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Characterization and origin of organic and inorganic pollution in urban soils in Pisa (Tuscany, Italy). --Manuscript Draft--

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Abstract:	<p>We assessed the quality of 31 urban soils in Pisa by analyzing total petroleum hydrocarbons (TPH), Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn and the platinum group (PGEs). The risk assessment was evaluated by the geological accumulation index (Igeo) and the enrichment factor (EF). Results were compared with those obtained from a non-urban site and with the quantitative limits fixed by Italian legislation. In nearly all the monitored sites, the legal limit for TPH of 60 ppm in residential areas was exceeded, indicating widespread and intense pollution throughout the entire city area. The Igeo indicated no Cd, Cu, Mn, Ni and Zn pollution and minimal Pb and Cr pollution, due to anthropogenic enrichment. Legal Hg and Zn limits were exceeded in about 20% of sites, Cd, Cr and Cu in only one site, the Ni legal limit was never exceeded. Some urban soils showed a higher Hg level than the more restrictive legal limit concerning areas for industrial use. Mn and Zn showed the highest mobility, suggesting a more potential risk of soil contamination than the other metals. The TPH and both Cr and Hg amounts were not correlated with any of the other monitored metals. The total contents of Cd, Pb, Zn and Cu in soils were positively correlated with each other, indicating a common origin from vehicular traffic. The PGE values (Pt and Pd) were below the detection limits in 75% - 90% of the monitored areas, suggesting that their accumulation is at an early stage.</p>
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1 **Abstract**

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3 Mn, Ni, Pb, Zn and the platinum group (PGEs). The risk assessment was evaluated by the geological accumulation
4 index (Igeo) and the enrichment factor (EF). Results were compared with those obtained from a non-urban site and with
5 the quantitative limits fixed by Italian legislation. In nearly all the monitored sites, the legal limit for TPH of 60 ppm in
6 residential areas was exceeded, indicating widespread and intense pollution throughout the entire city area. The Igeo
7 indicated no Cd, Cu, Mn, Ni and Zn pollution and minimal Pb and Cr pollution, due to anthropogenic enrichment. Legal
8 Hg and Zn limits were exceeded in about 20% of sites, Cd, Cr and Cu in only one site, the Ni legal limit was never
9 exceeded. Some urban soils showed a higher Hg level than the more restrictive legal limit concerning areas for
10 industrial use. Mn and Zn showed the highest mobility, suggesting a more potential risk of soil contamination than the
11 other metals. The TPH and both Cr and Hg amounts were not correlated with any of the other monitored metals. The
12 total contents of Cd, Pb, Zn and Cu in soils were positively correlated with each other, indicating a common origin from
13 vehicular traffic. The PGE values (Pt and Pd) were below the detection limits in 75% - 90% of the monitored areas,
14 suggesting that their accumulation is at an early stage.

15 **Keywords**

16 Urban soils; total petroleum hydrocarbons; heavy metals; platinoids; enrichment factor

18 **Introduction**

19 More than half of the world's population lives in cities (United Nations 2012). The degree of urbanization exceeds 80%
20 both in Europe (Antrop 2004) and the United States (Pickett et al. 2011) and is expected to increase rapidly worldwide
21 over the next 20 years. Urban areas are responsible for alterations in biogeochemical cycles (Pouyat et al. 2007), air
22 pollution (Seto and Satterthwaite 2010), water contamination (Choqfi et al. 2004), soil accumulation of trace elements
23 (Wei and Yang 2010), global and local climate change (Heisler and Brazel 2010), soil consumption, desertification, and
24 sealing (Scalenghe and Ajmone-Marsan 2009).

25 In the “Thematic Strategy on the Urban Environment” (Commission of the European Communities 2006), the EU
26 highlighted the importance of urban environment quality indicators and their monitoring. Among the indicators
27 determining the quality of urban green areas, one of the main features is soil quality. According to the European
28 Environment Agency (EEA), 250,000 soils have been identified as contaminated across the EU, mainly by metals and
29 mineral oils. In urban soils, pollutants accumulate from either localized or diffuse sources. Typical contaminants
30 include toxic substances, such as trace elements and persistent organic pollutants, which represent a potential danger to
31 human health and ecological systems.

32 The main source of hydrocarbons in soil is anthropogenic, originating from the incomplete combustion of fossil fuels
33 from residential heating, industrial processes, and vehicular traffic (Andreou et al. 2008). Other sources of hydrocarbons
34 in soils are the disposal of waste materials, road run-offs and car tyre shredding, as well as accidental fuel spills and
35 leakages (Jones and de Voogt 1999). Consequently, the hydrocarbon contamination of topsoil has been detected in
36 urban areas worldwide (Ma et al. 2009), where hydrocarbons usually lead to widespread contamination, characterized
37 by large areal extents, relatively low concentrations and the lack of identifiable sources (Johnsen et al. 2006). In
38 addition contamination due to accidental oil spills during transport or near gas stations is frequent (Vega et al. 2009).

39 The level of soil hydrocarbons is not affected by accumulation ("memory" effect), because they are subject to microbial
40 degradation (Baboshin and Golovleva 2012), which in turn is influenced by environmental and soil conditions (Riffaldi
41 et al. 2006; Zhang et al. 2006). However, linkages between metals and hydrocarbons are possible, due to the fact that
42 some additives, especially lead, promote the formation of hydrocarbons (Yuan et al. 1999).

43 The effects of heavy metal pollution on the urban ecological environment and human health are of increasing concern
44 (Burt et al. 2014; Chen et al. 2015; Doležalová Weissmannová et al. 2015; Luo et al. 2015; Qing et al. 2015; Wei et al.
45 2015). Calculating the total quantity of heavy metals in soils can provide information on possible enrichment, but
46 generally heavy metals are poor indicators for estimating environmental and biological effects. In fact, the mobility,
47 bioavailability, and persistence of soil heavy metals are influenced not only by their concentrations, but also by soil
48 properties and their interaction with the chemical organic and inorganic substances of the soil matrix (Acosta et al.
49 2015). It is thus important to recognise the speciation of metals in different fractions.

50 In order to assess the amounts of mobile or potentially mobile species in soil, selective extraction methods have been
51 used to release the individual forms of elements. Among the sequential extraction procedures proposed, the modified
52 version (Rauret et al. 1999) of the three-step scheme proposed by the former European Community Bureau of
53 Reference (BCR), has been widely used in urban soil studies (Wu et al. 2008; Mossop et al. 2009). This procedure
54 differentiates between four heavy metal species with a different degree of bioavailability. The four species are: a) the
55 labile form, including both the exchangeable form (subjected to soil particle sorption-desorption processes) and the
56 carbonate-bound form; b) the reducible form (bound to Fe and Mn oxides); c) the oxidizable form (bound to sulphides
57 and organic matter); d) the residual form (containing primary and secondary minerals, which may hold trace metals
58 within their crystal structure).

59 With the introduction of automobile catalytic converters, Pt and Pd (PGEs) have been extensively released into the
60 environment and have thus been increasingly studied by environmental scientists (Dubielła-Jackowska et al. 2009;
61 Wiseman and Zereini 2009; Almeida et al. 2016). In addition to vehicular traffic, PGE emissions can also derive from
62 effluents from hospitals, dental laboratories and jewellery manufacturing (Jollie 2006). In the past, PGEs were believed

63 to be relatively inert but they have now been shown to undergo environmental transformations into more reactive
64 species through complexation with organic matter or solubilization in low pH rainwater (Dubiella-Jackowska et al.
65 2009).

