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Geochemical and Pb isotopic characterization of soil, groundwater, human hair, and corn samples from the Domizio Flegreo and Agro Aversano area (Campania region, Italy)

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ABSTRACT

A geochemical survey was carried out to investigate metal contamination in the Domizio Littoral and Agro Aversano area (Southern Italy) by means of soil, groundwater, human hair and corn samples. Pb isotope ratios were also determined to identify the sources of metals. Specifically, the investigation focused on topsoils ($n = 1064$), groundwater ($n = 26$), 25 human hair ($n = 24$) and corn samples ($n = 13$). Topsoils have been sampled and analysed in a previous study for 53 elements (including potentially harmful ones), and determined by ICP-MS after dissolving with aqua regia. Groundwater was analysed for 72 elements by ICP-MS and by ICP-ES. Samples of human hair were prepared and analysed for 16 elements by ICP-MS. Dried corn collected at several farms were also analysed for 53 elements by ICP-MS. The isotopic ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in selected topsoil ($n = 24$), groundwater ($n = 9$), human hair ($n = 9$) and corn ($n = 4$) samples were analysed from both eluates and residues to investigate possible anthropogenic contamination and geogenic contributions. All data were processed and mapped by ArcGis software to produce interpolated maps and contamination factor maps of potentially harmful elements, in accordance with Italian Environmental Law (Legislative Decree 152/06). Results show that soil sampling sites are characterized by As, Cd, Co, Cr, Cu, Hg, Pb, Se, and Zn contents exceeding the action limits established for residential land use (RAL) and, in some cases, also the action limits for industrial land use (IAL) as established by Legislative Decree 152/06. A map of contamination factors and a map showing the degrees of contamination indicate that the areas in the municipalities of Acerra, Casoria and Giugliano have been affected by considerable anthropogenic-related pollution. To interpret the isotopic data and roughly estimate proportion of Pb from an anthropogenic source we broadly defined possible natural and anthropogenic Pb end-member fields based on literature data. For example, we summarized data for Vesuvius and Campi Flegrei volcanic rocks, gasoline, and aerosol deposits.

Lead isotope data show mixing between geogenic and anthropogenic sources. Topsoil, groundwater, human hair and corn samples show a greater contribution from geogenic sources like the Yellow Tuff (from Campi Flegrei) and volcanic rocks from Mt. Vesuvius. Aerosols, fly ash and gasoline (anthropogenic sources) have also been contributors. In detail, 46% of the topsoil residues, 96% of topsoil leachates, 88% of groundwater, 90% of human hair, and 25% of corn samples indicate that >50% percent of the lead in this area can be ascribed to anthropogenic activity.

1. Introduction

This paper presents the results of a comprehensive geochemical study of the Domizio Littoral and Agro Aversano area (Southern Italy) based on analyses of topsoil, groundwater, vegetable (corn) and human hair samples, conducted in order to determine the impact of human activities on the environment. Preceding studies have documented the heavy metal pollution of topsoils across this area (Albanese et al., 2011; Bove et al., 2011; Grezzi et al., 2011; Lima et al., 2012) as well as an increased rate of cancer mortality compared to the regional average (Senior and Mazza, 2004). Many studies in recent years have focused on environmental issues using isotope ratios of lead. (Ayuso et al., 2013; Ayuso and Foley, 2016; Chen et al., 2016; Galušková et al., 2014; Jiao et al., 2015; Kumar et al., 2013). The $^{206}Pb/^{207}Pb$ ratio is the most commonly used as tracer of environmental pollution sources because it can be precisely determined (Komárek et al., 2008). A detailed study of Pb isotope ratios was used as a key method to discriminate and apportion

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the contribution of various sources (Duzgoren-Aydin and Weiss, 2008). This is possible because the composition of lead resulting from burning of fossil fuels, lead emanating from industrial sources and lead contributed by the use of pesticides (Ayuso et al., 2004; Cheng and Hu, 2010) can be estimated for comparison,

The Domizio Flegreo Littoral and Agro Aversano area is located in northwestern Campania in an area that is of continuous environmental concern due to illegal dumping and burning of waste since the 1990s. This area is also characterized by a high degree of urbanization and by continuously changing land-use patterns. The isotopic composition of anthropogenic Pb sources has been investigated recently in the region. Bove et al. (2011) showed that topsoil, surface water and groundwater have been influenced in various ways by human-derived pollution in the Agro-Aversano's area. They showed a considerable anthropic influence recorded by the soil isotopic compositions, in agreement with previous studies of soils in the Domizio Flegreo-Litorall (Grezzi et al., 2011).The isotopic compositions have proven very useful to improve geo-environmental characterization throughout the region and to discriminate different sources of pollution in different media.

