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**Linking bioaccessibility and solid phase distribution of potentially toxic elements in extractive
waste and soil from abandoned mine site : Case study of Campello Monti, NW Italy**

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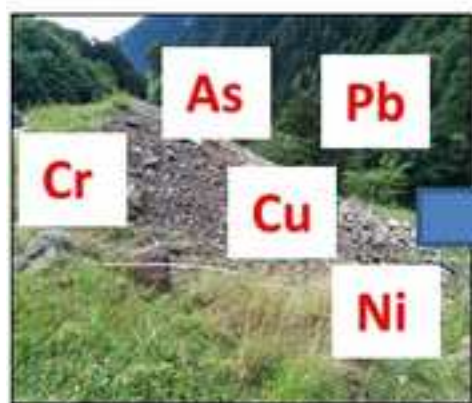
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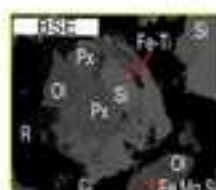
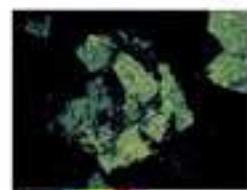
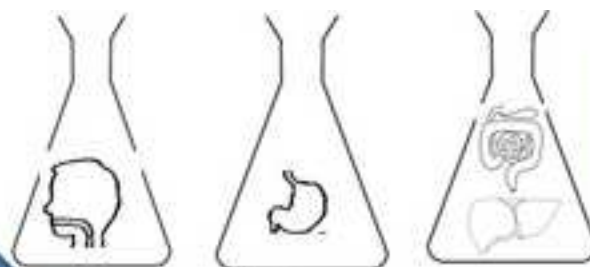
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ABANDONED
MINE SITES



Bioaccessible fraction <
100%

PTE in clay and Fe oxide
fractions

Fe Mg silicates, olivine, and
pyroxene major minerals in
soil

Highlights

- Extractive waste and soil at abandoned mines pose a risk to human health.
- Cr, Cu and Ni were present in high total concentrations at Campello Monti site.
- Potentially toxic elements were associated with clay and Fe oxide fractions.
- Mean BAF <11% for both Cr and Ni. Non-mobile form in Fe oxide fraction.
- PTE were found to be embedded in mineral grains of soil.

1 **Abstract**

2 Mining activities have led to the introduction of high levels of potentially toxic elements (PTE)
3 concentrations in soils. This has attracted governmental and public attention due to their non-
4 biodegradable nature and hazards posed to human health and the environment. However, total
5 concentrations of PTE are poor indicators of actual risk hazard to human health and can lead to
6 overestimation of risk. In this study, oral bioaccessibility, the fraction available for absorption via
7 oral ingestion, was used to refine human health risk assessment at an abandoned mine site from
8 Campello Monti, north-west Italy. The solid phase distribution was performed to characterise the
9 distribution and the behaviour of PTE within the extractive waste streams and impacted soil nearby.
10 Mineralogical information was obtained from micro-XRF and SEM analysis used to identify
11 elemental distribution maps. The results showed that the total concentrations of PTE were high, up
12 to 7400 mg/kg for Ni due to the presence of parent material, however, only 11% was bioaccessible.
13 Detailed analysis of the bioaccessible fraction (BAF) showed that As, Cu and Ni varied from 7 to
14 22%, 14 to 47%, 5 to 21%, respectively. The variation can be attributed to the difference in pH,
15 organic matter content and mineralogical composition of the samples. The non-specific sequential
16 extraction also showed that the non-mobile forms of the PTE were associated with the clay and Fe
17 oxide components of the environmental matrices. The present study demonstrates how
18 bioaccessibility, solid phase distribution and mineralogical analysis can help decision making and
19 inform the risk assessment of abandoned mine sites.

20 Keywords: abandoned mine site, oral bioaccessibility, potentially toxic elements (PTE), risk
21 assessment, solid phase distribution.

22

23 **1. Introduction**

24 Since the onset of industrial revolution, mining and smelting activities have been at forefront of
25 economic development of many countries. Mining activities generate employment, while also

26 producing a wide variety of minerals that can have countless uses in various contexts (Ono et al.,
27 2016 ; Dino et al., 2018a). Yet, mining and dressing activities have resulted in the generation of
28 large quantities of waste and degraded soils. After the closure of mining activities, these waste
29 dumps were abandoned, resulting in poor management and maintenance. Further to this, the
30 degraded soils, waste dumps and tailings are often geotechnically unstable and sources of
31 contamination by PTE (Gál et al., 2007). As PTE tend to persist in the environment, these extractive
32 waste dumps and soils often become a matter of concern for human health (Lim et al., 2009).

33 There is growing awareness and concern about the harmful effects of elevated
34 concentrations of toxic elements on human health (Golia et al., 2008). However, there is a growing
35 evidence that an elevated concentration of elements may not be indicative of the actual damaging
36 effects. Consequently, it has been proposed that bioavailable concentrations should be used to
37 inform human health risk assessment (HHRA). Bioavailable concentration is the concentration of
38 the contaminants reaching to the systemic circulation and thereby the remainder of the body
39 (Oomen, 2000). However, measuring bioavailability in-vivo is a difficult and lengthy procedure
40 (Maddaloni et al., 1998). Therefore, a number of in-vitro bioaccessibility methods have been
41 developed to measure the oral bioaccessibility of a contaminant (Cox et al., 2013). The oral
42 bioaccessible fraction is defined as the fraction that, after ingestion, may be mobilized into the gut
43 fluids (chyme). Bioaccessible concentration is greater than or equal to the bioavailable
44 concentration and can be used as a conservative measure to the bioavailability for HHRA
45 (Paustenbach, 2000).

46 The present research used the unified BARGE method (UBM) developed by the
47 Bioaccessibility Research Group of Europe (BARGE) for measuring the oral bioaccessibility of
48 contaminants in extractive waste and soils from abandoned mining sites. The UBM method has
49 been validated against in vivo studies for As, Cd and Pb (Denys et al., 2012) and has been used to
50 provide guidance data on a wider range of chemical elements to facilitate inter-laboratory trials
51 (Hamilton et al., 2015). Therefore, many studies have used the UBM method to assess

52 contamination due to PTE in mining affected areas. For example, Pelfrêne et al., (2012) quantified
53 bioaccessible concentrations of Cd, Pb and Zn as 78%, 32%, and 58% respectively on smelter-
54 contaminated agricultural soils in a coal mining area of northern France. Foulkes et al., (2017)
55 applied the UBM method to measure bioaccessibility of Pb, Th, and U on solid wastes and soils
56 from an abandoned uranium mine site in South West England. However, in Italy there is little to no
57 attention towards inclusion of oral bioaccessibility in studies reporting HHRA (Kumpiene et al.,
58 2017). Consequently, the present study provides evidence towards evaluating bioaccessibility to
59 support the HHRA procedures for two abandoned mine sites in Italy.

60 Potentially toxic elements (PTE) are associated with the various components in soils and the
61 mineral phases of solid wastes in different ways, and these associations can lead to variation in both
62 mobility and availability (Cipullo et al., 2018). A wide range of soil properties can thus lead to
63 variation in bioaccessibility of PTE such as mineralogy, soil pH, organic matter content, presence of
64 clay, iron oxides alumino-silicates in matrix as reported in other studies (Ruby et al., 1999;
65 Peijnenburg and Jager, 2003; Martin and Ruby, 2004; Basta et al., 2005; Palumbo-Roe and Klinck,
66 2007; Denys et al., 2009; Reis et al., 2014; Palumbo-Roe et al. 2015). Therefore, in order to assess
67 bioaccessibility of PTE, it becomes imperative to study geochemical data and encapsulation of PTE
68 in mineral phases.

69 Considering the challenges linked with evaluating bioaccessibility and understanding factors
70 influencing bioaccessibility, the present study focuses on extractive waste (EW) and soils from the
71 abandoned mine site at Campello Monti, which was important for Ni exploitation from mafic
72 formations in north-west Italy. Specifically in this study, the total concentration, bioaccessible
73 fraction and the distribution of PTE were determined using non-specific sequential extraction and
74 chemometric analysis along with mineralogical analysis of the extractive waste and soil samples.

