

1 **Metal release under anaerobic conditions of urban soils of four European** 2 **cities**

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20 **Abstract**

21 Urban soils contamination may represent an environmental threat in view of their proximity to
22 humans. The ecological homogenization of urban areas has been postulated and, as the sources of
23 pollution are the same in most European cities, it is possible that soil contamination is another
24 factor of convergence. The current climate change with consequent increase of extreme rain events
25 may affect the mobility of potentially toxic elements (PTE) thus increasing the risks. If the soil is
26 submerged, Eh decreases and causes the solubilization of Fe and Mn oxides, which are important
27 carriers of PTE. We compared the release of Cu, Pb and Zn from 48 soils of four cities (namely
28 Glasgow, Ljubljana, Sevilla and Torino) when submerged for up to 30 days. A decrease of the
29 redox potential was observed in all soils after a few days and an increase of Mn and then Fe in
30 solution. Cu, Pb and Zn were consequently released to the solution according to the general soil
31 contamination. Despite the marked differences in soil properties, the reaction to anaerobiosis
32 appeared to be similar in all samples indicating that waterlogging of urban soil contaminated with
33 PTE may pose a serious environmental risk and substantiating the hypothesis of ecological
34 convergence.

35

36 **Keywords:** urban soils; climate change; potentially toxic elements; redox; flooding

37

38 **1. Introduction**

39 Urban soils are a well-known sink for the pollutants that are produced by a variety of human
40 activities. A review of available data (Ajmone-Marsan and Biasioli 2010) has shown that most
41 world cities are contaminated by potentially toxic elements (PTEs). Burning of fossil fuels,
42 industrial production and waste disposal are among the main sources of contaminants such as Cu,
43 Pb and Zn. In fact, these elements have been recognized as being characteristic diffuse
44 contaminants of urban areas (Imperato et al. 2003; Biasioli et al. 2006; Sharma et al. 2015). Indeed,
45 many of the studied cities are more similar in soil contamination than any other characteristic. The
46 hypothesis of a general ecological homogenization caused by urbanization was postulated by
47 McKinney (2006) and was later confirmed for six urban areas in the United States of America
48 (Groffman et al. 2014). Subsequently, Pouyat et al. (2015) compared the soils of five cities and
49 observed a convergence of the properties affected by anthropogenic processes and associated with
50 biogenic processes. In urban areas of Europe, the sources of contamination are similar, so it is
51 possible that soil contamination is another indicator of convergence of urban environments.

52 The total PTE content is but one parameter that can define the quality of a soil but it carries little
53 information about the actual threat that the presence of the PTEs pose to human health or to other
54 ecosystems. It is now generally accepted that chemical fractionation or solution data (NRC 2003)
55 give a better insight into the risk connected to PTE contamination, and several studies (Madrid et
56 al., 2008; Poggio et al. 2009; Sialleli et al. 2011) have confirmed the importance of the available
57 and bioaccessible fractions of PTE in the assessment of their hazardousness to humans in the urban
58 context.

59 The transfer of the contaminants to an adjacent environmental compartment – water, air or biota -
60 is not solely dependent on the chemical reactivity of the element; the soil matrix can abruptly
61 change its properties and reduce its equilibrium concentration for contaminants, thus releasing
62 some bound components. This is the case with rapid changes of the redox potential that occur, for
63 example, when a soil is submerged. Although trace metals are rarely directly involved in the redox
64 reactions, during submersion iron and manganese oxides are solubilized, thus releasing the PTEs
65 that are adsorbed onto their surfaces or occluded within their mineral structure (Davranche and
66 Bollinger 2000; Cornell and Schwertmann 2003; Du Laing et al. 2009; Violante et al. 2010;
67 Vodyanitskii and Plekhanova 2014). This would increase the potential toxicological effects that
68 come from PTE contamination of the soil (Alderman et al. 2012). Schulz-Zunkel et al. (2013)
69 described PTE contamination of the sediments of the river Elbe in Germany and indicated that
70 changes in redox potential were one of the main factors that may switch sediment from sink to
71 source of pollutants. Analogously, Popescu et al. (2013) reported an increase of the release of

