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ORIGINAL ARTICLE

Potentially harmful elements and lead isotopes distribution in a heavily anthropized suburban area: the Casoria case study (Italy)

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Abstract This study presents the results of 12 trace elements that have been classified by Italian Environmental law as potentially dangerous to human health and new Pb isotope data for topsoils and soil profiles collected in the Casoria municipal area (Napoli). Elemental concentrations were determined in 126 topsoil samples and were produced interpolated distribution (MIDW) and baseline maps using GeoDAS software. Results show Casoria soils to be significantly enriched in several elements (e.g., Cd, Cu, Pb, Zn). Two geochemical sources were determined associating elemental distribution with the background values of Neapolitan soils: one geogenic and another one anthropogenic. High As, Co, Se and Tl concentrations are coherent with bedrock lithology, and elemental concentrations show the same values typical of Neapolitan volcanic soils. Higher Cd, Hg, Pb and Zn concentrations can be linked with anthropic activities coherent with previous studies in the Neapolitan area. Cr, Cu, Sb and V geochemical concentration and distribution shows both geogenic and anthropogenic influence. Pb isotope analyses allow the determination of the source of the Pb and the level of anthropogenic/geogenic influence on their concentration. Pb sources in the Casoria soils overlap the isotopic compositions typical of industrial soils/aerosols. This anthropic influence on Pb concentration is quantified by anthropogenic fraction (AF%). Casoria topsoil shows very high amount of anthropogenic Pb: AF% is 41–58 %. In profile soil samples leached (L) AF(%) is 31–43 % (topsoils) and 38–56 % (bottom soils); in profile soil samples residues (R) AF(%) is shifted toward the geologic signature, 18–43 % (topsoils) and 25–50 % (bottom soils).

Keywords Environmental geochemistry · Urban geochemistry · Pb isotope geochemistry · Potential toxic elements

Introduction

In recent years, environmental pollution in the Campania region (Italy) has attracted worldwide attention. Illegal waste disposal, both domestic and from external sources, coupled with the uncontrolled burning of trash piles has raised human health concerns in areas adjacent to the city of Naples and around the town of Caserta known as "Land of fires." Metal contaminants (Pb, Zn, Hg, Cd, Cr) have an intense effect on the quality of air, water and soil (Flament et al. 1996; Monna et al. 1997; Jensen et al. 1999; Steckerman et al. 2000; Denaix et al. 2001; Citeau et al. 2003; Cicchella et al. 2008; Ayuso et al. 2008; Geagea et al. 2008; Bove et al. 2011; Grezzi et al. 2011; Cicchella et al. 2014; Guagliardi et al. 2015) and could be harmful to environmental quality and human health, particularly in urban, suburban and industrial areas (Albanese et al. 2008; Albanese and Cicchella 2012; Filippelli et al. 2012; Valera et al. 2014).

This paper presents the results of a study based on trace element distributions and Pb isotopic analysis of soils in

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the municipality of Casoria, which is a urban and suburban area adjacent to the city of Naples. The concentrations of 53 elements were determined but the study is focused on 12 elements considered as "pollutants" and potentially toxic by Italian environmental legislation D.L. 152/2006 (Italian Department of the Environment 2006). Geochemical data distribution patterns for the considered elements were described, and the health of urban environment has been monitored, using contamination factors and degree of contamination (Håkanson 1980) calculated for 3 potential toxic elements (Zn, Cd and Pb). Lead isotopes allowed us to detect different source of Pb in Casoria soil (anthropic or geogenic) and quantify the "anthropogenic fraction".

Lead in soil has a low solubility and a stable and long residence time (Zhang et al. 2014), and up to 30 years ago, Pb was used as additive in gasoline and in the principal industrial activities. Lead released from vehicles, and industrial emissions are accumulated in the soil profile, overlapping natural Pb concentration from Neapolitan volcanic rocks. For these reasons, Pb isotopes analysis is an important geochemical tool to discriminate and quantify the anthropic source vs the geogenic one. Lead has four stable isotopes: ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb; three of them (^{208}Pb, ^{207}Pb, ^{206}Pb) derive from radioactive decay of ^{232}Th (^{208}Pb), ^{235}U (^{207}Pb) and ^{238}U (^{206}Pb), while ^{204}Pb is the only non-radiogenic isotope. Natural materials have characteristic Pb isotope ratios, as a result of the different half-lives of Th and U and geological evolution (Doe 1970; Dickin 1995; Galer and Goldstein 1996). Environmental and industrial processes do not fractionate Pb isotopes during near-surface physical and chemical processes. The isotopic stability makes Pb isotopes powerful tools to trace the source of contamination and possibly distinguish the contribution from geologic (natural Pb contents in bedrocks) and anthropogenic sources (D'Antonio et al. 1995; Kramers and Tolstikhin 1997; Veron et al. 1999a, b; Tarzia et al. 2002; De Vivo et al. 2006; Ayuso et al. 2008; Cicchella et al. 2008; Bove et al. 2011; Grezzi et al. 2011).

Casoria is a densely populated area characterized by multiple uses of land, and diversity of commercial enterprises located in the northeastern part of Naples. Casoria extends for about 12 km^2 in the Campanian Plain (Fig. 1a) and displays the effects of human activities related to the processes of urbanization and industrialization mostly developed in the last 100 years. Traditional agriculture and farming activities have been overshadowed by new land use practices. In the last 40 years, industrial development has made Casoria one of the most important industrial centers in the Neapolitan area. Past and present industrial activities include the manufacture of chemicals (Montefibre-Rhodiatoce and Resia), steel manufacture (ADS—Acciaierie del Sud), cement factories (Calcobit), highly sophisticated aeronautic industrial plants and other activities related to the International Airport of Naples (Capodichino) located between Casoria and Naples. In the last few years, Italian and local governments have taken under serious consideration the extremely precarious environmental situation due to the combination of high-density population and the presence of highly polluting economic and illegal activities, which represent an obstacle for economic and social growth. The Italian law D.L. 136/2013 (Italian Department of the Environment 2013), which has defined as "Land of Fire" the areas northwest of Napoli metropolitan territory because of environmental pollution by illegal or industrial activities, tries to fight illegal pollutant activities, giving new guidelines aimed at environmental monitoring and soil remediation.

The aim of this research is to evaluate the availability of potentially toxic elements (e.g., Pb, Zn, Cd, Hg) in soils that are of concern for human health, in accordance with the Italian Environmental Law D.L. 152/06 (Italian Department of the Environment 2006), and quantify the contribution due to anthropogenic contamination. We attempt to identify pathways for these metals and use Pb isotopes to help identify the contribution from natural and/or anthropogenic sources by calculating the anthropogenic factor %. Detecting the possible emission sources, according to Italian legislation D.L. 136/2013 (Italian Department of the Environment 2013), would be useful for national and local authorities to plan measures for the inhabitant's health, soil remediation and economic development.

Characterization of the studied site

Geological and geomorphological settings

Casoria is in the Campania Plain, a Lower Pleistocene graben structure (Brancaccio et al. 1994) bordered by the Campanian Apennines to the east–northeast, the Tyrrhenian Sea to the west, Mt Massico to the northwest and Mt Lattari to the southeast (Fig. 1b). Generally, Casoria is a geographically low-lying suburb (between 10 and 70 m above sea level), and the underlying bedrock is the Neapolitan Yellow Tuff (NYT) up to a depth of about 20 m from the surface (De Vivo 2006). The NYT consists mostly of pyroclastic flow deposits and minor fall deposits constituting two different facies, namely the lithified facies and the non-lithified facies (Scherillo 1955). The lithified facies is yellow, highly consolidated and made of pyroclastic flows. The non-lithified facies includes pozzolana ash (gray unlithified) and lapilli layers. Morphologically, the southern sector of Casoria is the lowest lying part of the Campanian Plain. Until the nineteenth century, Casoria was characterized by swamps, which were drained and improved for agriculture.