The aims of this study are to determine the degree of contamination in the area and provide a preliminary attempt to quantitatively identify the influence of possible pollution sources. In our study, Geographic Information System (GIS) and related spatial analysis served as an important tool to generate a georeferenced geochemical database, to produce interpolated maps of the distribution of the different elements, and to assess the degree of contamination in the study area.

2. Study area

The Domizio Flegreo Littoral and Agro Aversano areas cover about 1287 Km^2 and include 90 municipalities. The total population is about 1,300,000. Morphologically, the areas include part of the Campania Plain. The region is surrounded by Mesozoic limestone of the Southern Apennines (N and E), Roccamonfina volcano (N), Somma-Vesuvius volcano (SE), the Phlegrean Fields (Campi Flegrei) volcanic area (SW) and the Tyrrhenian Sea (S and W). The Domizio Flegreo Littoral has three different lithologies: loose pyroclastic materials, lithoide tuffs (Campanian Ignimbrite, Yellow tuff) and lava with composition that is mostly trachytic and phonolitic (De Vivo et al., 2006; Grezzi et al., 2011). The Agro Aversano area contains abundant limestone and dolomite; the Caserta Mts. occur to the north, the Avella Mts. are in the NE part of the area, and the Lattari Mts. are found in the south. The entire region is also characterized by alluvial and volcanic deposits where the older sediments derived from the Volturno river are silty and clayey-sandy; the most recent sediments are derived from tuffs and lapilli originating from volcanic activity from Campi Flegrei (Fig. 1A) (Bove et al., 2011). On the basis of its hydrogeological features the study area can be divided into two interconnected groundwater bodies related to the Volturno river plain and the Phlegrean Fields pyroclastic hills. (Corniello and Ducci, 2014). The Regi Lagni, a system of artificial canals running for about 56 km with a basin covering an area of 1300 km across the provinces of Caserta, Naples and Benevento, is also included in the Agro Aversano area. In the past, the system was used as a source of irrigation water, but now it mostly collects sewage from factories of Nola, Naples, and from Marcianise and Acerra.

The area has become highly urbanized since the 1950s. Approximately 58% of the total study area is in agricultural use, while urban and peri-urban areas cover 19%; the remaining area comprises orchards, woodland and non-cultivated land (Fig. 1A) (Corine Land Cover, 2006). Agriculture is thus the most important economic activity. Farms specialize in the cultivation of olives, grapes (for wine production), tobacco, and corn for animal (especially water buffalo) husbandry. Numerous water buffalo farms are located in the area between the towns of Mondragone and Villa Literno; most of the milk production is used for the preparation of mozzarella cheese.

A representative of the Italian automotive industry, namely FIAT, has facilities with about 6000 employees in the town of Pomigliano d'Arco. Also, in the northern sector of Acerra, an industrial settlement presently covers an area of 2,6 Km^2. The area is mostly occupied by the Montefibre factory, which produces polyester fibres and is a potential source of industrial pollution in the area since 2009. Moreover, close to the industrial zone of Acerra, an incineration plant burns mixed waste from most of the municipalities situated around the city of Naples.

3. Sample preparation and chemical analysis

3.1. Topsoil

Geochemical data for 1064 topsoil samples were retrieved from former studies focused on the area (Lima et al., 2012; Grezzi et al., 2011; Bove et al., 2011). The sampling density was one sample for approximately 5 km^2 (Fig. 1c). Topsoil samples were collected in accordance with international methods described in Salminen et al. (1998). Each sample consisted of 1 kg of material taken from the depth of 0–20 cm. All samples were dried at the temperature below 35 °C and sifted to a fraction <100 mesh. Samples were sent to Bureau Veritas (Vancouver, Canada), where they were analysed by inductively coupled plasma mass spectroscopy (ICP-MS) after digestion with aqua regia (Cicchella et al., 2008; Bove et al., 2011; Grezzi et al., 2011). The analyses included the following 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, and Zr.

3.2. Groundwater

A total of 26 groundwater samples were collected at different times during the spring of 2012 using two 1 L HDPE plastic bottles. One sample out of the two was acidified by adding ultra-pure nitric acid. Samples were sent to Bureau Veritas for the determination of 72 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, C, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se,Si, Sm, Sn, Sr, Ta,Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb , Zn and Zr. Samples were analysed directly by inductively coupled plasma mass spectroscopy (ICP-MS) to determine trace to ultra-trace concentrations of elements, and by ICP-ES to confirm higher concentrations.

