapped in the vesicles that are more  
503 abundant in the 1 mm particles than in the 0.25 mm and 0.5 mm, and then may be  
504 related to the presence of gaseous F in the vesicles of the coarse ash particles of 1 mm  
505 grain size, which can compensate the lower active surface of this grain size.

Myriam 14/10/15 11:32  
**Eliminato:** whose

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

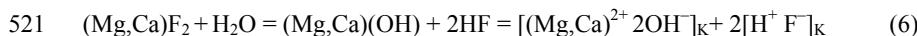
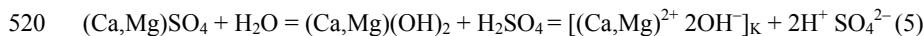
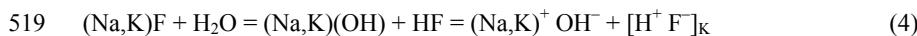
511

#### 512 | 4.4 Origin of pH changes

513 The changes in pH values of leachates with respect to those of mQ and lake water  
514 relates to the release of OH<sup>-</sup> and H<sup>+</sup> ions due to hydrolysis reactions of the salts  
515 dissolved from the ash surfaces (§ 6. 1).

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

517



522

523 Equation (3) is neutral for pH, producing a strong base and a strong acid that are totally  
524 dissociated in water. Equation (4) produces a strong base and a weak acid, which is only  
525 partially dissociated to supply H<sup>+</sup> ions. It induces alkalization of the leachates.

526 Equation (5) produces a strong acid and a weak base, which induce acidification of the  
527 leachates. Equation (6) produces a weak acid and a weak base. Being the equilibrium  
528 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  
529 alkalization of the leachates. Being the sublimates on Etna ash dominated by F salts  
530 (Tables 1 and 2), the hydrolysis reactions are dominated by equations (4) and (6). This  
531 explains why the pH of Etna leachates is more alkaline with respect to the mQ water.  
532 The alkalisation is less effective when considering leachates in lake water, due to the  
533 presence of dissolved carbonates (Table 2) that buffers the hydrolysis reactions.

534 The same hydrolysis equations hold for the Popocatépetl samples, although they are  
535 dominated by dissociation of  $(\text{Ca,Mg})\text{SO}_4$  salts (Tables 1 and 2). This explains why the  
536 Popocatépetl leachates are more acid with respect to the mQ water (Fig. 5). The  
537 correlation of pH value with  $\text{SO}_4^{2-}$  is also testified by the higher acidification of 0.063  
538 mm leachates with respect to the 0.125 mm ones (Fig. 5; Tables 1 and 2). The pH varies  
539 very little when considering lake water also for Popocatépetl samples, due to the  
540 buffering effect of already dissolved carbonates (Fig. 5; Tables 1 and 2).

mac 5/11/15 15:21

Eliminato: 6

mac 5/11/15 15:23

Eliminato: 3

544 | **4.5. Drinkability of water leachates**

545 Drinking water quality is commonly regulated using a two-tier system. Primary  
546 standards are legally enforceable limits set for contaminants posing a health risk (Table  
547 S7). Secondary standards are non-enforceable guideline values for contaminants which  
548 are not known to be a health risk but which make drinking water unacceptable to  
549 consumers because of aesthetic factors such as taste, colour or odour (Table S7), or  
550 effects on the supply system such as staining or scale deposition (Stewart et al., 2006).  
551 Inspection of Etna and Popocatépetl mQ leachates shows that F<sup>-</sup> and Mn<sup>2+</sup> elements are  
552 always well above the legal limits for drinkable water (Table 1). Also Fe exceeds the  
553 limits in most of the Etna samples and in all the Popocatépetl ones (Table 1). This  
554 makes it the water dark in colour, bitter, with metallic taste and can induce dental  
555 fluorosis and gastrointestinal disease on consumers. The SO<sub>4</sub><sup>2-</sup> also exceeds the limits in  
556 the Popocatépetl samples, adding salty taste to the water and possible diarrhoea disease  
557 to consumers.  
558 The inspection of leachates with lake water shows a similar behaviour of mQ water for  
559 F<sup>-</sup>, which exceeds the legal limits in all the samples. Mn<sup>2+</sup> is in excess for all the Etna  
560 2011 and Popocatépetl samples, but only in two samples of Etna 2012 (Table 2). Fe  
561 exceeds the limits for most of the analysed samples, while SO<sub>4</sub><sup>2-</sup> is in excess in all the  
562 Popocatépetl samples (Table 2). Overall, the effects on water and consumers are the  
563 same than in mQ water.  
564 The inspection of Tables 1, 3 and S4 highlights how the F<sup>-</sup> content is the most sensitive  
565 element for drinkability of leachates of Etna samples, being its abundance 6 to 14 (mQ  
566 water) or 1.5 to 10 (lake water) times the acceptable limit for potability (Tables 1, 3 and  
567 S4). The Mn<sup>2+</sup> and Fe are the most sensitive elements for Popocatépetl samples in mQ  
568 water (Tables 1, 3 and S4), with abundances between 10 and 50 times (Mn<sup>2+</sup>) and 7 to  
569 58 times (Fe) the legal limits. Considering lake water, the most sensitive element for  
570 Popocatépetl is Mn<sup>2+</sup> (Tables 1, 3 and S4), being its abundance 3 to 50 times the legal  
571 limits for potability.  
572 Taking into account the concentration of these elements in Etna and Popocatépetl  
573 leachates, it is possible to calculate the minimum weight of ash needed to exceed the  
574 legal limits of potability. As an example, for Etna 2011 samples in lake water, only 12  
575 kg of ash per m<sup>3</sup> of water are sufficient for making it undrinkable (using F<sup>-</sup> as  
576 benchmark). It means that, depending on the bulk density of the ash deposit, a thickness

mac 5/11/15 15:21

Eliminato: 6

mac 5/11/15 15:24

Eliminato: 4

579 of 8 mm/m<sup>2</sup> (bulk density of 1500 kg/m<sup>3</sup>) or 6 mm/m<sup>2</sup> (bulk density of 2000 kg/m<sup>3</sup>) is  
580 sufficient for contaminating the water beyond the potability limits. The same exercise  
581 for Popocatépetl samples yields a mean weight of only 8 kg of ash per m<sup>3</sup> (using Mn<sup>2+</sup>  
582 as benchmark), which corresponds to 5 mm/m<sup>2</sup> (bulk density of 1500 kg/m<sup>3</sup>) or 4  
583 mm/m<sup>2</sup> (bulk density of 2000 kg/m<sup>3</sup>). If applied to lake Ohrid (water volume of ca. 5.5.  
584 km<sup>3</sup>), the required thickness of tephra deposited over the lake area is 12-15 cm for Etna  
585 compositions and 6-8 cm for Popocatépetl ones. Taking into account the thickness of  
586 past tephra layers recognised in lake Ohrid succession (Sulpizio et al., 2010), the only  
587 deposits with similar thicknesses is the Campanian Ignimbrite-Y5 (Leicher et al., 2015).

mac 7/11/15 22:17

Formatto: Apice

588 It is evident that to contaminate a big water reservoir like lake Ohrid it is necessary an  
589 amount of volcanic ash compatible only with super eruptions. Nevertheless, limited  
590 amounts of ash can impinge significantly the availability of a primary resource like  
591 drinkable water in many smaller water reservoirs then lake Ohrid. This is an  
592 underestimated volcanic hazard, which can impact large areas and severely affect  
593 population if no preventive civil protection actions are taken in advance. Authorities  
594 were generally unable to allay public fears because of a lack of supporting information  
595 on specific effects of volcanic ash on water supplies, including considerations such as  
596 the quantity of ash necessary to produce adverse effects, and the specific nature of  
597 contaminants that may pose a health risk to consumers or otherwise compromise the  
598 integrity of water supplies. A good example of this hazard is the potential contamination  
599 of water reservoirs of southern Italy, which are exposed to ash deposition in case of  
600 renewal of explosive activity of Italian volcanoes (Sulpizio et al., 2014). ▲

mac 7/11/15 22:31

Eliminato: how such small

#### 601 4.6 Effects on living biota

602 The ash leachates obtained in mQ water were diluted in FETAX solution to obtain  
603 sequential dilutions from 1:5 to 1:100 vol/vol. This was planned to mime natural  
604 conditions in which ash leachates are likely progressively diluted in the water basins.  
605 Under these experimental conditions both Etna and Popocatépetl leachates results mild  
606 toxic to developing *Xenopus laevis* and no significant differences exist between the  
607 toxic profiles of the two materials. Anyway, we outline that the higher content in F  
608 exhibited by the leachates from Etna may represent a potential teratogenic risk. Indeed,  
609 F<sup>-</sup> is known to be a powerful teratogen, as also demonstrated in *Xenopus laevis* (Goh  
610 and Neff, 2003). In this optic, it may be useful to focus on the induced malformations  
611 more than on the deaths of embryos. It is evident that for both leachates the number of

mac 7/11/15 22:31

Formatto: Colore carattere: Automatico

mac 5/11/15 15:22

Eliminato: 6

mac 5/11/15 15:24

Eliminato: 5

Myriam 14/10/15 11:38

Eliminato: ring a bell in term of

617 malformations is greater for low dilutions (Fig. 13), with a good logarithmic fit of the  
618 data. This means that even few % of leachates (high dilutions) suddenly increases the  
619 malformations above 20%, which only augment of about 10% at higher concentrations  
620 (Fig. 13).