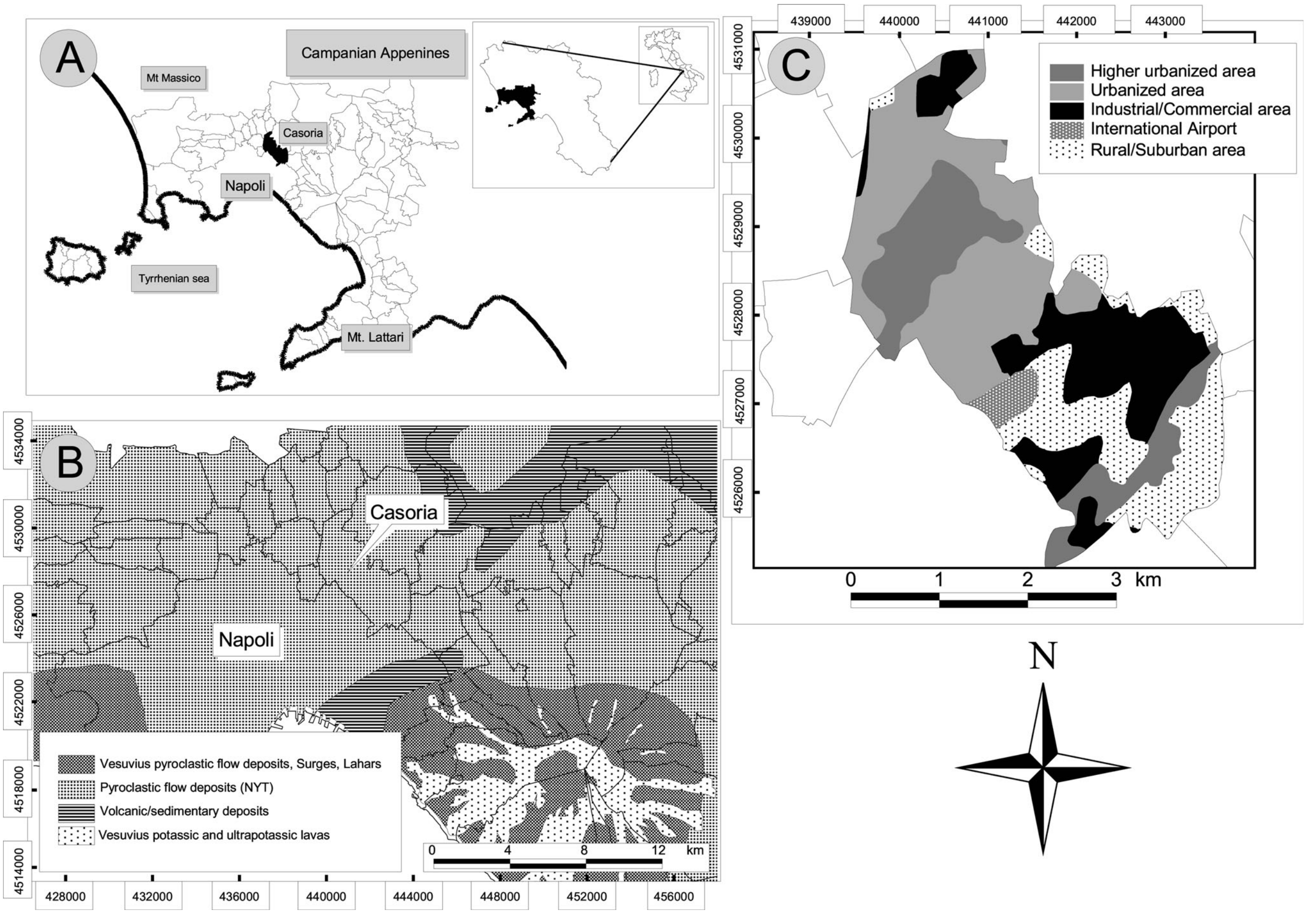

Fig. 1 **a** Map of Casoria and Neapolitan Province, **b** Geological setting of Campanian Plain, **c** Land use map of Casoria municipal area (EEA Corinne Project)

Land use

Using data collected by CORINE Land Use Project (European Environmental Agency 1985), most of Casoria is characterized as a highly urbanized area (~60 %). The northern sector of Casoria represents the oldest urban settlement, and the southern sector (Frazione Arpino) contains recent urban settlements. Industrial and commercial areas (~30 % of the total area) are located in the central-southern sectors along or close to highly used transportation routes. Rural or agriculture activities are less extensive than urban–commercial areas and often linked to family supplies and use. Local farmer business decreased as a result of municipal urbanization during the last 50 years and the increased retail trade of food supplies. Family agriculture activities are still present in the southern and northern sectors of the municipal area (Fig. 1c).

Casoria was one of the main industrial areas in the south of Italy around the middle of the last century, when important industrial centers were built. For example, petrochemical works (Montefibre-Rhodiatoce), production of chemical resins (Resia), steel manufacture (ADS—Acciaierie del Sud) and cement factories (Calcobit) are all located in this area. Also, the International Airport of Naples and supporting infrastructures represent significant possible point sources of human-derived contaminants (Fig. 2a).

Industrial development has been the main reason for the high level of urbanization of Casoria. Since the 1960s, the population increased by 30,000 inhabitants in 30 years. In the 1990s, new regional economic trends led to the closure of all the main industrial centers in Casoria. The industrial development from the 1960s to the 1990s has resulted in numerous brownfield sites in the area, representing therefore point sources of potentially high levels of metal and organic chemical contamination. According to several studies (Tarzia et al. 2002; Albanese et al. 2008; Cicchella et al. 2008; Geagea et al. 2008), the potential human health effects are at present the highest concern for the population living in Casoria.

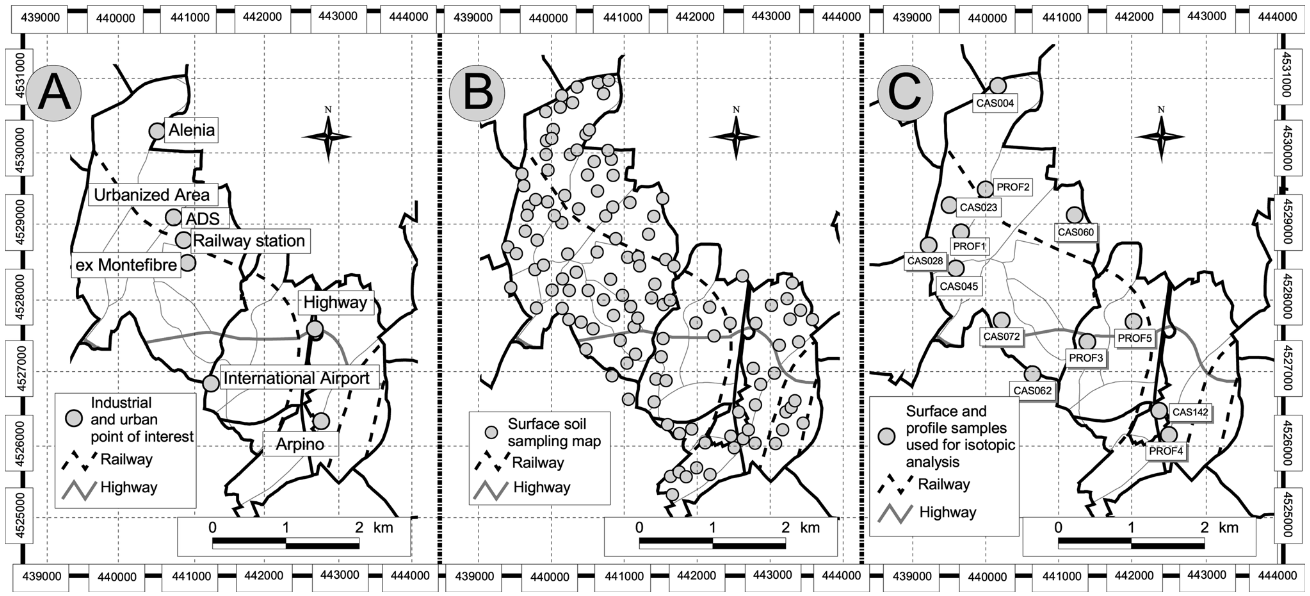

Fig. 2 **a** Casoria urbanized areas and ex-industrial settlements, **b** surface soil sampled for chemical analysis, **c** surface and profile soils sampled and analyzed for Pb isotopes

Materials and methods

Sampling

Fieldwork activity consisted of two main stages. The first working session was carried out between June and August 2008, by collecting 126 topsoil samples (depth 5–15 cm). Samples were collected following a sampling grid cell of 300 × 300 m (Fig. 2b). The protocol for soil sampling followed that used for the FOREGS project (Darnley et al. 1995; Plant et al. 1996; Salminen et al. 1998), according to European procedures, in order to link the results of this research to European and Italian geochemical cartography. A second soil sampling session was completed during July 2009; 50 samples were collected from five soil profiles (0–100 cm, 1 sample every 10 cm of depth) in areas that had been previously identified as having high Pb contents. Ten samples from 50 soil profiles (depth 0–10 and 90–100 cm) and seven selected surficial soil samples were analyzed for Pb isotopes (Fig. 2c).

Sample preparation, analyses and geochemical data elaboration

The soils were dried with infrared lamps at constant temperature <35 °C. The 126 surface soils were pulverized in a ceramic mortar and sieved to <100 mesh fraction (150 µm). The pulps were stored in plastic bags containing at least 30 g of samples and shipped to ACME Analytical Laboratories Ltd (Vancouver, Canada). The soil samples were analyzed by ICP-MS after aqua regia digestion (Cicchella et al. 2008), for 53 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr). The aqua regia approach is considered to be one of the best total dissolution processes. In fact the digestion by modified aqua regia is considered to be total for the dissolution of metals bound as water-soluble salts, in cation exchange sites, statically bound to clay particles, in organic chelates in amorphous oxides and hydroxides of Mn and Fe, in carbonates, in sulfides and some sulfates. Also, aqua regia partially dissolves metals in ferromagnesian-rich silicates and some Fe, Ti and Cr oxides. The most resistant minerals to this kind of approach are Ta, Hf, Zr, Nb and Ba bearing sulfates. About a 15-g-split of each powdered soil sample was digested in 45 ml of aqua regia (2:2:2 of $HCl:HNO_3:H_2O$) at 95 °C for about 1 h; the obtained solution was then brought to a final volume of 300 ml with 5 % HCl. Aliquots of sample solution were aspirated into a PerkinElmer Elan 6000 ICP-mass spectrometer. Instrumental detection limits (DL), accuracy and precision of the analyses are shown in Table 1.

