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Abstract

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

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

1. Introduction

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

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

The transfer of the contaminants to an adjacent environmental compartment – water, air or biota - is not solely dependent on the chemical reactivity of the element; the soil matrix can abruptly change its properties and reduce its equilibrium concentration for contaminants, thus releasing some bound components. This is the case with rapid changes of the redox potential that occur, for example, when a soil is submerged. Although trace metals are rarely directly involved in the redox reactions, during submersion iron and manganese oxides are solubilized, thus releasing the PTEs that are adsorbed onto their surfaces or occluded within their mineral structure (Davranche and Bollinger 2000; Cornell and Schwertmann 2003; Du Laing et al. 2009; Violante et al. 2010; Vodyanitskii and Plekhanova 2014). This would increase the potential toxicological effects that come from PTE contamination of the soil (Alderman et al. 2012). Schulz-Zunkel et al. (2013) described PTE contamination of the sediments of the river Elbe in Germany and indicated that changes in redox potential were one of the main factors that may switch sediment from sink to source of pollutants. Analogously, Popescu et al. (2013) reported an increase of the release of metals from mine-spoil contaminated soils in response to submersion and ensuing anaerobiosis. Shaheen et al. (2014) established that the periodic inundation of contaminated floodplain soils affected the temporal dynamics of Cd, Co, Cu, Ni, and Zn due to changes in Eh-pH, dissolved organic carbon, and in the chemistry of Fe, Mn and S. An increase of metal mobility in flooded urban soils was observed by Florido et al. (2011) and was attributed to the dissolution of Fe and Mn oxides. Notable examples of the consequence that soil submersion can have on PTE release comes from the work of Su et al. (2008) and of Fox et al. (2009) who studied the mobilization of contaminants after the flooding caused by hurricane Katrina in New Orleans (USA). Apart from that exceptional and extensive episode, local conditions that are conducive to the onset of anaerobiosis are frequent in urban soils, due mainly to the alteration of soil hydrology because of soil sealing and compaction (Du et al. 2015). In recent years, however, an increase in the number and intensity of extreme rain events has been observed (IPCC 2013; Gallant et al. 2014). Buzatu (2016) reported that Europe has seen a 60% increase in extreme weather events over the past three decades. Global climate change not only causes warming, but also alters the precipitation patterns, so that ecosystems will have to deal with an increased frequency of extreme precipitation events (IPCC 2013; NASEM 2016).

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

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

2. Materials and methods

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

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

Surface soil horizons were sampled using stainless steel shovels from 0 to 10 cm. Samples were air-dried, gently crushed and sieved to <2 mm with plastic sieves to reduce metal contamination (ISO 11464). A portion of the sample was further ground to <0.15 mm for *aqua regia* (HCl/HNO_3, 3:1 solution) digestion (ISO 11466). The *aqua regia* extracts were analysed for Cu, Fe, Mn, Pb, and Zn by ICP-OES. Triplicates were made for all samples and results accepted when the coefficient of variation was under 5%. A blank and soil CRM BCR 141 R reference material (Joint Research Centre - Institute for Reference Materials and Measurements, Geel, Belgium) were included in each batch of analyses for quality control. Results were considered satisfactory when within a range of ± 10% from the certified value. Particle size distribution was determined by sedimentation and sieving; the pH was measured in a $CaCl_2$ solution at a 1:5 soil:solution ratio and organic carbon and sulphur by elemental analyzer. The content of sulfur was always lower than the detection limit.

Anaerobic microcosms were set up by placing 45 g of soil in 250 ml dark glass bottles and 150 ml of a 0.01 M $CaCl_2$ solution (Supplementary Material, Fig. 1S). The flasks were flushed with CO_2-free N_2 and tightly sealed. Ten ml of the suspension were sampled at 6 hours, and 1, 5, 9, 14, 21, and 30 days, filtered with 0.45 µm nylon filters and the metals in solution (Cu, Fe, Mn, Pb and Zn) were measured having had care to maintain anoxia. The pH and Eh of the solutions were measured under N_2 in a parallel set of samples. Measurements of pH were done by a polymer combination electrode, and the Eh was estimated by a redox platinum electrode (Crison Micro CM, 2201, Crison Instruments S.A. Spain). At the end of the experiment, the soil samples were air-dried at 40°C and gently crushed in an agate mortar. Sequential extraction was carried out before and after the experiments according to the revised BCR protocol (Rauret et al. 1999). The procedure is summarised below:

- Step 1 (water/acid soluble and exchangeable fraction): 40 ml of 0.11 mol l^{-1} acetic acid was added to 1 g soil and shaken for 16 h at room temperature. The extract was separated from the solid by centrifugation, decanted and stored at 4 °C. The residue was washed with distilled water and the washings discarded.