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

623 Although promising, these preliminary data on ecotoxicity of Etna and Popocatépetl ash  
624 leachates claim for more experimental evidences to fully understand the specific and  
625 comparative reactivity of the different leachates in term of teratogenicity.

626

## 627 | **5. Conclusions**

628 Leaching experiments on fresh ash samples from Etna 2011, Etna 2012 and  
629 Popocatépetl 2012 eruptions highlights some interesting clues about behaviour of  
630 compound release in mQ and lake water. Surface analysis on unwashed ash  
631 demonstrates the presence of sublimated salts, and their leaching accounts for the  
632 observed composition of leachates in mQ water. The balance of leachates in lake water  
633 is more complex, due to the reaction of leached compounds with chemical elements  
634 dissolved in the lake water.

635 The hydrolysis reactions of the leached compounds accounts also for the observed pH  
636 variations in mQ and lake water, with Etna 2011-2012 samples that induce  
637 alkalinisation and Popocatépetl samples that induce acidification of the original water  
638 samples.

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

642 Grain size of ash particles has different and sometimes contrasting effects on release of  
643 compounds, with general inverse correlation only for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  
644 and  $\text{Mn}^{2+}$ .

645 Saturation calculations highlights how Etna samples are always saturated for F and Si in  
646 mQ water, while leachates in lake water are saturated in F, Si, and carbonates, reflecting  
647 the contribution of elements already present in the used solvent. Popocatépetl samples  
648 show general saturation in some Ca, Si, F, and Fe compounds in mQ water, similar to  
649 those calculated for lake water.

mac 5/11/15 15:22

Eliminato: 7

651 When compared with limits for potability imposed by [European](#) laws, it emerges of  
652 both mQ and lake leachates from Etna and Popocatépetl samples are classified as not  
653 allowed for human drinking due to the excess of F<sup>-</sup>, Mn<sup>2+</sup>, Fe, and SO<sub>4</sub><sup>2-</sup> (only  
654 Popocatépetl samples).

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

660

### 661 **Acknowledgements**

662 This research was carried out within the PRIN'09 project "Study of tephra layers in  
663 lacustrine sediments of the ICDP project "Scientific Collaboration on Past Speciation  
664 Conditions in Lake Ohrid (SCOPSCO)". Evaluation of the environmental impact and  
665 contributions to chronology of sediments and to volcanic hazard assessment in distal  
666 areas" to RS. Technician M. Pallara (DSTG-UNIBA) performed the XRF analyses.  
667 Thanks to Damiano Sarocchi (UASLP, Mexico) for providing sample of Popocatépetl  
668 ash, and to Rosa Anna Corsaro (INGV Catania, Italy) for providing the Etna samples.  
669 Marco Cantù and Sara Meschiari are greatly acknowledged for his contribution to living  
670 biota experiments. [F.A. Viehberg and an anonymous reviewer are acknowledged for the](#)  
671 [suggestions that improved the manuscript.](#)

672

### 673 **References**

- 674 Araya, O., Wittwer, F., Villa, A. and Ducom, C.: Bovine fluorosis following volcanic  
675 activity in the southern Andes., Vet. Rec., 126(26), 641–642, 1990.
- 676 Araya, O., Wittwer, F. and Villa, A.: Evolution of fluoride concentrations in cattle and  
677 grass following a volcanic eruption., Vet. Hum. Toxicol., 35(5), 437–40, 1993.
- 678 Armienta, M. A., De la Cruz-Reyna, S., Morton, O., Cruz, O. and Ceniceros, N.:  
679 Chemical variations of tephra-fall deposit leachates for three eruptions from  
680 Popocatépetl volcano, J. Volcanol. Geotherm. Res., 113(1-2), 61–80.
- 681 Ayris, P. M. and Delmelle, P.: The immediate environmental effects of tephra emission,  
682 Bull. Volcanol., 74, 1905–1936.
- 683 Baxter, P. and Ancia, A.: Human health and vulnerability in the Nyiragongo volcano  
684 crisis Democratic Republic of Congo 2002: Final report to the World Health  
685 Organisation, World Heal. Organ., 2002.

- 687 Blong, R.: Volcanic hazards. A sourcebook on the effects of eruptions., 1984.
- 688 Boyd, P., Watson, A., Law, C. and Abraham, E.: A mesoscale phytoplankton bloom in  
689 the polar Southern Ocean stimulated by iron fertilization, *Nature*, 407, 695–702, 2000.
- 690 Clesceri, L.S., Grrenberg, A. E., Eaton, A. D.: Standard Methods for the examination of  
691 Water and Wastewater. 20th Edition, 1998.
- 692 Collins, C.: Contamination of water supplies and water courses. Appendix 2, *Erupt.*  
693 Ruapehu, New Zealand, 22 June 1969. DSIR Bull., 224, 1978.
- 694 Cronin, S. J. and Sharp, D. S.: Environmental impacts on health from continuous  
695 volcanic activity at Yasur (Tanna) and Ambrym, Vanuatu., *Int. J. Environ. Health Res.*,  
696 12(2), 109–23.
- 697 Cronin, S. J., Neall, V. ., Lecointre, J. ., Hedley, M. . and Loganathan, P.:  
698 Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano,  
699 New Zealand, *J. Volcanol. Geotherm. Res.*, 121(3-4), 271–291.
- 700 Cronin, S. J., Stewart, C., Zernack, A. V., Brenna, M., Procter, J. N., Pardo, N.,  
701 Christenson, B., Wilson, T., Stewart, R. B. and Irwin, M.: Volcanic ash leachate  
702 compositions and assessment of health and agricultural hazards from 2012  
703 hydrothermal eruptions, Tongariro, New Zealand, *J. Volcanol. Geotherm. Res.*, 286,  
704 233–247.
- 705 Duggen, S., Croot, P., Schacht, U. and Hoffmann, L.: Subduction zone volcanic ash can  
706 fertilize the surface ocean and stimulate phytoplankton growth: Evidence from  
707 biogeochemical experiments and satellite data, *Geophys. Res. Lett.*, 34(1), L01612.
- 708 Flaathen, T. K. and Gíslason, S. R.: The effect of volcanic eruptions on the chemistry of  
709 surface waters: The 1991 and 2000 eruptions of Mt. Hekla, Iceland, *J. Volcanol.*  
710 *Geotherm. Res.*, 164(4), 293–316.
- 711 Frogner, P., Reynir Gíslason, S. and Óskarsson, N.: Fertilizing potential of volcanic ash  
712 in ocean surface water, *Geology*, 29, 487.
- 713 Fruchter, J., Robertson, D. and Evans, J.: Mount St. Helens ash from the 18 May 1980  
714 eruption: chemical, physical, mineralogical, and biological properties, *Science* (80- .),  
715 209(4461), 1116–25, 1980.
- 716 Gíslason, S. R., Snorrason, Á., Kristmannsdóttir, H. K., Sveinbjörnsdóttir, Á. E.,  
717 Torsander, P., Ólafsson, J., Castet, S. and Dupré, B.: Effects of volcanic eruptions on  
718 the CO<sub>2</sub> content of the atmosphere and the oceans: The 1996 eruption and flood within  
719 the Vatnajökull Glacier, Iceland, *Chem. Geol.*, 190, 181–205.
- 720 Grattan, J. and Charman, D. J.: Non-climatic factors and the environmental impact of  
721 volcanic volatiles: implications of the Laki fissure eruption of AD 1783, *The Holocene*,  
722 4(1), 101–106.
- 723 Gudmundsson, A. and Oskarsson, N.: The 1991 eruption of Hekla, Iceland, *Bull.*  
724 *Volcanol.*, 54(3), 238–246, 1992.