In addition, other 50 soil samples, representing depth profiles, were prepared at the USGS Laboratories in Reston (VA, USA) to be used for Pb isotope analysis. The soils were leached using a mixture of 1.5 N HCl + 3 HNO_3 to dissolve amorphous Fe and Mn oxyhydroxides, since these minerals are considered to capture anthropogenic Pb (Ayuso et al. 2013). About 200 mg of each sample have been leached with 3 ml of acid solution, placed in an ultrasonic bath and centrifuged for 5 min. This operation

Table 1 Trace elements accuracy (A), precision (RPD) and detection limit (DL)

	A (%)	RPD (%)	DL (mg/kg)
As	0	0	0.10
Be	17	14	0.10
Cd	8	12	0.01
Co	3	1	0.10
Cr	3	7	0.50
Cu	1	2	0.01
Hg	3	11	0.005
Pb	3	2	0.01
Se	3	0	0.10
Tl	4	3	0.02
V	1	0	2.00
Zn	5	4	0.10

produced two fractions of samples: one liquid (leached, L) and one solid (residue, R). The residue samples have been directly placed on warm hot plates to dry at <50 °C, while the leached portion of the soils has been first digested in an Ethos Plus Microwave Lab Station for 15 min and then dried. Once dried, the samples have been processed and evaporated using a multistep chemistry procedure employing HNO_3, concentrated HF, 4 N HCl and 0.5 N HBr. Lead was purified using Pb exchange columns (anion exchange resin, 0.5 N HNO_3 and 0.5 N HBr) (Ayuso et al. 2013). This step was repeated in order to ensure the maximum purity of the extracted Pb.

Lead isotopic analyses on seven selected surface soils and 50 soil profiles have been processed in the Radiogenic Isotope Laboratory of the US Geological Survey (USGS) in Reston, VA. For these analyses, we used a multicollector Spectromat modified Finnigan-MAT 262 thermal ionization mass spectrometer (TIMS).

Pb was loaded on a single Re degassed filament using the method of silica gel and phosphoric acid (Ayuso et al. 2013). Isotopic mass fractionation has been constantly monitored by periodic analysis of a standard (NIST-SRM981), and the obtained isotopic ratios were corrected for mass fractionation relative to repeated runs of this standard (Ayuso et al. 2013).

Analytical data on surface soils were processed using ArcView GIS software for statistics and map elaboration, and topsoil samples geochemical maps for each of the 53 analyzed elements were produced. A univariate statistical analysis was performed on the chemical data by means of a geochemistry-dedicated GIS software GeoDAS, producing MIDW and baseline geochemical maps for each of the 53 analyzed elements, even if only select ones will be discussed. MIDW maps showing the estimated elements content in non-sampled areas and baseline maps were produced using a multifractal inverse distance weighted (MIDW) method by Cheng (1999) and (Cheng et al. 2000) available in the software GeoDAS (Cheng 2003) with a search distance of 1 km and a map resolution of 60 m. Baseline concentrations have been obtained by S-A method that use a fractal filtering technique based on Fourier spectral analysis to separate the anomalies from baseline values (Cheng 2003; Lima et al. 2003; Cicchella et al. 2005; Lima 2008).

Results

Toxic element geochemical patterns

Statistical parameters of the soils analytical data (Sinclair 1976; Reimann et al. 2002) for 53 elements are reported in Table 2, even if attention was focused on 12 toxic elements (As, Cd, Co, Cr, Cu, Hg, Pb, Sb, Se, Tl, V and Zn) for which the Italian Environmental Law (D. Lgs 152/06) fixed two limits, one for residential and recreational land use (Residential Action Limit—RAL) and the second one for industrial/commercial land use action limit (IAL). Figure 3 shows histograms and cumulative frequency curves for selected elements very harmful for human health (As, Cd and Pb). Figures 4 and 5 report MIDW and baseline maps for the 12 selected toxic elements.

The geochemical distribution of As, Cd, Pb and Zn (Fig. 4) has been considered indicative of different sources. Cd, Pb and Zn show high concentrations probably influenced by human activities, while As concentrations are mostly related to the volcanic bedrock lithologies. The geochemical background changes regionally depend on geology and nature of the overburden. The geochemical baseline (as described by Salminen and Tarvainen 1997) for an element refers to its natural variation in concentration in the surface environment, which may be a combination of natural and anthropogenic activities.

Arsenic (As)

Soils from the Neapolitan region are characterized by high As content up to 60 mg/kg (Cicchella et al. 2005). These values coincide with natural background values because of the active volcanism present in this area. The high As concentrations in the investigated soils (20–27 mg/kg) that only in a very small area exceeds the Italian RAL (of 20 mg/kg) are consistent with the local background values (Fig. 4 As).

Cadmium (Cd)

Cadmium distribution is strongly influenced by anthropogenic activity in this region, especially in the western

Table 2 Summary statistics of the entire group of 53 elements analyzed as part of this project. Please note: this includes the 12 potentially harmful elements of interest listed in Table 1

Statistical parameters							
Element	Units	Max	Min	Media	Median	Standard deviation	Skewness
Ag	µg/kg	3844.00	32.00	378.58	262.00	463.44	4.90
Al	%	5.61	1.98	4.12	4.11	0.71	−0.45
As	mg/kg	33.90	5.80	14.06	13.70	3.40	1.46
Au	µg/kg	333.50	0.50	25.78	16.20	38.09	5.37
B	mg/kg	44.00	20.00	26.07	23.00	7.73	1.91
Ba	mg/kg	2630.60	191.00	404.90	367.95	270.38	6.88
Be	mg/kg	8.40	1.80	5.12	5.10	1.30	−0.10
Bi	mg/kg	1.53	0.21	0.50	0.48	0.17	3.26
Ca	%	14.25	0.77	3.13	2.15	2.54	2.08
Cd	mg/kg	3.50	0.10	0.52	0.43	0.44	3.82
Ce	mg/kg	102.90	31.10	74.34	75.80	14.11	−0.68
Co	mg/kg	25.00	3.20	8.98	9.00	2.52	1.91
Cr	mg/kg	486.10	2.20	20.69	15.50	43.10	10.26
Cs	mg/kg	21.45	5.57	13.89	14.04	3.31	−0.20
Cu	mg/kg	1034.30	11.42	108.81	95.57	101.93	6.38
Fe	%	3.12	1.26	2.19	2.18	0.35	−0.04
Ga	mg/kg	10.90	3.50	8.13	8.35	1.52	−0.67
Ge	mg/kg	0.20	0.10	0.13	0.10	0.04	1.08
Hf	mg/kg	0.47	0.09	0.25	0.24	0.07	0.22
Hg	µg/kg	986.00	11.00	227.87	178.50	171.29	1.55
In	mg/kg	0.07	0.02	0.03	0.02	0.01	3.06
K	%	2.37	0.65	1.35	1.33	0.36	0.59
La	mg/kg	52.40	17.50	39.17	39.55	7.04	−0.69
Li	mg/kg	38.80	9.60	21.22	21.45	4.72	0.02
Mg	%	1.10	0.22	0.58	0.61	0.14	−0.37
Mn	mg/kg	978.00	332.00	658.12	663.00	113.82	−0.01
Mo	mg/kg	5.70	0.77	1.53	1.36	0.69	3.57
Na	%	1.13	0.20	0.47	0.45	0.16	1.10
Nb	mg/kg	13.35	0.87	6.33	6.32	2.66	0.26
Ni	mg/kg	70.20	3.00	14.46	14.45	6.84	4.47
P	%	1.66	0.04	0.19	0.17	0.15	7.40
Pb	mg/kg	821.42	25.28	125.70	103.14	104.65	3.93
Pd	µg/kg	119.00	10.00	28.45	17.50	27.11	2.54
Pt	µg/kg	64.00	2.00	6.68	4.00	9.06	4.59
Rb	mg/kg	211.10	71.50	141.48	142.40	34.39	0.07
Re	mg/kg	3.00	1.00	1.63	2.00	0.65	0.54
S	%	0.17	0.02	0.05	0.04	0.03	2.27
Sb	mg/kg	11.15	0.02	1.44	1.16	1.43	4.09
Sc	mg/kg	2.50	0.80	1.70	1.70	0.35	−0.07
Se	mg/kg	1.30	0.20	0.45	0.40	0.16	1.56
Sn	mg/kg	35.40	1.90	6.63	5.60	4.20	3.33
Sr	mg/kg	284.70	100.30	175.53	175.50	33.98	0.44
Te	mg/kg	0.10	0.02	0.04	0.04	0.01	0.98
Th	mg/kg	22.80	1.80	11.68	12.10	3.70	−0.10
Ti	%	0.17	0.05	0.11	0.11	0.02	−0.08
Tl	mg/kg	2.55	0.60	1.63	1.63	0.38	−0.19
U	mg/kg	6.40	1.80	3.51	3.40	0.91	0.67

Table 2 continued

Statistical parameters							
Element	Units	Max	Min	Media	Median	Standard deviation	Skewness
V	mg/kg	85.00	30.00	57.07	56.50	11.91	0.30
W	mg/kg	1.90	0.40	1.13	1.10	0.19	0.25
Y	mg/kg	17.14	5.42	11.15	11.21	1.98	−0.08
Zn	mg/kg	1765.10	42.50	199.75	141.10	211.22	4.63
Zr	mg/kg	46.20	6.30	23.45	23.30	7.85	0.36

area adjacent to the city of Naples, in which higher Cd concentrations up to 2 mg/kg (Fig. 4 Cd) have been detected. The latter, however, never exceed the Italian RAL and IAL (respectively, of 2 and 15 mg/kg). Most of soils are characterized by lower Cd concentrations between 0.1 and 0.7 mg/kg that are exactly the uncultivated soils Cd average content (Connor et al. 1975; Shacklette and Boerngen 1984).