3.3. Hair and corn

Human hair samples were collected at local barber and hairdresser shops. The samples were stored in plastic bags. Each hair sample, weighing 50 g, was a composite from five adults of the same gender, and coming from the same municipality. A total of 24 samples were collected. The samples were cleaned using methanol and purified water, and dried prior to analysis. After this, they were dissolved using a microwave digestion with ultrapure nitric acid and hydrogen peroxide. All samples were further dried in the laboratory of DISTAR (University of Naples, Federico II), and shipped to Act Labs laboratories (Toronto, Canada) for the determination of the following 16 elements by inductively coupled plasma mass spectroscopy (ICP-MS) technique: Al, As, Cd, Co, Cr, Cu Hg, Mn Mo, Ni, Pb, Th, U, Sc, Ni, V.A total of 13 corn (*Zea mays*) samples were collected at different farms in this area. After collection, 100 g of each sample was dried in a temperature of 60 °C and ground to a powder. Then 20 g of each sample was shipped to Bureau Veritas for analysing 53 elements (Ag, Al, As, Au, B, Ba, Be, Bi, ca, Vd, 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, U, V, W, Y, Zn, Zr) by inductively coupled plasma mass spectroscopy (ICP-MS) technique. Before the analysis, the samples were dissolved with nitric acid and digested in a hot water bath. After cooling a modified aqua regia solution consisting of equal parts of concentrated