66 The “2006 Report on the State of Municipality of Pisa” (Comune di Pisa 2007) reported that in the municipal area
67 (approximately 187 km²), the artificial surface (impermeable urban area) was approximately 27 km², with a high soil
68 consumption, with around 1.25 km² of green areas. Built-up areas have been steadily increasing, with the largest
69 increases since the 1950s (+ 260% increase from 1954 to 2003).

70 The aim of this study was to monitor the pollution level of 31 urban green areas in Pisa by measuring the content of
71 total petroleum hydrocarbons (TPHs), and the amount and mobility of the most harmful elements, including the PGEs.
72 The evaluation of the contaminated sites involved two terms of comparison: a) a rural site at the S. Rossore – Migliarino
73 - Massaciuccoli Natural Regional Park (latitude 43°42'48.84N; longitude 10°21'44.47E), used as a control; b) the
74 quantitative limit of Italian legislation (Repubblica Italiana 2006) for each substance, used as a reference.

75

76 **Materials and Methods**

77 **Sampling procedure**

78 Soil samples were collected from 31 sites around the urban areas of the city of Pisa. As the control, a sample soil was
79 collected from a rural area of a similar lithogenic origin, located in “S. Rossore – Migliarino – Massaciuccoli Natural
80 Regional Park” (latitude 43°42'48.84N; longitude 10°21'44.47E), near Pisa (Figure 1). At each site, three samples, each
81 formed by 5 sub-samples, were randomly collected from the topsoil (depth 0-20 cm), after removing the herbaceous
82 cover. The sub-samples were taken within a 2×2 m square, four from the corners and one from the middle of the square.
83 The sampling was performed with a stainless steel hand auger and all the soils that came into contact with the metallic
84 digging tools were carefully eliminated, before packing the soil into plastic bags, to avoid cross-contamination. For each
85 main sample, a total of 5 kg of soil was taken. In the laboratory, the samples were air-dried at room temperature (20 ± 1
86 °C), and, after removing any plant material such as roots and leaves, they were stored at 4°C until analysis.

87 **Soil characteristics**

88 General soil physical and chemical features (Table 1), including bulk density, texture, maximum water holding
89 capacity, pH, inorganic C (CaCO₃), were determined according to the official Italian methods (Repubblica Italiana
90 1999). Total carbon was measured by dry combustion with an automatic C analyzer FKV induction furnace 900 CS,
91 Eltra (F.K.V.) The organic carbon content of the soil samples was obtained by the difference between the total and
92 inorganic carbon.

93 **Total petroleum hydrocarbons (TPHs)**

94 The TPH soil content was determined by the Platen's method (1995). Briefly, 1.5 g of air dry soil was dehydrated with
 95 Na₂SO₄ and then thoroughly mixed with 1,1,2-trichlorotrifluoroethane (C1CF₂CCl₂F) in a dark glass vial for 120 min
 96 (extraction ratio 1:10) by mechanical agitation. The extracts were filtered on Florisil (MgO₃Si) columns (Bond Elut
 97 Varian; Agilent Technologies Inc. - Santa Clara, CA, USA). The CH₃ and CH₂ groups of TPH extracts were
 98 quantitatively determined using an infrared spectrometer (Perkin Elmer 1600 IR Spectrometer; Perkin Elmer Inc.,
 99 Waltham, MA, USA) in a range of wavelengths of between 3200 and 2800 cm⁻¹. The values were elaborated using
 100 Spectrum 2.0 (Perkin Elmer Inc., Waltham, MA, USA).

101 **Total content of heavy metals and platinum group elements (PGEs)**

102 Soil heavy metals and PGE (Pd and Pt) contents were determined following ISO 11466 (International Organization for
 103 Standardization 1995). This entails the mineralization of 1 g of soil sieved to 200 microns (≅ 80 mesh) with aqua regia,
 104 a mixture of nitric and hydrochloric acid (1:3 ratio). Individual elements were determined by inductively coupled
 105 plasma mass spectrometry (ICP-MS). Detection limits for heavy metals are reported in Table 2, while the limits for
 106 PGEs were: Pd: 5.0 µg/kg; Pt: 2.0 µg/kg.

107 **Heavy metal forms**

108 The speciation of selected metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) was carried out in the most polluted areas by the
 109 BCR method (European official method) as modified by Rauret et al. (1999). The extraction was performed in four
 110 steps, as follows:

Extraction procedure				Extracted element species	
step	Substance	Temperature	Time	Chemical forms	Name
1	Acetic acid 0.11M	22±2 °C	16h	Soluble, exchangeable and bound carbonate	Labile
2	Hydroxylamine hydrochloride 0.1 M	22±2 °C	16h	Fe and Mn oxide and bound hydroxide	Reducible
3	Hydrogen peroxide 27%	85±2°C	1h+1h	Organic matter and bound sulphides	Oxidizable
	Ammonium acetate 1M	22±2 °C	16h		
4	Aqua regia	22±2 °C	16h	Residual	Residual
		130±2°C	2h		

111 Heavy metals were determined in supernatants and digests by a flame atomic absorption spectrophotometer (Perkin
112 Elmer Lambda 25 UV/VIS Spectrometer; Perkin Elmer Inc., Waltham, MA, USA).

113 **Risk assessment**

114 In order to quantify the degree of pollution or enrichment of potentially toxic elements in soils, and their potential
115 environmental hazard, a geological accumulation index (Igeo) and enrichment factor (EF) were calculated. Igeo was
116 calculated according to the equation: $I_{geo} = \log_2 [C_x/1.5B_x]$, where C_x represents the concentration measured of the
117 element x , and B_x is the geochemical background value of the element. The factor 1.5 was introduced to minimize the
118 possible variations in the background values. Igeo values were interpreted as: <0 = practically unpolluted; $0-1$ =
119 unpolluted to moderately polluted; $1-2$ = moderately polluted; $2-3$ = moderately to strongly polluted; $3-4$ = strongly
120 polluted; $4-5$ = strongly to very strongly polluted and >5 = very strongly polluted. The EF calculation was based on the
121 normalization of a measured element against a reference element. In this study, Fe was used as a reference element
122 (data not shown) (Li and Feng 2012). Values of EF close to 1 indicate natural origin, whereas amounts >10 are
123 considered to originate mainly from anthropogenic sources. The EF values were interpreted as: <2 = deficiency to
124 minimal enrichment; $2-5$ = moderate enrichment; $5-20$ = significant enrichment; $20-40$ = very high enrichment, and $>$
125 40 = extremely high enrichment.

126 **Statistical analyses**

127 Tests were carried out in triplicate. Results were expressed on a dry soil basis, and were presented as means \pm standard
128 deviation (SD). For each parameter, a one-way ANOVA (site as variability factor) was performed using CoStat version
129 6.311 (CoHort Software; Monterey, CA, USA). Means were compared by Tukey's HSD test. Differences at $P < 0.05$
130 were considered statistically significant.

131 A correlation coefficient analysis (CCA) was carried out by Pearson's product-moment correlation coefficient. The
132 CCA was performed using NCSS (2004 version, Number Cruncher Statistical Systems; Kaysville, UT, USA).

133

134 **Results and Discussion**

135 **Petroleum hydrocarbons**

136 Table 2 shows the total petroleum hydrocarbon (TPH) content of urban soils in Pisa. The TPH content was in a wide
137 range of between 38.3 and 419.1 mg kg⁻¹ dry soil, which is comparable with values reported by several authors in soils
138 from many cities worldwide (Müller et al. 2001; Adeniyi and Afolabi 2002; Azimi et al. 2005; Henriquez et al. 2006;
139 Aichner et al. 2007; Pies et al. 2007; Morillo et al. 2007; Manzo et al. 2008; Teaf et al. 2008; Ma et al. 2009). The
140 highest level of TPH was in a green space located close to a gas station and a flowerbed traffic divider, in which there
141 were clear signs of the disposal of bituminous material from a recent tarmacking of the adjacent road. The areas where

142 the value of 100 mg kg⁻¹ soil was exceeded were characterized by particularly intense vehicular traffic. However, the
143 control site showed 54.5 mg kg⁻¹ soil, which was not statistically different from values observed in most ($\cong 75\%$) of the
144 monitored areas.

