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This is an **author produced version** of a paper published in:

Science of the Total Environment 625 (2018): 16-26

DOI: <https://doi.org/10.1016/j.scitotenv.2017.12.223>

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**TOTAL AND FRACTION CONTENT OF ELEMENTS IN VOLCANIC SOIL: NATURAL OR
ANTHROPOGENIC DERIVATION**

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Abstract

Soil element composition derives from parent material disaggregation during pedogenesis and weathering processes but also by anthropogenic inputs. Elements are present in soils in different chemical forms that affect their availability and mobility. The aim of the study was to evaluate the main derivation, natural or anthropogenic, of elements in the soils of the Vesuvius National Park (a natural environment strongly affected by human impacts). Besides, the effects of age of the lava from which soils derive, different vegetation covers, traffic fluxes along the two roads connecting the Vesuvius crater and altitudes of the sites on the pseudo-total element concentrations and on their contents in different fraction of soil were investigated. To reach the aims, BCR (Bureau Commun de Référence) sequential extraction was performed in order to determine the distribution of elements into: acid-soluble, reducible, oxidizable and residual fractions. The relationship between the main environmental media and distribution of elements was discussed using non-metric multidimensional scaling (NMDS). The findings showed that, with the exception of Cd, Cu, Pb and Zn that would seem to derive also from human activities, the other investigated elements (Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, Si, Ti, V, W and Zn) mainly had a natural derivation. Among the investigated elements, only Cd could represent a potential high risk for the studied andosols. The highest element accumulations in the soils at low altitude could be attributable to an integrated effect of plant cover, vicinity of downtowns and traffic flux. The acid-soluble fraction of elements appeared more linked to lava age; the reducible and oxidizable ones to plant cover; the residual one to the chemical composition of the parent material that gave origin to the soils.

Keywords: pseudo-total content; element fractionation; contamination factor; pollution load index, risk assessment code

1. Introduction

Soil element composition derives from the integration of local conditions such as geology, climate and hydrology, and it strongly depends on parent material disaggregation during pedogenesis and weathering processes (De Nicola et al., 2003; Martínez Cortizas et al., 2003). Nevertheless, also external factors, such as anthropogenic activities, directly affect the element composition of soil surface layer (Buccianti et al., 2015). In fact, during the last years, human activities (*i.e.* tourism, agriculture, urbanization and industrialization) have caused an increase of major and trace elements in soils (Wiseman et al., 2013). In addition, human activities are confirmed as primary sources of elements in the air gaseous phase or particulates that can reach the surface soils through dry or wet depositions (De Nicola et al., 2003; Werkenthin et al., 2014). For instance, As, Se, Sb and Hg, showing high affinity for the volatile phase, can be aerial transported and are often associated to long distance contamination (Buccianti et al., 2015). As a result, the human activities can determine a significant modification of the elemental status of the soils. Therefore, the identification of the main derivation of a single soil element by geogenic or anthropogenic sources could be difficult especially originate from both (Cicchella et al., 2005; Buccianti et al., 2015).

Elements are mainly present in soils as acid-soluble, carbonate-associated, Fe-Mn oxide-associated and organic-associated forms (Fernández-Ondoño et al., 2017). Besides, some elements can be strongly bound to silicates, representing the residue form, and cannot be available from organisms (Denaix et al., 1999; Tanneberg et al., 2001). Recently, in order to evaluate element fate in soil system, element mobility along the soil profile and the potential element bioavailability or toxicity, the identification of the element amount in different soil geochemical phases and not only the total content is required (Adamo et al., 2007). Soil element fractionation, distribution and mobility depend not only on chemical composition of the parental material (Maeda et al., 2003), but also on various chemical and physical characteristics of soil, such as pH, cationic exchangeable capacity, water and organic matter contents (Peijnenburg et al., 2007; Degryse et al., 2009). By

72 now, studies dealing with associations of elements in the various fractions in andosols are poorly
73 present in the scientific literature (Hernandez-Moreno et al. 2007).

74 In this framework, the Vesuvius National Park is a good environmental model to provide a
75 contribution to the present knowledge about the evaluation of natural or anthropogenic derivation of
76 some elements in the soils. In fact, the soils of the Vesuvius are mainly andosols or present andic
77 character (Arnalds et al., 2007) and, deriving by pyroclastic materials (Shoji et al., 1978), are rich in
78 neoformed amorphous aluminosilicates and organo-mineral compounds that have high capacity to
79 bind elements (Eswaran et al., 1993; Tanneberg et al., 2001). It is been reported that the chemical
80 species composition of the Vesuvius substrates is a function of the age of the lava and pyroclastic
81 materials and of the time and degree of alteration. In fact, Belkin et al. (1998) have reported that
82 silicate-melt inclusions showed a decrease of some components such as total alkalis, SO_3 , Cl, Li, B
83 and Sr and a decrease of Zr and Y passing from samples of lava of 25000 yr B.P. to 1631-1944
84 A.D. The Vesuvius is located at few kilometres from Naples, one of the most populated cities in
85 Campania (Southern Italy) where various and intensive human activities occur, emitting pollutants
86 in the atmosphere (*i.e.* intensive vehicular traffic, small industries, domestic heating). In addition,
87 itself is a touristic destination of thousands of people per year who reach the crater by any kinds of
88 vehicles.

89 The aims of the study were to evaluate the main derivation (natural or anthropogenic) of
90 elements in the soils of the Vesuvius National Park and their behaviour in the soils. The
91 identification of the main source of contaminants can be useful to contain their emissions in order to
92 preserve and/or restore the soils quality inside the park. To reach the aims, the element fractions
93 were detected according the BCR (Bureau Commun de Référence) sequential extraction
94 (recommended by the Commission of the European Communities, 1987, and modified by Ure et al.,
95 1993) in order to separate the elements into: acid-soluble, reducible (associated to Fe-Mn oxides),
96 oxidizable (associated to organic matter content and sulphides) and residual fractions (associated to
97 primary and secondary well-crystallized minerals). The acid-soluble fractions are considered as

98 bioavailable, the reducible and oxidizable fractions can be potentially bioavailable, whereas the
99 residual fraction is considered not available for organisms (Ma and Rao, 1997; He et al., 2006;
100 Rodriguez et al. 2009). In addition, the element pseudo-total content (calculated as the sum of the
101 content of the four fractions) was also used. Other aim of the research was to investigate the
102 relationships between the element pseudo-total or fraction contents to different: i) age of the lava
103 from which soils derive, ii) vegetation covers, iii) traffic fluxes along the two roads (one accessible
104 over the year long and the other one accessible only for six months a year) connecting the Vesuvius
105 crater, iv) microclimate conditions, considering sites at two altitudes (approximately 600 and 900 m
106 a.s.l.).

107

108 **2. Materials and methods**

109 **2.1 Study area**

110 The Vesuvius National Park was established in 1995 and is located 12 km SE of Naples. It
111 covers an area of 8482 ha and contains Mt. Somma (maximum height: 1132 m a.s.l.), the original
112 volcano, and Mt. Vesuvius (maximum height: 1281 m a.s.l.), originated from 79 A.D. eruption. The
113 soil of Mt. Vesuvius are classified as Lepti-Vitric Andosols according to the FAO soil classification
114 (Di Gennaro and Terribile, 1999) and the vegetation is constituted by native Mediterranean
115 vegetation based in trees (such as holm oak, maple, alder) and shrubs (such as myrtle, laurel,
116 viburnum, brambles, brooms), but are present some species such as black pine and black locust (De
117 Nicola et al., 2003; De Marco et al., 2013). In addition, especially on soils of recent origin and on
118 emergent rocks inside mature soils, lichens and mosses were also present.