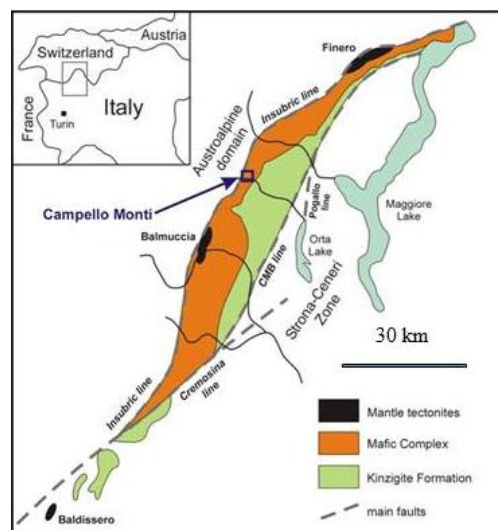
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76 **2. Methodology**

77 **2.1 Site description**

78 Campello Monti is a small settlement of Valstrona village in the northern sector of Piemonte, Italy.
 79 Geologically, the site (**Figure 1**) is present in the ultramafic layers of mafic complex of Ivrea
 80 Verbano Zone. Ivera- Verbano zone is a tectonic unit which has preserved the transition from
 81 amphibolite to granulite facies (Redler et al.,2012). The mafic formation consists of a sequence of
 82 cumulate peridotites, pyroxenites, gabbros and anorthosites, together with a large, relatively
 83 homogeneous body of gabbro-norite, grading upwards into gabbro-diorite and diorite. Campello
 84 Monti area consists of lherzolites, in places with titanolivin, in large and smaller masses.

85 The rocks in this area are rich in nickel, copper and cobalt. The area was exploited for nickel
 86 production from Fe-Ni-Cu-Co magmatic sulphide deposits occurring from the Sesia to Strona
 87 valleys from 19th Century (1865) until 1940s. The ore was extracted using underground mining
 88 activities which left waste rocks near the mine tunnels (Mehta et al., 2018).

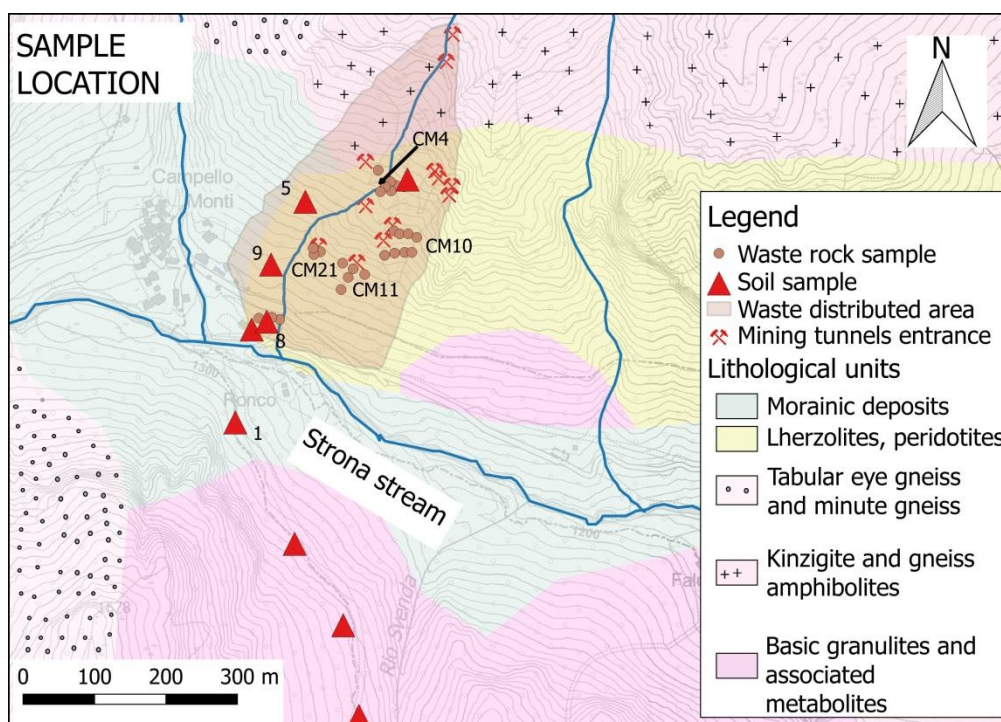


89
 90 Figure 1. Geological setting of Campello Monti (modified from Fiorentini and Beresford, 2008).

91 **2.2 Sample collection and preparation**

92 Site investigation was performed to collect information about waste typology and location, in order
 93 to ensure that the facilities are suitable for characterisation and sampling. The sampling site at
 94 Campello Monti is composed of different waste rock dumps. These waste rock dumps were placed
 95 on the north of the Strona stream and were formed by the dumping in vertical sequence of non-

96 valuable mineralisations and non-mineralised rocks. A systematic sampling strategy was adopted in
 97 order to obtain representative data of the whole waste facility. Waste rock material was sampled
 98 using hand shovel and a hammer (where necessary). In total 26 samples of waste rock were
 99 collected at the site in July 2016 (Error! Reference source not found.). Each sample (8-10 kg) was
 100 collected in an area of 1.5 m², after removing organic residues. Additionally, a total of 9 soil
 101 samples were taken near the waste rock dumps to the north and south of the Strona stream during
 102 the sampling campaigns in June 2016 and March 2017. In order to obtain representative soil
 103 samples, the samples taken were formed by mixing 4 subsamples taken at the vertices of a 1m x 1m
 104 square. All samples were taken at depth of 0-15 cm. The extractive waste samples and soil samples
 105 were dried in an oven for a period of 24 h to remove any moisture. Samples were then sieved
 106 through 2 mm sieves and quartered to obtain a representative sample size of 10 g. The pH was
 107 measured in a 1: 2.5 suspension of each sample in water (ISO 10390, 2005).



108
 109 Figure 2. Waste rock and soil sample locations at Campello Monti. Sample numbers are shown for
 110 the samples analyzed for bioaccessibility.

111 **2.3 Total concentrations measurement**

112 The samples were analyzed for their concentrations of chemical elements on the 2 mm fraction
113 using the method described in U.S. EPA, 3051 A, (2007) and U.S. EPA, 6010 C, (2007). Briefly,
114 0.5 g of sample was digested using 3 ml concentrated HNO₃ and concentrated HCl (1:3). The
115 concentrations of As, Be, Cd, Co, Cr (total), Cu, Ni, Pb, Sb, Se, V and Zn were measured using an
116 Ametek Spectro Genesis Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).
117 The instrument was provided with an Ametek monochromator, a cyclonic spray chamber and a
118 Teflon Mira Mist nebulizer. The instrumental conditions included a plasma power of 1.3 kW,
119 sample aspiration rate of 30 rpm, argon nebulizer flow of 1 l/min, argon auxiliary flow of 1 l/min
120 and argon plasma flow of 12 l/min. All the reagents used were of analytical grade. All metal
121 solutions were prepared from concentrated stock solutions (Sigma Aldrich). High-purity water
122 (HPW) produced with a Millipore Milli-Q Academic system was used throughout the analytical
123 process. All samples were analyzed in duplicate.