- Step 2 (reducible fraction): 40 ml of 0.5 mol l^{-1} hydroxylammonium chloride (adjusted to pH 1.5) was added to the residue from step 1, and the extraction performed as described for step 1.
- Step 3 (oxidisable fraction): the residue from step 2 was digested with hydrogen peroxide then 50 ml of 1.0 mol l^{-1} ammonium acetate (adjusted to pH 2) was added and the extraction performed as described for step 1.
- Step 4 (residual fraction): the residue from step 3 was extracted with *aqua regia* using the same procedure as described above for the whole soil.

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

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

3. Results and Discussion

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

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

In this work we investigated the effect of changing redox conditions on the release of Cu, Pb and Zn, typical contaminants of urban soils (Madrid et al. 2006), thus we calculated correlations between the soil properties and metal concentrations using data for all the soils (Supplementary Material, Table 2S). Although the soil properties are widely changing, Pb, Zn and Cu are significantly, though moderately (r_{Cu-Pb}=0.70; r_{Cu-Zn}=0.65; r_{Cu-Pb}=0 .50), correlated, corroborating the observation that, at least in respect of PTE contamination, these urban soils tend to converge.

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
S.D.	*0.6*	*7.3*	*4.9*	*2.9*	*2.3*	*0.5*	*164*	*46*	*141*	*149*
CV%	*11*	*11*	*19*	*38*	*33*	*16*	*35*	*52*	*47*	*57*
					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
S.D.	*0.2*	*5.6*	*4.8*	*2.8*	*1.2*	*0.5*	*319*	*24*	*87*	*79*
CV%	*2*	*12*	*12*	*21*	*21*	*22*	*37*	*38*	*46*	*35*
					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
S.D.	*0.1*	*14.3*	*9.8*	*6.7*	*1.0*	*0.3*	*324*	*71*	*311*	*79*
CV%	1	39	24	30	40	15	60	62	85	44
					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
S.D.	*0.8*	*12.2*	*9.2*	*3.3*	*1.3*	*0.5*	*233*	*82*	*431*	*123*
CV%	12	18	44	31	40	16	32	60	101	47

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

The maximum acceptable PTE concentrations in soils are regulated in all countries of this study, although with different thresholds or guideline values in the different states. As found in previous studies (Madrid et al. 2006), Torino, Glasgow and, to a lesser extent, Sevilla, were the most contaminated cities but the definition of contamination may not be applicable, as the trigger values differ widely between countries.

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

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

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

Country/ Region	Cu	Pb	Zn
Italy[a]	120	100	150
Andalucia[b]	150-300 300-500	250-350 400-500	300-600 500-1000
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

3.1 Incubation experiments

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

The pH values (Supplementary Material, Fig. 2S) varied accordingly, increasing in most soils. The Sevilla soils showed more erratic values, presumably as a result of the dissolution of the CO_2 derived from the carbonates.

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

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

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

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

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

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

In the case of copper (Figure 4), a peak in the concentration in solution was observed in all soils although some differences emerged between cities. While the Cu peak appeared as early as day 5 of submersion in Ljubljana and Sevilla, most of the soils in Glasgow and Torino showed the maximum release around day 10. After the first peak, another increase was observed in Ljubljana and Sevilla soils after the 21st day of the experiment. The decrease in concentration of an element in solution following a maximum is usually attributed to changes in the matrix that are brought about by anoxia:

Fe and Mn oxides are only partially dissolved and new surfaces are exposed that can re-adsorb the metals or they can adsorb to, or coprecipitate with, Fe(II)-compounds while organic matter can similarly contribute to the lowering of the concentration in solution (Cornu et al. 2009; Borch et al. 2010; Vink et al. 2010; Frohne et al. 2014). The rise in pH would increase the negative charge on variable-charge minerals, such as Fe-oxides, and augment the probability of surface sorption. The chemistry of Cu in soil, especially in urban settings, is particularly complex (Biasioli et al. 2010; Borch et al. 2010) as the sources can be very variable: metallurgical and energy-related industry as well as automotive traffic can release Cu in different forms. This can partly justify the very high levels of readily soluble Cu in some soils from Glasgow, Sevilla and Torino, the latter showing a concentration as high as 15.3 mg/kg of Cu (7% of the total Cu) released after the first 6 hours of the experiment. The affinity of this element for organic matter can further obscure the overall picture, as part of the metal can pass into solution as a complex or subsequently to the oxidation of organic complexes rather than the reduction of Fe and Mn oxides.

While there are sources of point contamination of Pb, this element is a typical diffuse contaminant of urban soils due to its former use as antiknock in gasoline. Similarly to Cu, Pb was promptly released to the solution in many soils of Glasgow, Sevilla and Torino (Figure 5) indicating that there are soluble forms of these elements in the soils of all three cities. In Glasgow, most soils showed an increase in concentration towards the end of the experiment, indicating that a substantial Fe dissolution (Figure 3) is necessary for Pb to be released. The soils of Torino presented the highest release considering absolute values, but the general trend was similar to that of the other cities. For the soils of Ljubljana, a peak in Pb concentration was observed after 5 days of submersion, in correspondence with Mn peaks and another close to the 21 days Fe peak, reinforcing the hypothesis that Pb could be closely associated with redox-sensitive oxides.

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

3.2 Chemical fractionation

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

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

		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, $p<0.05$)

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

The exchangeable fraction of Cu increased significantly in all cities after submersion (Table 4); the residual fraction decreased in all city soils in favour of more labile forms, although the differences were not significant. In the case of Pb it was observed that in GLA samples the exchangeable fraction significantly increased as did the oxidisable and residual forms while the reducible fraction significantly decreased after submersion. In TOR and LJU there was a significant increase in the exchangeable fraction and a decrease in the oxidisable form while the SEV soils did not show any significant differences between fractions before and after submersion. These results are in line with the results of Furman and co-workers (2007), who observed an increase in Pb bioaccessibility on drying of wet soils. Silvetti et al. (2014) report an increase of Pb bioaccessibility after an anaerobic treatment of soils treated with industrial by-products. The trend was also observed for Zn that, in general, shifted from less mobile to more labile forms at the expenses of either the residue or oxidizable and reducible forms. The differences were statistically significant in GLA, LJU and SEV but not in TOR as for other metals, probably because Torino soils presented the highest variability of metal concentrations.

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

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

3.3 Statistical treatment

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

The first factor (PC 1), representing the 28% of the total variance, present the highest loading for all Fe variables and for Zn released promptly after submersion and after 5 days. This association is probably driven by the Zn release from Glasgow soils, fostering the attribution to Fe dissolution and pH increase. The PC 2 represented the dissolved fractions of Pb and Cu at the beginning of the experiment, associated with the exchangeable fraction of the metals, and toward the end of it, when oxides already released the associated metal content.

The third factor is characterized by high loadings of the reducible fraction of Cu, Pb and Zn, representing the similar behaviour of anthropic elements in urban soils, as represented also from PC

4, where the oxidizable fraction of the metals is associated to the Mn release in solution at day 5, with Pb.

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

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

4. Conclusions

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

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Conflict of Interest

The authors declare that they have no conflict of interest.