119 Vesuvius is one of the most studied volcanoes because it has been active for about 25000 years
120 and for the alternation of explosive and effusive activities. At the present, Vesuvius is in a quiescent
121 phase and the last eruption started in 1913 and finished with the paroxystic phase in 1944 (Rolandi,
122 2010). Because of the various eruptions, the slopes of the Vesuvius present diversified landscapes
123 as result of different lava flows. In the last decades, Vesuvius is subject to intensive touristic flux.

124 Ercolano road was, for a long time, the unique road to reach the crater, but in 2012 also Matrone
125 road was opened to reach the crater only by old military vehicles and only from April to October.

126

127 2.2 Soil sampling

128 In this concern, the study focused on the soils in proximity of the two roads that lead to the
129 Vesuvius cone: Matrone (M) and Ercolano (E). At high altitude (H), the soils derive from the 1937
130 and 1891-1893 eruptions, respectively at Matrone and Ercolano roads, whereas at low altitude (L),
131 the soils in proximity of Matrone road derive from the 1906 eruption whereas those in proximity of
132 Ercolano by the 1944 one (Table 1).

133 In order to highlight probable differences according the traffic flow and microclimatic
134 conditions, on November 2016 a total of eight sites were selected along each road (Fig. 1): four
135 sites were selected at high altitude (approximately, 900 m a.s.l.) and four at low altitude
136 (approximately, 600 m a.s.l.). At each altitude, two sites were selected at each edge of the road and
137 two at approximately 30 m from the previous towards the vegetation (Table 1). At each site, five
138 subsamples of surface soil (0-10 cm) were collected, after litter removal, and mixed to obtain a
139 homogeneous sample, in order to perform the physico-chemical analyses.

140

141 2.3 Physico-chemical analyses

142 All the physico-chemical analyses were carried out on triplicates of sieved ($< 2\text{mm}$) soil samples
143 according to the methods reported by Colombo and Miano (2015). pH was measured, on fresh
144 samples, with pH-meter on aqueous extract obtained adding distilled water to soil (2.5:1; v:v). The
145 water content was determined by drying fresh soil at $105\text{ }^{\circ}\text{C}$ until to reach constant weight. The
146 total carbon, nitrogen and sulfur concentrations were determined, on dry and pulverized samples, by
147 elemental analysis (Thermo Finnigan, CNS Analyzer). The organic carbon (C_{org}) content was
148 measured as above described for total carbon on dry samples previously treated with HCl (10%).

149 The soil organic matter content was calculated multiplying the C_{org} concentrations by 1.724 as
150 reported by Pribyl (2010).

151 The sequential extraction was applied to study the fractionation of metals in the soils (Fig. 2) and
152 determine their mobility and potential bioavailability as suggested by Community Bureau of
153 Reference, BCR (Rauret et al., 2000). Therefore, in order to determine the acid-soluble fraction
154 (F1), 40 mL of acetic acid 0.11M were added to 1 g of dry soil. The samples were shaken for 16 h
155 at 30 ± 10 rpm at 22 ± 5 °C in a mechanical shaker. The extract was separated by centrifugation at
156 5000 rpm for 20 min, the supernatant passed through 0.45 mm filter, collected in polyethylene
157 bottles and stored at 4°C until analyses. The residue was washed shaking for 15 min with 20 mL of
158 doubly deionised water and then centrifuged, discarding the supernatant. To determine the reducible
159 fraction (fraction associated to Fe-Mn oxides, F2), 40 mL of hydroxylamine hydrochloride 0.5M at
160 pH 1.5 was added to the residue of first step. The samples were treated as reported for the first step.
161 To determine the oxidizable fraction (fraction associated to organic matter content and sulphides,
162 F3), 10 mL of 8.8 M hydrogen peroxide was added to the residue of the second step. The mixture
163 was digested for 1 h at 22 ± 5 °C and for another 1 h at 85 ± 2 °C, and the volume was reduced to
164 less than 3 mL. A second aliquot of 10 mL of H_2O_2 was added, the mixture was digested for 1 h at
165 85 ± 2 °C, and the volume was reduced to about 1 mL. The residue was extracted with 50 mL of 1M
166 of ammonium acetate, adjusted to pH 2.0, at 30 ± 10 rpm and 22 ± 5 °C for 16 h. The extract was
167 separated and the residue was washed as reported for the first step. To determine the residual
168 fraction (associated to primary and secondary well-crystallized minerals, F4) 9 mL of HCl (37%)
169 and 3 mL of HNO_3 (69%) were added to 250 mg of soil and the samples were digested in
170 microwave oven (CEM MarsX press, USA) according to the procedure described in García-
171 Delgado et al. (2012). The element concentrations in the solutions obtained in each step were
172 determined by ICP-MS (Perkin-Elmer NexION 300). The sum of the concentrations of each
173 element in the four fractions is considered as pseudo-total. One lake sediments (BCR-701) certified
174 or with indicative values for extractable metal contents in the three steps of the modified BCR

175 sequential extraction procedure, and indicative values for *aqua regia* extraction (Rauret et al.,
176 2000), were used to ensure the quality of the results obtained. The accuracy of the obtained values
177 ranged between 80 and 140%.

178

179 2.4 Quantification of soil pollution

180 In order to assess the soil contamination level and the risk index, the contamination factor (CF),
181 pollution load index (PLI) and risk assessment code (RAC) were calculated. The contamination
182 factor (CF), the ratio between the pseudo-total concentration of each element in the soil at each
183 edge of the road and its background value (*i.e.* the element concentration in soil collected at the
184 natural reserve inside the Vesuvius National Park), was calculated using the equation reported
185 below and proposed by Tomlinson et al. (1980):

$$CF = \frac{C_{element}}{C_{background}}$$

186 The pollution load index (PLI), the geometric mean of the CF values for the n elements (Madrid
187 et al., 2002), was calculated only for the elements with CFs higher than 1 according to the following
188 equation:

$$189 \quad PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \dots \times CFn}$$

190 The risk assessment code (RAC), used as a risk index for Cd, Cu, Pb and Zn was calculated as
191 follows (Liang et al., 2017):

$$RAC = \frac{\text{amount of HM in F1}}{\text{total amount of HM}} \times 100$$

192 where *HM in F1* is the concentration of each investigated element in F1, *total amount of HM* is the
193 correspondent pseudo-total concentration. $RAC < 1\%$ indicates no risk; RAC ranging between 1–
194 10% indicates low risk; RAC ranging between 11–30% indicates medium risk; RAC ranging

195 between 31–50% indicates high risk; *RAC* ranging between 51–100% indicates very high risk
196 (Sundaray et al., 2011).