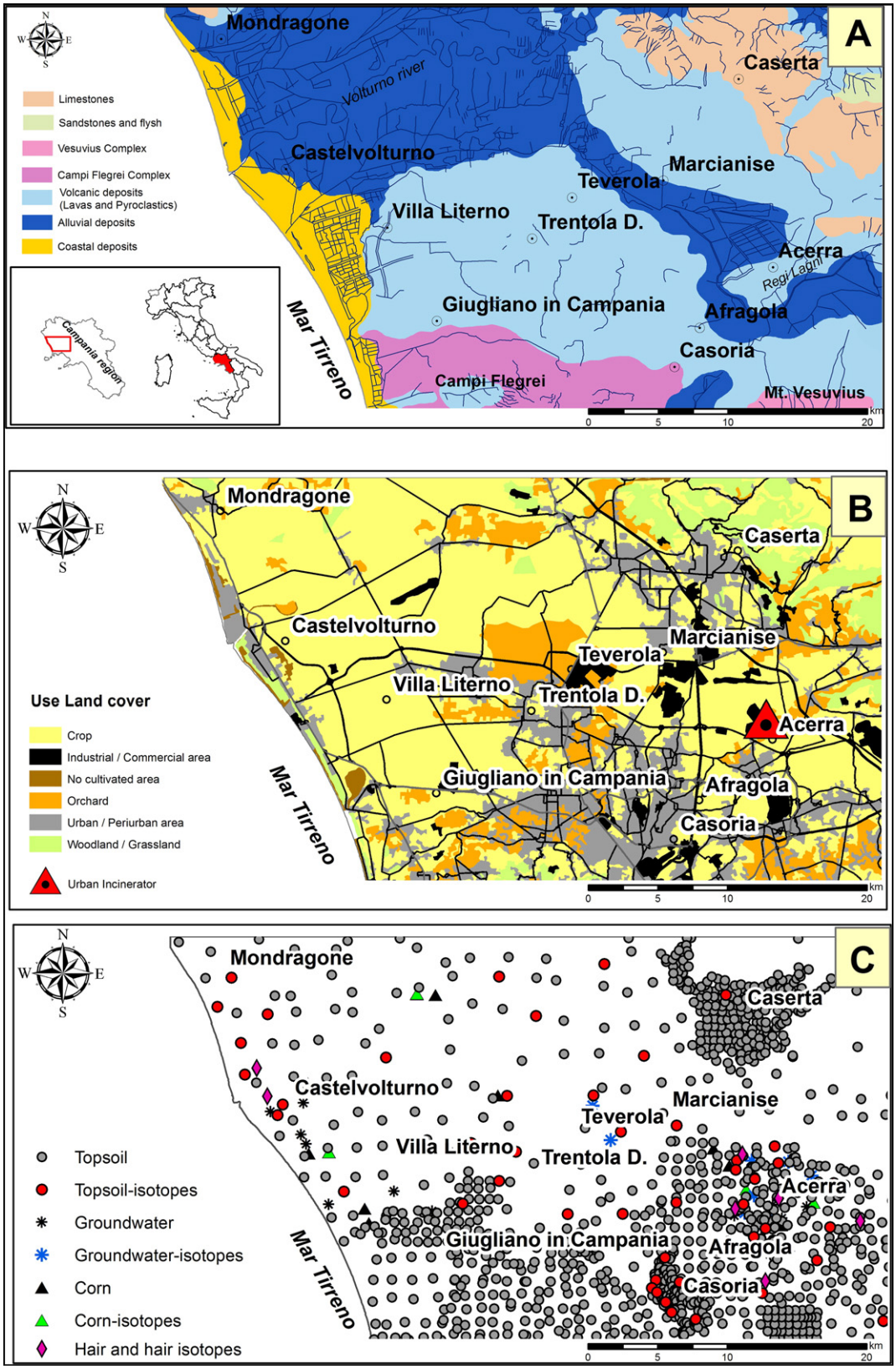

Fig. 1. Geo-lithological map of study area (A); Land Cover use map (B); Sampled site for isotopic analysis (C).

HCl, HNO_3 and DI H_2O was added to each sample to dissolve it in a heating block within a hot water bath. Sample was further diluted with HCl and filtered. Finally, 5 g of each sample was taken for the analysis.

3.4. Pb isotopes

Lead is present in the environment as four isotopes: ^{208}Pb, ^{206}Pb, ^{207}Pb, ^{204}Pb. Variations in the abundance of these isotopes arise from

the radioactive decays off ^{238}U, ^{235}U and ^{232}Th to ^{206}Pb, ^{207}Pb and ^{208}Pb over the geological time (Faure, 1986). The only non-radiogenic isotope is ^{204}Pb, which has remained stable since the Earth solidified. The abundances of ^{208}Pb, ^{206}Pb, ^{207}Pb change as a function of time. A combination of various processes and a mixture of Pb from different sources cause the isotopic composition characteristics of different types of Pb-containing minerals. (Cheng and Hu, 2010).

For the lead isotopic analysis, 24 topsoil samples, 9 groundwater samples, 9 hair samples and 4 corn samples were processed at the USGS Radiogenic Isotope Laboratory in Reston (Fig. 1c). Each topsoil sample was first sifted to 60 mesh (250 μm) and about 200 mg dissolved with 3 ml of a solution containing 1.5 N HCL and 3 N HNO_3. Finally, the samples were centrifuged for 5 min to separate the leachate from the solid residue. The residues were processed using a multistep treatment with the solution of HNO_3, 4 N HCL and 0.5 N HBr. Each leachate was digested in a microwave (Ethos Plus Microwave Lab station) for 15 min and treated using the same multistep process. A total of 48 samples (leachates and solubilized residues) were run through columns filled with anion exchange resin and using 0.5 M HNO3 and 0.5 HBr. (for details of procedures see Ayuso et al., 2013; Ayuso and Foley, 2016).

Groundwater samples were filtered using 0.4 μm micro pore cellulose filter to eliminate all solid particles, dried and then processed with same Pb chemistry and Pb elution of the topsoil samples. Hair samples were collected in plastic bags, between 5 and 25 g for each sample. Before digestion, each sample was cleaned with 6 N HNO3 and with 10 ml of *aqua regia*. Samples were digested with ultrapure HNO_3 and placed in a microwave with a solution of 9 ml HNO3. The analytical method was the same as the method used in analysing topsoil and groundwater samples.

About 1 g of corn samples was used for isotopic analyses (TIMS/Spectromat) at the USGS Laboratory in Reston. Each sample underwent a digestion process using 100 ml of pure HNO3. After drying, T2 HNO3 and T2 HCL and 6 N HCL were added stepwise to the samples. Then each sample was placed in a microwave and further exposed to the same treatment as the topsoil, groundwater and hair samples.