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

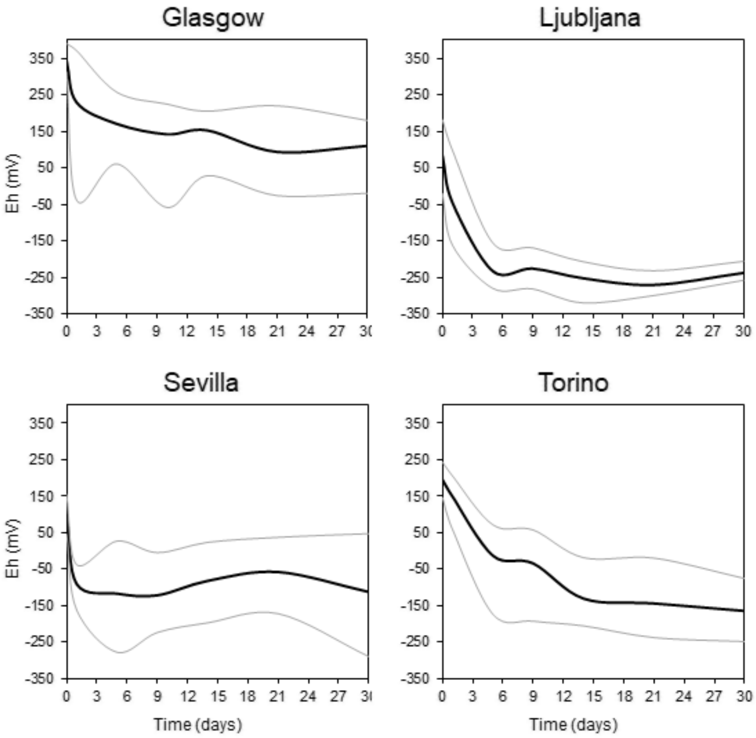

Fig. 2 Concentration of Mn in solution (percentage of the exchangeable and reducible fraction). The average value (n=12) for each city is reported in black with standard deviations, while grey lines report the maximum and the minimum value showed from soils at each time

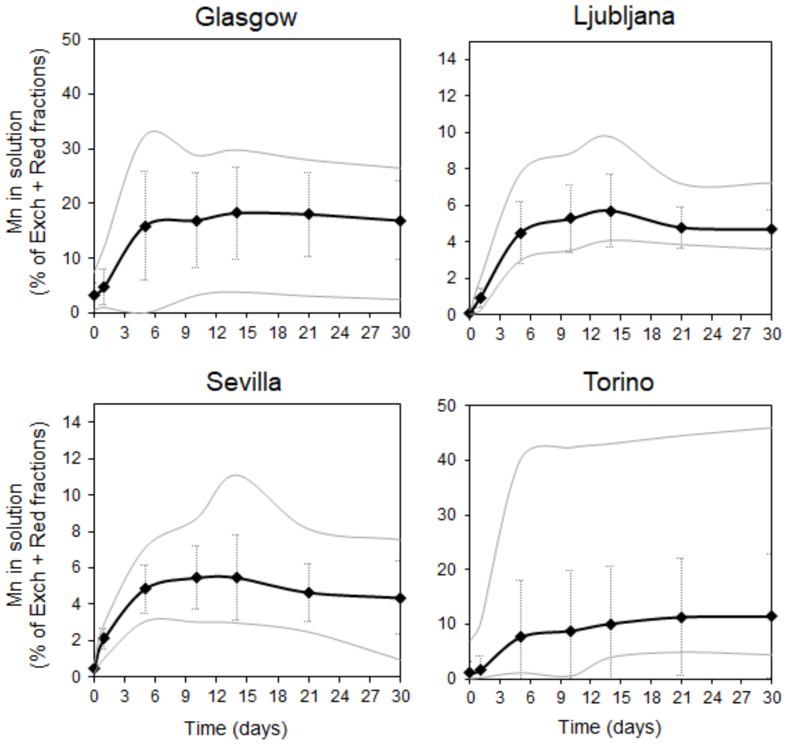

Fig. 3 Concentration of Fe in solution (percentage of the exchangeable and reducible fraction). The average value (n=12) for each city is reported in black with standard deviations, while grey lines report the maximum and the minimum value showed from soils at each time