197

198 2.5 Statistical analyses

199 The unpaired t-test was performed in order to evaluate the differences between soils samples
200 from the two roads (Ercolano and Matrone) or altitudes (high and low) for each element fractions of
201 the BCR sequential extraction procedure. The similarity of the sites according to the mean value of
202 the contents of each element in the fractions (F1 - F4) was investigated through the multivariate
203 analysis of the non-metric multidimensional scaling (NMDS) based on the Euclidean distance and
204 performed on a matrix of 22 columns and 24 rows. In addition, the confidence ellipses (for $\alpha =$
205 0.05) for lava ages, traffic flows and vegetation covers were superimposed on the NMDS in order to
206 evaluate their effects on element distribution. The NMDS analyses were performed using the R
207 3.1.1 programming environment (R Core Team 2016) with functions from *Vegan*^ package,
208 whereas t-test was performed using Sigmaplot 12.0.

209

210 3. Results

211 The results of the physico-chemical characteristics of the soils collected at the investigated sites
212 are reported in Table 2. The soil pH values ranged from 6.5 to 8.0 (Table 2). The organic matter
213 and water contents showed wide variability among the sites as well as total C, N and S contents
214 with ranges of 1.78 - 26.3% d.w., 0.11 - 0.67% d.w. and 0.01 - 0.07% d.w., respectively (Table 2).

215 The pseudo-total element concentrations and their contents in different fractions (F1-F4) of the
216 investigated soils are reported, respectively, in Table 3 and Supplementary material. The pseudo-
217 total element concentrations showed that, at all the sites, the elements found in the lowest
218 concentrations were Cr, W and Cd, whereas Al, K, Ca and Fe were the most abundant.

219 The CFs showed differences according the site typologies, in fact they were higher than 1 for 12
220 (*i.e.* As, B, Ca, Cd, Cu, K, Na, P, Pb, Si, W and Zn) out of the 22 investigated elements with values
221 particularly high for Cd, Cu and Zn for the soils collected along Ercolano road (Table 4); they were
222 higher than 1 for 11 elements (*i.e.* Ba, Ca, Cd, Cr, Cu, Mg, Mn, Ni, Pb, Si and Zn) with values of
223 Cd particularly high for the soils collected along Matrone road (Table 4). The CFs showed values
224 higher than 1 for 4 (*i.e.* Cd, Cu, Si and Zn) out of the 22 investigated elements for the soils collected
225 at high altitude (Table 4); they were higher than 1 for all the elements (particularly higher were the
226 values for Cd, Cu, Pb and Zn) with the exception of La, P and Ti for the soils collected at low
227 altitude (Table 4).

228 The PLIs were 1.55, 1.37, 1.29 and 1.52, respectively, for the soils collected along Ercolano
229 road, Matrone road, at high altitude and low altitude (Table 4).

230 As Cd, Cu, Pb and Zn appeared the main contaminants in the investigated soils, the RAC were
231 calculated for these four elements. The results showed high risk for Cd in MH_1 and MH_2 (67%)
232 and EL_2 (63%), medium risk for Zn (25% in EL_1 and 50% in EH_1), and low risk for Cu and Pb
233 with RAC < 10%.

234 The most mobile elements in the Vesuvius soils, based on the element recovery in F1, were B,
235 Ca, Cd, Mn, Mg, Na, Si and Zn. The elements associated to oxi-hydroxides of Fe and Mn in F2
236 were Cd, Mn, Pb and Zn; whereas those associated to the oxidazable fraction of the soil (organic
237 matter and sulfides) in F3 were Al, As, Ba, Ca, Cr, Cu, La, Na, Ni, P, Pb, Si, V and W. Finally, F4,
238 associated to aluminosilicates and resistant fraction, was the most important fraction for all the
239 analyzed elements with the exception of Cd and Pb.

240 The NMDS performed using the results of F1 showed that the soils distributed according both
241 the altitude (axis 1) and the road (axis 2); that performed using the results of F2 and F3 (Fig. 3a, 3b
242 and 3c) showed that the soils mainly separated according to the altitude (axis 1); whereas that
243 performed using the results of F4 showed a soil separation mainly due to the road (Fig. 3a, 3b and

244 3c). The variability among the soils was wider in the first three NMDS, also showing similar values,
245 but it was narrower in the NMDS performed with F4 results (Fig. 3a, 3b and 3c).

246 The soils originated by the four lava ages clearly separated for F1 and F2, whereas the soils
247 originated from the lava flow of 1906 (ML), with similar concentrations of Mg, Mn and K in F1,
248 and 1944 (EL), with similar concentrations of Pb and B in F2, separated from those originated from
249 the lava flow of 1891-1893 (EH) and 1937 (MH) for F3 (Fig. 3a). By contrast, no separation among
250 the soils coming from lava with different ages was observed for F4 (Fig. 3a).

251 The soils covered by different plant (shrub or tree) mainly separated according to the element in
252 F2 and F3 (Fig. 3b). The soils covered by shrubs were characterized by similar concentrations of K,
253 As, Si and La in F2 and by similar concentrations of La, W, V, Si, Cd, Ca and Na in F3. Instead, the
254 soils covered by trees showed similar concentrations of Mn, Ca, Fe, Al, W and Ba in F2 and similar
255 concentrations of Al in F3 (Fig. 3b).

256 According to the kind of traffic flow (intense or less intense), the soils clearly separated for the
257 element contents in F1, a narrow separation was observed for F2 and F3 and no separations were
258 observed for F4 (Fig. 3c). In F1, the soils affected by low traffic flow showed similar concentrations
259 of As, Ba, V and Mg, whereas those affected by high traffic flow showed similar concentrations of
260 Cd, Na, Si, Zn, Ca and Al (Fig. 3c).

261 The soils collected along Ercolano road, with high traffic flow, showed statistically higher
262 concentrations of Na in F1, Na and Si in F2, P and La in F3 as compared to the soils collected along
263 Matrone road, with low traffic flow (Table 5). Instead, the concentrations of Mn in F1, Cd, Ni, Ti
264 and Zn in F2, Mg and Ti in F3 were statistically higher in the soils collected along Matrone road
265 (Table 5). No statistically significant differences for the element contents in F4 between the soils
266 collected along the two roads were observed (Table 5). The percentage ratios between fraction and
267 pseudo-total content showed the same distribution for all the elements, with the exception of B, Ni,
268 Si, Ti and Zn, in the soils collected along both the roads (Fig. 4).

269 The soils collected at high altitude showed statistically higher contents of Ti in F3; whereas the
270 soils collected at low altitude showed statistically higher contents of Mn, Na and Ni in F1, Cd, Na,
271 Ni, Si and Zn in F2, and Cr, La, Mg, Pb and Zn in the F3 fractions (Table 5). No statistically
272 significant differences for the element contents in F4 fractions between the soils collected at the two
273 altitudes were observed (Table 5). The percentage ratios between fraction and pseudo-total content
274 showed the same distribution for of the elements in the soils collected at both the altitudes (Fig. 5).
275 Exceptions were found for As, B, Ba, Cd, Mn, Pb and Zn that differed for the soils collected at the
276 two altitudes with higher values in F3 than in F4 (Fig. 5).

277

278 **4. Discussion**

279 The wide variability of pH values, organic matter, C, N and S contents observed in the sampled
280 soils likely was linked to the parent material disaggregation, weathering processes and topography
281 (Lozano-Garcia et al., 2016, Li et al., 2017). Besides, also plant cover gave an important role; in
282 fact, the different plant species differently contribute to litter amount, chemical composition and
283 decay, influencing the soil organic matter quality (De Marco et al., 2012).