72 metals from mine-spoil contaminated soils in response to submersion and ensuing anaerobiosis.
73 Shaheen et al. (2014) established that the periodic inundation of contaminated floodplain soils
74 affected the temporal dynamics of Cd, Co, Cu, Ni, and Zn due to changes in Eh-pH, dissolved
75 organic carbon, and in the chemistry of Fe, Mn and S. An increase of metal mobility in flooded
76 urban soils was observed by Florido et al. (2011) and was attributed to the dissolution of Fe and
77 Mn oxides. Notable examples of the consequence that soil submersion can have on PTE release
78 comes from the work of Su et al. (2008) and of Fox et al. (2009) who studied the mobilization of
79 contaminants after the flooding caused by hurricane Katrina in New Orleans (USA). Apart from
80 that exceptional and extensive episode, local conditions that are conducive to the onset of
81 anaerobiosis are frequent in urban soils, due mainly to the alteration of soil hydrology because of
82 soil sealing and compaction (Du et al. 2015). In recent years, however, an increase in the number
83 and intensity of extreme rain events has been observed (IPCC 2013; Gallant et al. 2014). Buzatu
84 (2016) reported that Europe has seen a 60% increase in extreme weather events over the past three
85 decades. Global climate change not only causes warming, but also alters the precipitation patterns,
86 so that ecosystems will have to deal with an increased frequency of extreme precipitation events
87 (IPCC 2013; NASEM 2016).

88 In the Piemonte region, in NW Italy, a study of the data between 1930 and 2004 has revealed an
89 increase in the intensity of extreme rain events (Ciampittiello et al. 2013). Similarly, Jones et al.
90 (2014) observed an increase of the probability of extreme rain events in south Scotland in the
91 period 1961-2010. As thunderstorms are generally more frequent over urban areas, due to the
92 formation of a *heat island* (Scalenghe and Ajmone-Marsan 2009), the risk of local soil flooding is
93 enhanced (Jha et al. 2011).

94 The scope of this work was to evaluate the effects that changing redox conditions caused by
95 flooding can have on the potential release of Cu, Pb and Zn from contaminated soils from four
96 European cities. A more general aim was to verify if the postulated ecological homogenization of
97 urban environment would also apply to these biotic reactions of soils.

98

99 **2. Materials and methods**

100 Twelve soils were selected from each of the cities of Glasgow (UK), Ljubljana (SL), Sevilla (ES)
101 and Torino (IT) (Table 1) among those that had been previously described by Madrid et al. (2006)
102 and Biasioli et al. (2007). The selection was made to obtain a variety of soil properties and of
103 concentrations of Cu, Pb and Zn in order to represent the wide diversity of these urban soils. In
104 addition to potential flooding from exceptional rain events, all four cities are built on riverbanks so
105 there is also a possibility that their soils could be inundated. Indeed, the city of Torino was flooded
106 in 1994 and 2000 when heavy rains occurred over the steepest areas of its catchment.

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Table 1 Description of the cities

City	Location Lat/Long	Size of urban area (km ²)	Population	Climate	
				Mean annual rainfall (mm)	Mean annual temperature (°C)
Ljubljana	46°N/14°E	95	260 000	1352	10.8
Sevilla	37°N/6°W	135	706 000	540	18.2
Torino	45°N/8°E	130	865 000	750	12.6
Glasgow	55°N/4°W	176	600 000	1100	8.9

111

112 Surface soil horizons were sampled using stainless steel shovels from 0 to 10 cm. Samples were
113 air-dried, gently crushed and sieved to <2 mm with plastic sieves to reduce metal contamination
114 (ISO 11464). A portion of the sample was further ground to <0.15 mm for *aqua regia* (HCl/HNO₃,
115 3:1 solution) digestion (ISO 11466). The *aqua regia* extracts were analysed for Cu, Fe, Mn, Pb,
116 and Zn by ICP-OES. Triplicates were made for all samples and results accepted when the
117 coefficient of variation was under 5%. A blank and soil CRM BCR 141 R reference material (Joint
118 Research Centre - Institute for Reference Materials and Measurements, Geel, Belgium) were
119 included in each batch of analyses for quality control. Results were considered satisfactory when
120 within a range of ± 10% from the certified value. Particle size distribution was determined by
121 sedimentation and sieving; the pH was measured in a CaCl₂ solution at a 1:5 soil:solution ratio and
122 organic carbon and sulphur by elemental analyzer. The content of sulfur was always lower than the
123 detection limit.