Lead (Pb)

The highest Pb contents (182–821 mg/kg) were found in the western area of Casoria, near the border with Naples and in the urbanized area (Fig. 4 Pb). In the same areas, the Pb baseline shows the highest values (126–158 and 158–206 mg/kg). A large portion of the investigated area exceeds the Italian RAL (of 100 mg/kg). The lowest Pb content found is higher than uncultivated soils Pb average content (2.5–25 mg/kg; Connor et al. 1975; Shacklette and Boerngen 1984), likely due to the background volcanic rocks as well.

Zinc (Zn)

High zinc values (up to 1765 mg/kg) are found in the western sector of Casoria, in the urbanized area and near the highway (Fig. 4 Zn). The distribution of Zn overlaps that of Cd and Pb, with higher Zn concentrations (213–419 mg/kg) observed in the mostly urbanized portion along the border with Naples. Soils of the suburban areas show Zn concentrations (23–125 mg/kg) in line with uncultivated soils Zn average content (25–67 mg/kg; Connor et al. 1975; Shacklette and Boerngen 1984). Most of the soil samples exceed Italian RAL (150 mg/kg), and only few samples exceed Italian IAL (1500 mg/kg).

Geochemical distributions of other potential toxic element like Sb, Cr, Co, Cu, Hg, Se, Tl and V (Fig. 5) can be indicative of natural and anthropic sources as well.

Antimony (Sb)

Casoria soils show the highest contents of Sb (2.72–11 mg/kg) in its urban areas, near the border with Naples (Fig. 5 Sb). Suburban and rural areas have Sb contents being considered the natural background values (0.5–1 mg/kg) (Cicchella et al. 2005). Only in a very small area, Sb content exceeds the Italian RAL (of 10 mg/kg).

Chromium (Cr)

The spatial distribution of Cr (Fig. 5 Cr) shows the highest values (158–300 mg/kg) in the southern sector of Casoria. Suburban northern, central and eastern areas are characterized by values that can be assumed to represent the natural background of all the Naples territory (5–15 mg/kg) (Cicchella et al. 2005). Only in a very small area, Cr content exceeds the Italian RAL (of 150 mg/kg).

Cobalt (Co)

The spatial distribution of Co values (Fig. 5 Co) in Casoria area shows the same trends of the Neapolitan volcanic soils (highest values range 12–19 mg/kg). Almost all the values of the Casoria municipal area are totally coherent with Neapolitan soils background values (3–14 mg/kg) (Cicchella et al. 2005). No sample exceeds Italian Action Limits.

Copper (Cu)

Copper anomalous values are present in the southern sector of the Casoria territory (Arpino) and locally in the northeast urbanized area (Fig. 5 Cu) showing the influence of anthropogenic pollution (218–636 mg/kg). Copper values that characterize the rest of the Casoria municipal soils can be assumed to represent the natural background levels, coherently with the Neapolitan soils (20–120 mg/kg) (Cicchella et al. 2005). Most of the soil samples exceed Italian RAL (120 mg/kg), and only few samples exceed Italian IAL (600 mg/kg).

Mercury (Hg)

The highest Hg contents (0.38–0.98 mg/kg) occur in the highly urbanized areas and near Capodichino international