284 The trace (*i.e.* Cr and Cd) and dominant (*i.e.* Al, K, Ca and Fe) elements likely derive from the
285 mineralogical composition of the soil samples such as leukite, $K[AlSi_2O_6]$ and augite
286 $(Ca,Mg,Fe)_2(Si,Al)_2O_6$, two of the most abundant minerals in Vesuvian rocks (Vingiani et al.,
287 2013). These minerals were identified by XRD in all the investigated soils. Other secondary
288 crystalline phases detected by XRD in the soils samples were iron oxides and multiple aluminum
289 silicates of K, Ca, Fe, Mg and Na.

290 In addition, pseudo-total concentrations of some elements in the investigated soils agreed with
291 those reported for volcanic rock powder by Ramos et al. (2017). The low concentrations of toxic
292 elements (such as Cr, Cd and Pb) could be attributable to the scarce potentiality of volcanic rocks to
293 bind them, whereas the abundance of Al, a widely recognized toxic element, could derive from the
294 alteration of aluminosilicate glassy matrix (Ramos et al., 2017), that are peculiar components of

295 andosols. The less abundant elements were traceable also in each fraction (F1-F4), whereas Ca was
296 the most abundant element in F1 and F2, Al in F3 and K in F4, suggesting that these elements
297 outnumber in different chemical forms. Among the investigated elements, Al, Fe and Mn were
298 extensively extracted in F4 (56-75%, 52-92% and 29-73%, respectively, of their correspondent
299 pseudo-total content), the less extractable fraction, endorsing the supposition that they were mainly
300 part of the solid phase (*i.e.* oxi-hydroxides and aluminosilicates) of the soils. Besides, a key role of
301 organic matter content in the distribution of Fe and Al in soil fractions cannot be excluded as, for
302 instance, ML_1 and ML_2 soil samples, with the highest content of organic matter (46.7 and 40.8%
303 d.w., respectively), also showed the lowest percentage of these elements in F4. In addition, at these
304 sites, the soils presented higher percentage of Al (36 and 31%, respectively, at ML_1 and ML_2)
305 and Fe (34 and 22% respectively, at ML_1 and ML_2) in F3 as compared to the other soil samples.

306 The main drivers of element fractionations in the soils would seem to be linked to specific site
307 characteristics such as altitude and proximity to the two roads. These site characteristics integrate
308 the effects due to different lava ages, plant covers, traffic flows and types, and microclimatic
309 conditions. The outcomes of the NMDS suggested that the chemical composition of the soils mainly
310 depended on lava age. In fact, the similar element contents of the residual fraction (F4), which
311 represents the portion of elements bound to the primary and secondary well-crystallized minerals,
312 suggested a comparable chemical composition of the lava, whereas the weathering time of the lava
313 would seem to affect the availability and mobility (F1, F2 and F3) of different elements. In
314 particular, the soils deriving by the lava of 1906 showed similar concentrations of Mg, Mn and K in
315 F1, whereas those deriving by the lava of 1944 showed similar concentrations of Pb and B in F2.

316 Also plant cover appeared to have an important role in element fractionations, especially for F2
317 and F3, as a clear separation was observed in the NMDS. Plants have a direct effect on soil
318 elemental composition as root exudates, changing the rhizosphere pH, modifying the oxidation
319 status of the elements and, in turns, their mobility and fate in the soil (Houben and Sonnet, 2015). In
320 addition, also the amount and quality of litter deriving from different plant species, affecting the soil

321 organic matter content, are important drivers the soil element mobility (Degryse et al., 2009; Abreu
322 et al., 2012). In the Vesuvius National Park, a clear role of soil element fractionations due to
323 different types of plant cover is evident. In fact, the element mobility and availability of the soils
324 collected at low altitude of Ercolano road, deriving by the lava flow of 1944 and covered by lichens
325 and herbaceous species clearly separated by those of the other soils.

326 However, in addition to the natural derivation of the elements of the soils inside the Vesuvius
327 National Park the anthropogenic one can not be excluded, especially for Cd, Cu, Pb and Zn that are
328 widely recognized as markers of vehicular traffic (De Silva et al., 2016; Wang et al., 2017) and that
329 are the main responsible of the higher CFs and PLIs for the soils collected at low altitude. These
330 soils, more than those at high altitude, were more exposed to the direct effect of the traffic flow
331 along the two roads connecting the crater of the Vesuvius for microclimatic conditions and plant
332 cover, and they also endured the effects of air particulates coming from the nearby cities. The
333 deposition of air particulate deriving by direct and indirect inputs decreases with the increase of
334 distance from the source of emission (Zhang et al., 2017).

335

336 **Conclusions**

337 The investigated elements in the soils of the Vesuvius National Park would mainly seem to be of
338 natural derivation. Exceptions were observed for Cd, Cu, Pb and Zn that would seem to derive also
339 from human activities. These elements, especially Cd, can represent a potential high risk for the
340 investigated soils. The highest element accumulations in the soils at low altitude could be
341 attributable to an integrated effect of the site characteristics (*i.e.* plant cover, vicinity of downtowns,
342 traffic flux and microclimatic conditions). The investigated andosols presented high capacity to
343 hold elements. Lava age and plant cover strongly affected the soil element fractionation. In
344 particular, the acid-soluble fraction appeared more linked to lava age, whereas the reducible and
345 oxidizable fractions to plant cover. The residual fraction of elements, that was comparable among

the investigated soils, suggested a similar chemical composition of the parent material that originated, over the time, the present soils.

The findings provide innovative information both at local and global scales. In fact, the individuation of the main origin of major, minor and trace elements in the soils can be useful in management practices inside and outside the investigated National Park; besides, the obtained data increase the scarce current knowledge dealing with associations of elements in the various fractions of volcanic soils that represent peculiar but widespread environments. Anyway, investigations on element composition of lava from which soils derive could be useful in order to relate it to that of soils as well as studies on soil biomass and activity could provide information about the effects of element contents in various fractions on biota.

5. Acknowledgments

This research activity has been realised in collaboration of the Biology Department of University Federico II of Naples and the Vesuvius National Park within the “Azione di Sistema - Impatto antropico da pressione turistica nelle aree protette: interferenze su territorio e biodiversità” funded by “Ministero dell’Ambiente e della Tutela del Territorio e del Mare”, Direttiva Conservazione della Biodiversità. The authors wish to thank Mrs. Roberta Leandri for English revision. Dr. García-Delgado thanks the Spanish Ministry of Economy and Competitiveness for his post-doctoral contract (JCFI-2015-23543). Chemical analysis has been economically supported by Ministry of Economy and Competitiveness of Spain (CTM2013-47874-C2-2-R).

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Figure captions

Fig. 1 – Map of the investigated area with the sampling sites.

Fig. 2 – Scheme of the procedure of the sequential extraction of elements from various soil fractions (F1-F4).

Fig. 3 – NMDS biplot for the element concentrations in each fraction (F1, F2, F3 and F4) in the investigated soils with the superimposition of the confidence ellipses (for $\alpha = 0.05$) relative to (a) lava ages (1891-1893, 1906, 1937, 1944), (b) plant covers (shrub or tree) and (c) traffic flows (less intense or intense).