- 725 Harvey, D.: Modern analytical chemistry,, 2000.
- 726 Johnston, D. and Houghton, B.: Impacts of the 1945 and 1995–1996 Ruapehu eruptions,  
727 New Zealand: an example of increasing societal vulnerability, Geol. Soc. Am., 112,  
728 720–726, 2000.
- 729 Jones, M. T. and Gislason, S. R.: Rapid releases of metal salts and nutrients following  
730 the deposition of volcanic ash into aqueous environments, Geochim. Cosmochim. Acta,  
731 72(15), 3661–3680.
- 732 Leicher, N., Zanchetta, G., Sulpizio, R., Giaccio, B., Wagner, B., Nomade, S., and  
733 Francke, A.: First tephrostratigraphic results of the DEEP site record in Lake Ohrid,  
734 Macedonia. Biogeosciences, this volume, 2015.
- 735 Martin, R. S., Watt, S. F. L., Pyle, D. M., Mather, T. a., Matthews, N. E., Georg, R. B.,  
736 Day, J. a., Fairhead, T., Witt, M. L. I. and Quayle, B. M.: Environmental effects of  
737 ashfall in Argentina from the 2008 Chaitén volcanic eruption, J. Volcanol. Geotherm.  
738 Res., 184(3-4), 462–472.
- 739 Oppenheimer, C., Barclay, D. M. and Pyle, J.: Volcanic Degassing., 2003.
- 740 Óskarsson, N.: The interaction between volcanic gases and tephra: Fluorine adhering to  
741 tephra of the 1970 hekla eruption, J. Volcanol. Geotherm. Res., 8, 251–266.
- 742 Qu, W.J., Zhang, X.Y., Arimoto, R., Wang, D., Wang, Y.Q., Yan, L.W., Li, Y.:  
743 Chemical composition of the background aerosol at two sites in southwestern and  
744 northwestern China: potential influences of regional transport, Tellus, 60B, 657–673,  
745 2008.
- 746 Rose, W., Bonis, J. and Stoiber, S.: Studies of volcanic ash from two recent Central  
747 American eruptions, Bull. Volcanol., 37(3), 338–364, 1973.
- 748 Rubin, C., Noji, E. and Seligman, P.: Evaluating a fluorosis hazard after a volcanic  
749 eruption, Arch. Environ. Heal. An Int. J., 49(5), 395–401, 1994.
- 750 Ruggieri, F., Saavedra, J., Fernandez-Turiel, J. L., Gimeno, D. and Garcia-Valles, M.:  
751 Environmental geochemistry of ancient volcanic ashes., J. Hazard. Mater., 183(1-3),  
752 353–65.
- 753 Shanks, D.: Clinical implications of volcanic eruptions on livestock: case studies  
754 following the 1995 and 1996 eruptions of Mt. Ruapehu, Proc. from 27th Semin. Soc.  
755 Sheep Beef Cattle Vet. NZVA NZVA Conf. Week 1997 29 June-4th July 1997,  
756 Wairakei Resort Hotel. 1997., 1997.
- 757 Smith, M. and White, M.: Observations on lakes near Mount St Helens: phytoplankton,  
758 Arch. für Hydrobiol., 104(3), 345–362, 1985.
- 759 Smithsonian Institution: Soufriere Hills, Bull. Glob. Volcanism Netw., 22(5), 2–4, 1997.
- 760 Smithsonian Institution: Copahue., Bull. Glob. Volcanism Netw., 25(6), 7–10, 2000.

mac 7/11/15 22:49
<b>Formattato:</b> Sottotitolo
mac 7/11/15 22:47
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman, 12 pt, Non Grassetto
mac 7/11/15 22:49
<b>Formattato:</b> Controllo ortografia e grammatica
mac 7/11/15 20:52
<b>Formattato:</b> Normale
mac 7/11/15 20:49
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman
mac 7/11/15 20:49
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman
mac 7/11/15 20:49
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman
mac 7/11/15 20:49
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman
mac 7/11/15 20:49
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman
mac 7/11/15 20:49
<b>Formattato:</b> Codice campo modificato
mac 7/11/15 20:49
<b>Formattato:</b> Tipo di carattere:(Predefinito) Times New Roman
mac 7/11/15 20:49
<b>Formattato</b> ... [1]
Unknown
<b>Codice campo modificato</b>
mac 7/11/15 20:49
<b>Formattato</b> ... [2]
Unknown
<b>Codice campo modificato</b>
mac 7/11/15 20:49
<b>Formattato</b> ... [3]
mac 7/11/15 20:49
<b>Formattato</b> ... [4]
mac 7/11/15 20:49
<b>Formattato</b> ... [5]
mac 7/11/15 19:26
<b>Formattato</b> ... [6]
mac 7/11/15 19:26
<b>Formattato</b> ... [7]
mac 7/11/15 19:26
<b>Formattato</b> ... [8]
mac 7/11/15 19:26
<b>Formattato</b> ... [9]
mac 7/11/15 20:52
<b>Formattato</b> ... [10]

- 761 Stefánsson, K. and Sigurjónsson, J.: Temporary increase in fluorine content of water  
 762 following the eruption: The eruption of Hekla, 1947–1948, Soc. Sci. Islandia, 2, 1–13,  
 763 1957.
- 764 Steingrímsson, J. and Kunz, K.: Fires of the earth: the Laki eruption, 1783–1784, Univ  
 765 Icel. Pr., 1998.
- 766 Stewart, C., Johnston, D. M., Leonard, G. S., Horwell, C. J., Thordarson, T. and Cronin,  
 767 S. J.: Contamination of water supplies by volcanic ashfall: A literature review and  
 768 simple impact modelling, J. Volcanol. Geotherm. Res., 158(3–4), 296–306.
- 769 [Sulpizio, R., Zanchetta, G., D’Orazio, M., Vogel, H., Wagner, B.: Tephrostratigraphy](#)  
 770 [and tephrochronology of lakes Ohrid and Prespa, Balkans. Biogeosciences, 7, 3273–](#)  
 771 [3288, 2010.](#)
- 772 Sulpizio, R., Zanchetta, G. and Caron, B.: Volcanic ash hazard in the Central  
 773 Mediterranean assessed from geological data, Bull. Volcanol., 76(10), 1–8, 2014.
- 774 Thorarinsson, S.: The Lakagigar eruption of 1783, Bull. Volcanol., 33(3), 910–929.
- 775 Thorarinsson, S. and Sigvaldason, G.: The Hekla eruption of 1970, Bull. Volcanol.,  
 776 36(2), 269–288, 1972.
- 777 Uematsu, M.: Enhancement of primary productivity in the western North Pacific caused  
 778 by the eruption of the Miyake-jima Volcano, Geophys. Res. Lett., 31.
- 779 Wardman, J. B., Wilson, T. M., Bodger, P. S., Cole, J. W. and Johnston, D. M.:  
 780 Investigating the electrical conductivity of volcanic ash and its effect on HV power  
 781 systems, Phys. Chem. Earth, Parts A/B/C, 45–46, 128–145.
- 782 Weniger, B. and Blaser, M.: An outbreak of waterborne giardiasis associated with  
 783 heavy water runoff due to warm weather and volcanic ashfall., Am. J. Public Health,  
 784 73(8), 868–872, 1983.
- 785 Wilcox, R. and Coats, R.: Some effects of recent volcanic ash falls with especial  
 786 reference to Alaska, US Gov. Print. Off., 1959.
- 787 Wilson, T. M., Stewart, C., Sword-Daniels, V., Leonard, G. S., Johnston, D. M., Cole, J.  
 788 W., Wardman, J., Wilson, G. and Barnard, S. T.: Volcanic ash impacts on critical  
 789 infrastructure, Phys. Chem. Earth, 45–46, 5–23.
- 790 Witham, C. S., Oppenheimer, C. and Horwell, C. J.: Volcanic ash-leachates: a review  
 791 and recommendations for sampling methods, J. Volcanol. Geotherm. Res., 141(3–4),  
 792 299–326.