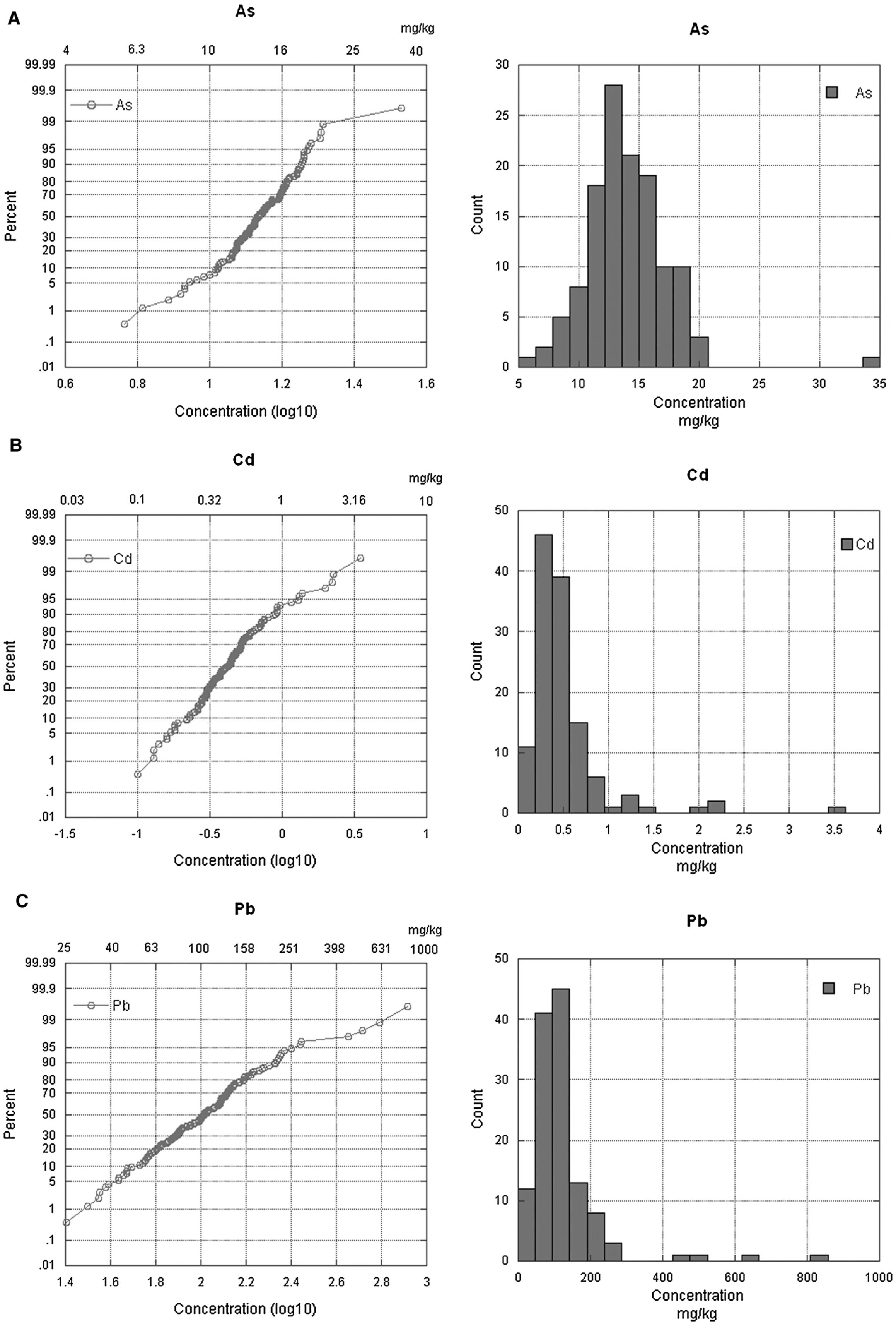

Fig. 3 Histograms and cumulative frequency *curves* of As, Cd and Pb

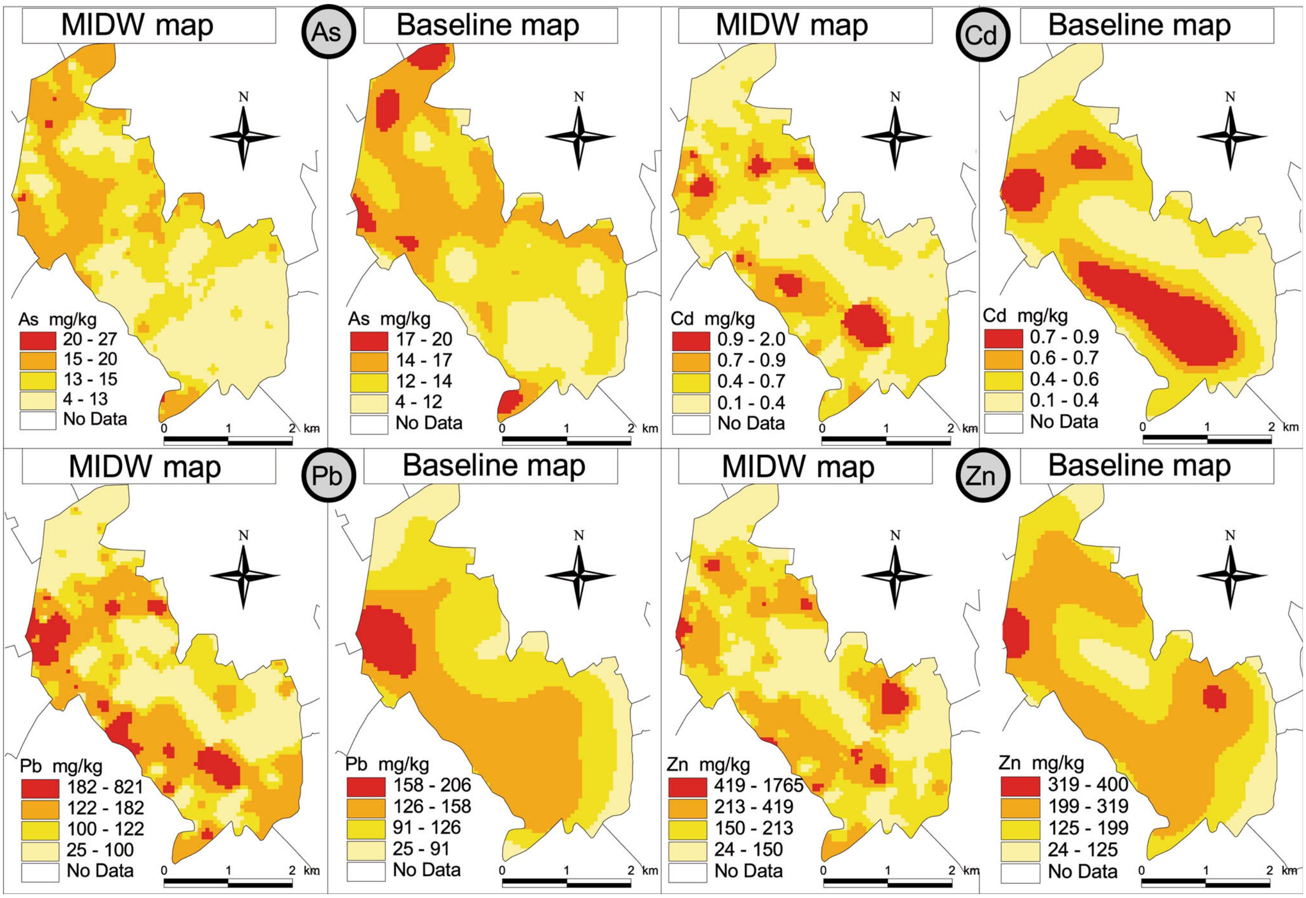

Fig. 4 Interpolated and baseline maps of As, Cd, Pb and Zn

airport and the highway. The soils of the suburban areas are characterized by values that are identified as the natural background in the Neapolitan territory (0.05–0.2 mg/kg) (Cicchella et al. 2005) (Fig. 5 Hg). No sample exceeds Italian Action Limits.

Selenium (Se)

The soils of the whole Casoria territory (Fig. 5 Se) are characterized by values (0.63–1.3 mg/kg) considered as coincident with natural background values for soils of the entire Neapolitan area (0.2–1.1 mg/kg) (Cicchella et al. 2005). No sample exceeds Italian Action Limits.

Thallium (Tl)

The spatial distribution of Tl concentration (Fig. 5 Tl) (highest values range 2–2.5 mg/kg) in the soils of Casoria (as for the entire Neapolitan area) indicates that the Tl is strictly geogenic, being related to the alkalic nature of the Neapolitan volcanic rocks (1.7–2.7 mg/kg). For this reason, even if almost all soils exceed Italian RAL (mg/kg), the obtained values represent no concern for the population's health.

Vanadium (V)

Vanadium higher contents (70–85 mg/kg) are found in the central-southern sector of Casoria municipal area from the international airport to the highway (Fig. 5 V). According to the literature, these values reflect mostly a geogenic source (30–120 mg/kg) (Cicchella et al. 2005), but at least locally, some high values might be influenced by anthropogenic activities (airport, vehicular traffic). No sample exceeds Italian Action Limits.

Contamination factor and degree of contamination

The degree of contamination due to potential harmful elements such as Pb, Zn, Cd needs to be quantified and spatially bounded to support the ecological risk assessment (ERA) process. In this work, *contamination factor* (C_f^i) has been calculated, on a GIS basis, for the considered harmful element, to evaluate the effects on the urban/suburban

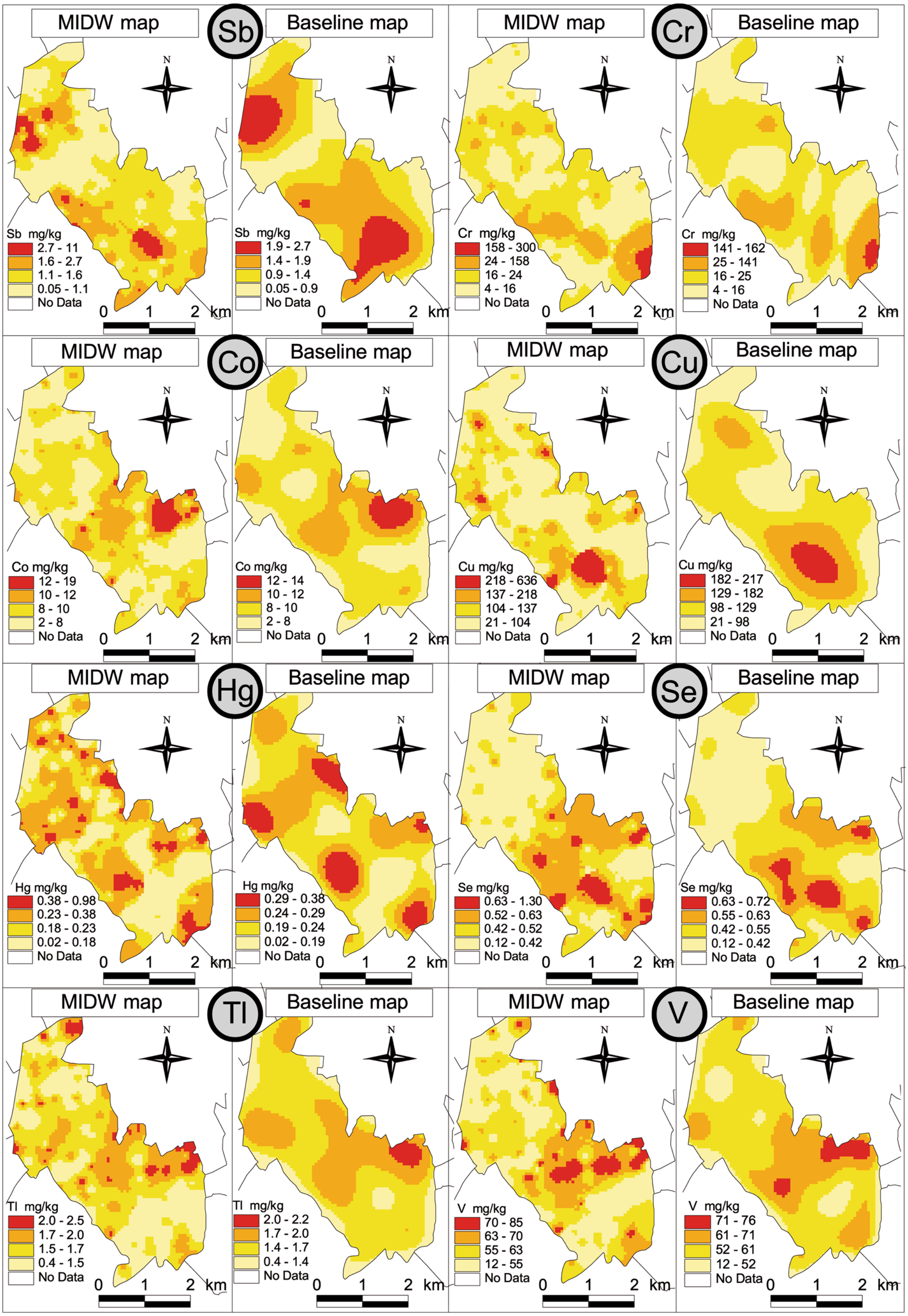

Fig. 5 Interpolated and baseline maps of Sb, Cr, Co, Cu, Hg, Se, Tl and V

environment of Casoria due to anthropic activities. It expresses a potential ecological hazard of a given contaminant in relation to a given area (Håkanson 1980).

The original formula to calculate the *contamination factor* is as follows:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

where C_{0-1}^i is the mean content of the substance i from at least 5 sample sites, and C_n^i is the pre-industrial reference level for the substance.

The C_f^i for the evaluation of each element has been obtained in a GIS environment (ArcView GIS 3.2), by dividing the interpolated grid of elemental concentration by the background value of the element in Neapolitan volcanic soils (Cicchella et al. 2008), assumed to be as pre-industrial reference level.

The following terminologies have been used to describe the grade of contamination determined by means of C_f^i:

$C_f^i < 1$, low contamination; $1 \leq C_f^i < 3$, moderate contamination; $3 \leq C_f^i < 6$, considerable contamination; $C_f^i \geq 6$, very high contamination.

Observed *contamination factor* (C_f^i) for Cd shows considerable and very high values of contamination (ranging from 3 to 6 and > 6) in the urbanized historical city area, in the western area and in southern urbanized area of Arpino. The suburban eastern and northern areas present low and moderate contamination factor (<3) (Fig. 6a).