Fig. 4 – Percentage contributes of elements in acid-soluble (F1, oblique lines), reducible (F2, dots), oxidazable (F3, grey) and residual (F4, grid) fractions of the soils collected along Ercolano and Matrone roads.

Fig. 5 – Percentage contributes of elements in acid-soluble (F1, oblique lines), reducible (F2, dots), oxidazable (F3, grey) and residual (F4, grid) fractions of the soils collected at high and low altitudes.

Table 1. Description and characteristics of the investigated sites inside the Vesuvius National Park **along Ercolano (E) and Matrone (M) roads, at low (L) and high (H) altitudes, in proximity (1) and far (2) from the road.**

Site	Geographical coordinates	Age of the pedogenetic substrate	Altitude (m a.s.l.)	Distance from the road (m)	Traffic intensity and duration	Vegetation cover	Litter layer (cm)
EL_1	40°49'49.156"N 14°24'0.273"E	1944	596	0	High 12 months a year	Holm oak, broom, lichens, euphorbia, black locust, ivy	< 1 cm
EL_2	40°49'49.156"N 14°24'0.273"E	1944	596	30	High 12 months a year	Broom, euphorbia, lichens	0 cm
EH_1	40°49'51.935"N 14°25'28.606"E	1891-1893	900	0	High 12 months a year	Broom, euphorbia	< 1 cm
EH_2	40°49'51.935"N 14°25'28.606"E	1891-1893	900	30	High 12 months a year	Pine, broom	5-7 cm
ML_1	40°48'19.04"N 14°26'13.361"E	1906	570	0	Medium 6 months a year	Pine, broom, holm oak, mosses	5-7 cm
ML_2	40°48'19.04"N 14°26'13.361"E	1906	570	30	Medium 6 months a year	Pine, broom, holm oak, mosses	5-7 cm
MH_1	40°48'55.246"N 14°26'18.679"E	1937	820	0	Medium 6 months a year	Pine, broom, mosses, bramble	1-2 cm
MH_2	40°48'55.246"N 14°26'18.679"E	1937	820	30	Medium 6 months a year	Pine, broom, bramble, holm oak	4-5 cm

Table 2. Mean values (\pm s.e.) of pH, organic matter content and water content (OM and WC, expressed as % d.w.), total C, N and S concentrations (expressed as % d.w.) in soils collected inside the Vesuvius National Park along Ercolano (E) and Matrone (M) roads, at low (L) and high (H) altitudes, in proximity (1) and far (2) from the road.

	pH	OM	WC	C	N	S
EL_1	7.0 (± 0.1)	7.45 (± 0.09)	58.4 (± 0.40)	8.02 (± 0.53)	0.38 (± 0.02)	0.03 (± 0.003)
EL_2	7.0 (± 0.1)	10.4 (± 0.40)	28.9 (± 0.70)	3.57 (± 0.23)	0.23 (± 0.02)	0.02 (± 0.01)
EH_1	8.0 (± 0.1)	10.6 (± 0.13)	14.1 (± 0.32)	1.78 (± 0.17)	0.11 (± 0.01)	0.01 (± 0.01)
EH_2	6.5 (± 0.1)	15.4 (± 0.71)	38.7 (± 1.31)	5.95 (± 1.02)	0.30 (± 0.04)	0.05 (± 0.01)
ML_1	6.6 (± 0.1)	46.7 (± 0.92)	102 (± 1.45)	26.29 (± 0.75)	0.65 (± 0.04)	0.07 (± 0.01)
ML_2	6.7 (± 0.1)	40.8 (± 1.22)	102 (± 1.75)	22.13 (± 0.18)	0.67 (± 0.02)	0.06 (± 0.01)
MH_1	7.8 (± 0.1)	12.0 (± 0.75)	26.6 (± 0.26)	3.71 (± 0.48)	0.24 (± 0.03)	0.02 (± 0.01)
MH_2	7.4 (± 0.1)	13.6 (± 0.71)	23.0 (± 1.28)	5.72 (± 1.46)	0.34 (± 0.06)	0.05 (± 0.05)

Table 3. Mean values (\pm s.e.) of pseudo-total concentrations of elements in soil collected inside the Vesuvius National Park along Ercolano (E) and Matrone (M) roads, at low (L) and high (H) altitudes, in proximity (1) and far (2) from the road.

	Al	K	Ca	Fe	Na	Mg	Si	P	Ti	Ba	Mn	Zn	V	Cu	Pb	La	B	Ni	As	W	Cr	Cd
	$\mu\text{g g}^{-1}$ d.w.																					
EL_1	72015	60155	46752	37758	15976	11375	7374	2378	1898	1092	1025	156	138	131	119	71.8	31.4	27.0	17.1	12.4	6.45	0.47
	(± 379)	(± 414)	(± 348)	(± 93.8)	(± 72.7)	(± 115)	(± 56.0)	(± 13.5)	(± 18.4)	(± 6.47)	(± 3.91)	(± 1.82)	(± 1.23)	(± 1.05)	(± 1.62)	(± 0.35)	(± 0.92)	(± 1.84)	(± 0.21)	(± 0.02)	(± 0.07)	(± 0.01)
EL_2	76490	72019	41153	35354	14266	9075	7595	2858	1841	657	868	149	147	786	152	76.2	26.9	21.9	60.6	14.5	5.06	0.80
	(± 1519)	(± 983)	(± 1128)	(± 1124)	(± 211)	(± 386)	(± 110)	(± 38.2)	(± 74.0)	(± 20.3)	(± 25.5)	(± 6.12)	(± 2.81)	(± 50.4)	(± 3.62)	(± 0.94)	(± 0.68)	(± 2.05)	(± 13.4)	(± 0.74)	(± 0.25)	(± 0.04)
EH_1	38486	25774	44104	22588	8703	8441	5302	1770	1327	703	558	133	104	107	48.5	42.1	10.1	19.4	7.42	6.40	3.79	0.21
	(± 571)	(± 454)	(± 1468)	(± 371)	(± 46.1)	(± 304)	(± 21.5)	(± 63.3)	(± 27.8)	(± 9.23)	(± 7.83)	(± 6.62)	(± 1.30)	(± 2.34)	(± 1.67)	(± 1.13)	(± 0.66)	(± 1.20)	(± 0.16)	(± 0.20)	(± 0.12)	(± 0.02)
EH_2	51428	33339	30736	24301	6958	8031	4127	2071	1350	695	596	45.2	100	120	46.9	51.2	12.9	18.1	13.5	9.43	4.00	0.43
	(± 564)	(± 824)	(± 124)	(± 240)	(± 537)	(± 64.3)	(± 9.74)	(± 9.50)	(± 13.7)	(± 7.42)	(± 6.98)	(± 0.25)	(± 0.54)	(± 1.24)	(± 0.19)	(± 0.15)	(± 0.72)	(± 1.04)	(± 0.04)	(± 0.17)	(± 0.11)	(± 0.04)
ML_1	61231	38956	41960	28457	8763	12350	5880	1265	1278	1015	1281	166	121	102	152	46.3	17.2	31.0	10.5	8.96	10.1	0.93
	(± 870)	(± 864)	(± 413)	(± 2266)	(± 114)	(± 2059)	(± 76.8)	(± 22.2)	(± 14.6)	(± 12.2)	(± 14.8)	(± 1.65)	(± 0.92)	(± 1.03)	(± 2.24)	(± 0.53)	(± 0.40)	(± 0.71)	(± 0.18)	(± 0.44)	(± 0.35)	(± 0.02)
ML_2	54962	33804	40617	32904	7448	14451	4970	1453	1281	891	1373	162	106	84.5	149	45.4	14.5	36.2	10.5	9.73	9.68	0.77
	(± 319)	(± 98.8)	(± 65.4)	(± 77.5)	(± 40.9)	(± 263)	(± 25.0)	(± 17.7)	(± 49.7)	(± 5.54)	(± 0.67)	(± 2.70)	(± 1.21)	(± 0.58)	(± 1.03)	(± 0.44)	(± 0.38)	(± 2.20)	(± 0.29)	(± 0.47)	(± 0.09)	(± 0.02)
MH_1	45865	34434	31457	25348	9150	9537	6281	1402	1221	814	641	40.9	97.2	78.1	28.2	43.4	6.73	21.6	6.49	7.00	3.11	0.10
	(± 1214)	(± 475)	(± 238)	(± 508)	(± 77.2)	(± 126)	(± 42.3)	(± 31.2)	(± 42.3)	(± 5.90)	(± 6.51)	(± 0.74)	(± 2.86)	(± 1.18)	(± 0.05)	(± 0.21)	(± 0.26)	(± 0.24)	(± 0.08)	(± 0.62)	(± 0.09)	(± 0)
MH_2	34810	36971	33384	29962	8927	9908	4487	1865	1720	723	728	49.9	98.5	84.4	38.2	51.2	9.49	21.1	9.29	7.86	2.34	0.19
	(± 4829)	(± 116)	(± 694)	(± 359)	(± 107)	(± 125)	(± 229)	(± 36.1)	(± 125)	(± 13.6)	(± 9.60)	(± 0.77)	(± 1.73)	(± 1.84)	(± 1.20)	(± 0.85)	(± 0.44)	(± 1.27)	(± 0.42)	(± 0.22)	(± 0.06)	(± 0)