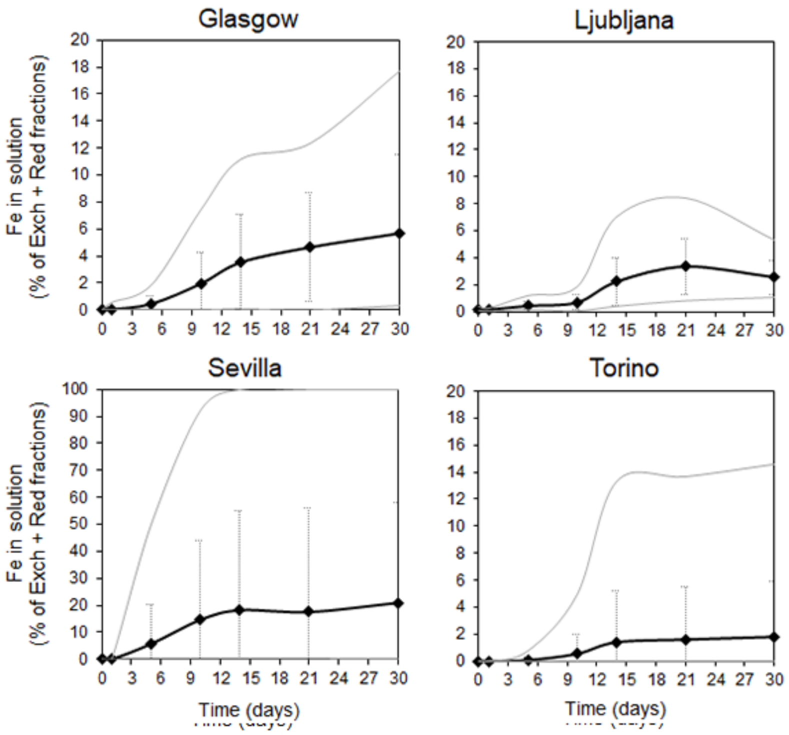

Fig. 4 Concentration of Cu in solution (percentage of the exchangeable and reducible fraction). The average value (n=12) for each city is reported in black with standard deviations, while grey lines report the maximum and the minimum value showed from soils at each time

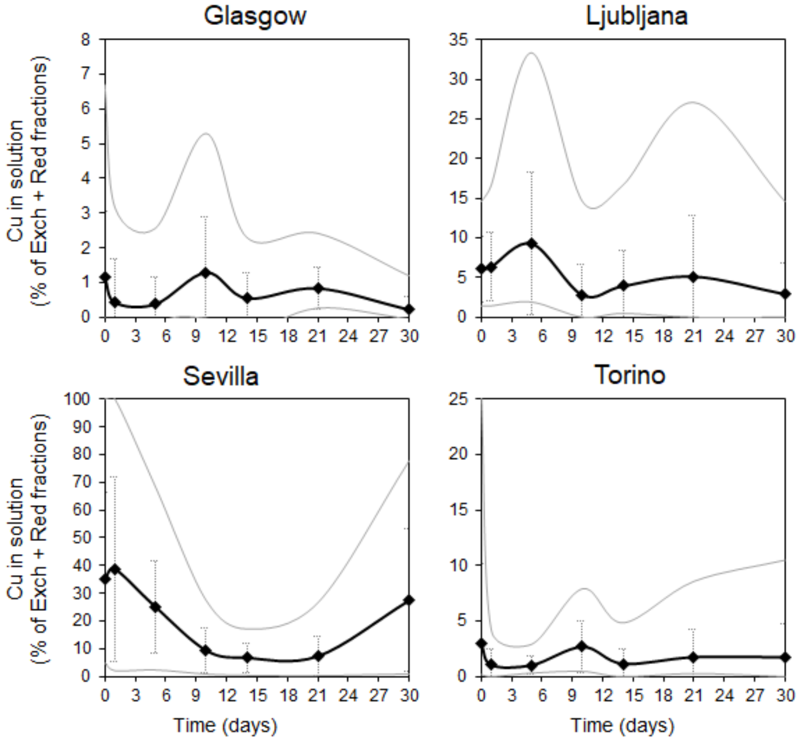

Fig. 5 Concentration of Pb in solution (percentage of the exchangeable and reducible fraction). The average value (n=12) for each city is reported in black with standard deviations, while grey lines report the maximum and the minimum value showed from soils at each time