4. Results

4.1. Data analysis and mapping

Before any statistical treatment, a value corresponding to 50% of the detection limit (DL) was assigned to all measurement results below the DL. Univariate statistical parameters for the results obtained from all analysed samples are shown in Table 1. Fig. 2 shows the probability plots of the concentration of some selected elements (Cu, As, Pb and Zn) in soils, groundwater, hair and corn; on soil plots also RAL and IAL established by the Italian Environmental Law (Legislative Decree 152/06 are graphically reported. In the plot presenting the results related to corn, the maximum European accepted level, where present, is also indicated (European Union, 2006). Geochemical maps for each considered element were obtained by means of Multifractal Inverse Distance Weighted (MIDW) interpolation method implemented in the GEODAS software and ArcGis 10.3 software (Cheng, 2003), with concentration intervals set on the basis of the concentration–area (C-A) method (Cheng, 2003; Xu and Cheng, 2001; Lima et al., 2003; Agteberg, 2012) (Fig. 3). In accordance with the Italian Environmental Law (Legislative Decree 152/06), a contamination factor map was produced for all potentially harmful elements: As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, Zn. A contamination factor (CF) for each potentially harmful elements was calculated using the following formula, presented by Hakanson (1980):

$CF = C_i / C_b$ where:

CF = *Contamination factor value of the element in a specific pixel*

C_i *is the concentration value of the element in a specific pixel of interpolated map;*

C_b *is the background concentration value of the element in the same pixel.*

In our case, C_b is equivalent to the uppermost value of the Background Concentration Reference Interval for Neapolitan soil (BCRIN) established for urban and provincial soils of Naples by De Vivo et al. (2006) (Table 1A).

4.2. Geochemical distribution of toxic elements

In this section we discuss the elements of concern with respect to impacts on human health as indicated by Italian Environmental Law (Legislative Decree 152/06). In order to keep the presentation concise, we use the interpolated maps of selected elements (Sb, As, Cu, Pb, Hg, Zn) that indicate the areas of concern (Fig. 3). Results related to human hair are compared to data reported by Cicchella et al. (2016) and by Dongarrà et al. 2011. Cicchella et al. (2016) studied hair specimens collected in the Sarno basin area (Campania region) using a methodology similar to the one described in this paper. The study by Dongarrà et al. (2011) focused on students living in Palermo city (Sicily).

Antimony (Sb)

The content of antimony in topsoil ranges from 0.01 to 42.8 mg/kg with a median of 0.7 mg/kg. Most of the samples (about 75%) have values <1 mg/kg and only 0.1% of the samples reach the highest concentrations (12.1–42.8 mg/kg) in the area of Giugliano in Campania and Quarto (Fig. 3A and Table 1A). Three samples exceed the Italian RAL of 10 mg/kg (D.lgs 152/06) (Table 1A).

In the groundwater, Sb concentrations range from <0.025 up to 1.42 μg/l, showing a median concentration (0.14 μg/l) much lower than median concentration (0.3 μg/l) established by Cicchella et al. (2010) for Italian groundwater (Table 1B). The Sb concentrations in corn range from <0.010 to 0.03 mg/kg with a median of 0.010 mg/kg (Table 1D).

Arsenic (As)

Arsenic content in topsoil ranges from 3.4 to 61 mg/kg, with a median of 13.7 mg/kg. Approximately 80% of the topsoil samples have values <20 mg/kg (Fig. 2A). The highest concentrations have been determined in correspondence with Giugliano in Campania and Acerra (61 and 60.9 mg/kg, respectively) (Fig. 3B and Table 1A). About 18% of the samples exceed the BCRIN (18 mg/kg) determined by De Vivo et al. (2006) and 5% of samples exceed the Italian RAL (20 mg/kg) (Table 1A).

Arsenic content in groundwater ranges from 0.25 to 57.8 μg/l, with a median of 3.8 μg/l. The latter is much higher than the Italian groundwater concentration median of 2.2 μg/l (Cicchella et al., 2010) (Table 1B). In hair, As ranges from 5 to 73 μg/kg, with a median of 35 μg/kg (Table 1C), very close to median value of 31 μg/kg reported by Cicchella et al. (2016) in the Sarno river basin. The As concentrations in corn range from values <0.050 up to 0.50 mg/kg with a median of 0.10 mg/kg (Table 1D).

Cadmium (Cd)

In topsoil, Cd ranges from 0.005 to 10.6 mg/kg with a median of 0.39 mg/kg (Fig. 3C and Table 1). Many sampled sites (32%) have Cd concentrations exceeding the corresponding uppermost limit of the BCRIN (0.5 mg/kg) (De Vivo et al., 2006) (Table 1A) but only 1% of topsoil is higher than the Italian RAL (2 mg/kg). Cadmium content in groundwater ranges from 0.02 to 0.3 μg/l with a median of 0,025 μg/l, which is higher than Italian groundwater corresponding value (0.003 μg/l) (Cicchella et al., 2010). Cadmium in hair ranges from 5 to 176 μg/kg with a median of 26.9 μg/kg, which is lower than the median reported by Dongarrà et al. (2011) and also higher than the median calculated for the Sarno river basin in Campania region (Cicchella et al., 2016) (Table 1C). The Cd concentration in corn ranges from 0.005 to 0.060 mg/kg with a median of 0.020 mg/kg.

