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The influence of a large city on some soil properties and metals content

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Abstract

Urban soils differ from the rural ones by the fact that they are more strongly influenced by anthropogenic activities. This influence is often reflected by a high degree of contamination. To investigate the influence a large city can have on its soils and on the surrounding ones, samples within the city of Torino, Italy were compared with a set of surrounding soils developed from the same alluvial parent material. City–country trends were investigated by spatially managing the samples. Results show that the city plays a key role in concentrating some pollutants, such as Pb, Zn, and Cu within its borders. Lead is the element most enriched in the city, presenting a pollution index of 7.5 calculated comparing the two sets of samples. Ni and Cr appear to have a strong natural contribution. The spatial distributions for Pb, Cu and Zn present an abrupt division between urban and rural samples. Unexpectedly, the transport of pollutants from the city to the surrounding areas seems to be limited as no city–country trends with distance are identified. The pH and the sand fraction result also influenced by the city, showing high values. The investigation of possible city–country distance trends has shown to be effective in evaluating the impact a city can have on its soils and on the transport and deposition of contaminants on the surrounding ones.

Keywords: Urban soils; Heavy metals; Soil contamination

1. Introduction

Nearly half of the world's population already lives in urban agglomeration and in Europe it has reached about 80% and is continuously increasing (Burghardt, 1994; Antrop, 2004). Urban soils consequently are often sealed, compacted, contaminated and generally influenced by the human presence and activity. This is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development (Bullock and Gregory, 1991; Pichtel et al., 1998; Stroganova et al., 1998; Alexandrovskaya and Alexandrovskiy, 2000).

During the last few years urban soils raised receiving attention by scientists, leading to studies focused on their description and investigation all over the

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world (Chronopoulos et al., 1997; Chatterjee and Banerjee, 1999; Thuy et al., 2000; Birch and Scollen, 2003; Lu et al., 2003; Madrid et al., 2004; Murray et al., 2004). These soils in fact play an important role in maintaining the environmental quality as they can act as both source and sink for pollutants that can easily affect human health (De Kimpe and Morel, 2000). Urban soils receive a load of contaminants usually greater than the surrounding rural areas, due to the concentration of anthropogenic activities typical of urban settlements.

Typical pollutants of urban soils are Heavy Metals (i.e. HM), PAHs, chlororganic compounds and radionuclides (Madrid et al., 2002; Imperato et al., 2003; Li et al., 2004; Murray et al., 2004). Main sources of pollution in urban settlements are industrial emissions, traffic, burning of fossil fuels and wastes from industrial and residential activities. Soils are therefore exposed to a continuous accumulation of contaminants that can come from either localized or diffuse sources.

In urban areas, pollutants in soils are a major threat because they can easily enter the food chain by dust ingestion, dermal contact or breathing (Abrahams, 2002). Children are particularly exposed as they play on floors and on the ground and they pick up dust and soil on their fingers and place fingers in their mouth (Mielke et al., 1999).

Among other pollutants, HM are of particular concern due to their long residence time in soils and their toxicity to humans (Kabata-Pendias and Pendias, 1992; Alloway, 1995). These elements in soils can come from pedological or anthropogenic sources and a major thread of current research is how to distinguish between these two origins (Bonifacio et al., 1995; Facchinelli et al., 2001). Urban soils often contain concentrations of heavy metals that exceed regulatory levels. These latter are usually based on a generic total metal content on the basis that its measurement is rapid and cost-effective. These limits however may not be suitable for application in urban environments where diffuse contamination prevails, having been developed for contaminated sites, i.e. small polluted areas and point-source pollution.

Although HM accumulation in soils of large cities has been documented, little information is available on their differential content with respect to the surrounding areas and on the influence of the city in the transport and deposition of contaminants outside its borders.

Estimating a city's influence on soil contamination is generally made by comparing either legislative limits mentioned above or background values obtained from natural, comparable soils. While legislative limits often do not consider diffuse pollution, which is prevalent in a city, background values are of questionable reliability either because of the lack of natural, uncontaminated soils in the proximity of the city or because they are valid only for large areas. A carefully chosen set of rural soils from the surroundings of a city can, however, provide baseline values even though these soils can be exposed to some form of contamination (pesticides, sewage sludge applications, manures, etc.). The comparison would then provide not the absolute level of contamination of city soils but the incremental pollution caused by the concentration of human activities in urban areas with respect to the less intense anthropogenic influence on soils in rural settings.