124 Anaerobic microcosms were set up by placing 45 g of soil in 250 ml dark glass bottles and 150 ml
125 of a 0.01 M CaCl₂ solution (Supplementary Material, Fig. 1S). The flasks were flushed with CO₂-
126 free N₂ and tightly sealed. Ten ml of the suspension were sampled at 6 hours, and 1, 5, 9, 14, 21,
127 and 30 days, filtered with 0.45 µm nylon filters and the metals in solution (Cu, Fe, Mn, Pb and Zn)
128 were measured having had care to maintain anoxia. The pH and Eh of the solutions were measured
129 under N₂ in a parallel set of samples. Measurements of pH were done by a polymer combination
130 electrode, and the Eh was estimated by a redox platinum electrode (Crison Micro CM, 2201, Crison
131 Instruments S.A. Spain). At the end of the experiment, the soil samples were air-dried at 40°C and
132 gently crushed in an agate mortar. Sequential extraction was carried out before and after the
133 experiments according to the revised BCR protocol (Rauret et al. 1999). The procedure is
134 summarised below:

- 135 – Step 1 (water/acid soluble and exchangeable fraction): 40 ml of 0.11 mol l⁻¹ acetic acid was
136 added to 1 g soil and shaken for 16 h at room temperature. The extract was separated from
137 the solid by centrifugation, decanted and stored at 4 °C. The residue was washed with
138 distilled water and the washings discarded.
- 139 – Step 2 (reducible fraction): 40 ml of 0.5 mol l⁻¹ hydroxylammonium chloride (adjusted to
140 pH 1.5) was added to the residue from step 1, and the extraction performed as described for
141 step 1.
- 142 – Step 3 (oxidisable fraction): the residue from step 2 was digested with hydrogen peroxide
143 then 50 ml of 1.0 mol l⁻¹ ammonium acetate (adjusted to pH 2) was added and the
144 extraction performed as described for step 1.
- 145 – Step 4 (residual fraction): the residue from step 3 was extracted with *aqua regia* using the
146 same procedure as described above for the whole soil.

147 All determinations were carried out in triplicate. The sum of fractions was compared with the
148 results of *aqua regia* digestion of the whole soils to determine metal recovery with the BCR
149 procedure and recoveries were within 90% and 110% for all samples.

150 Data interpretation and statistical analysis (Pearson correlations and analysis of variance) were
151 carried out using Microsoft Excel 2013 and IBM SPSS 25. To better define associations between
152 analytes, we used Principal Component Analysis (PCA). We carried out the chemometric treatment
153 on the whole data set of 48 samples and we used, alternatively, the chemico-physical
154 characteristics, the whole data on metals release and specific release times. All data sets were
155 normalized using Z-scores.

156

157 **3. Results and Discussion**

158 The four cities have soils with different pH: while Glasgow (GLA) has acidic soils, in Torino
159 (TOR) it ranges from acidity to above neutrality, with a mean value of 6.6, and in Ljubljana (LJU)
160 and Sevilla (SEV) the pH is slightly above neutrality (Table 2 and Supplementary Material, Table
161 1S).

162 The soils of the latter two cities have an average carbonate content of 19% and 21%, respectively.
163 The content of organic C is very variable within and between cities, being highest in Glasgow and
164 lowest in Sevilla. In general, the C concentrations parallel the climatic conditions of the cities with
165 a North-South organic matter decline. In contrast, the particle-size distribution appears to be
166 remarkably uniform as the majority of the textures are towards a sandy particle-size except for
167 some soils in Sevilla, which show a silty texture. Metal contents reflect the sample selection
168 criteria, showing a wide range of values. In most cases, however, the concentrations are above the
169 respective national legislative thresholds for contaminated soils, as described in Madrid et al.
170 (2006).

171 In this work we investigated the effect of changing redox conditions on the release of Cu, Pb and
 172 Zn, typical contaminants of urban soils (Madrid et al. 2006), thus we calculated correlations
 173 between the soil properties and metal concentrations using data for all the soils (Supplementary
 174 Material, Table 2S). Although the soil properties are widely changing, Pb, Zn and Cu are
 175 significantly, though moderately ($r_{\text{Cu-Pb}}=0.70$; $r_{\text{Cu-Zn}}=0.65$; $r_{\text{Cu-Pb}}=0.50$), correlated, corroborating
 176 the observation that, at least in respect of PTE contamination, these urban soils tend to converge.