Cobalt (Co)

In topsoil, Co ranges from 2.6 to 35.6 mg/kg with a median of 8.6 mg/kg (Table 1A). About 1% of samples exceed the uppermost value of the BCRIN (17 mg/kg) (De Vivo et al., 2006) (Table 1A). Three samples located in Giugliano and Casoria municipalities exceed the Italian RAL (20 mg/kg). Cobalt content in groundwater ranges from values <0.01 up to 5.04 μg/l with a median of 0.04 μg/l, which is well below the Italian groundwater reference value of 0.17 μg/l (Cicchella et al., 2010). Cobalt in hair varies from 24 to 1000 μg/kg with a median of 75 μg/kg.

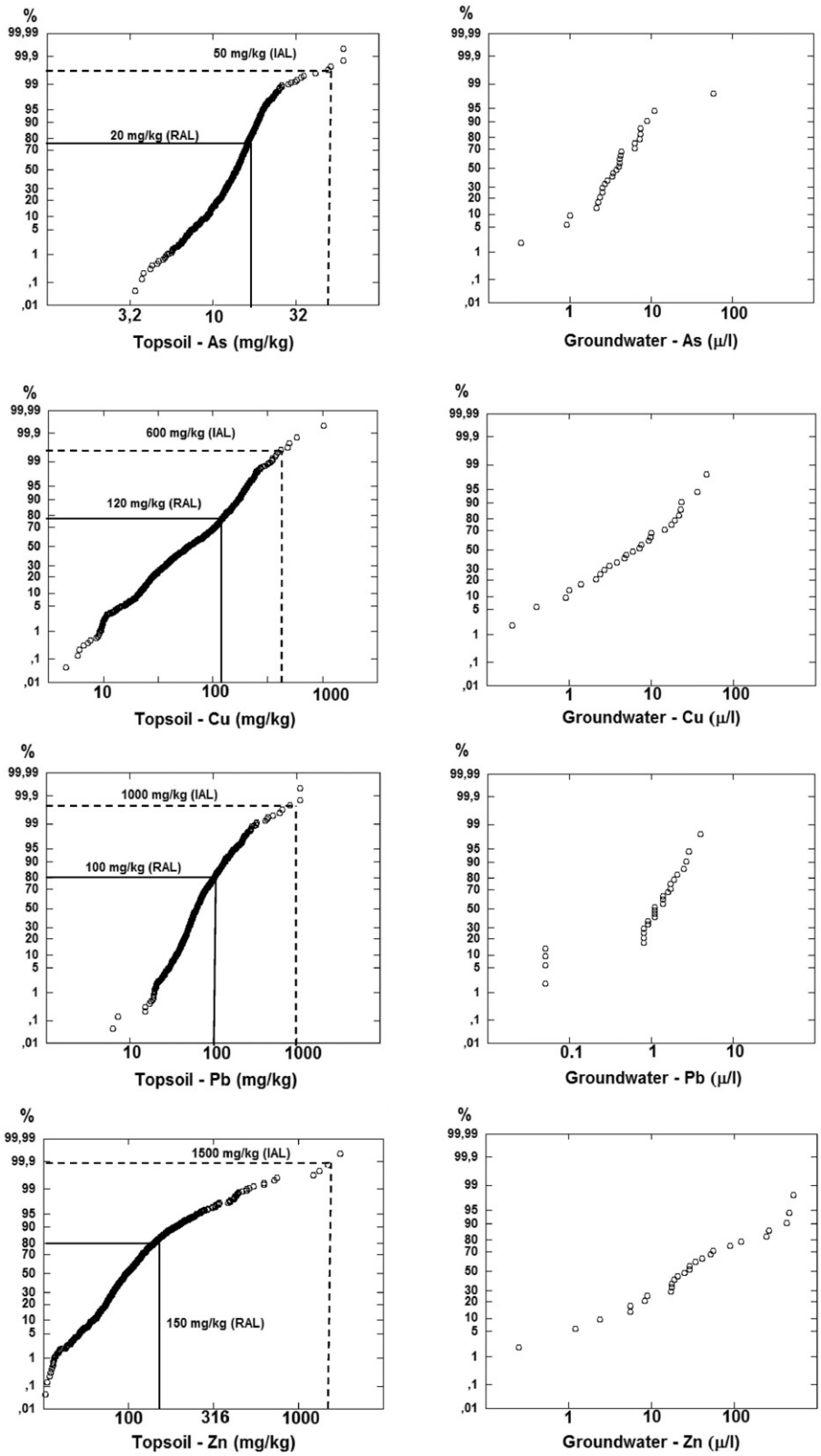

Fig. 2. A Cumulative frequency curves for As, Cu, Pb, Zn in the topsoil and groundwater samples. B Cumulative frequency curves for As, Cu, Pb, Zn in the human hair and corn samples.