145 Since the extraction method used in our experiment did not differentiate between different hydrocarbon categories, the
146 limit of 60 mg kg⁻¹ used as a reference was calculated by adding “light” hydrocarbon values, i.e. constituted by a
147 number of carbon atoms less than 12 (10 mg kg⁻³ soil), and “heavy” hydrocarbons ($C > 12$) (50 mg kg⁻¹ soil), as
148 established by Italian legislation for the maximum level of hydrocarbon content in public green, private and residential
149 areas (Repubblica Italiana 2006). Generally, the soils in the city of Pisa showed widespread pollution from petroleum
150 hydrocarbons, with very few areas under the legal threshold. This pattern agrees with findings on hydrocarbon pollution
151 in urban environments. The limit of 60 mg kg⁻¹ soil was exceeded in approximately two-thirds of the sites. The content
152 of the remaining areas was also close to this value.

153 **Heavy metals**

154 **Cadmium**

155 The Cd total content of urban soils in Pisa is shown in Figure 4. Values ranged widely between 0.13 and 1.90 mg kg⁻¹ of
156 soil, with a mean of 0.35 (Table 2). The largest differences may be explained by the findings of Huang et al. (2015),
157 who found that Cd pollution originates from point sources. In the control site, the Cd content was statistically no
158 different from most ($\cong 90\%$) of the monitored areas, and slightly lower than the mean value of soils in Italy (Bini et al.
159 1988). Total amounts of Cd measured were comparable with those found in several cities in Italy, such as Naples,
160 Benevento and Avellino (Cicchella et al. 2008), Ancona (Businelli et al. 2009), Rome (Cenci et al. 2008), as well as
161 Bangkok (Wilcke et al. 1998), Berlin (Birke and Rauch 2000), and Izmit Gulf (Canbay et al. 2010), while other cities
162 worldwide higher contents were found. The limit of 2.0 mg kg⁻¹ soil, established by Italian legislation (Repubblica
163 Italiana 2006), was exceeded in only one site.

164 The geological accumulation index (Igeo), a quantitative measurement of the degree of metal pollution, has been widely
165 used in urban soil studies. On the other hand, the enrichment factor (EF) of an element in a soil sample is used to
166 distinguish between heavy metals from an anthropogenic source and those of a natural origin (Chen et al. 2015). On
167 average, the Pisan urban soils showed a Cd Igeo of -0.40, typical of unpolluted areas, and the EF (1.63) indicated a
168 minimal Cd anthropogenic enrichment (Table 5). The Igeo index indicated a minimum level of Cd pollution for about
169 94% of the monitored sites (Table 5), while one site was classified as minimally polluted and another as moderately to
170 strongly polluted. The EF indicated no Cd anthropogenic enrichment in 80% of the areas, a moderate enrichment in
171 15% of the sites, while one site showed a significant enrichment (Table 5). The anthropogenic enrichment for Cd has
172 already been observed by Doležalová Weissmannová et al. (2015) in urban soils in Ostrava (Czech Republic).

173 Chromium

174 The Cr total content of urban soils in Pisa are reported in Figure 2. Values varied widely between 46.4 and 227.5 mg kg⁻¹
175 ¹ of soil (mean of 71.2) (Table 2) and were comparable with those found in Palermo (Salvagio-Manta et al. 2002),
176 Rome (Cenci et al. 2008), Ancona (Businelli et al. 2009), and Cesena (Gherardi et al. 2009), Bangkok (Wilcke et al.
177 1998), Berlin (Birke and Rauch 2000), Damascus (Moller et al. 2005), Seville and Ljubljana (Davidson et al. 2006),
178 Turku (Salonen and Korkka-Niemi 2007), and the Gulf of Izmit (Canbay et al. 2010).

179 The control site showed a significantly lower Cr value than observed in the urban areas, and considerably lower than
180 95.0 mg kg⁻¹ soil, which is the Italian soil background of the element (Bini et al. 1988). Contamination assessment
181 indexes are reported in Table 5. The Igeo classified 94% of the monitored sites as not significantly polluted, while the
182 remaining 6% were classified as moderately polluted. These latter values exceeded the limit of 150 mg kg⁻¹ soil
183 established by Italian legislation (Repubblica Italiana 2006). The EF generally indicated a minimal anthropogenic
184 enrichment, with about 10% of the areas showing a moderate enrichment, indicating that Cr originated mainly from
185 lithogenic substrate. The enrichment of Cr in some areas could be due to the disposal of the metal through contaminated
186 soils or waste, such as tannery sludge. Figure 3 shows that the labile fraction was absent in all areas. In sites with a
187 similar Cr total content to the control, the greatest amount was in the residual fraction (70-80%), while low quantities
188 (8-10% and 10-15%, respectively) were observed in the fractions bound to Fe/Mn oxides and hydroxides as well as to
189 organic matter and sulphides. These results are in agreement with Wang et al. (2006) and Plyaskina and Ladonin
190 (2009). In the enriched areas, an increase in both the reducible fraction (15%) and the oxidizable form (50%) was
191 found.

192 Copper

193 Copper is common in many urban soils because of its increased use in civil and industrial activities, such as coal and oil
194 combustion, pesticide and dye use, and especially from vehicular traffic (USEPA 2006). Figure 2 reports the total
195 amounts and Cu forms of urban soils in Pisa. The total content ranged widely between 30.9 and 142.3 mg kg⁻¹ of soil,
196 with a mean of 67.4 (Table 2). The control site showed a Cu value of 32.2 mg kg⁻¹ soil, which is statistically equal to
197 that observed in a small fraction (\cong 10%) of the urban soils. The Cu amount exceeded the limit value of 120.0 mg kg⁻¹
198 soil established by Italian legislation for residential areas in only two areas. The same two sites showed Igeo indexes
199 that are typical of moderately polluted areas, and typical EF values of a moderate anthropogenic enrichment (Table 5),
200 in line with the results of Doležalová Weissmannová et al. (2015). On average, urban soils in Pisa showed an Igeo of
201 0.40, which is typical of unpolluted areas, and an EF of 1.55, indicating a minimum anthropogenic enrichment. Similar
202 results were reported by Biasioli et al. (2007) in soils in Turin. There was no Cu labile fraction in any areas (Figure 3).
203 Most of the element was found in the residual fraction (approximately 60%), while in the oxidizable and reducible

204 forms, smaller quantities were found (10-20% and 20-30% respectively). In the most enriched sites, Cu was associated
205 with reducible and oxidizable fractions, which reached about 60% of the total content. These results are not in
206 agreement with Davidson et al. (2006), who reported that Cu was mostly in the fraction bound to the organic matter.