177

178 **Table 2** Soil properties and metal content (aqua regia)*. N is 12 for all cities

Samples	pH in CaCl ₂	Sand	Silt	Clay	Org. C	Fe	Mn	Cu	Pb	Zn
		%		%		mg/kg				
Glasgow										
Mean	5.0	66	26	8	7.0	2.9	475	89	300	263
Median	5.0	66	27	8	6.7	2.8	456	82	281	215
Max	5.8	81	35	15	13.0	4.0	686	194	618	621
Min	4.1	50	16	3	4.2	2.3	132	41	122	124
<i>S.D.</i>	<i>0.6</i>	<i>7.3</i>	<i>4.9</i>	<i>2.9</i>	<i>2.3</i>	<i>0.5</i>	<i>164</i>	<i>46</i>	<i>141</i>	<i>149</i>
CV%	<i>11</i>	<i>11</i>	<i>19</i>	<i>38</i>	<i>33</i>	<i>16</i>	<i>35</i>	<i>52</i>	<i>47</i>	<i>57</i>
Ljubljana										
Mean	7.1	46	40	14	5.7	2.3	866	65	190	223
Median	7.1	48	40	14	5.5	2.1	854	60	162	193
Max	7.3	57	48	19	8.6	3.2	1410	124	388	421
Min	6.9	37	34	8	4.2	1.3	412	39	115	134
<i>S.D.</i>	<i>0.2</i>	<i>5.6</i>	<i>4.8</i>	<i>2.8</i>	<i>1.2</i>	<i>0.5</i>	<i>319</i>	<i>24</i>	<i>87</i>	<i>79</i>
CV%	<i>2</i>	<i>12</i>	<i>12</i>	<i>21</i>	<i>21</i>	<i>22</i>	<i>37</i>	<i>38</i>	<i>46</i>	<i>35</i>
Sevilla										
Mean	7.2	37	41	22	2.5	2.1	544	116	364	182
Median	7.2	41	40	23	2.8	2.0	401	109	326	197
Max	7.4	54	58	33	3.7	2.7	1317	229	977	325
Min	7.0	10	27	13	0.9	1.6	294	25	30	21
<i>S.D.</i>	<i>0.1</i>	<i>14.3</i>	<i>9.8</i>	<i>6.7</i>	<i>1.0</i>	<i>0.3</i>	<i>324</i>	<i>71</i>	<i>311</i>	<i>79</i>
CV%	<i>1</i>	<i>39</i>	<i>24</i>	<i>30</i>	<i>40</i>	<i>15</i>	<i>60</i>	<i>62</i>	<i>85</i>	<i>44</i>
Torino										
Mean	6.6	68	21	11	3.2	3.4	736	137	428	264
Median	6.8	64	25	12	3.0	3.2	686	104	320	243
Max	7.5	88	32	15	5.8	5.0	1097	301	1440	440
Min	4.8	55	7	5	1.7	3.0	397	35	58	90
<i>S.D.</i>	<i>0.8</i>	<i>12.2</i>	<i>9.2</i>	<i>3.3</i>	<i>1.3</i>	<i>0.5</i>	<i>233</i>	<i>82</i>	<i>431</i>	<i>123</i>
CV%	<i>12</i>	<i>18</i>	<i>44</i>	<i>31</i>	<i>40</i>	<i>16</i>	<i>32</i>	<i>60</i>	<i>101</i>	<i>47</i>

179 *Max = maximum; Min = minimum; S.D. = standard deviation; CV% = coefficient of variation

180

181 The maximum acceptable PTE concentrations in soils are regulated in all countries of this study,
 182 although with different thresholds or guideline values in the different states. As found in previous

183 studies (Madrid et al. 2006), Torino, Glasgow and, to a lesser extent, Sevilla, were the most
 184 contaminated cities but the definition of contamination may not be applicable, as the trigger values
 185 differ widely between countries.

186 Despite these differences, all legislative limits refer to the total concentrations of PTEs, a metric
 187 that does not necessarily refer to the risk posed from the leaching of these elements from soil.

188 Bioavailable and bioaccessible fractions have been studied in last years to offer a more realistic
 189 representation of the risk posed to humans and the environment in general (Ajmone-Marsan et al.
 190 2008; Padoan et al. 2017) using extracting agents that mimic the human absorption of the
 191 contaminants. While availability and accessibility are estimates based on the nature (solubility,
 192 desorbability) of the element and of the soil, the release of PTE due to the chemical reduction and
 193 dissolution of the matrix (i.e. Fe, Mn oxides, organic matter) is usually not taken into account. The
 194 PTE release depends on various soil properties as the quantity and type of organic matter, Fe and
 195 Mn-oxides. Thus, these trigger values would not be suitable in case of flooded soils and a more
 196 specific risk-based approach that takes into consideration the parameters governing the metals
 197 release is required.

198

199 **Table 3** Maximum acceptable limits (mg kg⁻¹) in the studied countries or regions applicable to
 200 soils of residential or recreational areas (adapted from Madrid et al. 2006).

Country/ Region	Cu	Pb	Zn
Italy ^a	120	100	150
Andalucia ^b	150-300	250-350	300-600
	300-500	400-500	500-1000
Slovenia ^c	60/100/300	85/100/530	200/300/720
UK ^d	-	450	-

^a Limit values for residential and garden areas.