Geostatistics techniques have recently been used to describe urban soils contamination (Imperato et al., 2003). Nevertheless, this approach may reveal limitations as the assumptions of continuity and stationarity could be difficult to make. Urban soils in fact can hardly be considered as a continuous system as they are repeatedly interrupted by roads, buildings foundations, pipes, cables, and their development is strongly influenced by the human activity.

The aim of this study was to evaluate the influence of a large city on its soils and on the surrounding ones with reference to some soil properties and HM content.

2. Materials and methods

2.1. Study area

The city of Torino has approximately 1 000 000 inhabitants and has a long industrial history, mainly car factories and metallurgical industries. The city covers an area of almost 133 km^2 of which about 10% is devoted to green areas.

Soil samples were taken in the Piemonte region, located in north-western Italy (Fig. 1). The alluvial plains where the samples were taken are constituted

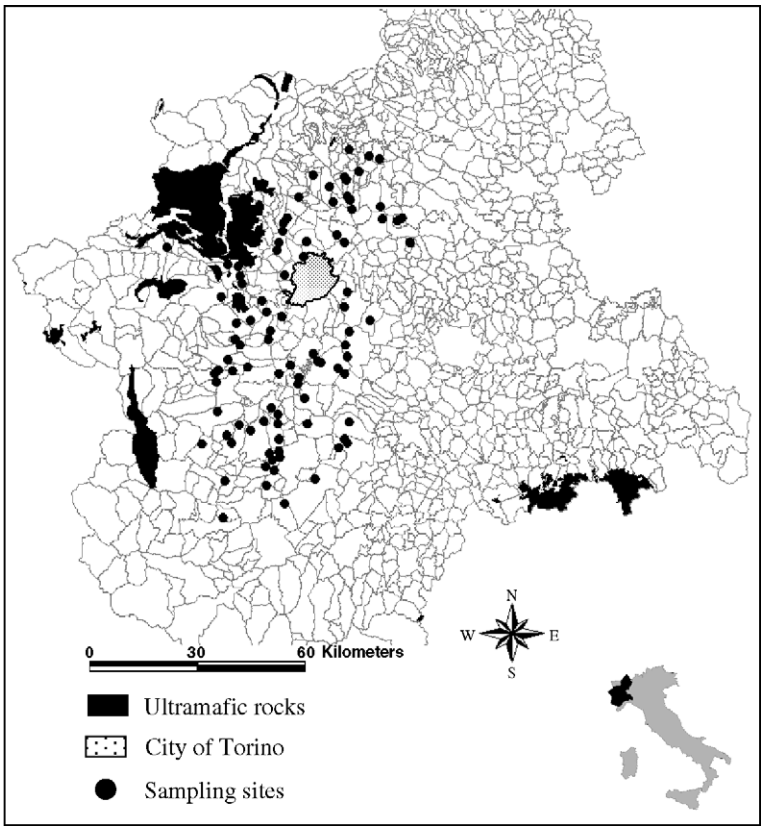

Fig 1. Rural sampling points and ultramafic rock outcrops.

by a sequence of fluvio-glacial and alluvial terraces formed during the Middle Pleistocene and Upper Pleistocene–Holocene periods (Arduino et al., 1984).

The city of Torino was built and sprawled on an alluvial plain, which has been formed by the rivers Po, Sangone, Stura di Lanzo and Dora Baltea. The watershed of these rivers contains a mixture of very diverse rocks that have contributed to the chemical composition of the deriving soils. In particular, serpentinites are present that might have increased Cr and Ni contents in the alluvial deposits (Alloway, 1995; Lombini et al., 1998). The outcrops of ultramafic rocks are represented in Fig. 1.

2.2. Soil sampling

Urban sampling locations were recorded by means of a GPS and are shown in Fig. 2. Samples from urban soils were collected in the city of Torino, Italy, in 1999. In total 70 sites chosen among parks and roadsides were sampled at a depth of 0–20 cm. At each sampling site composite samples were obtained by mixing subsamples from 4 points taken on the corners of a 1-m^2 square. The herbaceous cover of the site was removed and the sample was taken with a spade and stored in a plastic bag. The spade was washed with deionised water and wiped dry with paper towels after each use. About 3 kg of soil was taken at each location.

The topsoil (0–20 cm) samples from the surrounding rural fields (i.e. rural samples) were sampled by the local agency for the protection of the environment (ARPA) in 2001 and 2002. Samples were taken from the area delimited by those rivers that might have contributed to the deposition of materials of the alluvial plains where the city is located to limit the comparison to soils on similar parent materials. In total, 92 rural sites were considered (Fig. 1).