207 Mercury

208 The Hg total content of urban soils in Pisa ranged between 0.036 and 9.609 mg kg⁻¹ of soil (mean value 0.863) (Table
209 2). The Hg content of the control site was 0.081 mg kg⁻¹ soil, which is statistically no different from most (≅80%) of
210 the monitored areas, and similar to the mean values of 0.06 mg kg⁻¹ soil found in world soils (Adriano 2001). In the
211 remaining 20% of areas, much higher values were detected. In these sites the limit of 1.0 mg kg⁻¹ soil, established by
212 Italian legislation (Repubblica Italiana 2006), was exceeded. In two of these sites the limit of 5.0 mg kg⁻¹ soil,
213 established for industrial areas, was also exceeded. The total Hg amounts of urban areas were comparable with those
214 found in urban soils of Naples, Benevento, Caserta, Salerno and Avellino (Cicchella et al. 2008), Rome (Cenci et al.
215 2008), Chicago (Cannon and Horton 2009), Berlin (Birke and Rauch 2000), Bydgoszcz (Dąbkowska-Naskręt and
216 Róžański 2007), Changchun (Fang et al. 2004) and Trondheim (Andersson et al. 2010). Contamination assessment
217 indexes for Hg are reported in Table 5.

218 On average, Pisa urban soils showed an Igeo of 2.88, typical of polluted areas, and attributable to a significant
219 anthropogenic enrichment (mean value of 7.89). The Igeo showed that more than 50% of the areas were minimally
220 contaminated, almost 30% revealed a moderate degree of pollution, and the remaining areas were between strongly and
221 extremely polluted. The EF displayed a poor anthropogenic enrichment in more than 70% of the areas, about 20% of the
222 sites were significantly enriched and two sites revealed an extremely high degree of Hg enrichment. Given that Hg
223 accumulation does not originate from human activities typical of urban areas, such as vehicular traffic and domestic
224 heating, the enrichment is assumed to derive from the disposal of contaminated soils or waste, such as medical or
225 industrial sludge. Anthropogenic enrichment was also reported by Doležalová Weissmannová et al. (2015) in urban
226 soils in Ostrava.

227 Manganese

228 The Mn total contents of the urban soils in Pisa are shown in Figure 2. Values ranged between 509 and 1063 mg kg⁻¹ of
229 soil, with a mean of 705 (Table 2). The Mn content for the city of Pisa were comparable to those of the cities of
230 Ljubljana (Davidson et al. 2006) and Pretoria (Okonkwo et al. 2009). In the control site, Mn was 526 mg kg⁻¹ soil,
231 which is significantly lower than values observed in nearly all the monitored areas, and significantly lower than the
232 mean value of 873 mg kg⁻¹ soil, of Italian soils (Bini et al. 1988). Italian legislation does not set any limit with regard to
233 the content of manganese in soil. Igeo showed no soil pollution and the lack of a significant anthropogenic Mn
234 enrichment (Table 5). The predominant Mn fractions were the reducible form, which on average reached about 50%,

235 and the labile form, which was 28.9% (Figure 3). The residual and oxidizable fractions accounted for 16-19% and 3%
236 of the total content respectively. These results disagree with the findings of Okonkwo et al. (2009) in the urban soils in
237 Pretoria, where the residual fraction was the most represented, accounting for about 60% of the total amount.

238 Nickel

239 The Ni total content ranged narrowly between 43.0 and 77.1 mg kg⁻¹ of soil, with a mean of 55.2 (Table 2). The Ni
240 content of the control site was significantly lower compared to nearly all the monitored areas, and slightly lower than
241 the mean value of 65.0 mg kg⁻¹ of Italian soils (Bini et al. 1988). The total Ni content of the urban areas was very
242 similar to the Ni content measured at Sesto S. Giovanni (Torretta et al. 2005), Ancona (Businelli et al. 2009), Bologna
243 (Gherardi et al. 2009), Glasgow (Hursthouse et al. 2004), Seville and Ljubljana (Davidson et al. 2006), and Trondheim
244 (Andersson et al. 2010). Neither Igeo or EF showed any pollution and anthropogenic enrichment of the urban soils
245 (Table 5). Values were in any case lower than the limit of 120 mg kg⁻¹ soil established by Italian legislation (Repubblica
246 Italiana 2006). The residual fraction was clearly the highest, accounting for about 65% of the total amount (Figure 3).
247 The labile fraction was present in small quantities (3.5%) in almost all areas, while reducible and oxidizable fractions
248 were about 16-17% of the total content. These results are in agreement with those found by Davidson et al. (2006) in
249 urban soils from five European cities, by Thums et al. (2008) in an urban brownfield in Wolverhampton, and by
250 Plyaskina and Ladonin (2009) in urban soils in Moscow.

251 Lead

252 The Pb total content ranged widely between 19.6 and 275.4 mg kg⁻¹ of soil, with a mean of 83.6 (Table 2). In the
253 control site, the Pb content was 24.5 mg kg⁻¹ soil, which is similar to values observed in a small fraction (\cong 16%) of the
254 monitored areas, and comparable with the mean value of 26.0 in Italian soils (Bini et al. 1988). Although considerably
255 lower than those measured in the coastal cities of Tuscany (Bretzel and Calderisi 2006), the total Pb content in the urban
256 soils was comparable to values found in urban soils in Bologna (Bretzel and Calderisi 2006), Ancona (Businelli et al.
257 2009), Avellino and Caserta (Cicchella et al. 2008), Shanghai (Shi et al. 2008), Berlin (Birke and Rauch 2000) and
258 Trondheim (Andersson et al. 2010). Approximately 30% of the examined sites showed a Igeo typical of moderately
259 polluted areas, while 13% indicated a strong pollution trend (Table 5). The limit of 100.0 mg kg⁻¹ soil, established by
260 Italian legislation (Repubblica Italiana 2006) was exceeded in about 30% of the monitored areas. On average, the urban
261 soils in Pisa showed a Pb Igeo of 1.10, which is typical of minimally polluted areas, while the EF (2.58) indicated a
262 moderate anthropogenic enrichment (Table 5). The EF exhibited a moderate anthropogenic enrichment of Pb in 25% of
263 the sites, while 16% of Pisa urban soils showed a significant enrichment (Table 5), in line with the findings of
264 Doležalová Weissmannová et al. (2015). Lead is present in low amounts in the pedogenic substrate of coastal Tuscany
265 (APAT 2003), which suggests that its enrichment had an anthropogenic origin, mainly from its use in paints, glass, car

266 batteries and electronic waste (USEPA 2006). Although Pb use is banned by law in many areas in the world, another
267 source of pollution is vehicular traffic, as Pb is used as an additive in gasoline. The highest amount of Pb was in the
268 reducible fraction (70-80%) (Figure 3). The labile and residual fractions were small in all the examined areas.
269 Accordingly, in different types of soils and climates, Pb is found mostly in the reducible form, i.e. bound to soil oxides
270 and hydroxides of Fe and Mn, followed by the residual form (Wong and Li 2004; Davidson et al. 2006; Yang et al.
271 2006). However, in areas with a high total content of Pb, it was uniformly distributed within the single fractions.