Pb *contamination factor* (C_f^i) shows considerable and very high values of contamination (ranging from 3 to 6 and >6) in the western area on the border of Naples in the urbanized area and in southern urbanized area of Arpino. Moderate and low level of contamination (<3) is present in the eastern and northern suburban and rural areas (Fig. 6b).

Zn *contamination factor* (C_f^i) shows the same pattern of the previous elements; higher and considerable levels of contamination (ranging from 3 to 6 and >6) are detected in the urbanized areas, in the western area on the border of Naples and in southern urbanized area of Arpino. Northern and eastern suburban and rural areas show low and moderate level of contamination factor (<3), whereas high-considerable level of C_f^i is detected only near the highway (Fig. 6c).

The total *degree of contamination* (C_d), is the sum of all contamination factors (C_f) for a given area.

$$C_d = \sum_{i=1}^{3} \quad C_f^i = \sum_{i=1}^{3} \frac{C_{0-1}^i}{C_n^i}$$

With this approach, contamination factor (C_f) was obtained, which accounts for the contamination of single elements according to the concentration requirement, and a C_d value, which accounts for the total of the sediment pollution within an area. Elements that should be considered are PCB, Hg, Cd, Pb, As, Cr, Cu, Zn (Håkanson 1980).

In the Casoria territory were considered only 3 elements (Pb, Cd, Zn), which show the higher anthropic influence. The following terminology may be used to describe the degree of contamination (for 3 elements):

$C_d < 3$ = low degree of contamination; $3 < C_d < 6$ = moderate degree of contamination; $6 < C_d < 12$ = considerable degree of contamination; $C_d > 12$ = extreme degree of contamination.

The different *degrees of contamination* (C_d) show that considerable to extreme values (ranging from 6 to 12 and $C_d > 12$) characterize the municipal areas with some extreme values in correspondence of the shared administrative boundary of Naples, the northern historical center, the Arpino urban area and the highway area. Low and moderate degree of contamination is locally detected in the northern and eastern suburban and rural areas (Fig. 6d).

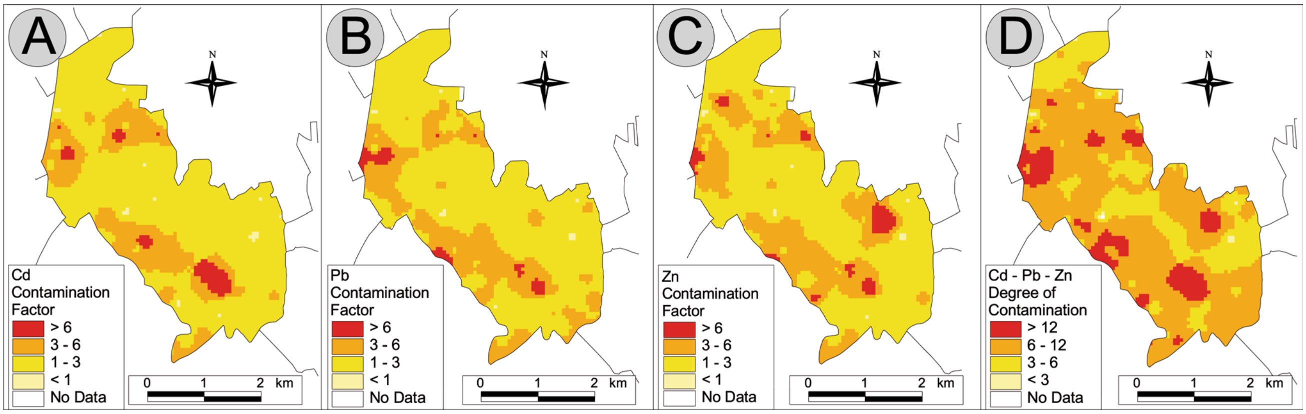

Fig. 6 **a**, **b** and **c** contamination factor (C_f^i) maps for Cd, Pb and Zn, **d** degree of contamination (C_d) map

Table 3 Casoria Pb isotopic ratios ($^{208}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$) for surface and profile soils. The letters L or R near sample ID indicate leach or residue

Sample	Pb^{208}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{206}/Pb^{204}	Pb^{208}/Pb^{207}	Pb^{206}/Pb^{207}
CAS004 L	38.773	15.633	18.775	2.480	1.201
CAS060 L	38.007	15.551	18.157	2.444	1.168
CAS023 L	37.611	15.507	17.929	2.425	1.156
CAS028 L	38.021	15.562	18.120	2.443	1.164
CAS045 L	37.679	15.524	17.920	2.427	1.154
CAS062 L	37.772	15.527	18.021	2.433	1.161
CAS072 L	37.511	15.507	17.856	2.419	1.151
CAS142 L	37.694	15.525	17.930	2.428	1.155
Profilo 1 0–10 L	38.192	15.559	18.343	2.455	1.179
Profilo 2 0–10 L	38.213	15.564	18.351	2.455	1.179
Profilo 3 0–10 L	38.058	15.558	18.216	2.446	1.171
Profilo 4 0–10 L	37.945	15.552	18.116	2.440	1.165
Profilo 5 0–10 L	37.934	15.552	18.139	2.439	1.166
Profilo 1 0–10 R	37.921	15.543	18.112	2.440	1.165
Profilo 2 0–10 R	38.441	15.578	18.537	2.468	1.190
Profilo 3 0–10 R	38.200	15.549	18.376	2.457	1.182
Profilo 4 0–0 R	38.291	15.569	18.445	2.460	1.185
Profilo 5 0–0 R	38.548	15.597	18.640	2.472	1.195
Profilo 1 90–100 L	37.877	15.552	18.029	2.435	1.159
Profilo 2 90–100 L	37.579	15.515	17.872	2.422	1.152
Profilo 3 90–100 L	38.084	15.562	18.224	2.447	1.171
Profilo 4 90–100 L	37.958	15.556	18.114	2.440	1.164
Profilo 5 90–100 L	37.778	15.527	18.018	2.433	1.160
Profilo 1 90–100 R	38.326	15.582	18.437	2.460	1.183
Profilo 2 90–100 R	37.759	15.538	18.000	2.430	1.158
Profilo 3 90–100 R	38.346	15.572	18.497	2.463	1.188

Lead isotopic composition and anthropogenic factor

Lead isotopic ratios for surface and profile soils (Table 3) are plotted in Figs. 7, 8 and 9. The letters L or R near sample ID (Table 3) distinguish the leach and residue sample compositions, obtained by chemical preparation. Leach (L) samples represent the portion of Pb that is readily leached from grains of soils and reflects possible anthropogenic contamination, whereas residue (R) samples represent the residual portion of soils and reveal Pb compositions of geogenic origin (Ayuso et al. 2008, 2013). Diagrams in Figs. 7, 8 and 9 show $^{208}Pb/^{207}Pb$ vs $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ ratios of soils from Casoria and from three pesticides commonly used in the studied area: Azin Pb30, Crittam WG and Cosan's (Ayuso et al. 2004; Bove et al. 2011; Grezzi et al. 2011); geologic and anthropogenic end-members from the literature are also shown.

Leached soil samples have isotopic compositions resembling Pb signature of aerosols and brownfield soils (Naples); only one soil sample (CAS004) shows an isotopic composition similar to the Neapolitan volcanic rocks (Vesuvius and Phlegraean Fields) (Fig. 7).

Figure 8 shows isotopic ratios for 5 soil profiles. Aliquots of leached and residue soils from 0 to 10 cm depth (the near-surface soils) show that Pb isotopic ratios overlap and define a regular trend. The residues are shifted toward the geologic Pb isotope signature and the leached aliquots plot closer to aerosol values. This level of soil profile shows the same trend of surface soils, with the isotopic signature typical of Neapolitan urbanized and industrialized (Bagnoli brownfield) soils (Tarzia et al. 2002; Cicchella et al. 2008).

Figure 9 shows Pb isotopic ratios for 5 soil profiles at depth of 90–100 cm. Residues were analyzed for 3 profile samples (# 1-2-3). Leached and residue Pb isotopic ratios show a similar trend with profile samples at depth 0–10 cm. Lead isotopic ratios of leach and residues (depth 90–100 cm) overlap and define a regular trend in which residues span more toward the geologic end-member field, and leached aliquots are closer to the aerosol values. The deep soil horizon composition indicates that metal contamination, especially Pb, is leached from the surface to deeper soil levels (Bove et al. 2011; Grezzi et al. 2011).