124

125 **2.4 Bioaccessibility analysis (Unified BARGE method)**

126 Following the analysis on total concentration of elements for the fraction under 2 mm, samples were
127 selected for measurement of bioaccessible concentrations. Waste rock samples and soil samples
128 were selected to ensure representation of each dump and lithology in the final selected samples. For
129 tailings, the two samples closest to the ground surface were measured for bioaccessible
130 concentrations. The total metal concentrations were measured on (<250 µm fraction of these
131 samples) using aqua regia extractions as described in section 2.3. Following the analysis on total
132 concentration of PTE on the <2 mm fraction, samples of waste rock, soil and tailings were selected
133 for measurement of bioaccessible concentrations, ensuring good representation of each matrix. For
134 tailings, the two samples at the nearest depth from the ground were measured for bioaccessible
135 concentrations. Each sample was sieved to <250 µm and total concentrations of PTE were measured
136 using aqua regia extractions as explained in section 2.3. The Unified BARGE method (UBM) was
137 also followed for measuring bioaccessible concentrations on the <250 µm fraction (BARGE 2010,

138 Denys et al., 2012). To ensure quality control of the extraction process each batch of UBM
139 extractions (n=10) included one procedural blank, six unknowns, one duplicate of two unknown
140 samples and one soil reference material (BGS102) (BARGE 2010; Hamilton et al., 2015). **Table 1**
141 shows the comparison of the certified and measured values of the BGS 102 extractions. As pH
142 plays an important role in controlling the leaching of the PTE from the matrix and overall extraction
143 process, the pH meter was calibrated before extraction of every batch of samples.

144 Unified BARGE method extractions were carried out using simulated digestive fluids
145 including saliva, gastric fluid, bile and duodenal fluid, which were prepared from inorganic and
146 organic reagents and enzymes one day prior to sample extractions. These fluids were used to
147 represent three main compartments of human digestive system: mouth, stomach and small intestine.
148 The extraction consists of two phases, gastric and gastro-intestinal for which 0.4 ± 0.0005 g of
149 sample was weighed in replicate in polycarbonate tubes (1 replicate for the gastric phase and 1
150 replicate for the gastro-intestinal phase). For gastric phase extractions, saliva and gastric fluids were
151 added to each tube (pH adjusted to 1.2 ± 0.05), followed by 1 h of end-over-end rotation. The
152 rotator was placed in oven at constant temperature of 37 °C. One of the replicates was extracted
153 through centrifugation at 4500 g for 15 min (G phase), while the second replicate was retained for
154 gastro-intestinal phase (GI phase) extraction. Simulated duodenal and bile fluids were added to this
155 tube (pH adjusted to 6.3 ± 0.5) and rotated end-over-end for 4 hours at 37 °C. This was followed by
156 an identical centrifugation procedure to obtain GI phase extracts. For both extractions, 10 ml of the
157 supernatant was collected and preserved with 0.2 ml concentrated (15.9 M) HNO₃. Determination
158 of PTE was performed by ICP-MS (Perkin-Elmer NexION 350X), while using internal standard
159 (Rh). The bioaccessible fraction (BAF) for both the phases was calculated using Equation 1. To
160 apply a conservative approach for human health risk assessment, BAF is reported as the percentage
161 of highest bioaccessible concentration from gastric or gastro-intestinal phase.

162

163
$$\text{BAF} = \frac{\text{Concentration of bioaccessible element } \left(\frac{\text{mg}}{\text{kg}}\right)}{\text{Total concentration of element } \left(\frac{\text{mg}}{\text{kg}}\right)} \times 100 \quad (1)$$

164

165 **2.5 Chemometric identification of substrates and element distribution (CISED)**

166 A non-specific sequential nitric acid extraction (Cave et al., 2004) was carried out on selected
167 samples (n=5) (n=2 waste rocks, n=3 soil). Briefly, 2 g of sample was sequentially extracted with
168 10 ml of deionized water and solution of increasing concentration of HNO₃ ranging from 0.01 M to
169 5.0 M. A total of 7 solutions were used twice (0.0 M, 0.01 M, 0.05 M, 0.1 M, 0.5 M, 1.0 M and 5.0
170 M), with progressive addition of H₂O₂ (0.25, 0.50, 0.75, and 1 ml) in the last 4 extracting solutions
171 to facilitate the precipitation of oxides. Each solution was mixed for 10 min in an end-over-end
172 shaker and centrifuged (4350 g for 5 min) to separate solid and liquid fractions. The solid fraction
173 was then resuspended in the following extracting solution. The recovered liquid fraction was
174 filtered with a 0.45 µm 25 mm nylon syringe filter and diluted 4 times with deionized water prior to
175 analysis. Extracts were spiked with internal standards (Sc, Ge, Rh, and Bi) and the following
176 elements Ca, Fe, K, Mg, Mn, Na, S, Si, P, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Li, Mo, Ni, Pb, Sb, Se,
177 Sr, V, Zn were measured using ICP-MS (NexION® 350D ICP-MS, Perkin Elmer). For data quality
178 control, acid blanks (1% nitric acid) and certified reference material (BGS102) were included in the
179 extraction procedure.

180

181 **2.6 Modelling**

182 Solid phase distribution of elements in soil and waste rock was calculated with MatLab (MatLab®
183 Version R2015a) using a self-modelling mixture resolution algorithm (SMMR) developed by Cave
184 et al. (2004). This modelling algorithm was used to identify (1) soil components with similar
185 physical-chemical properties, (2) chemical composition data (single elements in each soil
186 component expressed as percentage), and (3) amount of elements in each component (expressed in
187 mg/kg). The algorithm was run separately for waste rock and soil producing 7 and 8 distinct sets of

188 physico-chemical phases for each of these respective runs. In order to categorise these physio-
189 chemical phases into common distinct soil phases hierarchical clustering was used in combination
190 with geochemical profile interpretations. Briefly, heatmaps from hierarchical clustering were
191 produced with a mean-centered and scaled matrix of profile and composition data using the Ward's
192 method in R (v.3.4.1) and the results obtained were plotted with ggplot2, reshape2, grid and
193 ggdendro packages (Wickham,2007; Wickham, 2009; Chang et al. 2013).

194

195 **2.7 Mineralogical analysis**

196 The mineralogical analysis of waste rock samples was performed in a previous study (Rossetti et
197 al., 2017). Consequently, only the soil sample was analyzed for mineral phases in present study.
198 Micro-X-ray fluorescence (micro-XRF) was used to identify crystalline phases in the bulk soil
199 sample (sample code - 8). Element X-ray maps of soil sample were acquired using a micro-XRF
200 Eagle III-XPL spectrometer equipped with an EDS Si(Li) detector and with an EdaxVision32
201 micro-analytical system. The operating conditions were 2.5 μ s counting time, 10 kV accelerating
202 voltage and a probe current of 20 μ A. The spatial resolution was about 65 μ m in both x and y
203 directions. The elemental maps were processed to determine mineral phases in soil using software
204 program Petromod (Cossio et al., 2002). The micromorphology and associated chemical analysis of
205 solid phases in soil were analyzed with a Cambridge Stereoscan 360 scanning electron microscope
206 (SEM) equipped with an energy-dispersive spectrometry (EDS) Energy 200 system and a Pentafet
207 detector (Oxford Instruments). 10 kV accelerating voltage and 50 s counting time were used for
208 analysis of the minerals. SEM-EDS quantitative data (spot size 2 μ m) were acquired and processed
209 using the Microanalysis Suite Issue 12, INCA Suite version 4.01; natural mineral standards were
210 used to calibrate the raw data; the $\phi\rho Z$ correction (Pouchou & Pichoir, 1988) was applied. Absolute
211 error is 1 δ for all calculated oxides.