272 Zinc

273 The Zn total content ranged widely between 61.7 and 522.7 mg kg⁻¹ of soil, with a mean value of 121.5 (Table 2). In
274 the control site, the Zn content was 51.0 mg kg⁻¹ soil, which is statistically lower than values observed in nearly all
275 urban soils, and slightly lower than the mean value of 68.0 in Italian soils (Bini et al. 1988). Values were comparable to
276 those reported for coastal cities in Tuscany by Bretzel and Calderisi (2006), and very similar to those measured in
277 Palermo (Salvagio-Manta et al. 2002), Caserta and Avellino (Cicchella et al. 2008), Bologna and Cesena (Gherardi et
278 al. 2009), Bangkok (Wilcke et al. 1998), Tallinn (Bityukova et al. 2000), Seville (Davidson et al. 2006), Hong Kong (Li
279 et al. 2004), Berlin (Birke and Rauch 2000), and Trondheim (Andersson et al. 2010). On the basis of the Igeo
280 classification, the majority of soils were not polluted, while about 20% of sites exceeded the limit of 150.0 mg kg⁻¹ soil
281 established by Italian legislation (Repubblica Italiana 2006) (Table 5). Since the Zn amount is not a predominant
282 fraction in the pedogenic substratum in the Pisa area (APAT 2003), it can be assumed that there was a considerable
283 anthropogenic contribution. This is confirmed by the EF which indicated a moderate anthropogenic enrichment in 25%
284 of the areas and a significant enrichment in one site (Table 5). The main source of Zn enrichment in urban environments
285 may be vehicular traffic, related to emissions from the wearing of brake linings, tyres and road surfaces, loss of oil and
286 cooling liquids, and corrosion of galvanized steel safety fences and other road furniture (Blok 2005). The Zn
287 accumulated mainly in the reducible fraction, where the metal exceeded 25% in areas with a low Zn content, and was
288 up to 40-50% in soils with the greatest degree of pollution (Figure 3). The labile fraction, which was absent in the
289 control, was present in all other areas (10.1%), and was more marked in sites showing a higher total content. The
290 oxidizable fraction, which was absent in the control, showed relatively low values in all other areas (about 5%). The
291 residual fraction was around 50% of the total Zn, suggesting accumulation. These results are in agreement with the
292 findings reported for urban soils in Nanjing by Lu et al. (2003). However they disagree with the findings reported by
293 Öborn and Linde (2001), Plyaskina and Ladonin (2009), Davidson et al. (2006) who found that Zn was concentrated in
294 the labile forms or equally distributed in the various chemical fractions.

295 Table 3 shows the correlation analysis data in relation to soil pollutants in urban sites in Pisa. The total hydrocarbons
296 (TPHs) did not correlate with any of the heavy metals. The lack of a relationship between organic and inorganic

297 pollutants, indicating different behavior, has already been reported by Alloway (2004) and Dallarosa et al. (2008),
298 although a strict correlation was demonstrated by Wang et al. (2004). Among metals, Cr and Hg contents showed no
299 correlations with the other elements, suggesting a different source of contamination. The total soil content of Cd, Pb, Zn
300 and, although with a lower level of Cu correlation, showed positive relationships. Similar findings were reported by
301 Mielke et al. (2000), Wang et al. (2004), Maisto et al. (2006), Sun et al. (2010), Iqbal and Shah (2011), Qing et al.
302 (2015), who suggested a common origin from the vehicular traffic. The total content of Mn correlated positively with
303 that of Ni, in accordance with Huang et al. (2015), who suggested that both metals mainly originated from natural
304 sources.

305 Platinoids

306 The accumulation of platinoids (Pt and Pd) originated from the release of small particles containing these elements due
307 to “three way” catalytic converter abrasion and deterioration (Ek et al. 2004; Morcelli et al. 2005). Increasing amounts
308 of Pt and Pd were detected in the United States and Germany (Hodge and Stallard 1986; Schäfer and Puchelt 1998;
309 Zereini et al. 2001; Sutherland et al. 2007; Wiseman and Zereini 2009). Table 4 reports the total platinoid content in the
310 urban soils of Pisa. The Pt amounts were below the detection limits of $2 \mu\text{g kg}^{-1}$ of soil in about 75% of the monitored
311 areas. In 10% of the sites the Pt content was 8-10 $\mu\text{g kg}^{-1}$ soil. These areas were located at junctions with dense traffic.
312 A similar pattern was observed for Pd, which was below the instrumental limit of $10 \mu\text{g kg}^{-1}$ dry soil in 90% of the
313 monitored areas. In the remaining sites, the Pd content ranged from 11 to 27 $\mu\text{g kg}^{-1}$ soil. Since it was possible to
314 measure Pd in three of the areas where Pt was also detected, a similar origin for the two metals can be assumed. The
315 values of Pt and Pd found in urban soils in Pisa were comparable with findings observed in many urban soils in Italy
316 (Cinti et al. 2002; Spaziani et al. 2008; Fumagalli et al. 2010), where their accumulation has probably just begun.

317

318 **Conclusions**

319 More than 50% of the areas in Pisa showed TPH values in the range of 100 and 150 ppm, indicating widespread and
320 intense pollution throughout the entire city. The legal limit for TPH of 60 ppm (Repubblica Italiana 2006) in residential
321 areas was exceeded in almost all the monitored sites, including the control. The TPH values did not correlate with any
322 of the monitored metals.

323 Generally, urban soils in Pisa showed an Igeo of Cd, Cu, Mn, Ni and Zn typical of unpolluted areas. However, the
324 amounts of Zn were higher than the limit established by Italian legislation for residential areas (Repubblica Italiana
325 2006) in about 20% of the sites, where Zn was also always present in the labile and thus more available fraction. Cd, Cr
326 and Cu amounts exceed the limit established by Italian legislation in only one site, while the Ni total content was always
327 lower than the limit.

328 The Igeo showed a significant level of Cr pollution in about 6% of the urban soils in Pisa. The EF indicated a moderate
329 anthropogenic enrichment of Cr in about 10% of the areas, where the metal was mainly in the oxidizable form. In the
330 remaining sites, Cr was detected in the residual fraction, thus indicating that it originated mainly from the lithogenic
331 substrate. The urban soils in Pisa showed an Igeo typical of minimally polluted areas for Pb, with levels exceeding the
332 limit established by Italian legislation in about 30% of the monitored areas. The EF indicated a moderate anthropogenic
333 enrichment of Pb, mainly in the reducible fraction. The Igeo indicated a significant degree of Hg pollution in all sites,
334 due to an anthropogenic enrichment.

335 The mobility sequence of the heavy metals based on the soluble, exchangeable and carbonate-bound fractions decreased
336 in the order of Mn (28.9%) > Zn (10.1%) > Ni (3.5%) > Pb (2.3%) > Cr and Cu (absent), suggesting that Mn and Zn
337 pose more of a potential risk of soil contamination than other metals.

338 Total Cr and Hg contents showed no correlation with other metals, suggesting a different source of enrichment. The
339 total contents of Cd, Pb, Zn and Cu in soils correlated positively with each other, indicating a common origin from
340 vehicular traffic.

341 The Pt and Pd values of urban soils in Pisa were comparable with findings observed in many Italian urban soils. The Pt
342 and Pd amounts were below the detection limits in 75% - 90% of the urban soils, with the greatest amounts in sites
343 located at junctions with dense traffic. It can thus be hypothesized that their accumulation was at an early stage.

344 Further studies could be necessary to deepen the relation between factors that affect the mobility of metals and urban
345 soils. Also, our data represent a starting point for researches aimed at monitoring platinoids pollution in urban and
346 extra-urban areas.