^b Research required” values (ranges instead of single values are given);
 different values are given for pH below and above 7.

^c “Limit”, “warning” and “critical” values.

^d CLEA Soil Guideline Values, specific limits with a risk-based approach

201

202 3.1 Incubation experiments

203 Despite the differences between and within cities, the urban soils responded to treatment in a rather
 204 uniform way regarding Eh and pH values. The values of the redox potential (Eh, Figure 1)
 205 promptly decreased in all soils regardless of the content of the different redox couples in the soil,
 206 e.g. of organic carbon, that would act as an electron donor.

207 The pH values (Supplementary Material, Fig. 2S) varied accordingly, increasing in most soils. The
 208 Sevilla soils showed more erratic values, presumably as a result of the dissolution of the CO₂
 209 derived from the carbonates.

210 The redox system of the soil is controlled by several variables and the Eh is the result of numerous
211 redox couples acting simultaneously. Together with the pH, it gives a general representation of the
212 reduction or oxidation status, but its value cannot be attributed to any specific reaction, especially
213 in a complex matrix such as the soil. A more reliable indication that the soil has attained an anoxic
214 condition comes from the appearance of some elements in solution. After oxygen and nitrates have
215 been depleted, Mn first and Fe soon after are adopted as the final electron acceptors of the
216 anaerobic metabolism. The solubility of their reduced compounds – Mn^{2+} , Fe^{2+} – is greatly
217 increased with respect to the oxidized forms, and so was the concentration of these metals in
218 solution (Figures 2 and 3). In Figure 2 the average Mn concentration in the soil solution is reported
219 for all cities. The concentrations are represented as a percentage of the sum of the fractions
220 exchangeable and reducible of each soil, to improve readability, as soils had very diverse metals
221 concentrations. Exact amounts released from each soil at each time are in the Supplementary
222 Materials, in Tables 3S and 4S.

223 Manganese in solution (Fig. 2) increased from the very beginning of the experiment in almost all
224 soils, although the choice of the sampling aimed at representing the maximum variability in each
225 city, and its concentration appeared to stabilize after a peak at day 5 of submersion. This threshold
226 at day 5 was confirmed using mean release values; values recorded in samplings after 6 h and 1 day
227 were significantly different for subsequent samples (HSD Tukey test, $p=0.05$) for all cities but
228 Torino. In TOR samples, however, the trend was alike.

229 This indicated that most of the soils attained anoxic conditions in a very similar way, regardless of
230 the properties of the matrix. Electron donors such as low molecular weight organic matter is
231 sufficient to stimulate the action of anaerobic microorganisms that reduce Mn.

232 Iron concentration increased in solution on submersion (Fig. 3) and in general followed the
233 thermodynamic order, appearing in solution after day 5, i.e. after Mn reduction. A threshold day for
234 the concentrations to be significantly different from the beginning was found at day 14 for Torino
235 and Ljubljana soils while at day 21 for Glasgow and Sevilla.

236 The largest amounts of Fe were released from the GLA soils, despite their total Fe concentration
237 being similar to the soils of other cities. It is possible that the low pH and abundant organic matter
238 in those soils might have enhanced Fe dissolution by complexation (Vodyanitskii and Plekhanova
239 2014). The lowest values were recorded for the SEV and LJU soils where, in contrast, the high pH
240 and the presence of carbonates explain the low Fe solubility and the more homogeneous
241 concentration values.

242 The dissolution of Fe and Mn oxides brings about an increase in the solution concentration of the
243 PTE that are associated – adsorbed or occluded – to these compounds. Manganese oxides are
244 strong sorbents of PTE and act as natural sinks for contaminants (Borch et al. 2010) and Fe oxides
245 are used to sequester PTE from contaminated soils due to their strong affinity with the oxides
246 (Gasparatos 2013; Liu et al. 2014).