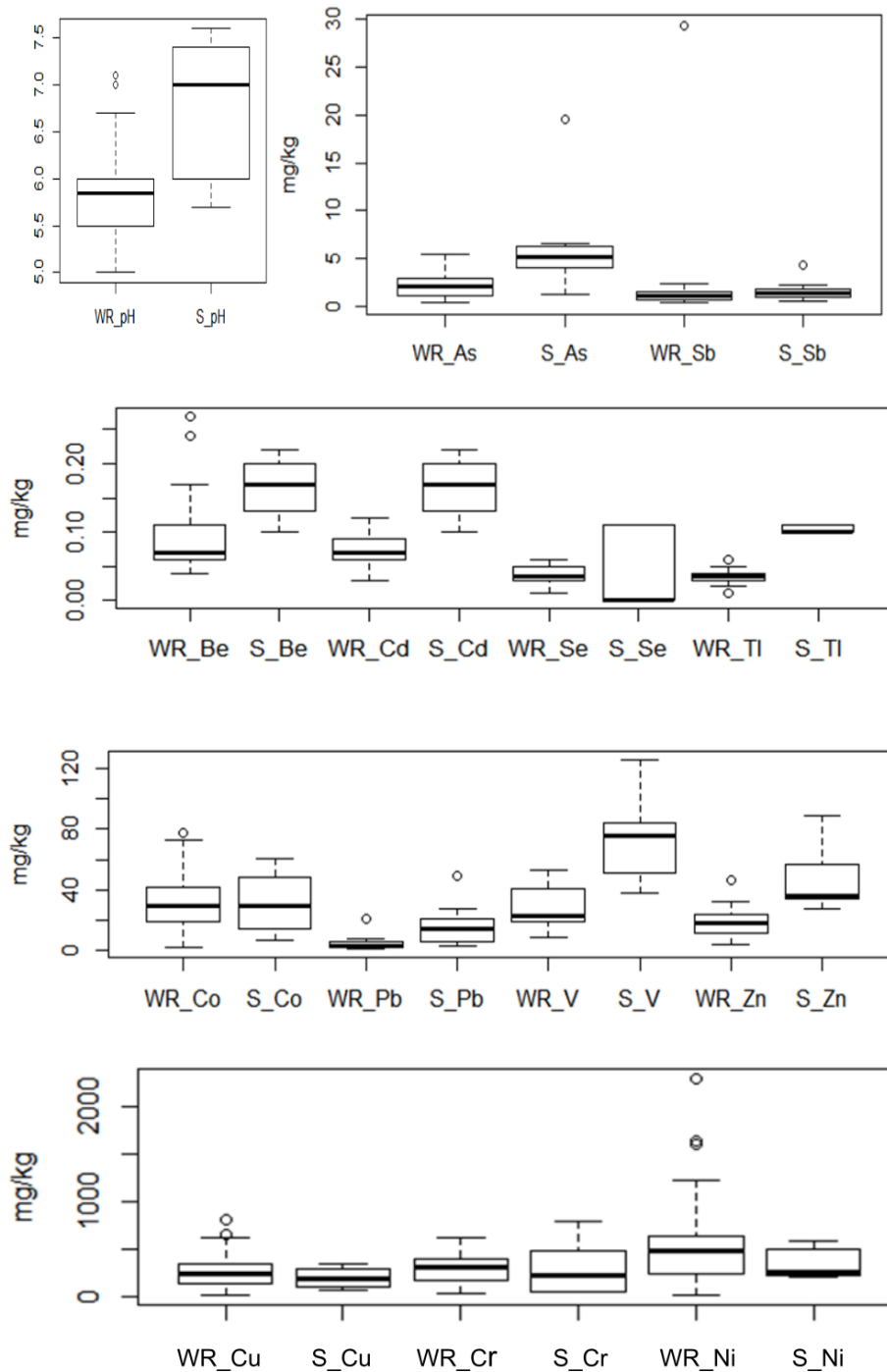
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213 **3. Results**

214 **3.1 Total concentrations of PTE**

215 The pH and total concentrations of PTE in waste rock samples (no. of samples, n = 26) and soil
216 samples (no. of samples, n = 9) are summarized in **Figure 3**. The value of pH varied from 5.0 to 7.1
217 with mean value of 5.9. The results showed that concentrations of Ni varied from 15.2 mg/kg to
218 2294 mg/kg with an average concentration of 640 mg/kg. The presence of slightly acidic samples
219 and high concentrations of Ni can be attributed to the presence of ultramafic lithology rich in
220 olivine and pyroxene in Campello Monti. The concentration of Cr varied from 39 mg/kg to 620
221 mg/kg with an average concentration of 299 mg/kg, while concentrations of Co ranged from 2.4
222 mg/kg to 77.8 mg/kg with a mean concentration of 32.1 mg/kg. The presence of Cr and Co is due to
223 the fact that Ni in earth's crust exhibits chalcophile and lithophile characteristics and is found to be
224 associated with Cr and Co. Copper was found to vary from 19 mg/kg to 806 mg/kg with mean
225 concentration of 284 mg/kg. The presence of Cu suggests sulphide rich minerals (e.g. pyrite and
226 chalcopyrite) that host both Ni and Cu, may be present at the site. It should be noted that
227 concentrations of (Ni, Cr, Co and Cu in waste rocks are higher than Italian permissible limits for
228 soils for recreational and habitation areas (Ministero dell'ambiente e della tutela del territorio, 2006,
229 decree no. 152/06). Analysis on soil samples showed that pH values ranged from 5.7 to 7.6 with
230 average value of 7.0. The samples were found to be in near neutral conditions and less acidic than
231 waste rocks samples. Total Ni, Cr and Cu ranged from 212 to 594 mg/kg, 46 to 795 mg/kg and 66
232 to 345 mg/kg respectively. Mean Ni, Cr, Cu concentrations, were 347, 296 and 200 mg/kg, an order
233 of magnitude above the Italian permissible limits for soils for recreational and habitation areas.
234 Concentrations of V were found to vary from 38 mg/kg to 126 mg/kg with a mean concentration of
235 72 mg/kg. Concentrations of other elements were found to be within permissible limits. The
236 presence of PTE in soil can be explained on the basis of lithogenic origin of soils and possible
237 transport of PTE from extractive waste dumps.

238



239

240 Figure 3. Box and Whisker plots showing pH and concentration of PTE in mg/kg in waste rock
 241 (n=26) and soil samples (n=9) on <2 mm size fractions at Campello Monti. pH and elements on X-
 242 axis are provided with sample identification code WR for waste rocks and S for soil samples.
 243

244 **3.2 Bioaccessible concentrations**

245 The total and bioaccessible concentrations of As, Cd, Co, Cr, Cu, Ni, Pb and V in waste rock and
 246 soil samples at Campello Monti are presented in **Table 2**. Total concentrations for the <250 µm size

247 fraction were considerably higher than total concentrations for size fractions under 2 mm (reported
248 in Figure 3) potentially due to an increase in surface area and thus higher the absorption of PTE to
249 particles (Yao et al., 2015). The bioaccessible concentrations were measured both for
250 gastrointestinal and gastric phases. It was observed that for all PTE except As, metals were more
251 bioaccessible in the gastric phase than the gastrointestinal phase. Bioaccessible fraction (BAF) was
252 calculated as the ratio of the higher value of bioaccessible concentration (either gastric or
253 gastrointestinal) to total concentration. The highest bioaccessibility value is used to ensure
254 conservative values are used during risk assessment.

255 Total concentrations of As in waste rock and soil samples varied from 5.6 to 11.1 mg/kg and
256 from 8.8 to 39.3 mg/kg respectively. The bioaccessible concentrations in gastrointestinal phase in
257 waste rock and soil samples varied from 0.6 to 1 mg/kg and from 1.8 to 2.7 mg/kg respectively.
258 Mean values of BAF were found to be 10.5% for waste rock samples and 12.8% for soil samples.
259 Waste rock and soil samples showed mean total concentrations of Cd as 1.3 mg/kg and 0.5 mg/kg.
260 The bioaccessible fraction were found to be varying from 3% to 19% and from 20% to 85%, for
261 waste rocks and soil, respectively.

262 Total concentrations of Co in waste rock and soil samples varied from 165 to 266 mg/kg and
263 from 45 to 175 mg/kg respectively. The bioaccessible concentrations in waste rock and soil samples
264 varied from 27 to 72 mg/kg and from 5 to 53 mg/kg respectively. Mean values of BAF were found
265 to be 20% for waste rock samples and 26% for soil samples. The results on Co bioaccessibility
266 showed that although total concentrations of Co were very less in comparison to Cr, the
267 bioaccessible concentrations were present in the same range as Cr due to higher bioaccessible
268 fractions of Co in comparison to Cr. Chromium in waste rock and soil samples was found to vary
269 from 931 to 1569 mg/kg and from 79 to 1643 mg/kg respectively. Mean values of BAF of Cr for
270 waste rock and soil samples was 1% and 2.75% respectively.