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

mac 7/11/15 22:45

Formattato: Tipo di carattere:Non Corsivo

mac 6/11/15 16:58

Formattato: Interlinea: singola

mac 6/11/15 16:58

Eliminato: -

mac 6/11/15 16:58

Eliminato: 4

mac 7/11/15 22:55

Sample	t (10 <sup>3</sup> s)	pH	ΔpH	Anions (mg/l)				Cations (mg/l)				Trace elements (µg/l)						
				NH <sub>4</sub> <sup>+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	B	Si	Mn	Fe	Hg	As	
mQ water	4,96	-	b.d.l.	b.d.l.	0	7,69	b.d.l.	0,57	0,02	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	3504,99	272,50	880,49	n.a.
E2011-0.25mm	3,8	6,15	1,19	1,82E-05	0,03	20,86	4,03	b.d.l.	33,88	14,72	4,33	3,13	11,90	89,25	314,47	194,63	158,00	2,68
E2011-0.25mm	10,8	6,32	1,36	1,99E-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.
E2011-0.25mm	21,6	5,93	0,97	1,51E-05	0,03	19,84	4,00	b.d.l.	35,04	14,87	4,29	3,28	12,41	58,14	1403,52	216,00	78,13	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	3,86	15,33	53,04	2123,64	280,13	70,00	n.a.
E2011-0.25mm	86,4	6,45	1,49	n.a.	n.a.	21,38	8,49	1,75	41,14	16,10	5,05	3,84	16,89	48,45	3174,75	n.a.	234,09	n.a.
E2011-0.50 mm	1,8	6,03	1,07	1,83E-05	0,03	15,87	3,32	b.d.l.	8,87	6,72	2,55	3,11	9,61	105,06	873,71	132,25	317,75	n.a.
E2011-0.50 mm	3,8	6,01	1,05	1,89E-05	0,03	16,64	3,74	b.d.l.	9,26	6,32	2,34	3,20	10,00	82,11	868,61	134,85	154,50	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.
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	164,83	449,50	n.a.
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	2,02	3,65	10,32	240,72	1378,02	147,23	167,5	n.a.
E2011-0.50 mm	86,4	6,11	1,15	2,63E-05	0,06	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.
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	2,04	4,04	11,81	n.a.	n.a.	n.a.	n.a.	n.a.
E2011-0.50 mm	432	6,48	1,52	8,75E-05	0,06	17,39	3,30	0,52	9,84	8,04	3,02	4,12	11,84	n.a.	5645,58	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.
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	2,18	7,66	435,03	462,57	123,25	22,50	n.a.
E2011-1 mm	3,8	5,82	0,86	8,11E-08	0,02	20,29	3,07	b.d.l.	7,79	7,94	1,88	2,85	8,43	236,04	3748,97	134,50	736,00	n.a.
E2011-1 mm	10,8	5,98	0,99	1,07E-05	0,02	20,81	2,95	b.d.l.	7,08	6,83	1,77	2,42	7,94	176,46	532,44	145,88	121,50	n.a.
E2011-1 mm	21,6	5,84	0,68	1,40E-05	0,08	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.
E2011-1 mm	43,2	5,91	0,95	7,89E-05	0,19	21,19	2,96	b.d.l.	7,31	7,55	2,09	2,68	8,79	132,86	2002,28	167,94	313,31	n.a.
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	0,1
E2011-1 mm	259,2	6,70	1,74	6,45E-05	0,02	21,32	2,96	b.d.l.	6,93	7,62	2,28	3,08	9,40	216,83	###	212,63	1470,38	n.a.
E2011-1 mm	432	6,71	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.	208,38	798,31	n.a.	n.a.
E2011-1 mm	604,8	6,69	1,73	1,05E-04	0,04	21,35	3,00	b.d.l.	7,06	8,58	2,70	3,39	10,57	n.a.	204,13	122,25	n.a.	n.a.
E2012-1 mm	1,8	6,70	1,74	1,86E-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.
E2012-1 mm	3,8	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.
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	42,75	n.a.	n.a.
E2012-1 mm	21,6	6,54	1,58	9,45E-04	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.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.
E2012-1 mm	86,4	6,37	1,41	5,83E-05	0,05	10,56	6,88	b.d.l.	3,48	6,00	9,50	3,00	10,00	71,91	1958,81	105,75	44,00	n.a.
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	18,80	209,00	3378,33	67,50	286,75	n.a.
E2012-1 mm	432	6,71	1,75	1,09E-04	0,06	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.
E2012-1 mm	604,8	6,63	1,87	2,15E-04	0,04	10,93	28,25	b.d.l.	44,19	7,50	10,00	4,00	12,00	17,00	4255,13	142,75	411,00	n.a.
Po2012-0.125 mm	1,8	4,52	-0,44	1,96E-05	0,93	3,39	8,45	b.d.l.	441,14	28,19	2,34	30,09	85,04	228,07	218,17	774,50	4194,00	n.a.
Po2012-0.125 mm	3,8	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.
Po2012-0.125 mm	10,8	4,55	-0,41	1,18E-05	0,63	4,27	6,01	b.d.l.	495,46	29,80	3,01	29,97	104,55	218,25	368,75	776,00	3732,25	n.a.
Po2012-0.125 mm	21,6	4,54	-0,42	1,38E-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.
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	110,30	348,83	747,83	524,67	2371,67	n.a.
Po2012-0.125 mm	86,4	4,7	-0,26	1,82E-05	0,70	3,70	5,27	b.d.l.	505,98	29,67	2,83	32,21	111,53	241,83	588,00	794,70	5027,60	n.a.
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.
Po2012-0.125 mm	432	4,66	-0,10	2,48E-05	0,66	4,25	9,91	b.d.l.	511,45	36,65	6,54	31,58	117,81	337,00	###	861,25	9336,38	n.a.
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.
Po2012-0.063 mm	1,8	4,01	-0,95	1,01E-05	1,91	3,35	10,1	b.d.l.	492,00	39,64	1,92	43,64	114,31	94,26	446,20	2510,84	6101,53	n.a.
Po2012-0.063 mm	3,8	4,04	-0,92	1,87E-05	3,29	5,29	13,6	2,1	77,00	49,67	2,79	60,53	213,66	84,38	466,40	2916,22	7302,96	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	538,88	1607,35	1808,90	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	775,88	1887,96	1458,51	n.a.
Po2012-0.063 mm	43,2	4,24	-0,72	3,29E-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.
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.
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	260	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.

Sample	t (10 <sup>3</sup> s)	pH	NH <sub>3</sub>
E2011-0.25mm	1,8	6,32	0,03
E2011-0.25mm	3,6	6,15	0,02
E2011-0.25mm	10,8	6,05	0,02
E2011-0.25mm	21,6	5,93	0,02
E2011-0.25mm	43,2	5,82	0,02
E2011-0.25mm			