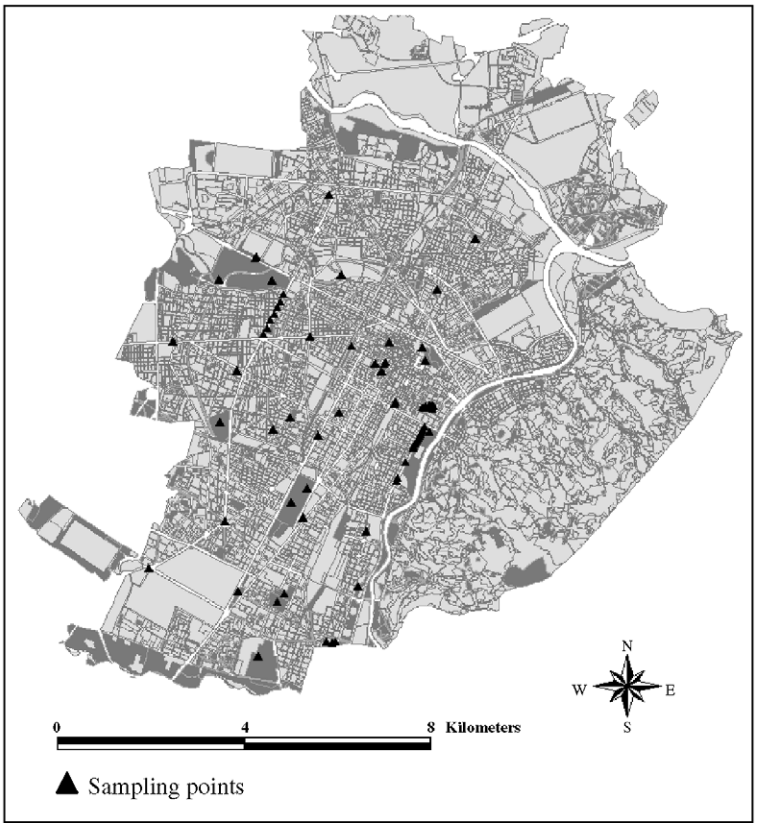

Fig 2. Urban sampling points.

2.3. Chemical analysis

Samples were air-dried, gently crushed and sieved at 2 mm with plastic sieves to avoid any contamination. A portion of each sample was further ground at 0.15 mm for *aqua regia* (HCl/HNO_3, 3:1 solution) digestion (ISO 11466, 1995). Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). Soil chemical properties were determined following ISO methods. The pH was determined in a $CaCl_2$ solution, 1:5 soil/solution ratio (ISO 10390, 1994), organic carbon by the CE Instruments NA2100 elemental analyser (ISO 10694, 1995), and cation exchange capacity with $BaCl_2$ at pH 8.1 (ISO 13536, 1995). The *aqua regia* extracts were analysed for metals with a Perkin Elmer 3030 flame atomic absorption spectrometer (FAAS). Duplicates were made for all samples and results accepted when the coefficient of variation was within 5%. A blank and the CRM (Certified Reference Material) 141 R (Community Bureau of Reference, Geel, Belgium) were included in each batch of analyses for quality control of HM measurements. Results were satisfactory when within a range of $\pm 10\%$ from the certified value. An internal reference material was also included in each batch of analyses for quality control of soil physical–chemical analyses.

2.4. Statistical analysis and data treatment

Statistical analysis was carried out using the software MINITAB 13 (Minitab Inc., USA) for Windows® and the data were geographically managed and processed with the GIS software Arcview 3.2 (ESRI Inc., California, USA).

3. Results and discussion

3.1. Soil properties

Table 1 shows the mean values, medians, standard deviations, number of samples and minimum and maximum of some soil properties for urban and rural samples. The pH in urban soils is mostly neutral to alkaline, with a mean value of 7.2 and only four samples below 6.5. Rural soils present a pH ranging from 3.7 to 8.0, with a mean value of 5.6. The wide pH range of rural soils reflects the influence of different land uses and agricultural practices. City soils show a pH higher than the surrounding ones; this has already been reported by several authors and could be partly explained by extraneous materials such as bricks and construction debris included in the soil that could increase the pH (Alexandrovskaya and Alexandrovskiy, 2000; Bullock and Gregory, 1991; Jim, 1998). This is confirmed by the observation that the present city ground level is, in the historical centre of the town, on average 2 m above the original roman settlement.

Urban soils present a high sand content, ranging from 439 to 889 g kg^{-1}, with a mean of 702 g kg^{-1}, while silt and clay have mean values of 210 g kg^{-1} and 88 g kg^{-1}, respectively. Sand, silt and clay for rural soils have a mean value of 565 g kg^{-1}, 352 g kg^{-1} and 79 g kg^{-1}, respectively. The high sand content of urban soils could be influenced, as for the pH, by the inclusion of extraneous coarse materials to the soils.