271 Total concentrations of Cu in waste rock and soil samples ranged from 953 to 2,006 mg/kg
272 and from 85 to 848 mg/kg respectively. The bioaccessible concentrations in waste rock and soil

273 samples varied from 129 to 921 mg/kg and from 27 to 222 mg/kg respectively. Mean values of
274 BAF were found to be 31% for waste rock samples and 26% for soil samples. Copper results
275 showed higher bioaccessibility for soil samples compared to waste rocks, indicating a contrasting
276 behavior with respect to the other PTE analyzed. The results on Cu bioaccessibility showed that
277 although total concentrations of Cu were not as high as Ni, the bioaccessible concentrations were
278 almost of the same magnitude as nickel. This can be attributed to the higher BAF values of Cu
279 when compared with Ni.

280 The samples were found to have very high total concentration of Ni in waste rock samples
281 with variation from 1181 to 7408 mg/kg. However, the bioaccessible concentrations of Ni in gastric
282 phase for waste rock samples was relatively low. The bioaccessible concentrations for gastric phase
283 for Ni varied from 119 to 776 mg/kg for waste rock samples, thus leading to a BAF (ratio of
284 bioaccessible concentration to total concentration) of about 10%. A similar observation was made
285 for soil samples. The total concentration and bioaccessible concentration for soil samples ranged
286 from 59 mg/kg to 1504 mg/kg and from 12 to 280 mg/kg, respectively. Thus leading to BAFs
287 varying from 5% to 20%.

288 Mean values of total concentration of Pb in waste rock and soil samples were found to be 25
289 mg/kg and 18 mg/kg respectively. The bioaccessible fraction of Pb in waste rock and soil samples
290 varied from 42% to 61%. Vanadium was found to vary from 34 mg/kg to 87 mg/kg for waste rock
291 samples, with mean BAF of 4%. The soil samples recorded mean values of total concentrations and
292 bioaccessible concentrations as 106 mg/kg and 7 mg/kg respectively.

293 The range of bioaccessibility values reported for the soils were found to be comparable to
294 those reported elsewhere, eg. Barsby et al. (2012) conducted bioaccessibility analysis in ultramafic
295 geological setting of Northern Ireland using UBM and reported mean values of gastric phase of
296 BAF of As, Co, Cr for soils as 14%, 18% and 1% respectively (here 13%, 26% and 3%
297 respectively). The same study reported mean value of BAF for Cu as 31 % (here 31%), Ni as 12%
298 (here 13%), V as 9% (here 7%). There was a marked difference in reported values of mean of BAF

299 of Pb as reported by Barsby et al. (2012) 33% (here 54%). However, the value was found to be
300 more comparable with smelter contaminated agricultural soil of northern France, which showed
301 BAF of 58% (here 54%) (Pelfrêne et al., 2012).

302

303 Table 1. Results of the UBM digests of certified reference material BGS 102 (n=3).

		As	Cd	Co	Cr	Cu	Ni	Pb	V
Gastric phase	Measured	3.17 ± 0.13	BDL ^b	9.57 ± 0.61	35.76 ± 0.58	8.66 ± 0.69	12.70 ± 0.51	15.35 ± 1.16	6.67 ± 0.40
	Reported ^a	3.90	0.02	9.50	36.70	8.60	13.00	15.30	6.10
Gastro-intestinal phase	Measured	2.54 ± 0.38		5.70 ± 0.75	6.19 ± 1.06	9.86 ± 0.82		2.23 ± 0.46	
	Reported	3.30		5.50	13.10	10.50		3.40	

304 ^aHamilton et al., 2015; ^bBDL- Below detectable limit.

305

306 Table 2. Total concentrations (mg/kg), bioaccessible concentrations (G and GI) (mg/kg) and BAF (%) measured on <250 µm size fractions for
307 samples at Campello Monti.

	Sample	As			Cd			Co			Cr		
		GI	total	BAF	G	total	BAF	G	total	BAF	G	total	BAF
Waste rock	CM4	0.6	5.6	11	0.1	0.9	6	27	188	14	25	1398	1
	CM10	1	11.1	9	0.3	1.4	19	69	266	26	20	1569	1
	CM11	0.6	7.5	9	0.2	1.9	13	58	295	20	26	1296	1
	CM21	0.7	6.3	13	0.0	1.1	3	30	165	18	9	931	1
Soil	5	1.8	15.3	11	0.2	1.0	20	53	175	31	54	1643	1
	1	2.9	39.6	7	0.6	0.7	85	23	68	34	3	79	3
	8	1.8	8.8	22	0.1	0.2	47	37	142	26	85	623	1
	9	1.2	9.4	12	0.2	0.2	73	5	45	10	124	701	6
	Sample	Cu			Ni			Pb			V		
		G	total	BAF	G	total	BAF	G	total	BAF	G	total	BAF
Waste rock	CM4	129	953	14	119	1181	10	10	21	49	2	87	2
	CM10	754	1955	39	502	4586	11	12	24	50	2	64	3
	CM11	921	2006	47	776	7408	10	10	25	42	2	34	6
	CM21	320	1367	23	256	2864	9	14	28	50	2	61	3
Soil	5	222	848	26	280	1504	19	8	15	51	9	149	5
	1	27	85	32	12	59	21	29	49	59	5	94	6
	8	135	441	31	73	1455	5	2	4	44	3	79	4
	9	45	256	17	38	763	5	2	4	61	12	101	12

308 G = gastric phase and GI = gastrointestinal phase of UBM. Total represents total concentration of PTE using *aqua regia*. Bioaccessible fraction is
309 represented as BAF.

310 **3.3 Interpretation of sequential extraction data**

311 Identified physico-chemical components for the most representative samples of waste rock (sample
312 code - CM 10) and soil (sample code - 8) at Campello Monti are highlighted in **Figure 4**. For these
313 samples, the chemometric data analysis identified 7 components in the waste rock sample and 8
314 components in the soil sample. Each row represents a component identified by the algorithm, where
315 the name is composed with the elements that make up >10% of the composition. The columns of
316 the heatmap are based on model output showing the composition (%) on the left side, and on the
317 right side the extraction profiles (E1-E14).

318 A combination of geochemistry knowledge, relative solubility of each component in the
319 extracts, major elemental composition, profile, and clustering obtained from the heat maps were
320 used to define 6 geochemically distinct clusters: pore-water, exchangeable, Fe oxide 1, clay related,
321 Fe oxide 2). The heatmap and clustergram for remaining waste rock and soil samples are shown
322 Supplementary Material (Figure 1).

323

324 Pore-water: In waste rock, the pore-water cluster was principally made up from S (*c.* 52.2%) and
325 Mg (*c.* 24.7%). Other elements extracted were Ca (*c.* 7.4%) and Ni (*c.* 8.8%). The presence of
326 nickel in the pore water component suggests mobility of Ni in the waste rock. The pore-water
327 cluster of soil was predominantly composed of S (*c.* 64%) and Na, Mg, K which were all present at
328 >5 %. These components in this cluster were extracted in water extractions and 0.01 M HNO₃ (E1-
329 E4). This was the most easily extracted cluster suggesting it could be associated with the residual
330 salts from the original pore water in the soil.

331

332 Exchangeable: In waste rock, the exchangeable component consisted of Cu (*c.* 36%), Mg (*c.* 17 %),
333 S (*c.* 12%) and Ca (*c.* 12%). It was removed by the HNO₃ extracts over the range 0.01 M to 0.05 M.
334 The presence of a Cu rich component could be due to the presence of Cu bearing ores, such as Cu
335 Fe sulphides (chalcopyrite, CuFeS₂ and cubanite, CuFe₂S₃) at the site. The exchangeable cluster of

336 soil was principally composed of Al (*c.* 48%), Ca (*c.* 27%), Cu (*c.* 7%) and S (*c.* 5%). It was
337 removed by the HNO₃ extracts over the range 0.01 M to 0.1 M. High Ca and Al concentrations
338 combined with removal on addition of relatively weak acid suggests that this cluster was associated
339 with the presence of K-feldspar, which was found in micro-XRF analysis of soil samples.