247 In the case of copper (Figure 4), a peak in the concentration in solution was observed in all soils
248 although some differences emerged between cities. While the Cu peak appeared as early as day 5
249 of submersion in Ljubljana and Sevilla, most of the soils in Glasgow and Torino showed the
250 maximum release around day 10. After the first peak, another increase was observed in Ljubljana
251 and Sevilla soils after the 21st day of the experiment. The decrease in concentration of an element
252 in solution following a maximum is usually attributed to changes in the matrix that are brought
253 about by anoxia: Fe and Mn oxides are only partially dissolved and new surfaces are exposed that
254 can re-adsorb the metals or they can adsorb to, or coprecipitate with, Fe(II)-compounds while
255 organic matter can similarly contribute to the lowering of the concentration in solution (Cornu et al.
256 2009; Borch et al. 2010; Vink et al. 2010; Frohne et al. 2014). The rise in pH would increase the
257 negative charge on variable-charge minerals, such as Fe-oxides, and augment the probability of
258 surface sorption. The chemistry of Cu in soil, especially in urban settings, is particularly complex
259 (Biasioli et al. 2010; Borch et al. 2010) as the sources can be very variable: metallurgical and
260 energy-related industry as well as automotive traffic can release Cu in different forms. This can
261 partly justify the very high levels of readily soluble Cu in some soils from Glasgow, Sevilla and
262 Torino, the latter showing a concentration as high as 15.3 mg/kg of Cu (7% of the total Cu)
263 released after the first 6 hours of the experiment. The affinity of this element for organic matter can
264 further obscure the overall picture, as part of the metal can pass into solution as a complex or
265 subsequently to the oxidation of organic complexes rather than the reduction of Fe and Mn oxides.
266 While there are sources of point contamination of Pb, this element is a typical diffuse contaminant
267 of urban soils due to its former use as antiknock in gasoline. Similarly to Cu, Pb was promptly
268 released to the solution in many soils of Glasgow, Sevilla and Torino (Figure 5) indicating that
269 there are soluble forms of these elements in the soils of all three cities. In Glasgow, most soils
270 showed an increase in concentration towards the end of the experiment, indicating that a substantial
271 Fe dissolution (Figure 3) is necessary for Pb to be released. The soils of Torino presented the
272 highest release considering absolute values, but the general trend was similar to that of the other
273 cities. For the soils of Ljubljana, a peak in Pb concentration was observed after 5 days of
274 submersion, in correspondence with Mn peaks and another close to the 21 days Fe peak,
275 reinforcing the hypothesis that Pb could be closely associated with redox-sensitive oxides.

276 The highest concentrations of Zn in solution were observed in the soils of Glasgow (Figure 6). In
277 contrast to other elements and to the soils from other cities the concentration of this metal
278 decreased steadily, after an initial peak. It appeared that Zn solubility followed Fe dissolution and
279 pH increase. In Ljubljana, Sevilla and Torino the release of Zn appeared to be connected with Fe
280 oxides solubilization. This confirms that this element is associated preferentially to Fe oxides (Van
281 Laer et al. 2010; Vodyanitskii and Plekhanova 2014). These results are in line with those reported
282 by Donner et al. (2012) for Mn and Fe rich soils and by Van Laer et al. (2010) for some Spodosols.

283

284 *3.2 Chemical fractionation*

285 The chemical fractionation of the metals in urban soils offers an insight into the transformations
 286 that these undergo after submersion and subsequent oxidation (Table 4).

287

288 **Table 4** Changes in the proportion of chemical fractions (expressed as % of the total content)
 289 before and after the anaerobiosis. Values are averaged by city.

290

		GLA	LJU	SEV	TOR
Mn	Exchangeable	35*	52*	29*	18*
	Reducible	-31*	-51*	-22*	-24*
	Oxidisable	3.1*	-0.2	-1.3	-0.6
	Residual	-7.5*	-0.8	-5.0*	6.3*
Fe	Exchangeable	0.7*	0.7*	0.1	0.2*
	Reducible	4.3*	2.2*	2.0*	1.2
	Oxidisable	2.0*	-0.7*	1.1	-0.2
	Residual	-7.1*	-2.1*	-3.1*	-1.2
Cu	Exchangeable	4.0*	3.3*	-1.4	5.0*
	Reducible	-0.9	2.1	-2.7	8.4
	Oxidisable	0.8	-3.8	10*	-6.3
	Residual	-3.8	-1.5	-5.9	-7.1
Pb	Exchangeable	3.0*	5.7*	0.0	5.0*
	Reducible	-6.2*	2.1	-1.4	0.8
	Oxidisable	1.5*	-17*	-1.8	-5.6*
	Residual	1.6*	8.9*	3.1	-0.3
Zn	Exchangeable	-1.2	4.3*	2.2*	5.3
	Reducible	0.7	-10*	-1.2	-5.1
	Oxidisable	6.7*	-1.1	0.1	-1.2
	Residual	-6.3	6.8	-1.1	1.0

* Significant changes (t-test, p<0.05)

291

292 An overview of these transformation is shown in Figure 7, where the average calculated over the
 293 12 soils for each fraction of each city are compared before and after the experiment, i.e. in the
 294 whole soil and on the samples at the end of the experiment after they had been dried and,
 295 consequently, re-oxidized. Differences between the fractions were tested using means before and
 296 after the submersion (Paired t-test, p=0.05). Qi et al. (2014) postulated that drying of paddy soils
 297 alters the distribution of metal fractions. Urban soils, however, more frequently undergo alternating
 298 reducing-oxidizing conditions while paddy soils are submerged for long periods. It seems therefore
 299 adequate for our soils to carry out the chemical fractionation after drying.