Table 1
Descriptive statistics for some soil properties for urban and rural samples[a]

	pH	Sand, g kg^{-1}	Silt, g kg^{-1}	Clay, g kg^{-1}	OC, g kg^{-1}	CEC, $cmol_c$ kg^{-1}
Urban						
Mean	7.2	702	210	88	16	11.3
Median	7.4	710	188	88	14	10.4
Max	7.8	889	430	170	48	26.3
Min	4.7	439	60	35	3	4.7
Std dev	0.6	81	81	32	9	4.1
n	70	70	70	70	70	70
Rural						
Mean	5.6	565	352	79	15	15.4
Median	5.3	561	347	71	13	13.2
Max	8.0	874	610	244	63	43.2
Min	3.7	272	98	14	3	3.3
Std dev	1.1	141	119	43	11	8.7
n	92	92	92	92	92	92

[a] OC: organic carbon; CEC: cation exchange capacity.

Table 2
Descriptive statistics for HM in urban and rural samples

	Pb, mg kg^{-1}	Zn, mg kg^{-1}	Cu, mg kg^{-1}	Ni, mg kg^{-1}	Cr, mg kg^{-1}
Urban					
Mean	149	183	90	209	191
Median	117	149	76	175	157
Max	870	545	283	790	870
Min	31	78	34	103	67
Std dev	120.6	97.3	47.9	117.9	132.4
n	70	70	70	70	70
Rural					
Mean	20	62	28	74	96
Median	19	57	23	56	87
Max	50	142	109	431	322
Min	2	27	6	13	14
Std dev	8.5	21.5	16.8	63.2	52.9
n	92	92	92	92	92

The organic carbon (OC) content in urban samples ranges from 3 g kg^{-1} to 48 g kg^{-1}, with a mean value of 16 g kg^{-1}. In rural samples, the OC content ranges from 3 g kg^{-1} to 63 g kg^{-1}, with a mean value of 15 g kg^{-1}. The organic carbon content of the two datasets is unusually similar and generally fairly low. It is commonly observed that OC of agricultural soils can be lower than the comparable virgin areas. This is because in nature the OC produced by the vegetation is returned to the soil. By contrast, in cultivated areas much of the plant material is removed for human or animal food. In addition, soil tillage breaks up the organic residues and brings them into contact with soil organisms, increasing the rate of decomposition (Brady, 1984; Baldock and Nelson, 2000). The agricultural fields that surround the city are mainly cultivated with maize (*Zea mays* L.) and ploughed, a fact that contributes to maintain a low OC. In urban areas, soils are usually covered by grass, which would be expected to accumulate OC in the upper layer. However, at many of the sampling sites, soils often did not have an herbaceous cover. Moreover microbiological activity is known to be hampered by pollutants (Alloway, 1995; Bullock and Gregory, 1991) that are likely to be more abundant in urban areas, this can cause a reduction of the OC content.

Cation Exchange Capacity (CEC) has a mean value of 11.3 $cmol_c$ kg^{-1} in urban soils, ranging

Table 3
Current legislation limits for contaminated sites in Italy for the five HM considered

Element	Public and private green and residential areas	Commercial and industrial areas
	Pseudototal content (mg kg^{-1})	
Pb	100	1000
Zn	150	1500
Cu	120	600
Ni	120	500
Cr	150	800

from 4.7 to 26.3 $cmol_c$ kg^{-1}. The CEC of rural soils ranges from 3.3 to 43.2 $cmol_c$ kg^{-1}, showing a mean of 15.4 $cmol_c$ kg^{-1}. The lower CEC of urban soils is in accordance with both the low OC and the low clay content.

3.2. Heavy metals

Descriptive statistics for HM pseudototal content (*aqua regia* extractable) for both urban and rural soils are given in Table 2.

The mean values of all the elements considered are higher in city samples. Minimum values of urban samples are always greater than the mean values of rural ones, reflecting a general and diffuse contamination of city soils. The mean metal content of urban soils in Torino always exceeds current legislation limits for contaminated sites designated for green and residential areas (Gazzetta Ufficiale delle Repubblica Italiana, 1999), except for Cu. These limits for clean up are based on the pseudototal metal content and are given in Table 3.