Lead isotopic composition (Pb^{208}/Pb^{207} versus Pb^{206}/Pb^{207}) of surface and soil profiles shows a high

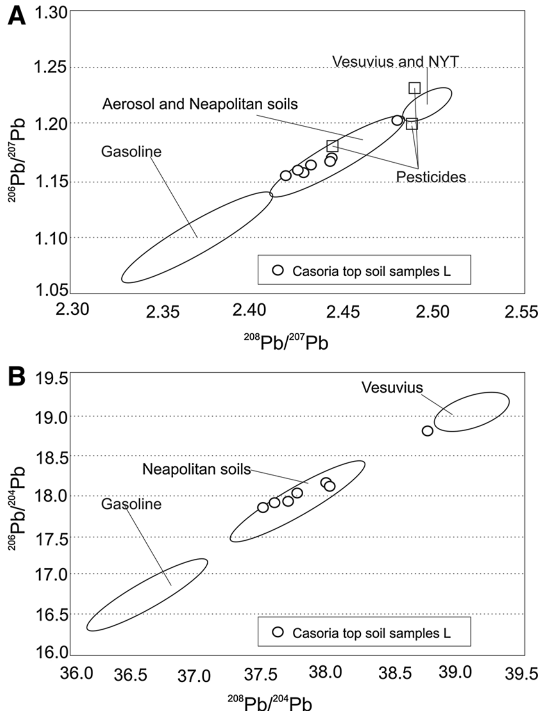

Fig. 7 Pb isotope composition of surface soil samples diagrams (Pb^{208}/Pb^{207} vs. Pb^{206}/Pb^{207}, **b** Pb^{206}/Pb^{204} vs. Pb^{208}/Pb^{204}). The *plots* show data for volcanic deposits from Vesuvius (Ayuso et al. 1998) and the NYT (Campi Flegrei) (D'Antonio et al. 1995, 2007), gasoline (Monna et al. 1997, 1999; Chiaradia and Cupelin 1999), aerosol deposits (Monna et al. 1999; Tommasini et al. 2000; Geagea et al. 2008), Bagnoli brownfield soils (Tarzia et al. 2002) and Neapolitan soils (Cicchella et al. 2008)

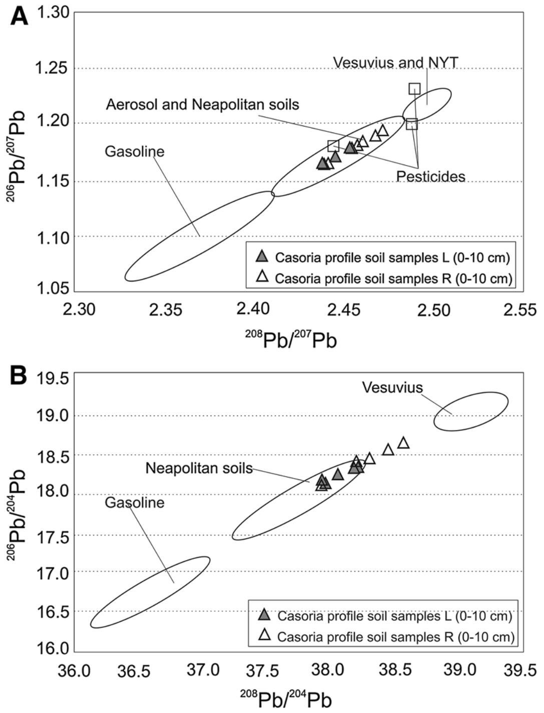

Fig. 8 Soil profiles samples (depth 0–10 cm) Pb isotopic ratio (**a** Pb^{208}/Pb^{207} vs. Pb^{206}/Pb^{207}, **b** Pb^{206}/Pb^{204} vs. Pb^{208}/Pb^{204}). The plots show data for volcanic deposits from Vesuvius (Ayuso et al. 1998) and the NYT (Campi Flegrei) (D'Antonio et al. 1995, 2007), gasoline (Monna et al. 1997, 1999; Chiaradia and Cupelin 1999), aerosol deposits (Monna et al. 1999; Tommasini et al. 2000, Geagea et al. 2008), Bagnoli brownfield soils (Tarzia et al. 2002) and Neapolitan soils (Cicchella et al. 2008)

correlation with industrial highly urbanized soils and aerosol depositions. In particular, Pb-rich gasoline that was used until the 1990s likely has influenced Pb isotopic signature of urban soils (Von Storch et al. 2002). In the case of Casoria, we have used two isotopic end-members (anthropogenic and geogenic) to calculate the anthropic fraction of the Pb isotopic contents of analyzed samples.

We have considered the average of $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ ratios of gasoline from the literature (Monna et al. 1997, 1999; Chiaradia and Cupelin 1999) as the anthropogenic end-member. For the geogenic end-member, we have considered the average of $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios of Vesuvius volcanic rocks (Ayuso et al. 1998).

The $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ systematics shows a good positive correlation between the analyzed soils and the two mentioned end-members (Fig. 10). The linear regression fitting the Pb isotopic trend is:

$$Pb^{206}/Pb^{207} = 0.9111\,Pb^{208}/Pb^{207} - 1.0576$$

This linear equation shows a correlation coefficient (R^2) of 0.9881. Based on this equation, we have recalculated the *y* values ($^{206}Pb/^{207}Pb$ isotopic ratios) of end-members and Casoria samples. We have calculated the distance (*d*) between geogenic end-member and the other data points (based on Pythagoras Theorem). Using the lever rule, we calculated the anthropogenic fraction of our samples by considering the distance $\Delta_{n\text{-}a}$ (with n = natural end-member and a = anthropogenic) as the 100 % natural (Table 4).

The estimated anthropogenic fractions indicate that the origin of Pb contamination in soils from Casoria is connected to human activities (e.g., gasoline and industrial activity).

The anthropogenic fractions of our surface soil samples range from 41 to 58 % with one exception (sample CAS004) that is less influenced by anthropogenic Pb (12 %).

Topsoil profiles (0–10 cm) show Pb isotopic compositions similar to those of the surface soils from Casoria and Neapolitan urbanized/industrialized areas (Bagnoli brownfield; Tarzia et al. 2002). Leached samples (L) show percentage of anthropogenic fractions varying from 31 to 43 %. Although the Pb isotopic compositions of residue samples (R) overlap with those of leached sample (L), some residue samples extend more through the geogenic end-member, ranging from 18 to 43 %.

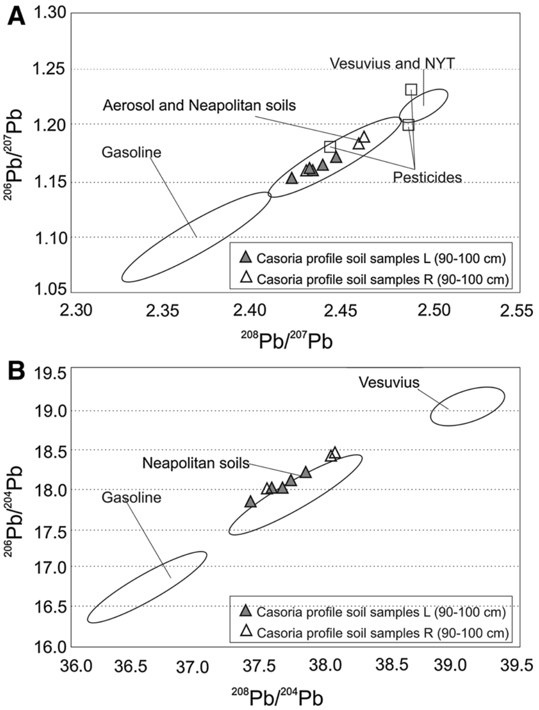

Fig. 9 Soil profile samples (depth 90–100 cm) Pb isotopic ratio (**a** Pb^{208}/Pb^{207} vs. Pb^{206}/Pb^{207}, **b** Pb^{206}/Pb^{204} vs. Pb^{208}/Pb^{204}). The plots show data for volcanic deposits from Vesuvius (Ayuso et al. 1998) and the NYT (Campi Flegrei) (D'Antonio et al. 1995, 2007), gasoline (Monna et al. 1997, 1999; Chiaradia and Cupelin 1999), aerosol deposits (Monna et al. 1999; Tommasini et al. 2000, Geagea et al. 2008), Bagnoli brownfield soils (Tarzia et al. 2002) and Neapolitan soils (Cicchella et al. 2008)

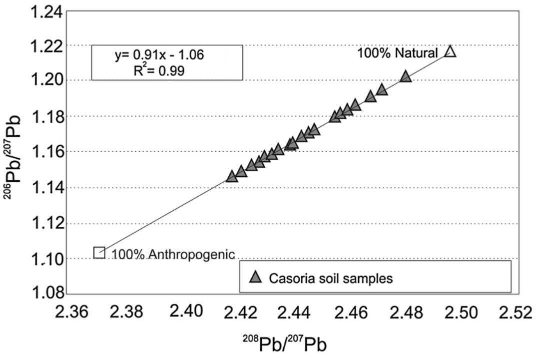

Fig. 10 Isotopic plot recalculated for anthropic fraction (ratios: Pb^{208}/Pb^{207} vs. Pb^{206}/Pb^{207}). The anthropogenic end-members used are gasoline $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratio (Monna et al. 1997, 1999; Chiaradia and Cupelin 1999). For the geogenic end-member, we have considered the average of $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios of Vesuvius volcanic rocks (Ayuso et al. 1998)

Lead isotopic compositions of bottom soil profiles (90–100 cm depth) show the same trend defined by Pb isotopic compositions of surface soil samples and topsoil profiles (sampled at 0–10 cm depth). The calculated anthropogenic fractions of bottom soil-leached profiles (L) range from 38 to 56 %, indicating that the anthropogenic Pb contamination is leached from the surface to deepest levels (e.g., 90–100 cm depth). Consistently with residues of topsoil profiles, Pb isotopic compositions of three residues of bottom soil profiles extend closer to the geogenic end-member (anthropogenic fraction from 50 to 25 %).