347

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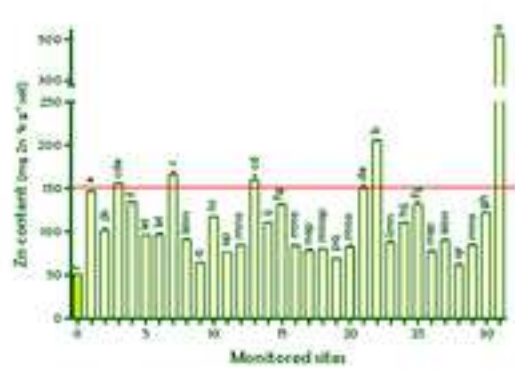
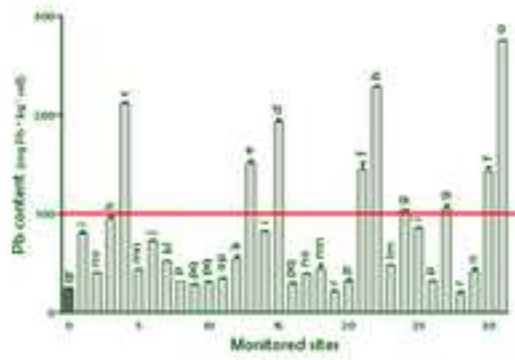
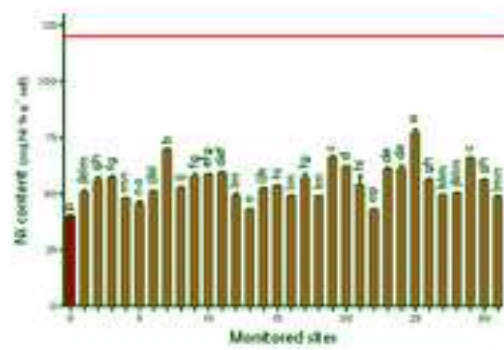
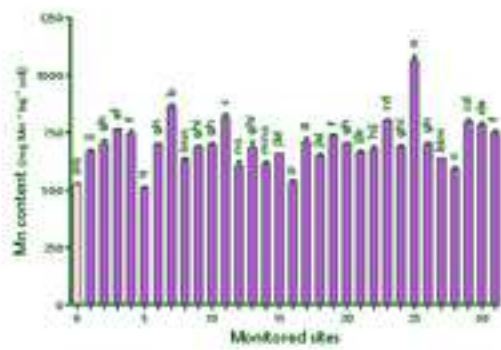
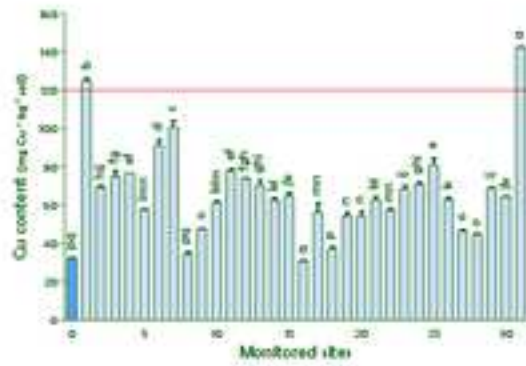
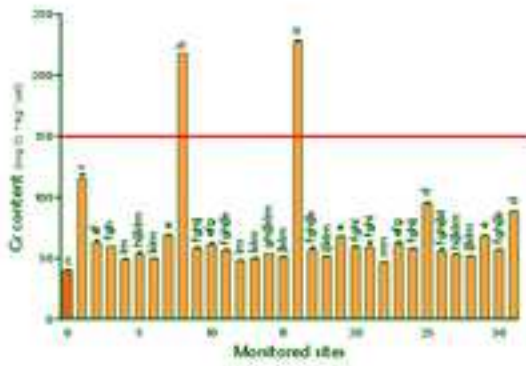
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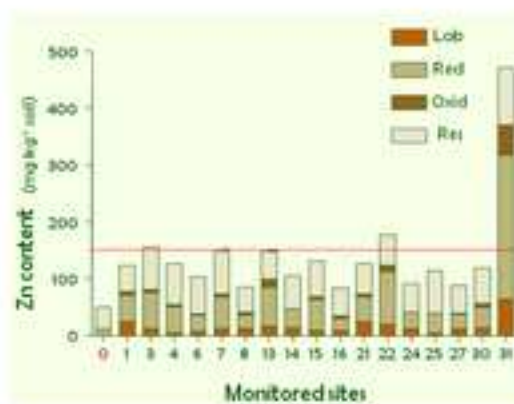
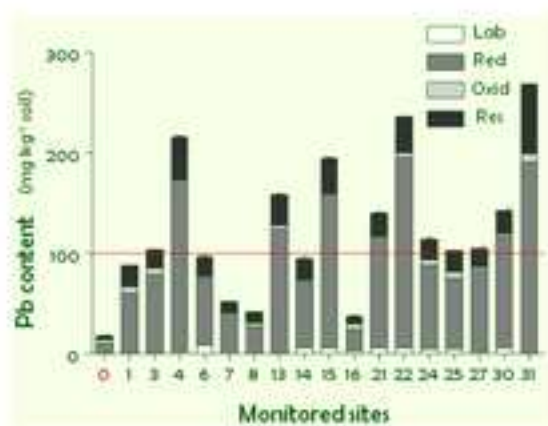
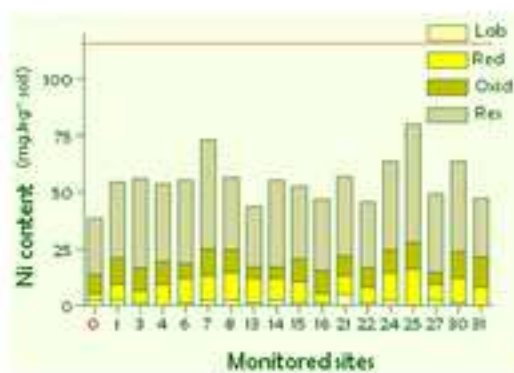
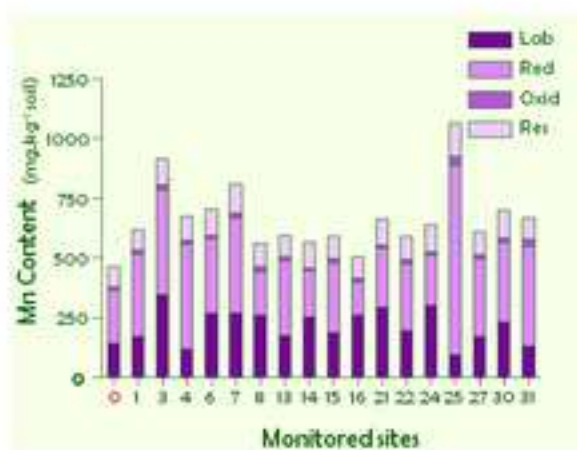
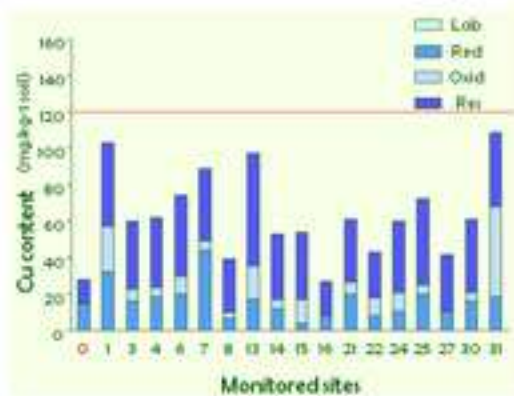
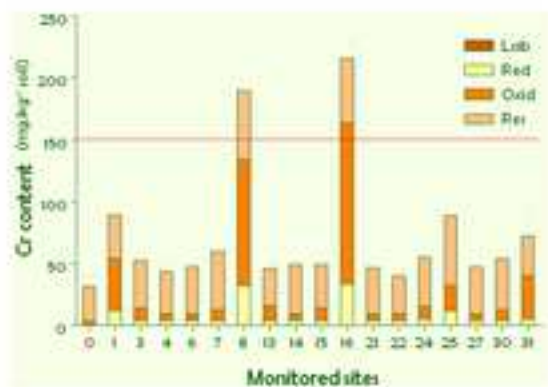
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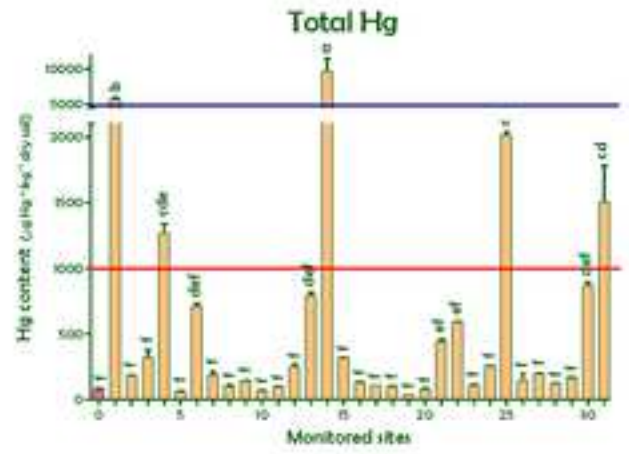
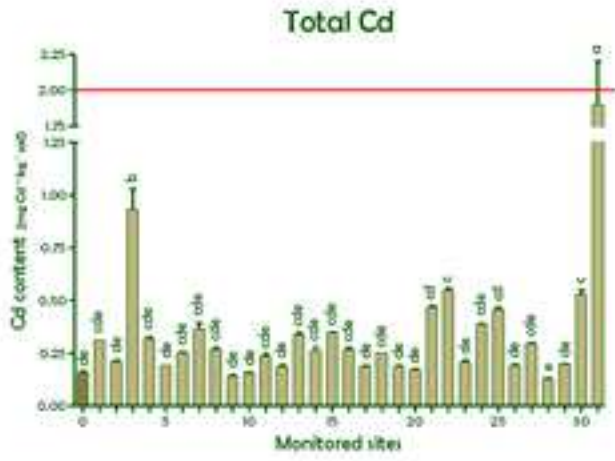
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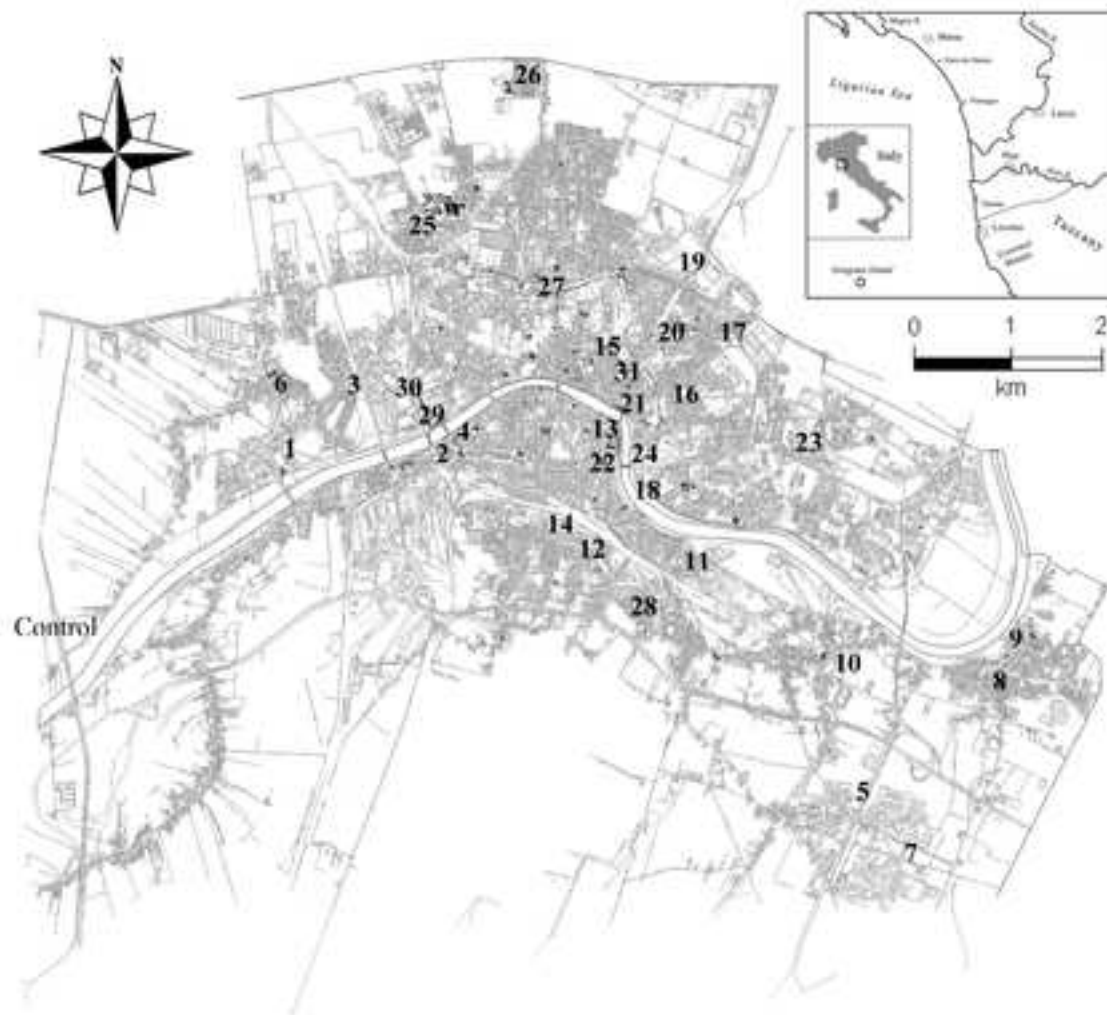