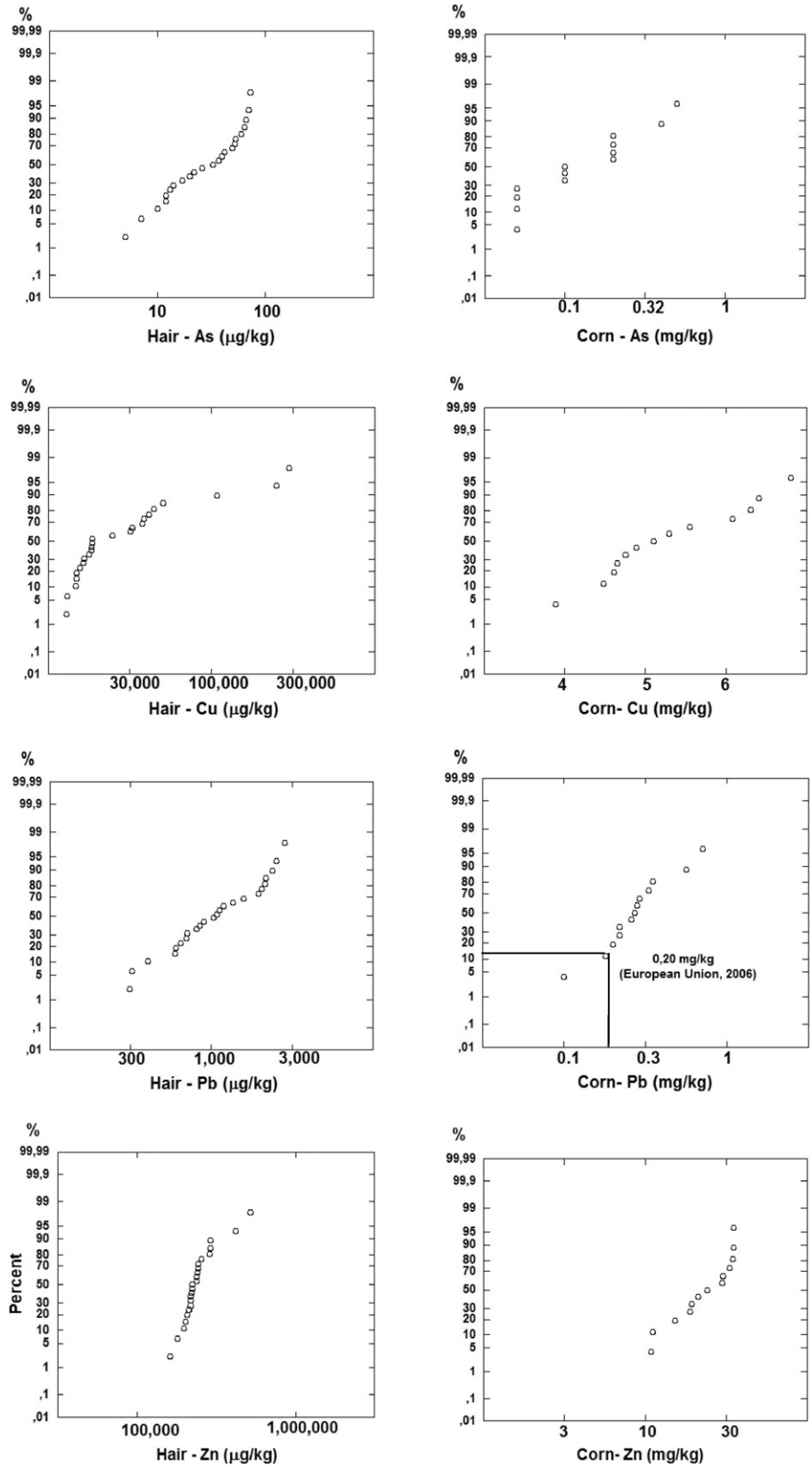

Fig. 2 (*continued*).