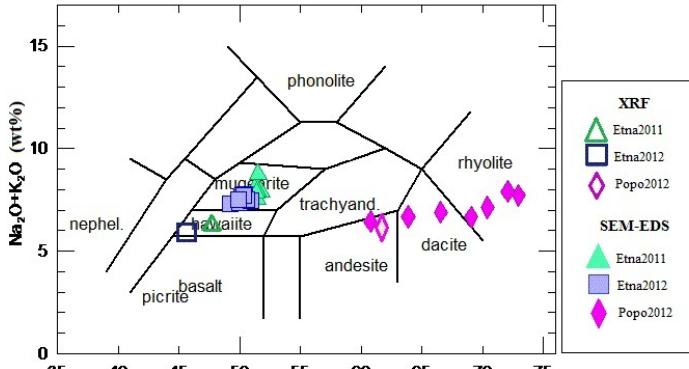
Sample	t (10 <sup>3</sup> s)	Anions (mg/l)				Cations (mg/l)				Trace elements (µg/l)									
		pH	Δ pH	NH <sub>4</sub> <sup>+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	B	Si	Mn	Fe	Hg	As		
mQ water	4,96	-	b.d.l.	b.d.l.	0	7,69	b.d.l.	0,57	0,02	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	3504,99	272,50	<b>880,40</b>	n.a.	
E2011-0.25mm	3,8	6,15	1,19	1,82E-05	0,03	20,86	4,03	b.d.l.	33,88	14,72	4,33	3,13	11,90	89,25	314,47	194,63	<b>158,00</b>	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	<b>418,00</b>	n.a.	
E2011-0.25mm	21,6	5,93	0,97	1,51E-05	0,03	19,84	4,00	b.d.l.	35,04	14,87	4,29	3,28	12,41	58,14	1403,52	216,00	78,13	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	3,86	15,53	53,04	2123,64	280,13	70,00	<b>n.a.</b>	
E2011-0.25mm	86,4	6,45	1,49	n.a.	n.a.	21,38	8,49	1,75	41,14	16,10	5,05	3,84	16,89	48,45	3174,75	n.a.	<b>234,00</b>	n.a.	
E2011-0.50 mm	1,8	6,03	1,07	1,83E-05	0,03	15,87	3,32	b.d.l.	8,87	6,72	2,55	3,11	9,61	105,06	873,71	<b>132,25</b>	<b>317,75</b>	n.a.	
E2011-0.50 mm	3,8	6,01	1,05	1,89E-05	0,03	16,64	3,74	b.d.l.	9,26	6,32	2,34	3,20	10,00	82,11	868,61	<b>134,85</b>	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.	
E2011-0.50 mm	21,6	6,14	1,18	2,25E-05	0,02	17,59	3,95	b.d.l.	10,20	7,15	2,55	3,57	10,00	430,44	2361,81	<b>164,83</b>	<b>449,50</b>	n.a.	
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	2,02	3,65	10,32	240,72	1378,02	147,23	16,75	n.a.	
E2011-0.50 mm	86,4	6,11	1,15	2,63E-05	0,02	17,36	3,34	b.d.l.	9,35	7,52	2,72	3,74	10,41	178,50	2659,14	<b>157,25</b>	<b>307,13</b>	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	2,04	4,04	11,81	n.a.	n.a.	n.a.	n.a.	n.a.	
E2011-0.50 mm	432	6,48	1,52	8,75E-05	0,06	17,39	3,30	0,52	9,84	8,04	3,02	4,12	11,84	n.a.	5645,58	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	11,78	271,83	6619,33	<b>210,75</b>	166,00	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	2,18	7,66	435,03	462,57	<b>123,25</b>	<b>22,50</b>	<b>n.a.</b>	
E2011-1 mm	3,8	5,82	0,86	8,11E-08	0,02	20,29	3,03	b.d.l.	7,79	7,94	1,88	2,85	8,43	236,04	3748,97	<b>134,50</b>	<b>736,00</b>	n.a.	
E2011-1 mm	10,8	5,98	0,99	1,07E-05	0,02	20,81	2,95	b.d.l.	7,08	6,83	1,77	2,42	7,94	176,46	532,44	<b>145,88</b>	<b>121,50</b>	0,77	
E2011-1 mm	21,6	5,84	0,68	1,40E-05	0,02	20,84	2,85	b.d.l.	7,24	7,39	2,04	2,58	8,47	145,35	1325,49	<b>158,50</b>	<b>468,63</b>	0,77	
E2011-1 mm	43,2	5,91	0,95	7,89E-05	0,19	21,19	2,98	b.d.l.	7,31	7,55	2,09	2,68	8,79	132,86	2002,28	<b>167,94</b>	<b>313,31</b>	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	<b>177,38</b>	158,00	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	3,08	9,40	216,83	<b>212,63</b>	<b>1470,38</b>	n.a.	n.a.	
E2011-1 mm	432	6,70	1,74	8,52E-05	0,02	21,13	3,02	b.d.l.	7,44	8,10	2,49	3,23	9,99	n.a.	n.a.	208,38	<b>798,31</b>	n.a.	n.a.
E2011-1 mm	604,8	6,69	1,73	1,09E-04	0,04	19,93	2,85	b.d.l.	7,06	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	1,86E-04	0,06	9,50	7,14	b.d.l.	3,54	6,00	9,00	2,50	8,50	228,48	1048,05	<b>101,25</b>	<b>170,00</b>	<b>n.a.</b>	
E2012-1 mm	3,8	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	1,03	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	<b>92,50</b>	5,50	n.d.	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	<b>108,75</b>	91,00	n.a.	n.a.
E2012-1 mm	86,4	6,37	1,41	5,83E-05	0,05	10,56	6,88	b.d.l.	3,48	6,00	9,50	3,00	10,00	71,91	1958,81	<b>105,75</b>	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	18,80	209,00	3378,33	<b>67,50</b>	<b>286,75</b>	n.a.	n.a.
E2012-1 mm	432	6,71	1,75	1,09E-04	0,02	11,19	n.a.	b.d.l.	n.a.	7,50	10,00	3,75	n.a.	189,50	3816,73	105,13	<b>348,88</b>	n.a.	n.a.
E2012-1 mm	604,8	6,83	1,87	2,15E-04	0,04	10,93	28,25	b.d.l.	44,19	7,50	10,00	4,00	12,00	17,00	4255,13	<b>142,75</b>	411,00	n.a.	n.a.
Po2012-0.125 mm	1,8	4,52	-0,44	1,96E-05	0,93	3,39	8,45	b.d.l.	<b>441,14</b>	28,19	2,34	30,09	85,04	228,07	218,17	<b>774,50</b>	<b>4194,00</b>	n.a.	0,2
Po2012-0.125 mm	3,8	4,57	-0,39	1,31E-05	0,68	3,42	10,22	b.d.l.	<b>466,39</b>	28,31	2,33	28,04	92,23	206,33	297,33	<b>784,00</b>	<b>3873,25</b>	n.a.	0,21
Po2012-0.125 mm	10,8	4,55	-0,41	1,18E-05	0,63	4,27	6,01	b.d.l.	<b>495,46</b>	29,80	3,01	29,97	104,55	214,25	368,75	<b>776,00</b>	<b>3732,25</b>	n.a.	0,56
Po2012-0.125 mm	21,6	4,54	-0,42	1,38E-05	0,76	4,67	7,12	b.d.l.	<b>519,61</b>	30,61	2,91	31,85	109,93	281,54	378,17	<b>926,88</b>	<b>4883,13</b>	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.	<b>496,57</b>	30,74	3,10	30,44	111,30	348,83	747,83	<b>524,67</b>	<b>2371,67</b>	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.	<b>505,98</b>	29,57	2,83	32,21	111,53	241,83	588,00	<b>794,70</b>	<b>5027,60</b>	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.	<b>528,55</b>	32,60	3,51	32,98	121,35	236,00	1695,00	<b>836,00</b>	<b>3422,83</b>	n.a.	0,1
Po2012-0.125 mm	432	4,66	-0,10	2,48E-05	0,66	4,25	9,91	b.d.l.	<b>511,45</b>	36,65	6,54	31,58	117,81	337,00	###	<b>861,25</b>	<b>9336,38</b>	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.	<b>531,74</b>	32,75	3,39	32,45	120,76	327,75	2326,75	<b>795,75</b>	<b>2565,75</b>	n.a.	0,87
Po2012-0.063 mm	1,8	4,01	-0,95	1,01E-05	1,91	3,35	10,1	1,33	<b>492,00</b>	39,64	1,92	43,64	114,31	94,26	446,20	<b>2510,84</b>	<b>6101,53</b>	n.a.	n.a.
Po2012-0.063 mm	3,8	4,04	-0,92	1,87E-05	3,29	5,29	13,6	2,1	<b>770,00</b>	49,67	2,79	60,53	213,86	84,38	466,40	<b>2916,22</b>	<b>7302,96</b>	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	<b>856,00</b>	55,80	4,47	63,33	234,98	237,00	538,88	<b>1607,35</b>	<b>1808,90</b>	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	<b>854,00</b>	54,06	3,98	60,31	231,09	268,41	775,88	<b>1887,96</b>	<b>1458,51</b>	n.a.	n.a.
Po2012-0.063 mm	43,2	4,24	-0,72	3,29E-05	3,63	6,58	12,7	1,47	<b>785,00</b>	48,45	7,25	56,71	219,33	78,47	1153,76	<b>2165,58</b>	<b>2483,93</b>	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	<b>899,00</b>	55,50	3,48	65,64	269,38	102,45	2809,21	<b>2635,04</b>	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.	<b>856,00</b>	53,5	4,3	62,8	260	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.	<b>845,00</b>	56,1	3,5	66,1	275	n.a.	n.a.	n.a.	n.a.	n.a.	

mac 7/11/15 23:02

Sample	t (10<sup>3</sup>s)	pH	Nl
<tbl\_info cols="

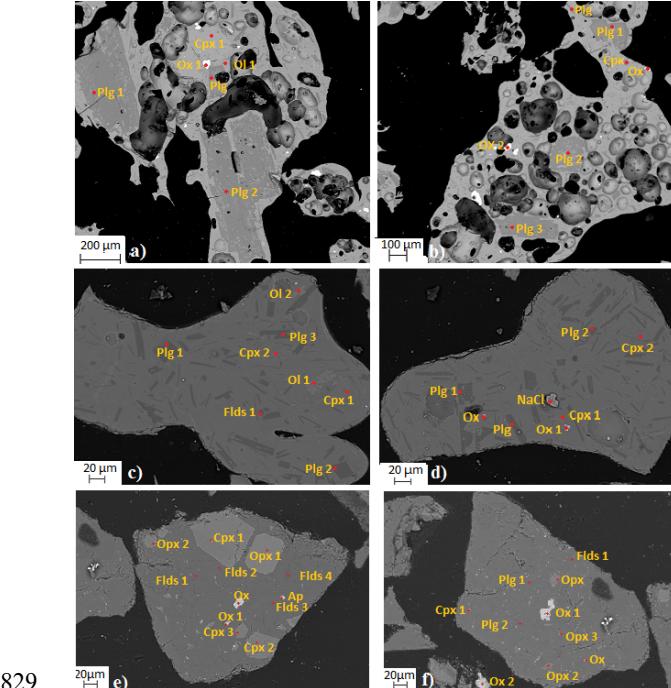
Sample	t (10 <sup>-3</sup> s)	Anions (mg/l)			Cations (mg/l)			Trace elements (µg/l)					
		F	Cl	SO <sub>4</sub>	Na	K	Mg	Ca	B	Si	Mn	Fe	As
E12/08/2011-1 mm	1.8	11.88	2.51	6.40	5.76	0.90	1.18	9.79	-240.00	-110.00	104.37	892.63	-0.22
E12/08/2011-1 mm	3.6	11.96	1.00	6.48	7.98	1.29	1.74	13.52	-240.00	10.00	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	-240.00	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	-0.17	5.05	-235.00	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	-230.00	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	-120.00	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	-120.00	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	-120.00	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	-220.00	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	-120.00	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	-210.00	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	-130.00	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	-60.00	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	-130.00	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	-230.00	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	-120.00	12350.00	n.a.	n.a.	0.63
E24/04/2012-1 mm	1.8	2.27	3.12	1.49	0.52	-0.25	0.01	6.66	-130.00	30.00	2.62	22.63	0.11
E24/04/2012-1 mm	3.6	1.31	0.26	-0.28	0.89	-0.92	0.35	7.55	-180.00	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	-120.00	910.00	35.62	260.63	0.19
E24/04/2012-1 mm	21.6	2.54	2.81	2.22	2.20	-0.38	-0.16	7.82	-220.00	1750.00	9.15	97.48	0.32
E24/04/2012-1 mm	43.2	4.30	2.44	0.33	0.57	-0.35	0.36	6.73	-210.00	1260.00	37.00	229.88	0.27
E24/04/2012-1 mm	86.4	4.35	2.98	0.81	0.91	-0.33	0.73	8.68	-130.00	1150.00	38.87	443.13	-0.12
E24/04/2012-1 mm	259.2	4.72	3.04	1.04	2.71	-0.51	1.34	9.44	-100.00	n.a.	47.87	663.88	-0.12
E24/04/2012-1 mm	432	9.21	6.66	3.10	3.97	-0.20	-0.01	6.66	-70.00	11410.00	283.65	11476.38	0.32
E24/04/2012-0.5 mm	1.8	2.42	3.14	2.66	0.91	0.58	-0.30	6.86	-110.00	510.00	5.65	189.08	0.19
E24/04/2012-0.5 mm	3.6	1.66	1.12	0.65	0.58	-0.90	0.25	7.01	-160.00	40.00	7.75	38.13	0.51
E24/04/2012-0.5 mm	10.8	0.97	8.67	0.27	-1.78	-1.68	-0.79	3.91	-280.00	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	-140.00	1150.00	53.00	250.63	9.87
E24/04/2012-0.5 mm	43.2	1.34	-0.07	-0.13	-1.59	-1.19	-0.09	6.97	-210.00	450.00	13.88	141.88	22.42
E24/04/2012-0.5 mm	86.4	0.65	-0.54	-0.79	-0.45	0.01	-0.03	6.18	-220.00	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	-381.22	333.45	1347.67	953.42	n.a.
Popo2012-0.125 mm	3.6	2.35	5.67	477.45	30.39	-0.08	36.85	114.52	-327.78	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	-391.75	1718.75	137.83	n.a.	n.a.
Popo2012-0.125 mm	21.6	2.19	3.84	486.45	29.92	2.80	34.02	128.70	-407.41	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	-401.55	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	131.50	-407.78	107.16	41.00	10.65	n.a.
Popo2012-0.125 mm	259.2	2.90	3.74	535.45	58.32	4.51	71.98	242.00	-388.55	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	-273.90	10831.68	2435.71	1904.28	n.a.
Popo2012-0.063 mm	1.8	2.62	12.70	755.45	49.86	3.38	62.11	203.52	-369.02	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	-362.76	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	-357.57	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	-343.98	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	-286.40	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.