300 The exchangeable fraction of Cu increased significantly in all cities after submersion (Table 4); the
 301 residual fraction decreased in all city soils in favour of more labile forms, although the differences
 302 were not significant. In the case of Pb it was observed that in GLA samples the exchangeable
 303 fraction significantly increased as did the oxidisable and residual forms while the reducible fraction

304 significantly decreased after submersion. In TOR and LJU there was a significant increase in the
305 exchangeable fraction and a decrease in the oxidisable form while the SEV soils did not show any
306 significant differences between fractions before and after submersion. These results are in line with
307 the results of Furman and co-workers (2007), who observed an increase in Pb bioaccessibility on
308 drying of wet soils. Silvetti et al. (2014) report an increase of Pb bioaccessibility after an anaerobic
309 treatment of soils treated with industrial by-products. The trend was also observed for Zn that, in
310 general, shifted from less mobile to more labile forms at the expenses of either the residue or
311 oxidizable and reducible forms. The differences were statistically significant in GLA, LJU and
312 SEV but not in TOR as for other metals, probably because Torino soils presented the highest
313 variability of metal concentrations.

314 In addition, after wet-dry cycles Fe and Mn oxides tend to decrease their crystallinity and
315 precipitate as amorphous phases upon oxidation (Grybos et al. 2007). This is reflected in the
316 changes of Fe fractions from the residual to the reducible and exchangeable forms. This was
317 observed in all cities and was statistically significant everywhere except in TOR where the changes
318 were smaller. Amorphous Fe would be more susceptible to reductive dissolution than a well
319 crystallized mineral and as a consequence the soils would be more prone to release metals on
320 subsequent anoxia. The results of a study conducted on mine-spoil soils of Romania (Balint et al.
321 2014) confirm the trend towards an increased mobility of metals after oxic-anoxic cycles.

322 The changes in Mn extractability were much more intense in all soils, with an increase in
323 exchangeable Mn from 18% in TOR up to the 52% in LJU soils, and a consequent decrease of the
324 reducible fraction of the same order. This could have lead to the release of associated PTEs,
325 explaining a fraction of the metals passed in solution after day 5 of the experiment, such as Pb,
326 previously found from other researchers as strongly sorbed on Mn oxides (Contin et al. 2007).

327

328 *3.3 Statistical treatment*

329 With the aim to better elucidate the main factors influencing metal releases we used Principal
330 Component Analysis in addition to the already explained statistical analysis. The better explanatory
331 results were obtained considering the concentrations of metals extracted in the first three BCR steps
332 and the amount of metals released at specific times, namely at the beginning of the experiment,
333 after 5 days and after 21 days of submersion. The PCA results indicate that the first four principal
334 components explain about 69% of the data variance and Table 5 presents the factor loadings
335 obtained using all samples.

336 The first factor (PC 1), representing the 28% of the total variance, present the highest loading for
337 all Fe variables and for Zn released promptly after submersion and after 5 days. This association is
338 probably driven by the Zn release from Glasgow soils, fostering the attribution to Fe dissolution
339 and pH increase. The PC 2 represented the dissolved fractions of Pb and Cu at the beginning of the

340 experiment, associated with the exchangeable fraction of the metals, and toward the end of it, when
 341 oxides already released the associated metal content.

342 The third factor is characterized by high loadings of the reducible fraction of Cu, Pb and Zn,
 343 representing the similar behaviour of anthropic elements in urban soils, as represented also from
 344 PC 4, where the oxidizable fraction of the metals is associated to the Mn release in solution at day
 345 5, with Pb.

346 Grouped, the information gathered from PCA reinforce the hypothesis of a common behaviour of
 347 the heavy metal fraction emitted from anthropic activities, that in urban soil is considered to be the
 348 majority.

349

350 **Table 5** Variable loadings in the four principal components (PC) extracted using Varimax rotation.

351

Bold values correspond to the highest loading of each variable.