340

341 Clay related: This cluster was found only in soil and consisted of 4 different components extracted
342 (Al-Si, Al-Si1, Al-Si2, Al-S). It was dominated by Al (*c.* 62%) and Si (*c.* 34%) and to a lesser
343 extent by Fe (*c.* 3%). This component also consisted of highest % of Co, Cr and Cu released during
344 CISED extractions. These components were extracted with acid concentrations from 0.01 M HNO₃
345 to 1 M HNO₃, however, the majority of elements were extracted in a narrower band of acid
346 concentrations ranging from 0.1 M HNO₃ to 1 M HNO₃ (E7-E12). The high acid strength for
347 extraction, predominance of Al, Si and Fe, along with presence of trace elements in this cluster are
348 likely to be extracted from clay related minerals and from the primary soil forming minerals such as
349 olivine and pyroxene (Wragg 2005). Clay like minerals such as montmorillonite and kaolinite were
350 identified during mineralogical analysis of soil sample using micro-XRF.

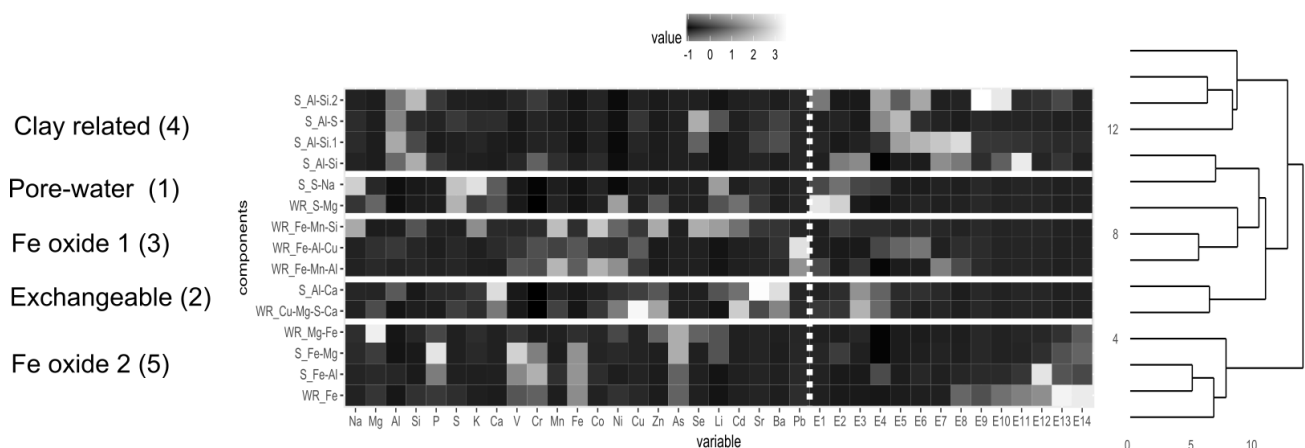
351

352 Fe oxide 1: The Fe oxide cluster was extracted only in waste rock. This cluster consisted of three
353 different Fe dominated components (Fe-Mn-Si, Fe-Al-Cu, Fe-Mn-Al). These Fe dominated
354 components were removed by acid concentrations ranging from 0.05 M HNO₃ to 0.5 M HNO₃ (E5-
355 E10). The important elements extracted were Fe (*c.* 39%), Al (*c.* 16%), Mn (*c.* 12%), Cu (*c.* 7%), Ni
356 (*c.* 6%) and Si (*c.* 6%), Mg (*c.* 5%). The presence of Fe, Cu, Ni rich components can be due to
357 presence of minerals like Fe Ni sulphide (pentlandite, (Fe,Ni)₉S₈) and Cu Fe sulphide (chalcopyrite,
358 CuFeS₂), which were found in mineralogy analysis of waste rocks from this site (Rossetti et al.,
359 2017). The presence of Al and Si in this Fe oxide cluster showed that in waste rock, both these
360 elements are more closely associated with iron unlike the soil sample, where Al was extracted in
361 clay related cluster.

362

363 Fe oxide 2: In the waste rock sample, the Fe oxide cluster was principally composed of Fe (c. 65%).
364 Other elements extracted were Al, Mg, Ni, Si, S with varying concentration from 2.6% to 12%. It
365 was removed by the HNO₃ extracts over the range 0.5 M to 5 M (E9-E14). The presence of Fe,S
366 rich components could be due to presence of Fe sulphide mineral (pyrrhotite, Fe_(1-x)S) observed in
367 microscopic images of waste rock from this site (Rossetti et al., 2017). The dominance of Fe and
368 high acid extracts required to extract these components could be due to presence of hematite
369 occurring naturally in the site (Rossetti et al., 2017). The presence of two different Fe containing
370 components for waste rock suggests the presence of different Fe oxide forms such as amorphous
371 and crystalline, that are being dissolved at different rates (Cave et al. 2004). The Fe oxide cluster in
372 soil included Fe (c. 75%), Al (c. 11%), Mg (c. 6%) and was removed by extracts containing HNO₃
373 over the range 1 M to 5 M and H₂O₂ (E11-E14). The Fe oxide 2 cluster was rich in Fe and Mg
374 which suggests that the important Fe and Mg bearing minerals of olivine group were mainly
375 extracted at very high acid concentrations. The cluster was also found to have concentrations of As,
376 Cr and Ni.