825



826

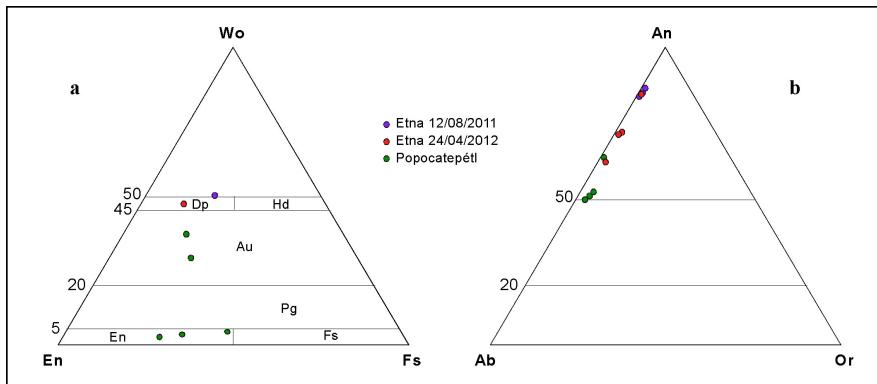
Figure 1 – Total alkali vs. silica (TAS) diagram for bulk rock and glass analyses of Etna 2011, Etna 2012 and Popocatépetl samples.



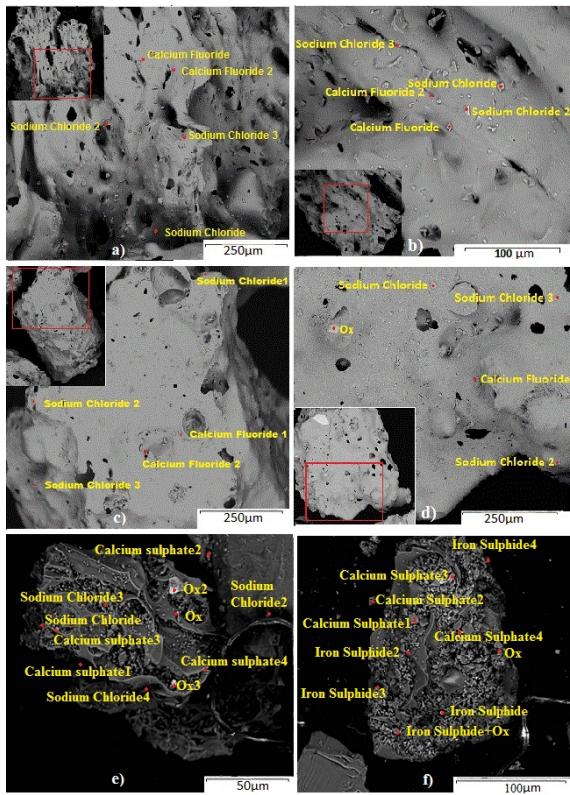
829

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

834

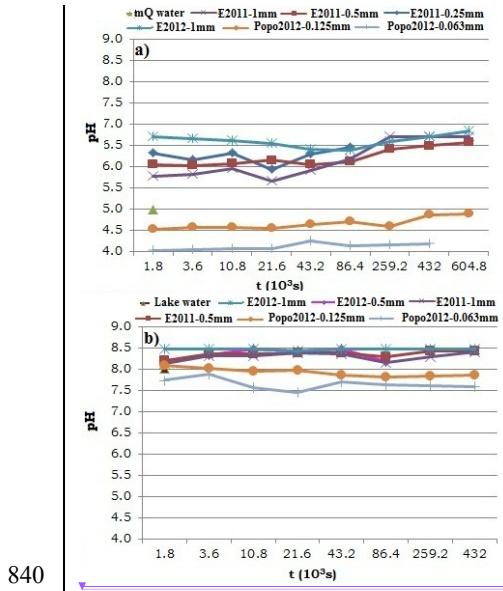


835 Figure 3 – Ternary diagrams for the classification of a) pyroxenes and b) feldspars.

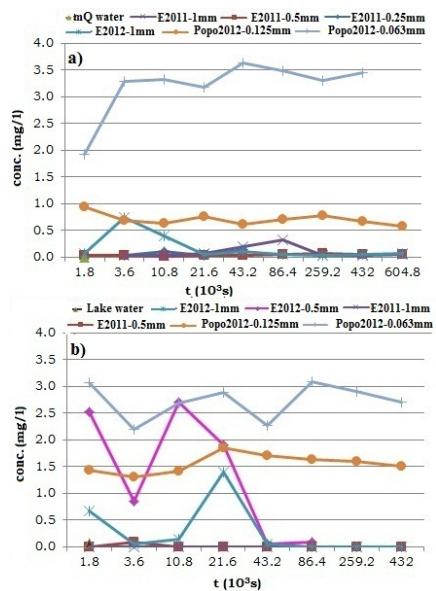
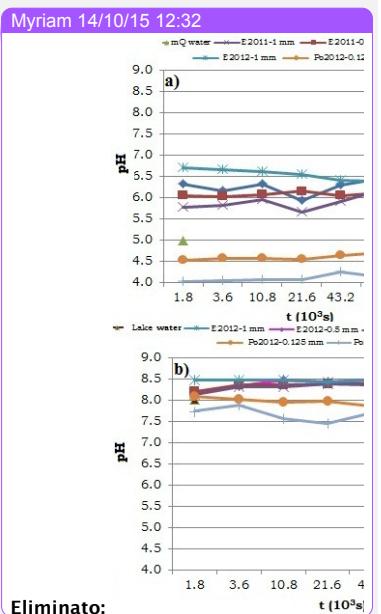


836

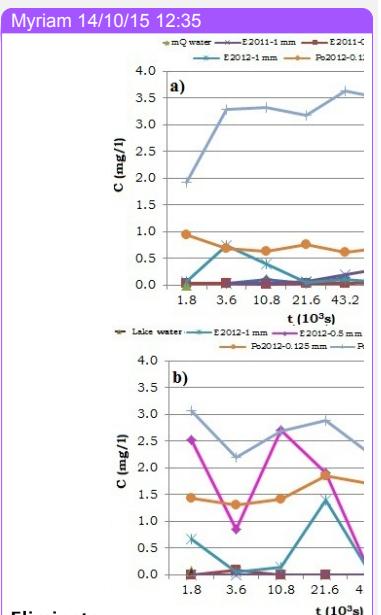
837 Figure 4 – SEM-BSE images of fresh ash particles from Etna 2011 (a and b), Etna 2012  
 838 (c and d), and Popocatépetl samples (e and f). The inserts in the lower left corner  
 839 indicate the investigated area. In yellow are the detected sublimated salts.