The 58% of the urban soils are above the legislation limit for Pb, this element ranging from 31 to 870 mg kg^{-1}. None of the rural samples is above the limit for this element, with values ranging from 2 to 50 mg kg^{-1}. The 49% of the urban samples pass the legislative limit for Zn, ranging from 78 to 545 mg kg^{-1}. The limit is never reached in rural soils, showing for Zn a maximum of 142 mg kg^{-1}. The mean content for Cu in urban soils is 90 mg kg^{-1}, with the 27% of the samples above the legislative limit. In rural samples, Cu varies from 6 to 109 mg kg^{-1}, with only a sample above the limit. Nickel and Cr range in urban soils from 103 to 790 mg kg^{-1} and from 67 to 870 mg kg^{-1}, respectively. The 94% of the urban samples are above the legislative limit for Ni and the 52% for Cr. In rural samples, the 12% of the samples are above the limits for Ni and the 13% for Cr.

Compared with other urban soils from different large cities in the world (see Table 4), the soils of Torino show the highest levels of Ni and Cr, while Pb and Zn concentrations are similar to values found in cities like Sevilla and Madrid. The Cu content is similar to those of the other two Italian cities, Napoli and Palermo.

In a city, HM can enter the soil by different sources such as traffic, emissions from industrial plants, burning of fossil fuels and municipal wastes. In particular, Pb, Cu and Zn seem to be mainly associated with traffic, Pb coming from the burning of leaded fuel (until its disappearance and the use of unleaded fuel only), Cu deriving from brakes and Zn from tyres consumption (Mielke et al., 1999; Van Bohemen and Janssen Van de Laak, 2003). Other sources of these three elements in urban environments can be incinerators, pipes, cables and paints (Alloway and Ayres, 1997). Nickel and Cr can have, as discussed before, a relevant natural contribution in the soils considered for this study, as they may be derived

Table 4
Mean metal content (mg kg^{-1}—*aqua regia* extractable) in urban soils from different cities in the world

City	Pb	Zn	Cu	Ni	Cr	References
Hong Kong	95	125	23.3	12	23	Li et al., 2004
Madrid	161	210	72	14.1	75	De Miguel et al., 1998
Nanjing	104	96	104		97	Lu et al., 2003
Napoli	262	251	74		11	Imperato et al., 2003
Palermo	253	151	77	19	39	Manta et al., 2002
Sevilla	137	145	68	22	39	Madrid et al., 2002
Warsaw	53	140	25		13	Pichtel et al., 1998
Torino	149	183	90	209	191	Present study