Table 4. Contamination factors (CFs) and **pollution load index (PLI)** for the soils collected inside the Vesuvius National Park along Ercolano (E) and Matrone (M) roads, at low (L) and high (H) altitudes. The values higher than 1 are reported in bold.

	Roads		Altitudes	
	E	M	H	L
Al	0.97	0.80	0.70	1.08
As	1.58	0.59	0.59	1.58
B	1.01	0.59	0.48	1.11
Ba	1.00	1.10	0.93	1.16
Ca	1.14	1.03	0.98	1.20
Cd	3.15	3.30	1.53	4.92
Cr	0.89	1.15	0.61	1.43
Cu	3.47	1.06	1.18	3.35
Fe	0.94	0.91	0.80	1.05
K	1.07	0.81	0.73	1.15
La	1.00	0.78	0.78	1.00
Mg	0.84	1.06	0.82	1.07
Mn	0.92	1.22	0.77	1.38
Na	1.28	0.96	0.94	1.29
Ni	0.95	1.20	0.88	1.27
P	1.10	0.72	0.86	0.96
Pb	1.77	1.77	0.78	2.76
Si	1.64	1.46	1.36	1.74
Ti	0.95	0.81	0.83	0.93
V	0.98	0.85	0.80	1.03
W	1.12	0.88	0.80	1.19
Zn	2.02	1.75	1.13	2.65
PLI	1.55	1.37	1.29	1.52

Table 5. P values of the t-tests performed on the elements contents in F1, F2 and F3 of soils collected inside the Vesuvius National Park to highlight differences between roads (Ercolano vs. Matrone) or altitudes (high vs. low). Only the elements that showed at least one statistically significant difference are reported.

	Ercolano vs. Matrone			high vs. low		
	F1	F2	F3	F1	F2	F3
Cd	n.s.	0.05	n.s.	n.s.	0.02	n.s.
Cr	n.s.	n.s.	n.s.	n.s.	n.s.	0.05
La	n.s.	n.s.	0.009	n.s.	n.s.	0.007
Mg	n.s.	n.s.	0.04	n.s.	n.s.	0.04
Mn	0.05	n.s.	n.s.	0.04	n.s.	n.s.
Na	0.009	0.02	n.s.	0.01	0.02	n.s.
Ni	n.s.	n.s.	n.s.	0.05	n.s.	n.s.
Ni	n.s.	0.04	n.s.	n.s.	0.05	n.s.
P	n.s.	n.s.	0.05	n.s.	n.s.	n.s.
Pb	n.s.	n.s.	n.s.	n.s.	n.s.	0.03
Si	n.s.	0.005	n.s.	n.s.	0.003	n.s.
Ti	n.s.	0.05	0.05	n.s.	n.s.	0.02
Zn	n.s.	0.006	n.s.	n.s.	0.002	0.03

n.s. = not significant ($P > 0.05$)