377

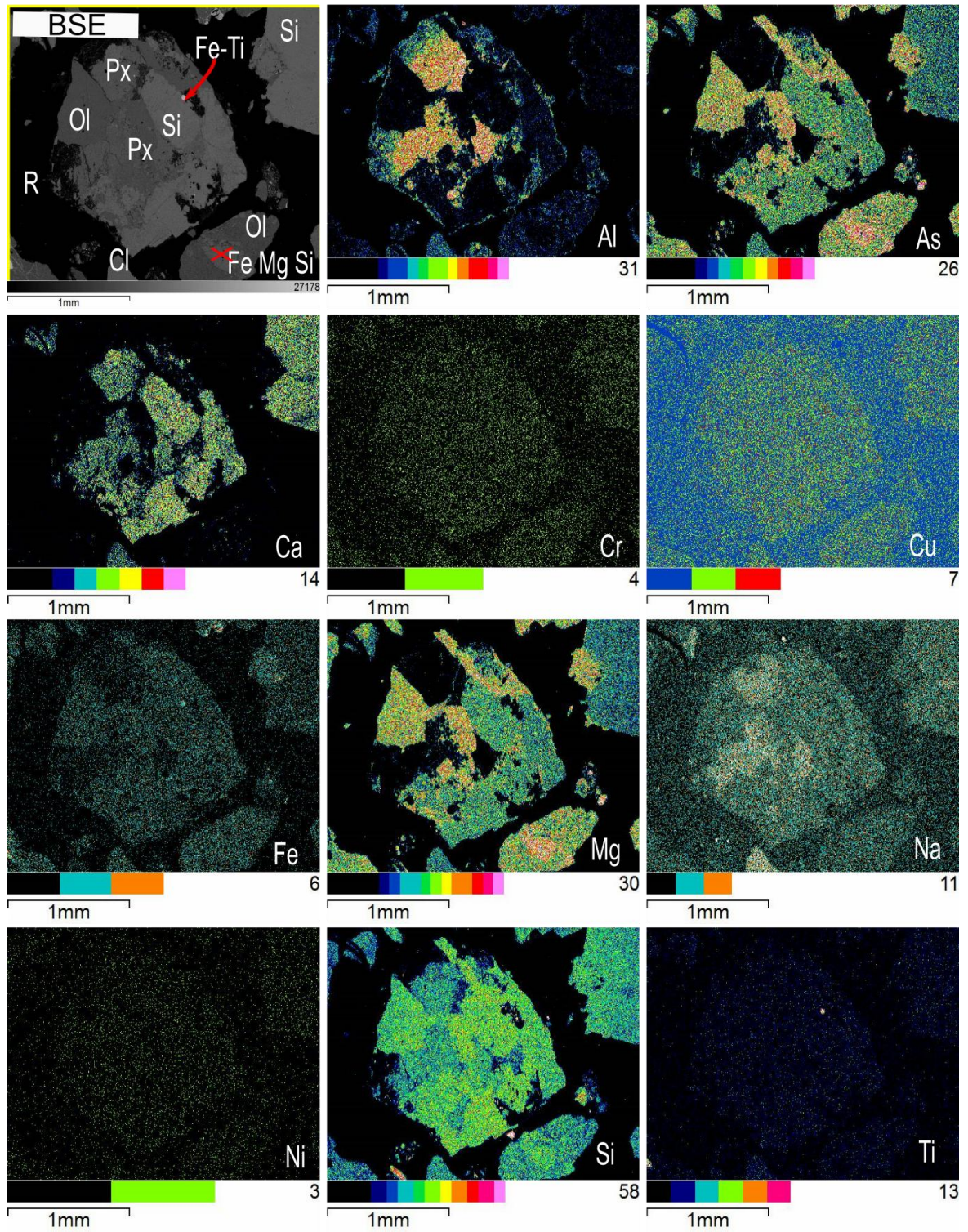


378 Figure 4. Heatmap and clustergram for CISED extracted waste rock and soil samples of Campello
379 Monti (CM 10, and soil sample code - 8). The dendrogram on the right hand side shows how
380 components link together. Elemental composition data is on the left-hand side separated with a
381 dashed vertical white line from the extraction number data (E1–14) on the right. The horizontal
382 white lines divide the map into clusters. High concentrations are depicted by white/light grey and
383 low concentrations by dark grey/black. Component names comprise a sample identification code
384 (WR and S) followed by the principal elements recorded for each component.

385 **3.4 Mineralogical analysis**

386 Semi quantitative analysis using micro-XRF showed that the dominant minerals present in soil
387 (sample code - 8) were clay related minerals (kaolinite and montmorillonite), Fe Al (Mg) silicates,
388 olivine, plagioclase and pyroxene. The secondary minerals determined during the analysis were Fe
389 oxides, K-feldspar, Mn phases and sulphides. The results from SEM analysis (**Figure 5**) showed
390 that As, Cr, Cu and Ni were locked within mineral grains. Arsenic was present in the minerals that
391 did not contain Al. One of the reason could be that in primary rock forming silicate minerals, As
392 can be incorporated in minerals through replacement of Al. It was also observed that As was found
393 to be occurring in the mineral phases rich in Fe-Mg, showing strong association of As with Fe-Mg
394 in the soil. This was also recorded in CISED analysis of soil sample where As was extracted in very
395 high percentage in Fe-Mg component. Chromium, Cu and Ni were found to be associated with both
396 Al rich and Fe-Mg silicate minerals.

397



398

399 Figure 5. Detail of elemental distribution and composition of soil (sample code 8) - Back scattered
 400 electron (BSE) image showing Cl : Clay related mineral (montmorillonite), FeMgSi : Fe Mg
 401 silicates, Fe-Ti : Fe-Ti oxide, Ol : Olivine, Px : Pyroxene, R : resin, Si : Ca Mg Fe silicates and
 402 corresponding X-ray maps (SEM) for Al, As, Ca, Cr, Cu, Fe, Mg, Na, Ni, Si and Ti.

403

404

405

406 **3.5 Relation of mineralogy and CISED to bioaccessibility**

407 The PTE extracted and their bioaccessible fraction are plotted in **Figure 6**. The waste rock sample
408 contained 11 mg/kg of As and only 1 mg/kg of this was bioaccessible. The total concentration of As
409 extracted by CISED was also 1 mg/kg, indicating that As extracted in both the methods was similar.
410 80% of total CISED extracted As was associated with the Fe oxide 2 cluster. The Campello Monti
411 site is rich in Fe bearing minerals suggesting that dissolution of Fe oxides/oxyhydroxides took place
412 leading to As in extracted solutions. 9 mg/kg of As was present in the soil sample, while 1.8 mg/kg
413 of this was bioaccessible and 1.2 mg/kg was extracted by CISED, suggesting that As could be
414 present in mineral phases which were not dissolved through CISED but were present in the
415 gastrointestinal phase of bioaccessibility extractions. It was observed through SEM analysis that As
416 was locked in mineral phases of soil sample. This could be due to the presence of organic reagents,
417 body temperature conditions and/or the longer reaction time for UBM solutions. In fact, Yunmei et
418 al. (2004) found that during dissolution of Fe-As-S rich mineral assemblages the concentration of
419 As in solution tends to increase with increase in temperature and time.

420 The total concentration of Cu in waste rock was 1955 mg/kg while only 650 mg/kg of Cu
421 (35%) was extracted by CISED extractions. Similar observations were made for Cu present in soil
422 where 33% of Cu was removed in CISED extractions with total concentration and total CISED
423 extracted concentrations of 441 mg/kg and 135 mg/kg, respectively.

424 The bioaccessible concentration of Cu in waste rock was 157 mg/kg resulting in higher
425 bioaccessible Cu concentrations than Cu concentrations recorded during CISED extractions. It
426 suggests that Cu associated with Fe and S present in Fe oxide 1 cluster, which did not get extracted
427 in CISED extractions, was extracted in bioaccessibility experiments. However in soil the
428 bioaccessible concentration was less than the CISED extracted concentration. Bioaccessibility of Cu
429 in soil was due to exchangeable, Fe oxide 2 and dissolution of clay related clusters, while Cu
430 present in the Fe oxide 2 component did not contribute to bioaccessible Cu. The differences in

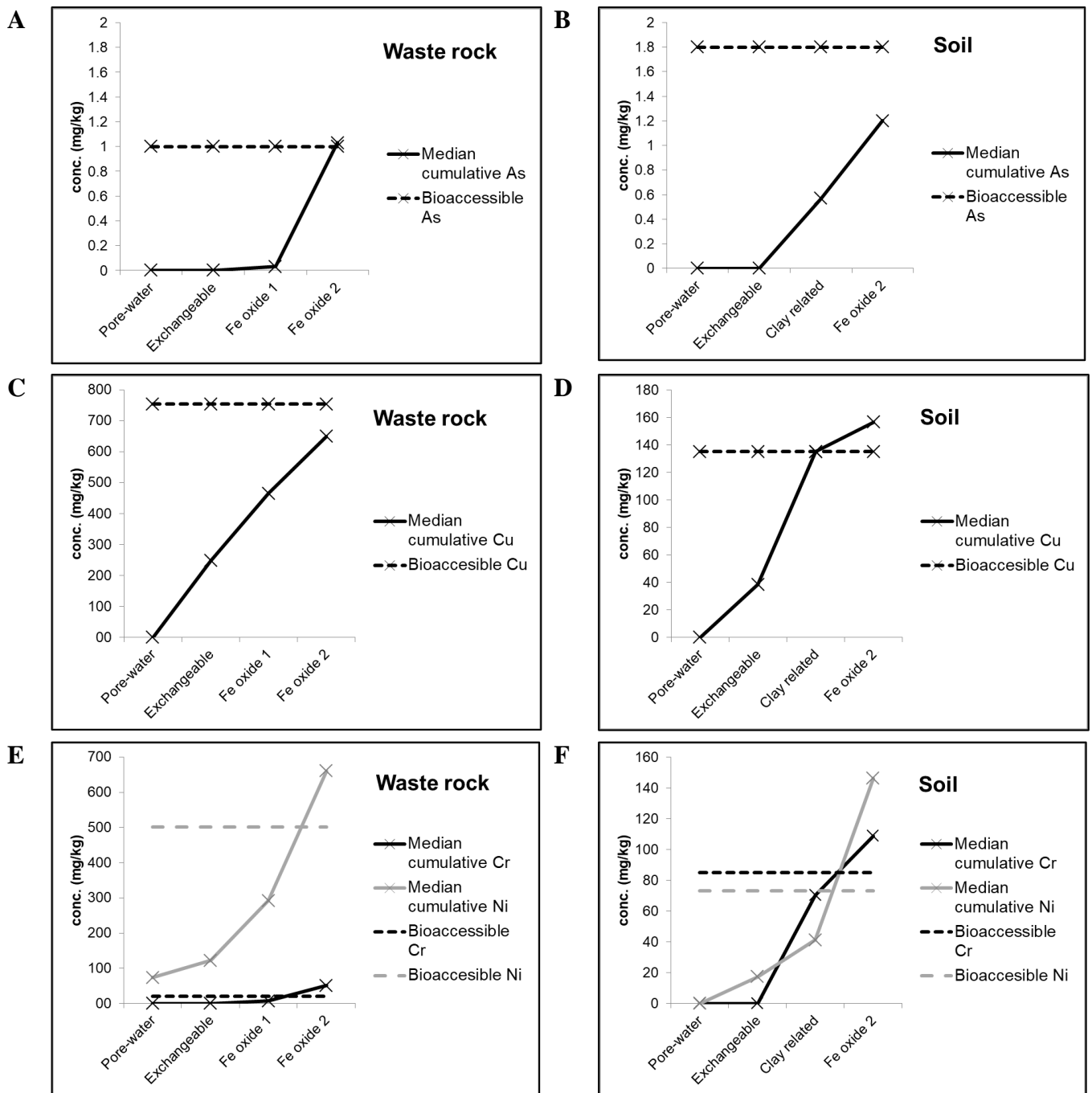
431 bioaccessible Cu concentrations in soil and waste rock could be due to a) the presence of Cu in clay
432 related minerals rich in metal silicate phases in soil. While in waste rocks Cu was associated with
433 metal sulphides. It has been found that Cu tends to form stable and relatively inert complex with Si
434 (Teien et al., 2006), leading to reduction in dissolution, b) the difference in CISED extracted ratio of
435 concentration of S/Fe. It is worth mentioning that the ratio of total S/Fe for CISED extracted
436 concentration in waste rock and soil was 12.8% and 7.6% respectively. Studies on dissolution
437 reactions of Cu has concluded that Cu is more chalcophile than siderophile and tends to dissolve
438 faster with increase in ratio of S/Fe in iron-sulphur based solutions (Holzheid and Lodders, 2001).