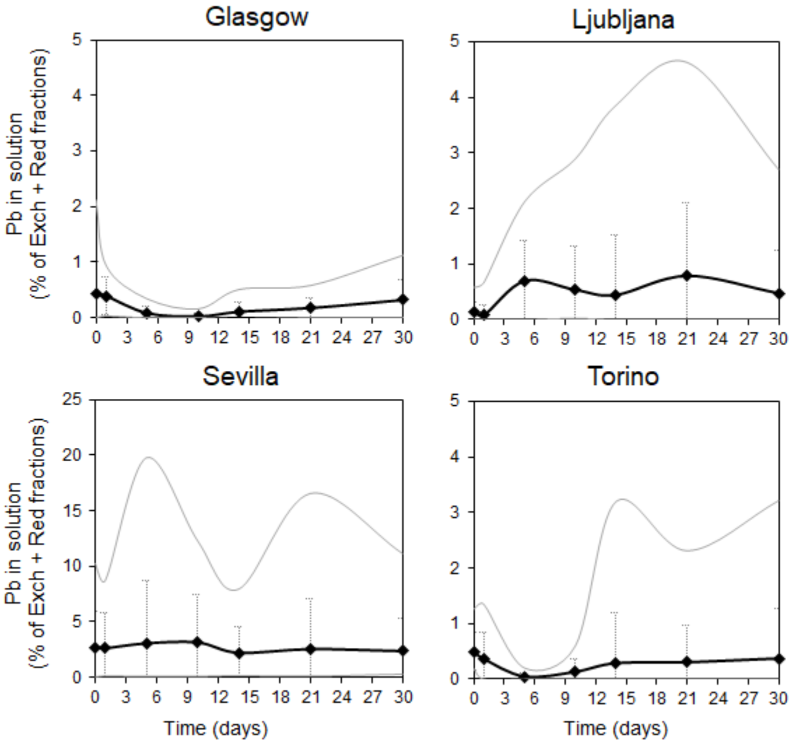

Fig. 6 Concentration of Zn in solution (percentage of the exchangeable and reducible fraction). The average value (n=12) for each city is reported in black with standard deviations, while grey lines report the maximum and the minimum value showed from soils at each time

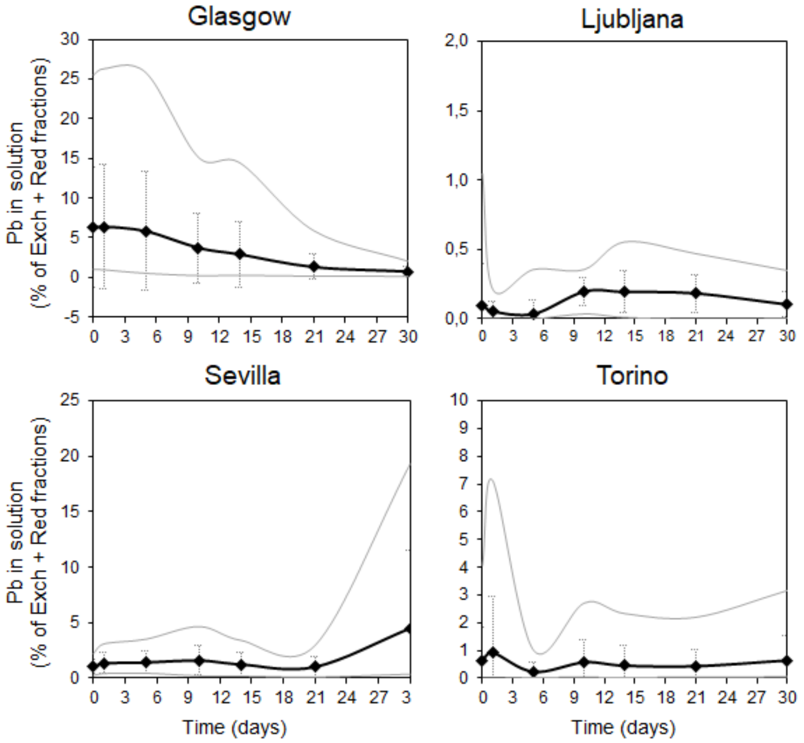

Fig. 7 Chemical fractions of dry soils before (on the left) and after the submersion experiment