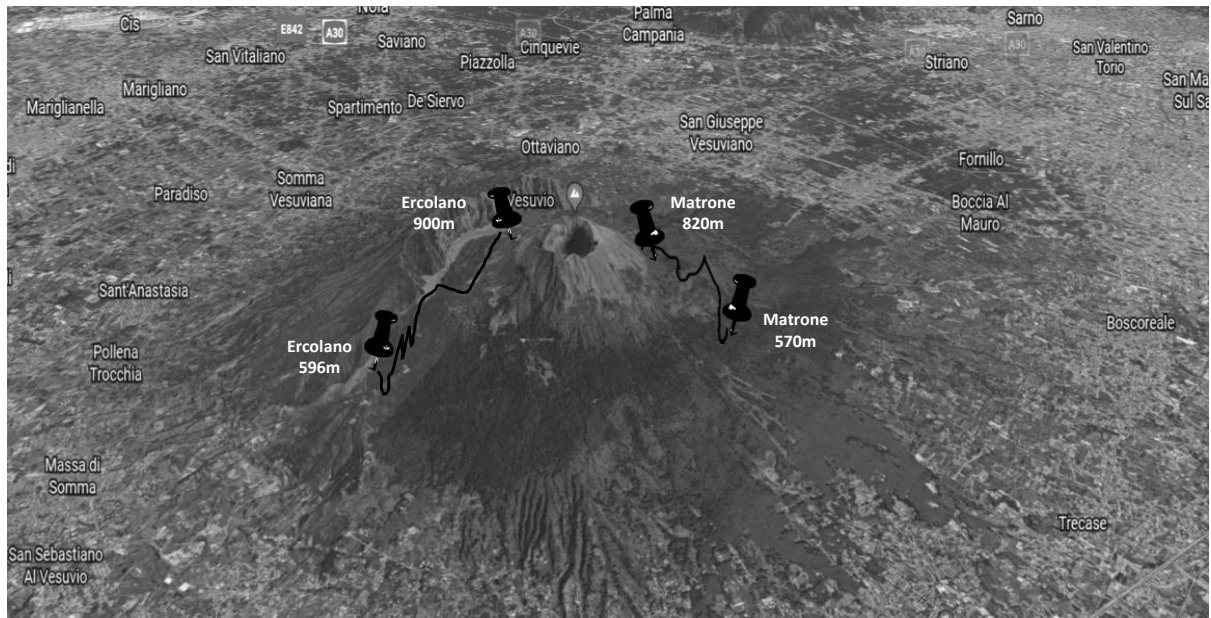


Fig. 1

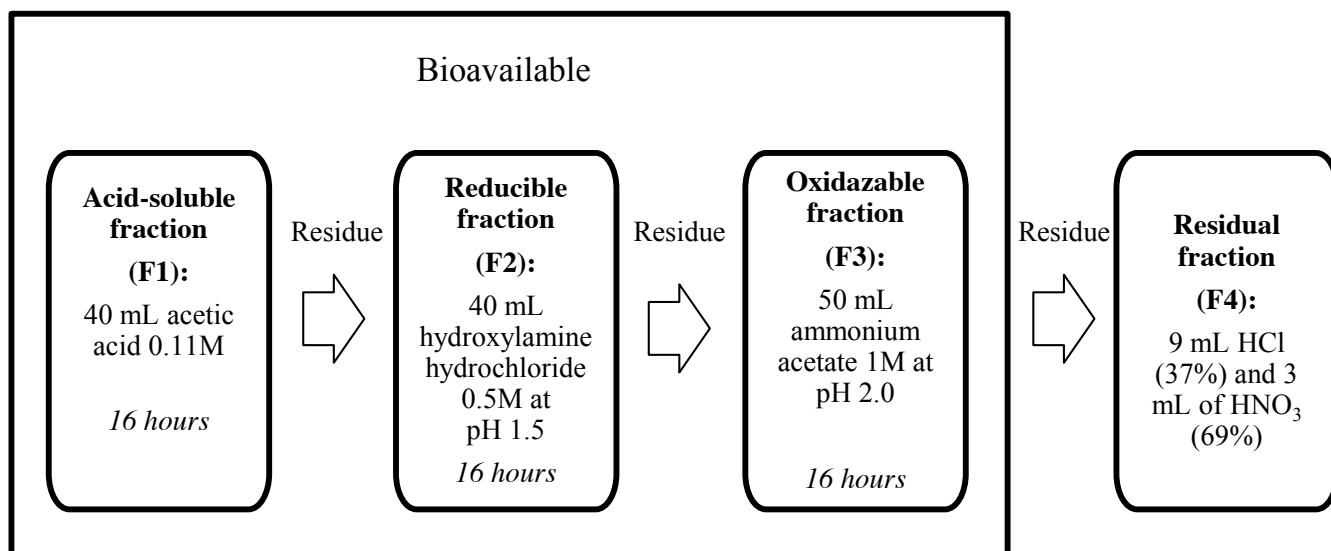


Fig. 2

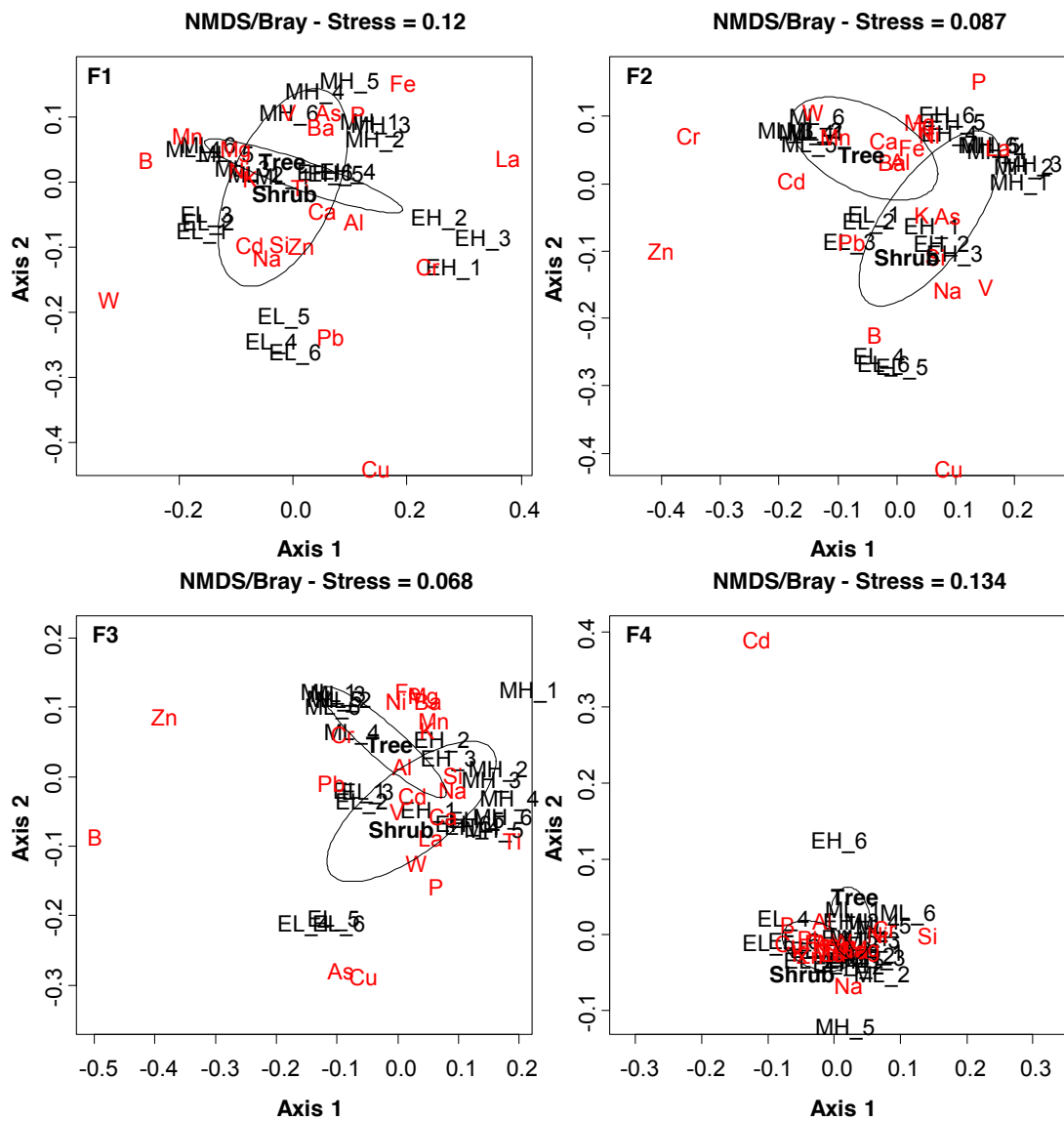


Fig. 3b