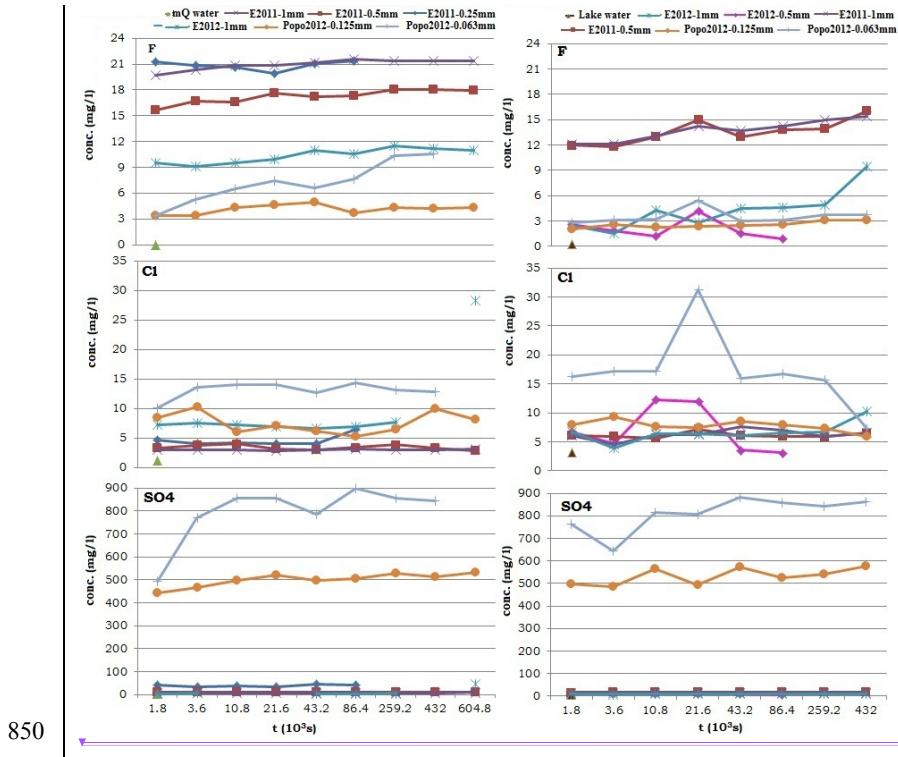


841 Figure 5 – a) pH variation of ash leachates in mQ; and, b) pH variation of ash leachates  
842 in lake water. The samples were washed using variable time of stirring and different  
843 grain-size. The pH of mQ and lake water is reported for comparison.

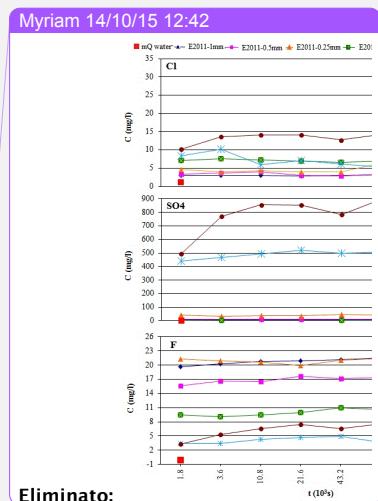


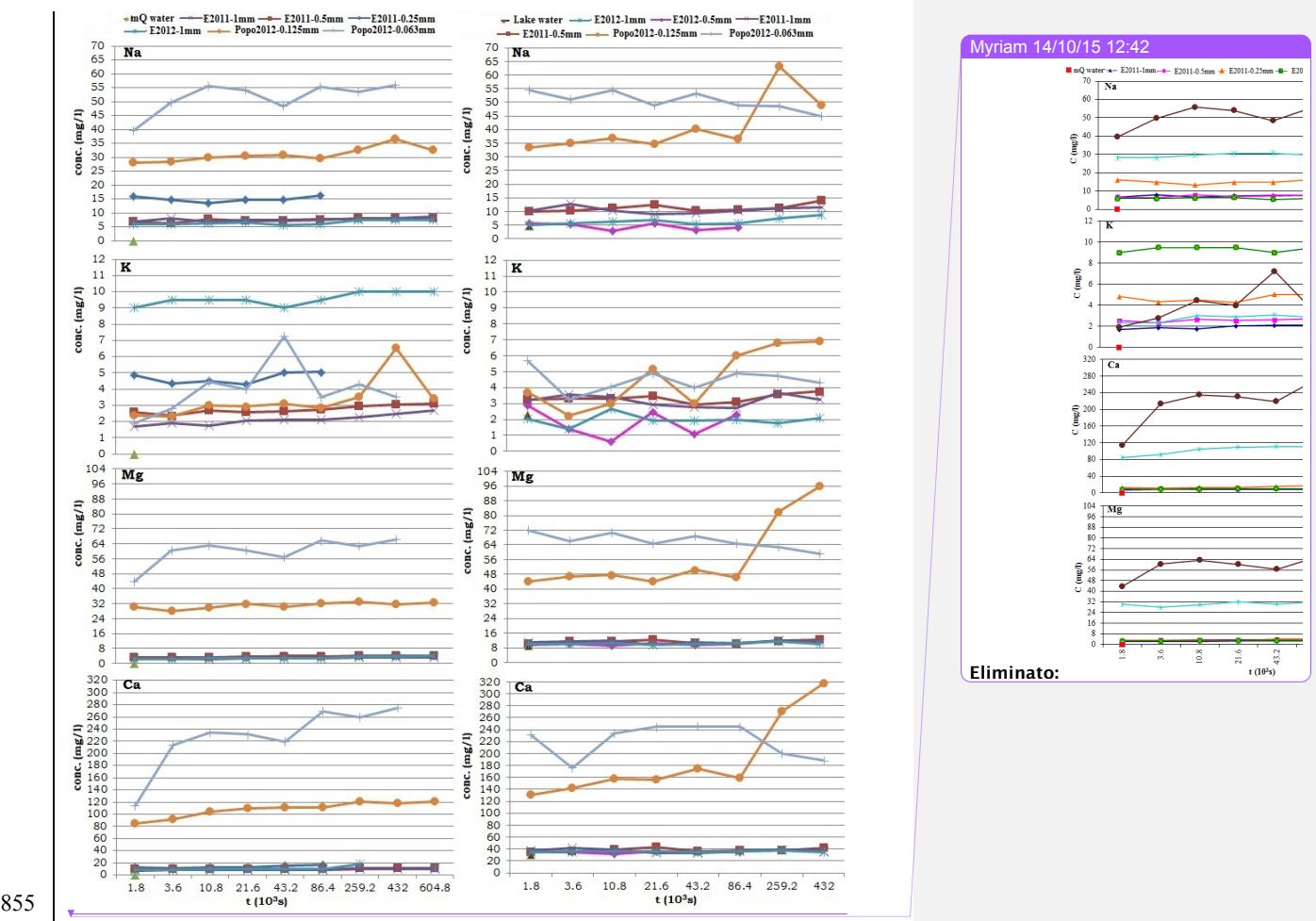
844 Figure 6 – NH<sub>3</sub> (ammonium) variation of ash leachates in: a) mQ; and, b) lake water for  
845 variable time of stirring and different grain-size. The NH<sub>3</sub> content of mQ and lake water  
846 is reported for comparison.  
847