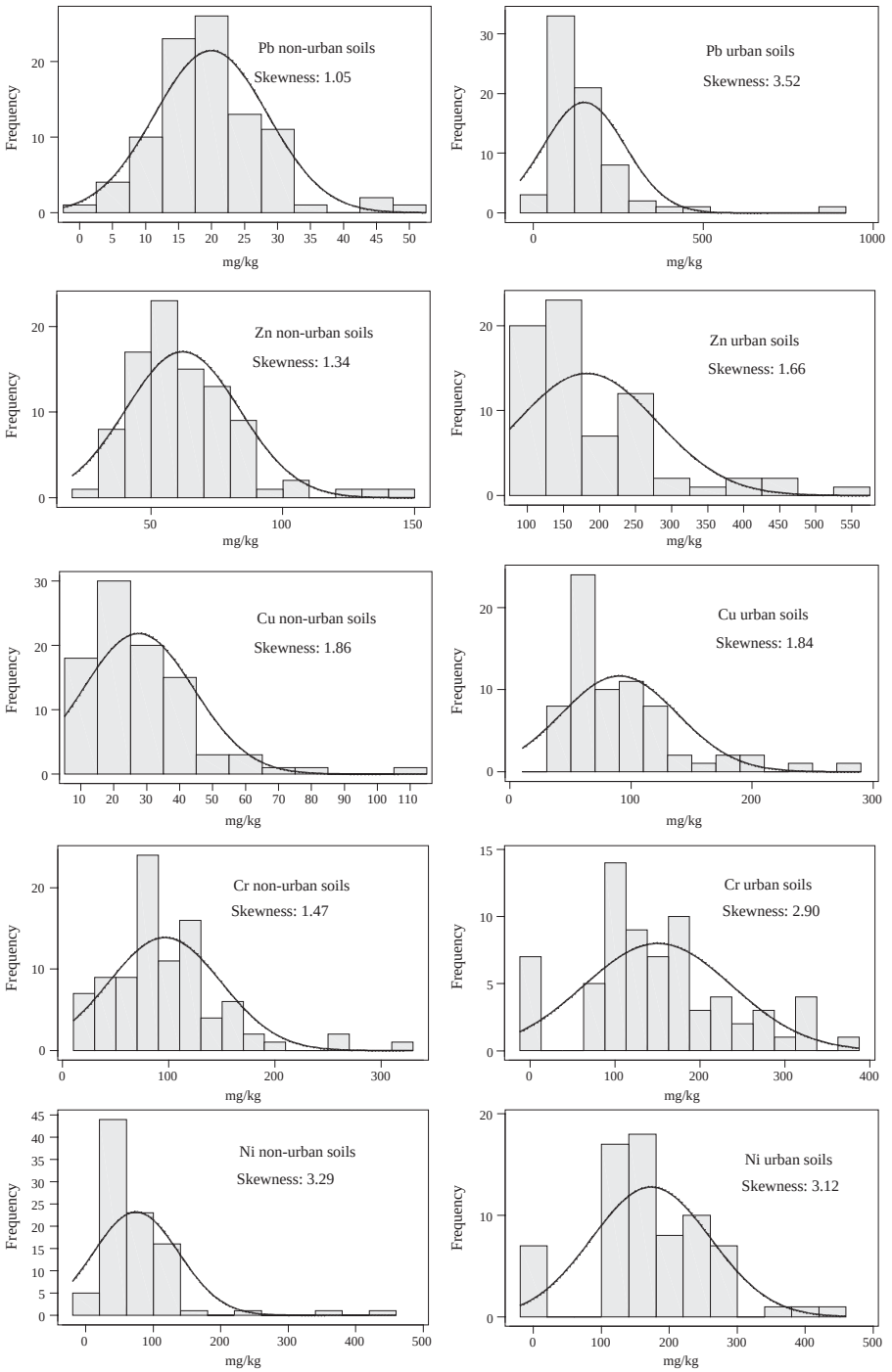

Fig 3. Frequency histograms of HM for urban and rural samples. In black is drawn the normal curve.

Table 5
Results of the *t*-test assuming unequal variances between urban and rural samples, calculated with the 95% confidence interval

	pH	OC	Pb	Zn	Cu	Ni	Cr
Stat *t*	11.26	0.60	10.27	11.53	11.65	9.34	6.21
$P(T \leq t)$	0.00	0.55	0.00	0.00	0.00	0.00	0.00
t critical	1.97	1.97	1.97	1.97	1.97	1.97	1.97

from the alteration of serpentinites. Other sources for these two elements can be heating plants, metallurgical industries, car factories and traffic.

Agricultural soils receive HM mainly from fertilizers, pesticides, manures, sewage sludge application and other scattered diffuse pollution sources such as incinerators, traffic, industries, etc. (Nicholson et al., 2003; Wong et al., 2002).

3.3. Frequency distributions and t-test

Frequency histograms with normal curves of the two datasets were obtained using the MINITAB 13 software and are compared in Fig. 3. The comparison of frequency histograms shows the characteristic positively skewed distribution of HM in contaminated sites (Imperato et al., 2003; Maiz et al., 2000). The metals considered as typically "urban" by some