439 In waste rock samples it was observed that the gastric phase bioaccessible concentrations of
440 Cr and Ni increased with increase in total concentration potentially suggesting that the majority of
441 bioaccessible Cr and Ni is derived from phases which contribute to the total Cr and Ni in the sample
442 (Cox et al. 2013). The total concentration of Cr in waste rock was 1,569 mg/kg while 51.2 mg/kg
443 was extracted by CISED. The total concentration of Ni in waste rock was 4,586 mg/kg, however
444 only 661 mg/kg was removed during the CISED procedure. The extraction of 4% of total Cr and
445 14% of total Ni by CISED suggests that the majority of Cr and Ni was present in less reactive
446 minerals such as olivine and pyroxenes that are resistant to attack by HNO₃. Pyroxene and olivine
447 are both known to host Cr and Ni are known to be the primary minerals at the site (Rossetti et al.,
448 2017). The source of bioaccessible Cr in the waste rock with the partial dissolution of Fe oxide 2 is
449 shown in Figure 6E. For Ni, it was observed that the same fraction was the source of
450 bioaccessibility, in addition to dissolution of pore-water, exchangeable and Fe oxide 1 components.
451 Higher concentrations of Ni than Cr in pore water and exchangeable components suggests easy
452 dissolution of Ni. It could be because Ni is primarily hosted by olivine in ultramafic rocks.
453 Dissolution of olivine has been found to be rapid in comparison to most silicate minerals as it has
454 simpler structure (Pokrovsky and Schott, 2000). Venturelli et al. (2016) while studying weathering
455 of ultramafic rocks, found that Ni tends to be more mobile than Cr and was found in higher
456 concentrations in weathered rocks. Another study reporting Cr and Ni mobility concluded that Ni

457 tends to be more readily transferred to secondary minerals (Quantin et al., 2008). Cox et al. (2017)
458 found that Cr concentrations in basaltic soils were related to highly recalcitrant chrome spinel and
459 primary iron oxides, while Ni was more widely dispersed within the soils including in more
460 extractable soil fractions which led to higher BAF measurements being recorded for Ni than Cr.

461 The total concentration of Cr in soil was 623 mg/kg with a bioaccessible Cr concentration of
462 85 mg/kg. The CISED method extracted 108 mg/kg of Cr. Differences in total bioaccessible and
463 CISED extracted concentrations suggest the non-mobile nature of Cr in soil. Dissolution of clay
464 related clusters and partial dissolution of Fe oxide 2 led to the bioaccessible forms of Cr. The total
465 concentration of Ni in soil was 1,455 mg/kg, however only 73 mg/kg was bioaccessible in gastric
466 phase extractions. The bioaccessible form of Ni was likely to come predominantly from the
467 exchangeable and clay related clusters, and to a lesser extent by the Fe oxide 2 cluster, identified by
468 the CISED extraction (**Figure 6E**). The possible reason could be that the clay related cluster
469 consisted of weathered minerals, while Fe oxide 2 cluster belongs to recalcitrant primary
470 mineralization at the site in form of pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), pentlandite ($(\text{Fe,Ni})_9\text{S}_8$), chalcopyrite
471 (CuFeS_2) (Rossetti et al., 2017). For As, Cr and Ni it was observed that the BAF was higher for soil
472 samples compared to waste rock samples. This could be because (a) elements in ultramafic
473 lithologies are more tightly bound in the mineral lattice of the waste rocks compared to soils, (b)
474 waste rock samples were more acidic than soil samples, which can cause some PTE to remain
475 immobile (Ruby et al., 1999), (c) elements with particle binding abilities may become immobilized
476 in rocks but can be released during weathering. However, the mean value of bioaccessible fractions
477 in soil for all PTE analyzed was less than 54%. The possible reason could be the embedment of
478 PTE within mineral grains of soil as observed in SEM analysis.

479



480 Figure 6. Median cumulative concentration of elements in different components of CISED
 481 compared with bioaccessible concentrations in samples of Campello Monti (mg/kg).
 482

483

484 4. Conclusions

485 This study investigated total concentrations and bioaccessible concentrations of PTE at abandoned
 486 mine site of Campello Monti. Data from mineralogy analysis, non-specific sequential extraction and
 487 chemometric analysis on selected samples were also related to the oral bioaccessibility to

488 understand the relationship between total concentrations, bioaccessible concentrations, the
489 mineralogy and solid phase distribution of these elements. The extractive waste facilities and local
490 soils around the old mining areas of Campello Monti (NW Italy) are strongly enriched in PTE. This
491 study provided evidence that total concentrations of PTE were higher in samples with particle size
492 $<250\ \mu\text{m}$ compared to samples ($<2\ \text{mm}$), due to higher specific surface area in the former case. The
493 results of total concentrations showed high concentrations of PTE. However, not all of these
494 elements were bioaccessible. The mean value of bioaccessible fraction (ratio of bioaccessible
495 concentration to total concentration) was observed to be significantly less than 100 % (11%, 1%,
496 and 31% for As, Cr, Cu respectively in waste rocks and 31%, 3%, and 26% for soils). The mean
497 value of BAF of Ni was 10%. Mean values of BAF of V in waste rock and soil were observed to be
498 4% and 9% respectively. It is clear that the release of PTE and potential risks to human health
499 strongly relies on pH, soil phases, and solubility of Fe-rich phases and presence of clay like
500 minerals. These results show that risk assessment of the site on the basis of total concentrations of
501 PTE alone would significantly overestimate the potential risks to human health at the site. The
502 research conducted highlights how geological and lithological structures together with rock
503 weathering and soil formation processes can lead to variations of bioaccessibility. Traditionally,
504 criteria for the assessment and intervention strategies of contaminated sites have been derived using
505 concentration-based standards and assuming that 100% of the contaminant is bioavailable.
506 However, the results outlined in this research clearly indicate that the bioaccessibility evaluations
507 can lead to more informed site based risk assessment.

508

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518

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