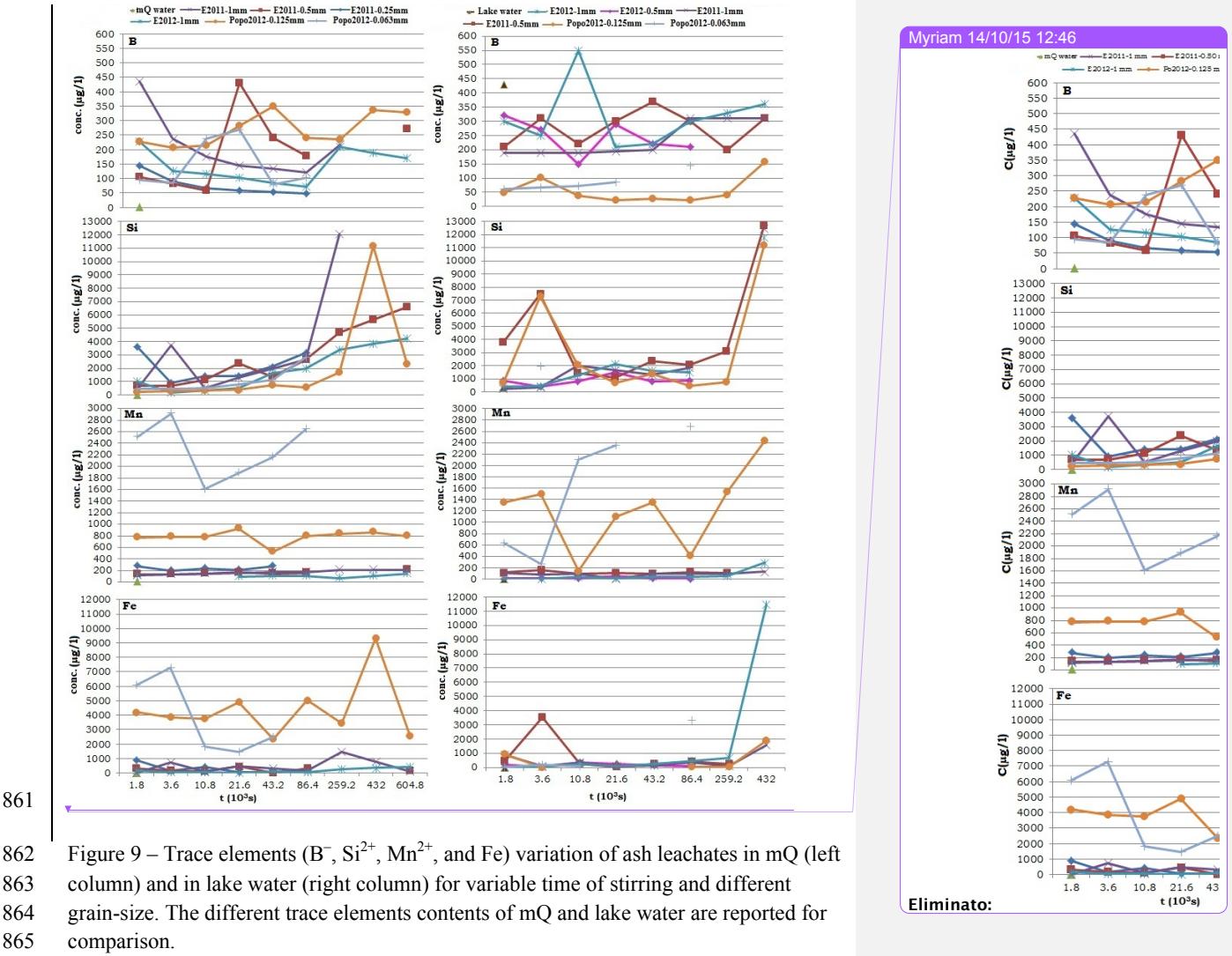




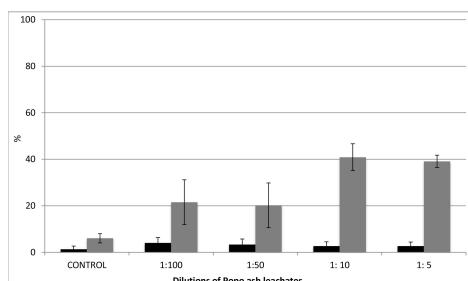
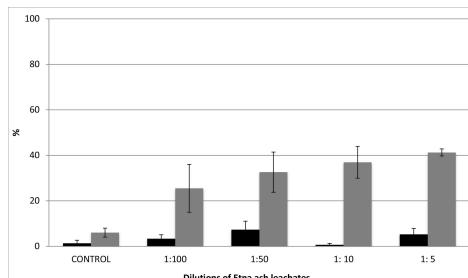
851 Figure 7 - Anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{F}^-$ ) variation of ash leachates in mQ (left column)  
852 and in lake water (right column) for variable time of stirring and different grain-size.  
853 The different anions contents of mQ and lake water are reported for comparison.





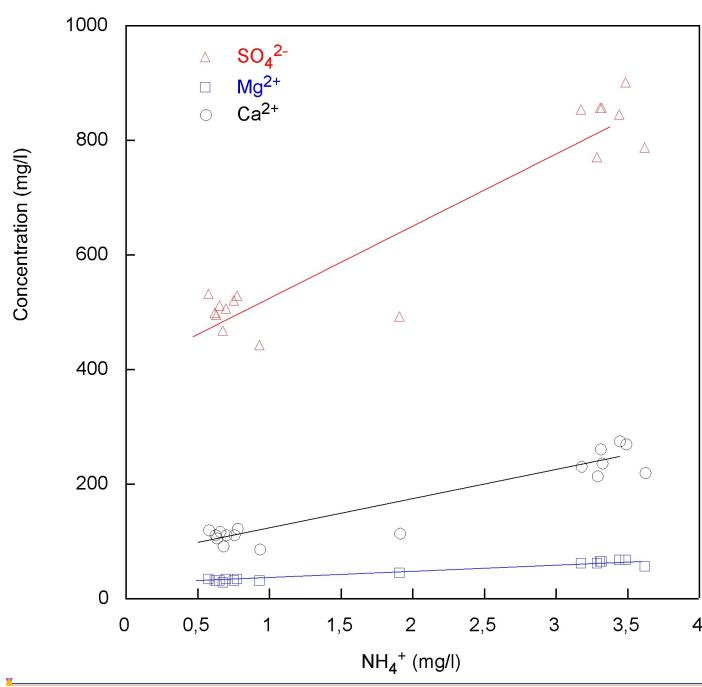


867

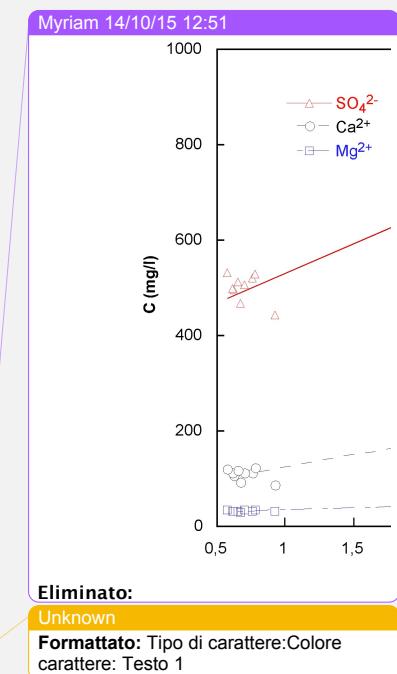


868 Figure 10 – Results of the FETAX test with ash leachates from Etna 2012 (a) and  
 869 Popocatépetl (b). Black histograms = mortality %; grey histograms = malformed larvae  
 870 %; bars = standard error of the mean.

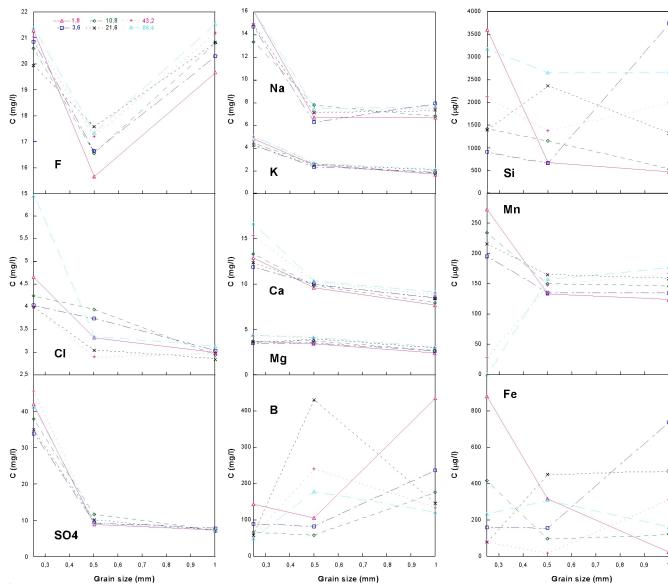
871



872

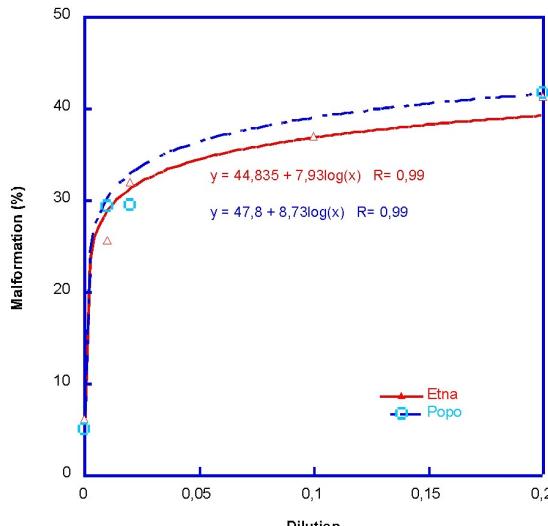


874 Figure 11 - Correlation of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  vs.  $\text{NH}_3$  for Popocatépetl samples.



875

876 Figure 12 – Dependence of element release to grain-size and times of stirring for Etna  
877 2011 samples. The colours indicate different time of stirring, expressed as  $s \times 10^3$ .



878

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

Myriam 14/10/15 12:57

**Commenta [1]:** Questa forse è da separare in 3: anioni, cationi e elementi in tracce.  
Così nn si vede nulla.