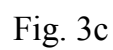


Fig. 3c

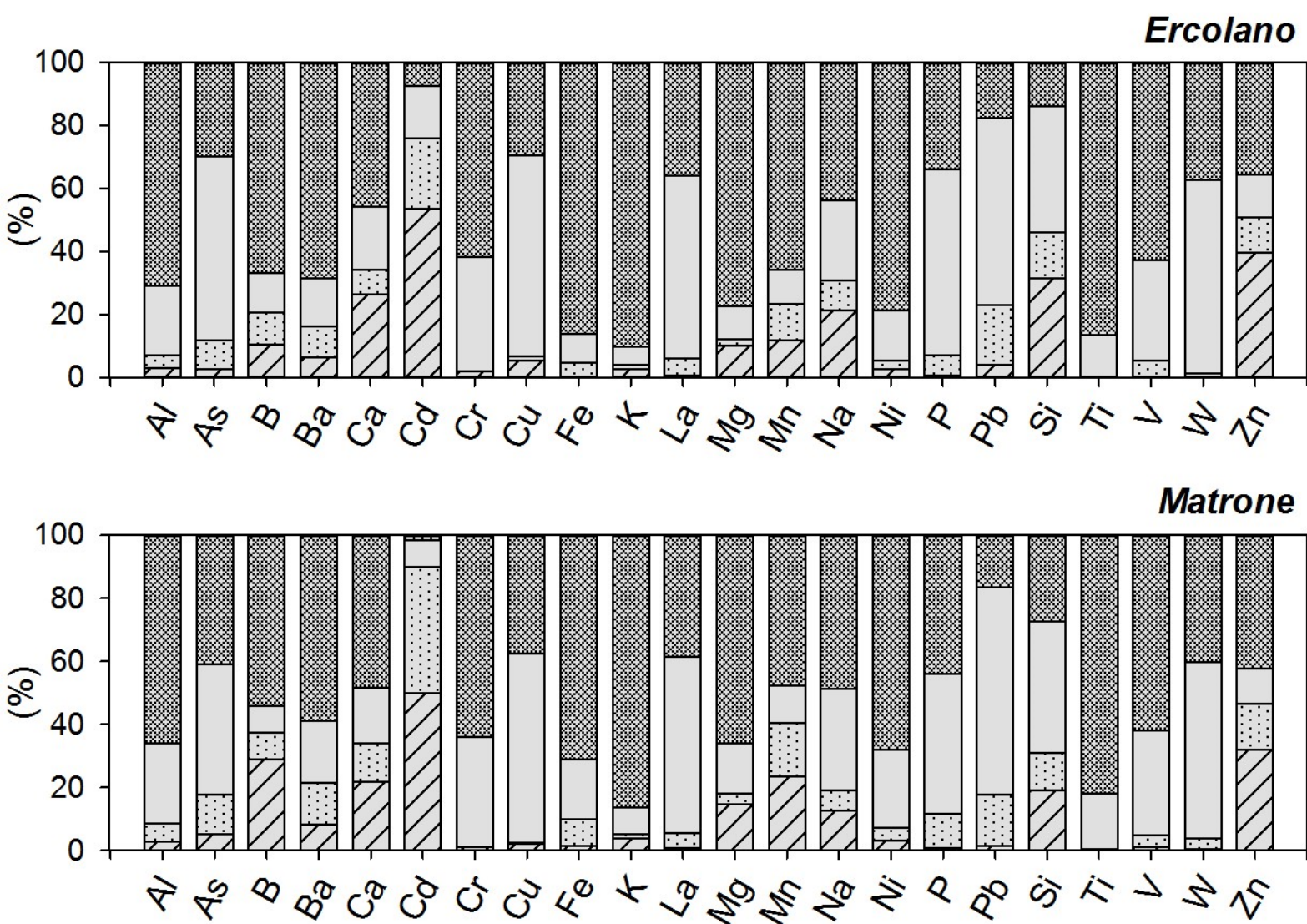


Fig. 5

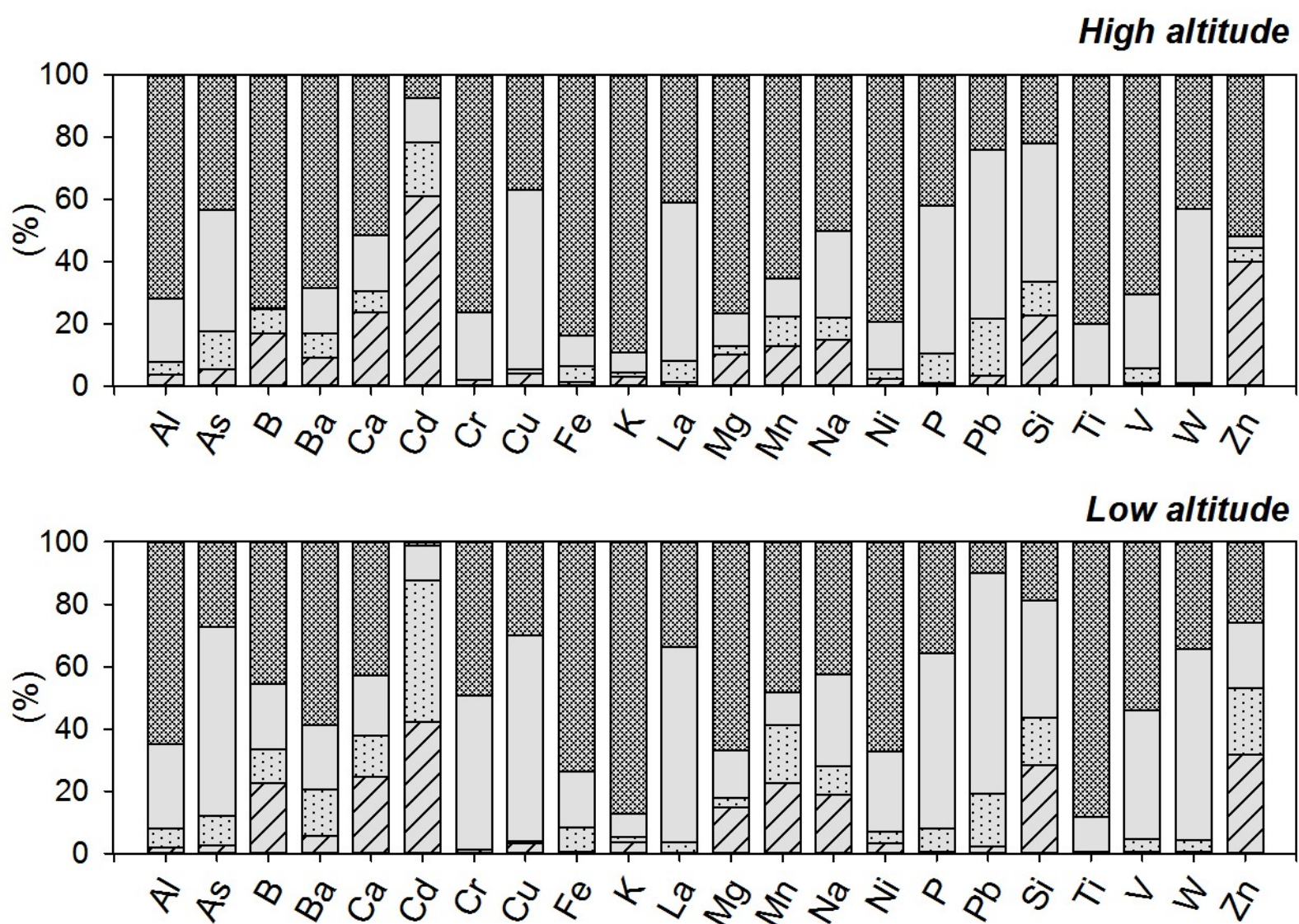


Fig. 6