Table 1 Selected characteristics of urban soils of Pisa.

		Mean	SD	Minimum	Maximum	Median	CV%
Bulk density	g/cm ³	1.70	0.17	1.39	2.09	1.72	10.0
Gravel	%	8.1	7.4	0.1	29.8	5.9	19.5
Sand	%	68.0	10.8	40.1	85.2	70.6	15.9
Silt	%	16.8	6.4	7.9	30.8	16.5	38.1
Clay	%	15.1	5.5	6.9	31.6	14.3	36.4
WHC	%	47	6	32	64	46	13.4
pH		7.63	0.27	7.21	8.29	7.59	3.5
Limestone	%	9.3	4.4	2.8	23.1	8.0	47.4
Organic C	%	3.27	1.24	1.32	7.57	2.98	37.9
Texture			Sandy-loam	Loamy-sand	Sandy-clay-loam	Loam	
			77.4%	9.7%	9.7%	3.2%	

Table 2 Descriptive statistics of total petroleum hydrocarbons and metals of Pisa urban soils.

	Units (dry soil basis)	Detection limits	Mean	SD	Minimum	Maximum	Median	Control site	Background value		Italian Law limits ^c	
									Pisa ^a	Italy ^b	residential	industrial
TPH	mg.kg ⁻¹	0.1	97.7	72.5	38.3	419.1	74.9	54.5		ND	60.0	1000.0
Cd	mg.kg ⁻¹	0.01	0.35	0.33	0.13	1.90	0.26	0.16	0.31	0.54	2.00	15.00
Cr	mg.kg ⁻¹	0.5	71.2	43.0	46.4	227.5	57.6	39.8	ND	100.0	150.0	800.0
Cu	mg.kg ⁻¹	0.01	67.40	23.50	30.94	142.35	64.38	32.24	34.70	37.00	120.00	600.00
Hg	mg.kg ⁻¹	0.005	0.863	1.943	0.036	9.573	0.183	0.081		ND	1.000	5.000
Mn	mg.kg ⁻¹	1	705	103	509	1063	696	526	ND	800	NA	NA
Ni	mg.kg ⁻¹	0.1	55.2	7.7	43.0	77.1	54.0	40.1	64.9	47.0	120.0	500.0
Pb	mg.kg ⁻¹	0.01	83.56	67.84	19.61	275.33	51.97	24.51	18.20	28.00	100.00	1000.00
Zn	mg.kg ⁻¹	0.1	121.5	82.1	61.7	522.7	96.7	51.0	94.2	103.0	150.0	1500.0

^a APAT (2003) *Annuario dei dati ambientali. Capitolo 12 Geosfera* – 2003 edition, APAT, Rome, Italy, pp. 648-734. (in Italian).