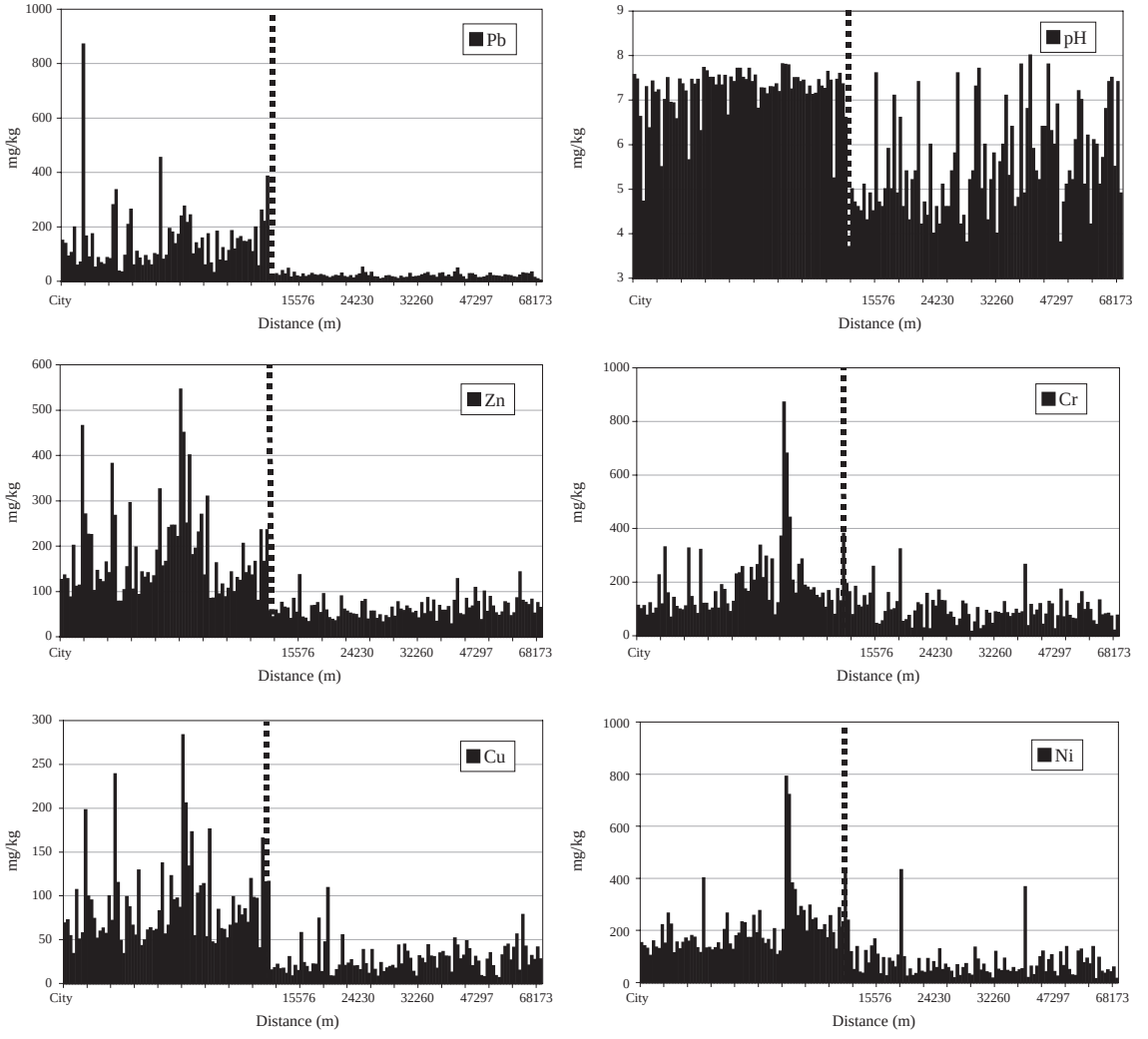

Fig 4. Histograms for parameters trends with the increase of the distance from the city. The dashed line shows city administrative borders.

Table 6
Correlation matrix between HM in urban samples; cells show the Pearson correlation coefficient and the corresponding *P*-value

	Cr	Cu	Ni	Pb
Cu	0.536			
	0.000			
Ni	0.702	0.256		
	0.000	0.043		
Pb	0.381	0.640	0.229	
	0.002	0.000	0.070	
Zn	0.514	0.892	0.121	0.709
	0.000	0.000	0.345	0.000

authors (Madrid et al., 2002; De Miguel et al., 1998; Manta et al., 2002) are the ones presenting greater deviation from the normal curve, reflecting the influence of some highly contaminated soils within the city. This is confirmed for example by Pb that shows a far lower skewness in rural soils than in the urban ones (1.04 vs. 3.52).

Theoretically, if a city does not have an influence on its soils these should have HM content and general soil properties similar to those of the surrounding areas developing on the same parent material. A *t*-test, assuming that city soils belong to the same population of the surrounding area as H_0, gave the results presented in Table 5. The test was run assuming unequal variances after a Levene's test for homoscedasticity had shown that the variances were unequal. The calculated values of *t* identify, except for OC, the two sets of samples as belonging to different populations, confirming the influence of the city on its soils (Table 5). As some of the parameters did not satisfy the assumption of normality for the *t*-test, the same hypothesis was tested by a non-parametric Wilcoxon–Mann–Withney test which confirmed the previous results.

3.4. Spatial patterns

Using an extension of the GIS software ArcView 3.2, distances of the rural sampling points from the city were automatically calculated and samples were then ordered with increasing distance, to investigate possible city–country patterns. Distances were calculated from a location in the centre of Torino (the royal castle) arbitrarily taken as the origin. Results are presented in Fig. 4. A line was drawn on the graph to separate urban samples, i.e. those within the city administrative border, from rural samples. The comparison of the graphs shows clearly the influence that a large city like Torino has on pH and on some contaminants. The city seems to have a strong influence on pH, this parameter being more evenly distributed within the city limits than in the country, confirming the general tendency of urban soils to being buffered towards high values.