Discussion

The higher concentration of Pb, Zn and Cd detected in the western area of the border of Naples is coherent with anthropogenic influence in the Neapolitan area (Cicchella et al. 2005). Geogenic contribution is evident in soils from the northeast suburban and rural areas of Casoria, in which trace element concentrations can be assumed to represent the natural background values of Neapolitan volcanic area soils (Cicchella et al. 2005).

Baseline geochemical elaboration confirms that the concentrations of trace elements detected are coherent with the Neapolitan province, in which an anthropogenic contribution made by different sources (vehicular traffic and industrial activities) overlaps the geogenic one (Cicchella et al. 2005).

Contamination factors (C_f^i) and *degrees of contamination* (C_d) values (Håkanson 1980) calculated for Zn, Pb and Cd show higher levels of contamination in the urbanized areas and in the administrative boundary of Naples. Suburban and rural areas located in the northeast show moderate and low levels of contamination, confirming the potential anthropogenic contribution detected by the geochemical data and the potential health risk of the inhabitants of Casoria urbanized areas.

Previous studies found that the urbanized and industrialized areas of the Neapolitan province have Pb contents that mainly reflect an anthropogenic source (Cicchella et al. 2005, 2008; De Vivo et al. 2006). To confirm the geochemical information made by the chemical analysis on trace elements, we compare Pb^{206}/Pb^{204} versus Pb^{208}/Pb^{204} isotopic ratio from Neapolitan area (Pb^{206}/Pb^{204} range 18.372–17.624; Pb^{208}/Pb^{204} range 38.485–37.359) and Casoria (Pb^{206}/Pb^{204} range 18.774–17.885; Pb^{208}/Pb^{204} range 38.773–37.510). Surface soils and soil profiles from Casoria show Pb^{206}/Pb^{204} versus Pb^{208}/Pb^{204} isotopic ratios overlapping those of the Neapolitan soils (Figs. 6, 7, 8) detected by Cicchella et al. (2008), showing the same Pb isotopic composition and source. As reported in the literature, Pb concentrations in Neapolitan soils are mainly influenced by anthropogenic activity related to the high levels of urbanization and industrialization (De Vivo et al. 2006; Cicchella et al. 2008). Casoria soils should be considered as part of the same trend.

Table 4 Casoria Pb isotopes samples ID, ratios ($^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$) distance (*d*) and anthropic fraction (AF%)

Sample ID	Pb^{208}/Pb^{207}	Pb^{206}/Pb^{207}	Recalculated y	Delta x	Delta y	*d*	Average %
CAS004 L	2.480	1.201	1.202	0.016	0.012	0.020	12
CAS060 L	2.444	1.168	1.169	0.052	0.046	0.069	40
CAS023 L	2.425	1.156	1.152	0.070	0.057	0.091	53
CAS028 L	2.443	1.164	1.168	0.053	0.049	0.072	42
CAS045 L	2.427	1.154	1.154	0.069	0.059	0.090	51
CAS062 L	2.433	1.161	1.159	0.063	0.053	0.082	48
CAS072 L	2.419	1.151	1.146	0.077	0.062	0.099	57
CAS142 L	2.428	1.155	1.155	0.068	0.058	0.089	52
Profilo 1 0–10 R	2.440	1.165	1.165	0.056	0.048	0.074	43
Profilo 2 0–10 R	2.468	1.190	1.191	0.028	0.023	0.036	21
Profilo 3 0–10 R	2.457	1.182	1.181	0.039	0.032	0.050	29
Profilo 4 0–10 R	2.460	1.185	1.183	0.036	0.029	0.046	27
Profilo 5 0–10 R	2.472	1.195	1.194	0.024	0.018	0.030	18
Profilo 1 90–100 R	2.460	1.183	1.183	0.036	0.030	0.047	27
Profilo 2 90–100 R	2.430	1.158	1.156	0.066	0.055	0.086	50
Profilo 3 90–100 R	2.463	1.188	1.186	0.033	0.026	0.042	24
Profilo 1 0–10 L	2.455	1.179	1.179	0.041	0.034	0.054	31
Profilo 2 0–10 L	2.455	1.179	1.179	0.041	0.034	0.053	31
Profilo 3 0–10 L	2.446	1.171	1.171	0.050	0.042	0.065	38
Profilo 4 0–10 L	2.440	1.165	1.165	0.056	0.048	0.074	43
Profilo 5 0–10 L	2.439	1.166	1.165	0.057	0.047	0.073	43
Profilo 1 90–100 L	2.435	1.159	1.161	0.060	0.054	0.081	47
Profilo 2 90–100 L	2.422	1.152	1.149	0.074	0.061	0.096	56
Profilo 3 90–100 L	2.447	1.171	1.172	0.049	0.042	0.064	38
Profilo 4 90–100 L	2.440	1.164	1.166	0.056	0.049	0.074	43
Profilo 5 90–100 L	2.433	1.160	1.159	0.063	0.053	0.082	48
Natural average	2.496	1.213	1.216				
Gasoline average	2.371	1.097	1.103	0.124	0.116	0.170	100

The Pb isotope investigation demonstrates that urban vehicular traffic and industrial aerosol are the main sources of metal pollution (Cicchella et al. 2008); the anthropogenic fraction of Pb shows values between 41 and 58 % in surface soil samples (with exception of CAS004 soil sample), and profile soil samples show similar % values.

Sample CAS004 shows high affinity with the geological isotopic signature of the bedrock (Ayuso et al. 1998; D'Antonio et al. 1995). The bedrock consists of pyroclastic rocks and lavas from Vesuvius and Campi Flegrei volcanoes (Somma et al. 2001; De Vivo et al. 2001 and reference therein). Sample CAS004 was collected in the northern area of Casoria where no apparent Pb contamination is present (i.e., where there is a lack of anthropic activity). The correlation between the uncontaminated areas detected by geochemical and statistical analysis and the predominant geogenic signature (Sample CAS004) detected by the Pb isotopic content is consistent.

It is possible to divide the area around Casoria into two different sectors, with two isotopic signatures:

- One controlled by bedrock lithology (northern and southeastern areas), with low Cd, Pb and Zn concentrations, where surface soils are characterized by lower anthropogenic fraction (12 %).
- One strongly influenced by anthropogenic activities (urbanized western area on the border of Naples) where potentially harmful heavy metals (e.g., Pb and Zn) show higher concentrations than the background, with surface soils characterized by higher anthropogenic fraction (41–58 %).

Conclusion

Trace metal concentration data were obtained for 126 soil samples. Geochemical maps were compiled using a MIDW interpolation method and spectral analysis (S-A) using a geochemistry-dedicated GIS (GeoDAS). In the Neapolitan region, soil geochemical baselines average the contribution of geogenic material (background) and the geochemical contamination from human activities (anthropogenic). Maps obtained by the S-A method point to high baseline concentrations for some toxic elements (Pb, Zn, Sb, Hg, Cd, Cr and Cu), and the anthropogenic impact is particularly evident for some elements (Pb, Zn, Hg and Cd). Contamination factors and degree of contamination calculated for Cd, Pb and Zn show high and extremely high levels in the urbanized and industrial areas.

Casoria can be divided into three main environmental sectors on the basis of potential harmful elements spatial distribution and correlation. The highest urbanized sectors of Casoria (historical urban center, Arpino village, international airport, highway) and the western area, along the shared administrative boundary with Naples, show Cd, Hg, Pb, Zn highest concentration. These concentrations are higher than the natural background, with contamination factor (C_f^i) and degrees of contamination (C_d) calculated for Cd, Pb and Zn ranging from considerable to very high values.

The south and southeast sectors of Casoria (suburbs and residential area of the Arpino) show Cu, Cr, Sb and V higher values, probably influenced by rural and anthropic activities. This area shows moderate to considerable contamination factor (C_f^i) for Cd, Pb and Zn and degrees of contamination (C_d) ranging from considerable to very high values.

As, Co, Se and Tl are coherent with natural background values for soils of the entire Neapolitan area.

Geochemical distribution of the potential toxic elements shows the lowest values of concentration in the northern, central and southeastern sectors. In these suburban and rural areas, values seem to be clearly influenced by volcanic bedrock lithology and less influenced by anthropic activities. These areas show moderate contamination factor (C_f^i) and degrees of contamination (C_d).

This pronounced spatial correlation between anthropogenic activities and high concentrations of Cd, Pb, Zn is corroborated by Pb isotopic composition of soils. In fact, Pb isotopic compositions were used to determine the anthropogenic impact on soils and soil profiles and confirm that Pb from anthropogenic sources modified the Pb from natural bedrock. Pb in surface soils from the urbanized and industrialized areas of Casoria show anthropogenic signature in a range 41–58 %. For the sample CAS004, the anthropogenic factor is 12 %, which confirms the influence of the bedrock on soils in the northern part of Casoria (less urbanized, used for non-intensive agriculture).

Anthropogenic contamination is confirmed by the soil profiles isotopic ratio: Leached samples (L) anthropogenic fraction is in a range 31–43 % (topsoils) and 38–56 % (bottom soils), showing a potential leaching of Pb from the topsoil to the bottom soil due to the solubility and mobility of Pb from gasoline.

Residues (R) are shifted toward the geologic signature with lower anthropogenic fractions in the range from 18–43 % (topsoils) and 25–50 % (bottom soils).

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