Element	PC 1	PC 2	PC 3	PC 4
Fe 21d	0.904	0.017	-0.151	-0.179
Mn 21d	0.258	-0.175	0.324	-0.481
Cu 21d	-0.119	0.896	0.225	0.091
Pb 21d	-0.078	0.915	0.079	0.064
Zn 21d	0.420	0.471	0.470	0.279
Fe 5d	0.807	0.035	-0.270	-0.148
Mn 5d	0.343	-0.236	0.126	-0.430
Cu 5d	-0.293	-0.317	-0.126	-0.013
Pb 5d	0.098	0.210	-0.180	0.627
Zn 5d	0.915	0.069	0.173	0.103
Cu 0d	-0.152	0.883	-0.087	0.131
Pb 0d	0.108	0.761	0.261	0.079
Zn 0d	0.892	0.213	0.242	0.051
Fe Exch	0.886	0.003	-0.112	-0.145
Fe Red	0.684	0.089	0.472	-0.412
Fe Ox	0.707	-0.120	0.236	0.028
Mn Exch	-0.365	-0.131	0.194	-0.517
Mn Red	-0.421	-0.383	0.337	-0.308
Mn Ox	-0.233	-0.225	0.051	0.654
Pb Exch	0.252	0.774	0.121	-0.024
Pb Red	0.240	0.510	0.727	-0.060
Pb Ox	-0.162	0.043	-0.059	0.715
Cu Exch	0.144	0.653	0.535	-0.124
Cu Red	0.038	0.420	0.719	-0.229
Cu Ox	-0.072	0.101	0.578	0.645
Zn Exch	0.167	0.173	0.871	-0.115
Zn Red	-0.206	0.065	0.836	0.051
Zn Ox	0.127	-0.094	0.206	0.872

352

353

354 **4. Conclusions**

355 The growing frequency of extreme rain events, especially in urban areas, increases the probability
356 that soils are temporarily submerged and undergo anoxia. The selected cities offer a wide variety of
357 climatic and urban settings and so do their soils, thus offering the opportunity of depicting a
358 general picture of the potential threat that PTE contamination poses at the onset of anaerobiosis.
359 The response of urban soils to submersion is more uniform than their diversity would suggest. This
360 would confirm the hypothesis that urbanization causes homogenization of soil biota in general and
361 soil quality in particular. Regardless of the starting pH, organic matter, Fe and Mn oxides content
362 in all urban soils the redox potential decreases within days from submersion. Soluble species of Fe
363 and Mn are released, and with them Cu, Pb and Zn are brought into solution. Although the absolute
364 concentrations in solution are generally a small fraction of the total contents, and that in most cases
365 the metals appear to be re-adsorbed by the solid matrix, the chemical fractionation before and after
366 the experiment shows that the PTE shift towards more labile form. Also, the Fe oxides, which are
367 the main ligand of the metals, shift towards more amorphous and easily reducible phases. The
368 danger coming from the instantaneous release of the metals is therefore reinforced by the threat
369 that, on subsequent submersions, these contaminants may become more and more prone to leaching
370 to the water table and reach the aquatic compartment.

371

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379

380 **Conflict of Interest**

381 The authors declare that they have no conflict of interest.

382

383

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538

539

540 **Figure captions**

541

542 **Fig. 1** Eh variation during 30 days submersion. The average value (n=12) for each city is reported
543 in black, while grey lines report the maximum and the minimum value showed from soils
544 at each time

545 **Fig. 2** Concentration of Mn in solution (percentage of the exchangeable and reducible fraction).
546 The average value (n=12) for each city is reported in black with standard deviations, while
547 grey lines report the maximum and the minimum value showed from soils at each time

548 **Fig. 3** Concentration of Fe in solution (percentage of the exchangeable and reducible fraction).
549 The average value (n=12) for each city is reported in black with standard deviations, while
550 grey lines report the maximum and the minimum value showed from soils at each time

551 **Fig. 4** Concentration of Cu in solution (percentage of the exchangeable and reducible fraction).
552 The average value (n=12) for each city is reported in black with standard deviations, while
553 grey lines report the maximum and the minimum value showed from soils at each time

554 **Fig. 5** Concentration of Pb in solution (percentage of the exchangeable and reducible fraction).
555 The average value (n=12) for each city is reported in black with standard deviations, while
556 grey lines report the maximum and the minimum value showed from soils at each time

557 **Fig. 6** Concentration of Zn in solution (percentage of the exchangeable and reducible fraction).
558 The average value (n=12) for each city is reported in black with standard deviations, while
559 grey lines report the maximum and the minimum value showed from soils at each time

560 **Fig. 7** Chemical fractions of dry soils before (on the left) and after the submersion experiment

561