The concentrations of the HM reveal interesting differences in their spatial patterns. Lead is the metal showing the strongest differences between urban and rural soils. In fact, even the samples closest to the city in all directions show a dramatically lower Pb content. The separation between rural and urban areas results clearly defined in the graph, closely fitting the administrative borders delimited on the graph by the dashed line. Zinc and Cu follow a similar pattern showing, especially for Zn, an abrupt division between the city soils and the surrounding areas. Air pollutants are supposed to be deposited according to a trend of decreasing concentrations with distance from the source. No trends with distance from the city are clearly identifiable from the graphs even though the amount of emissions could suggest the diffusion of pollutants over a wide area. In this study, transport of pollutants from the city to the surrounding areas seems therefore to be limited to about a 1-km strip around it.

For Ni and Cr, differences result lowered and a clear division between the two types of soil is no longer noticeable, reflecting a potential natural contribution on the content of these elements in both urban and rural soils. The accumulation of Pb, Cu and Zn in the city with respect to the rural area confirms their main anthropogenic origin, as sug-

Table 7
Correlation matrix between HM in rural samples; cells show the Pearson correlation coefficient and the corresponding *P*-value

	Cr	Cu	Ni	Pb
Cu	−0.043			
	0.614			
Ni	0.663	0.117		
	0.000	0.167		
Pb	0.408	0.076	0.092	
	0.000	0.366	0.277	
Zn	0.155	0.330	0.346	0.331
	0.065	0.000	0.000	0.000

gested by many authors. This can be somehow substantiated by the correlation coefficients obtained for the five metals considered in urban samples. The correlation matrices are shown the Tables 6 and 7. Chromium and Ni result well correlated in both urban and rural soils, confirming their probable common origin. Lead, Zn and Cu are well correlated in urban soils, but not in rural soils.

3.5. Urban pollution index (PI)

The evaluation of the degree of contamination is often made using an enrichment factor, usually calculated comparing surface vs. deep layers. This is based on the fact that in natural or semi-natural soils, contaminants coming from anthropogenic emissions are supposed to accumulate on surface layers. This is not necessarily true in urban settlements where soil is frequently mixed (e.g. for road and building construction, tree planting, etc.), new soil is added and extraneous materials such as bricks, wastes and construction debris are incorporated in the soil. Thus the common approach of calculating accumulation of contaminants down the profile by comparing concentrations of two layers cannot be used with urban soils. A different approach for the evaluation of the degree of contamination was used, using urban vs. rural samples, in an attempt to quantify the accumulation of HM caused by the urban activities, trying to estimate an enrichment of the city (Pollution Index, PI) with respect to the surrounding soils. Indices were calculated as mean urban/mean rural. The PI for Pb in urban soils is 7.5 on average, decreasing to 2.0 for Cr. Lead contamination seems therefore to be the most pronounced in the city of Torino, despite the quick increase of unleaded fuel utilization in the recent years (5% of the total fuel sold in the year 1991, 55% in 1997 and 100% in 2002). Lead is well known to be one of the less mobile elements in soils, which could explain the high values still found in urban soils. Moreover, among the metals considered for this study, it is the most toxic for humans, so the risks of its potential entry in the food chain must be carefully considered. Zinc, Ni and Cr are the elements presenting the lowest PI, 2.9, 2.8 and 2.0, respectively, reflecting a slight contamination of the city for these elements. The accumulation of Cr and Ni in the city soils indicates that, despite the natural high levels of these two elements in the area, there is a considerable contribution from diffuse pollution sources which doubles the average concentration of Cr and triples that of Ni.

Copper presents a PI of 3.3 showing, despite its general low values found, a moderate contamination of the city with respect of this element.

4. Conclusions

The comparison of a set of urban soils with a rural one shows that a large city like Torino has a strong influence in changing soil properties. In particular, the city appears to play a key role in concentrating within its borders some soil pollutants, such as Pb, Zn, and Cu. Lead is the most enriched HM in the city. Urban soils present for this element an average pollution index (PI) of 7.5, calculated comparing urban samples with a set of soils developing on the same parent material as the city. Nickel and Cr show a lower PI, reflecting a possible natural contribution. Ordering the samples with increasing distance from the city, an abrupt division between urban and rural soils is clearly identifiable for Pb, Zn, and Cu. Unexpectedly, the transport of pollutants from the city to the surrounding areas seems to be very low, as no trends with the distance are evident.

The city seems to also influence the pH of its soils, buffering it towards high values, and the particle size distribution, in favour of coarser fractions. This is probably due to the inclusion of extraneous materials to the soil.

The data comparison between urban soils and a set of soils from the surrounding area developing on the same parent material seems to be effective in quantifying the degree of soil contamination and evaluating the natural contribution to the HM content of urban soils. The investigation of possible city–country distance patterns represents an important tool towards the evaluation of the impact a city can have on the transport and deposition of contaminants outside its borders.

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