^b Bini et al. (1988)

^c Legislative Decree 152/2006

Table 3 Correlation coefficients among pollutants of Pisa urban soils.

	TPH	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
TPH	1	0.129	-0.058	0.216	-0.137	0.248	0.345	0.072	0.174
Cd	ns	1	0.051	0.607	0.078	0.215	-0.128	0.693	0.937
Cr	ns	ns	1	-0.164	0.023	-0.153	-0.012	-0.188	0.021
Cu	ns	**	ns	1	0.314	0.407	0.088	0.443	0.692
Hg	ns	ns	ns	ns	1	-0.044	-0.104	0.147	0.144
Mn	ns	ns	ns	*	ns	1	0.758	0.095	0.166
Ni	ns	ns	ns	ns	ns	**	1	-0.387	-0.202
Pb	ns	**	ns	*	ns	ns	*	1	0.744
Zn	ns	**	ns	**	ns	ns	ns	**	1

In the table are reported Spearman correlation coefficients and the obtained significances ** $p \leq 0.01$, * $p \leq 0.05$, ns $p > 0.05$


TPH = total petroleum hydrocarbons

Table 4 Platinum group elements (PGEs) of Pisa urban soils value (mean + standard deviation).
The sites where the amounts were below the instrumental limits are not reported.

site	1	2	3	5	7	8	14	29	30
Pt	2 ±0,0	3 ±1,0	2 ±0,3	7 ±1,0	10 ±2,0	2 ±0,3	2 ±0,7	2 ±0,7	8 ±4,6
Pd	nd	nd	nd	11 ±3,9	nd	nd	27 ±15,2	27 ±18,0	nd

Table 5 Geoaccumulation Index (Igeo) and Enrichment Factor (EF) for metal contamination assessment of Pisa urban soils.

Site	Cd		Cr		Cu		Hg		Mn		Ni		Pb		Zn	
	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF	Igeo	EF
1	0,37	1,70	0,95	2,54	1,37	3,40	5,56	62,30	-0,24	1,11	-0,26	1,10	1,12	2,86	0,94	2,52
2	-0,19	0,93	0,07	1,11	0,52	1,52	0,59	1,59	-0,16	0,94	-0,11	0,98	0,13	1,16	0,40	1,40
3	1,95	3,99	0,00	1,03	0,63	1,60	1,41	2,74	-0,04	1,00	-0,07	0,98	1,37	2,66	1,03	2,10
4	0,42	1,62	-0,30	0,99	0,67	1,93	3,38	12,68	-0,08	1,15	-0,33	0,97	2,52	6,98	0,81	2,12
5	-0,34	0,95	-0,19	1,06	0,25	1,43	-0,90	0,64	-0,63	0,78	-0,39	0,92	0,23	1,41	0,34	1,52
6	0,06	1,17	-0,27	0,93	0,91	2,11	2,54	6,55	-0,17	1,00	-0,23	0,96	0,97	2,21	0,34	1,42
7	0,62	1,52	0,20	1,13	1,06	2,04	0,59	1,48	0,13	1,08	0,21	1,14	0,50	1,39	1,11	2,12
8	0,17	1,38	1,87	4,48	-0,50	0,87	-0,24	1,04	-0,32	0,98	-0,19	1,08	-0,21	1,06	0,25	1,46
9	-0,78	0,64	-0,05	1,05	-0,02	1,08	0,25	1,29	-0,20	0,95	-0,06	1,05	-0,36	0,85	-0,25	0,92
10	-0,58	0,71	0,04	1,10	0,34	1,36	-0,75	0,64	-0,18	0,95	-0,04	1,05	-0,26	0,90	0,62	1,64
11	0,00	1,00	-0,08	0,95	0,68	1,61	-0,28	0,83	0,05	1,04	-0,02	0,99	-0,10	0,93	-0,01	1,00
12	-0,34	0,99	-0,31	1,01	0,62	1,91	1,05	2,58	-0,38	0,96	-0,30	1,02	0,56	1,84	0,14	1,37
13	0,50	2,13	-0,27	1,24	0,53	2,17	2,70	9,78	-0,20	1,31	-0,48	1,08	2,03	6,15	1,06	3,14
14	0,12	1,26	-0,14	1,05	0,37	1,50	6,31	91,88	-0,36	0,90	-0,20	1,01	1,16	2,60	0,53	1,67
15	0,54	1,69	-0,23	0,99	0,42	1,56	1,40	3,06	-0,26	0,97	-0,17	1,03	2,39	6,10	0,78	1,99
16	0,17	1,46	1,93	4,96	-0,64	0,83	0,09	1,38	-0,55	0,89	-0,29	1,06	-0,31	1,05	0,13	1,42
17	-0,34	0,81	-0,07	0,98	0,22	1,19	-0,18	0,90	-0,16	0,92	-0,07	0,98	0,08	1,09	0,03	1,05
18	0,06	1,30	-0,21	1,08	-0,38	0,96	-0,28	1,03	-0,28	1,03	-0,30	1,01	0,26	1,50	0,06	1,30
19	-0,34	0,75	0,18	1,07	0,17	1,07	-1,75	0,28	-0,09	0,89	0,14	1,04	-0,78	0,55	-0,15	0,85
20	-0,50	0,69	-0,02	0,96	0,16	1,09	-0,58	0,65	-0,16	0,87	0,05	1,00	-0,22	0,83	0,11	1,05
21	0,97	2,34	-0,01	1,19	0,37	1,55	1,87	4,37	-0,25	1,01	-0,16	1,07	1,97	4,69	0,97	2,35
22	1,20	3,05	-0,36	1,03	0,24	1,57	2,28	6,48	-0,22	1,14	-0,48	0,95	2,63	8,27	1,42	3,57
23	-0,19	0,83	0,04	0,98	0,50	1,35	-0,16	0,85	0,03	0,97	0,02	0,96	0,38	1,24	0,20	1,09
24	0,70	1,78	-0,05	1,06	0,55	1,60	1,08	2,32	-0,20	0,96	0,02	1,12	1,50	3,10	0,53	1,59
25	0,94	1,50	0,66	1,24	0,74	1,31	4,05	12,95	0,43	1,05	0,36	1,00	1,22	1,82	0,78	1,34
26	-0,34	0,85	-0,09	1,00	0,38	1,39	0,27	1,29	-0,17	0,95	-0,10	0,99	-0,22	0,91	0,02	1,08
27	0,32	1,60	-0,17	1,14	-0,06	1,23	0,70	2,08	-0,30	1,04	-0,28	1,05	1,51	3,66	0,24	1,51
28	-0,88	0,65	-0,21	1,04	-0,11	1,11	0,03	1,23	-0,42	0,90	-0,26	1,01	-0,91	0,64	-0,31	0,97
29	-0,26	0,80	0,19	1,09	0,51	1,36	0,48	1,34	0,02	0,97	0,13	1,04	0,16	1,07	0,14	1,05
30	1,14	2,32	-0,06	1,00	0,41	1,40	2,84	7,50	-0,01	1,04	-0,10	0,98	1,96	4,09	0,67	1,67
31	2,98	9,33	0,56	1,74	1,56	3,47	3,63	14,62	-0,08	1,12	-0,31	0,95	2,90	8,83	2,77	8,06



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