The latter value is lower than the median (80 μg/kg) reported by Dongarrà et al. (2011) and higher than the one (41.5 μg/kg) reported by Cicchella et al. (2016). Cobalt concentrations in corn range from 0.020 to 0.070 mg/kg with a median value of 0.040 mg/kg.

Chromium (Cr)

In topsoil, Cr concentrations range from 0.25 to 486 mg/kg with a median of 12 mg/kg (Table 1A). About 30% of samples exceed the

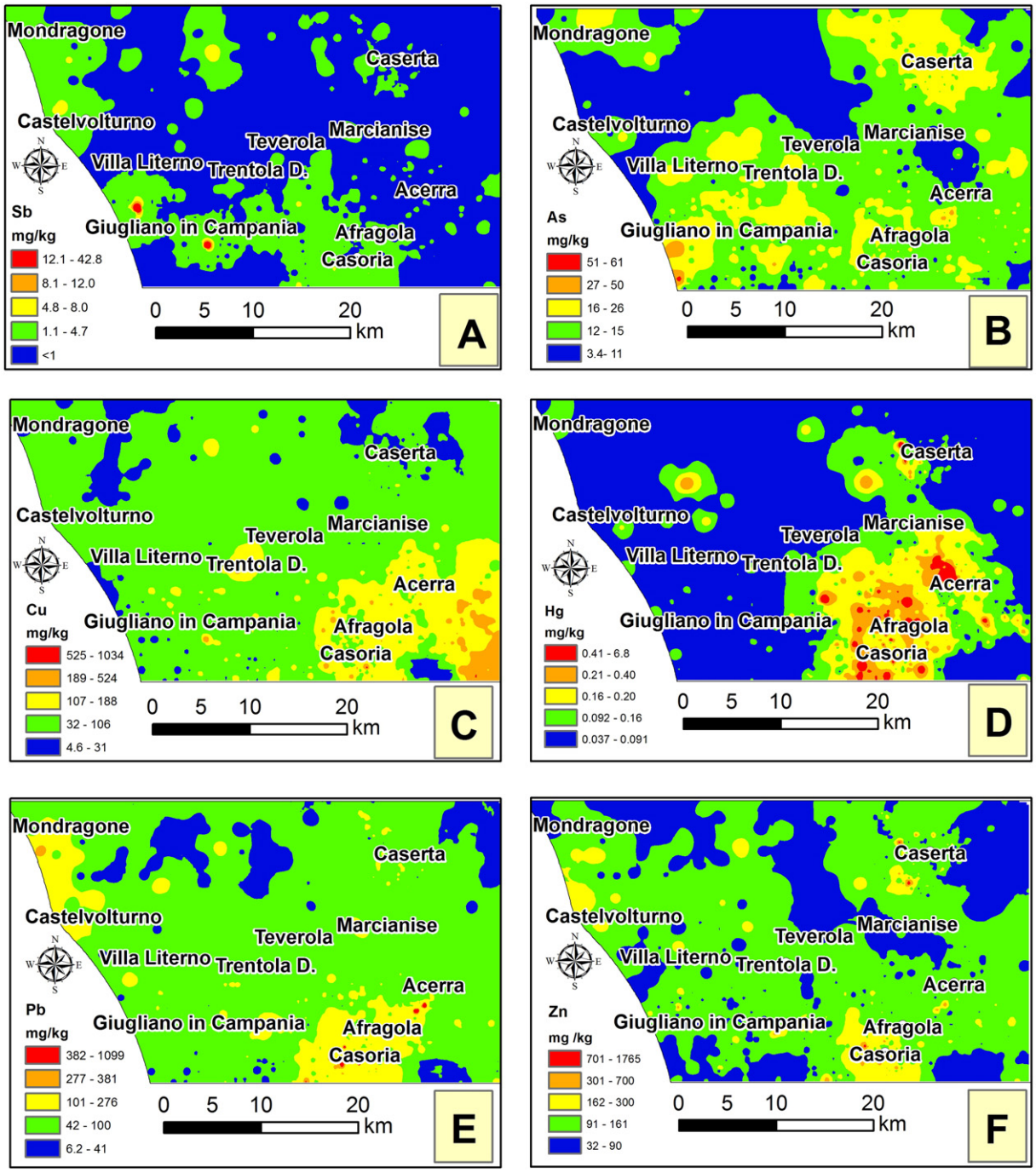

Fig. 3. Interpolated maps for Sb, As, Cu, Hg, Pb Zn in topsoil.

uppermost value of the BCRIN (16 mg/kg) reported by De Vivo et al. (2006) (Table 1A). Two samples exceed the Italian RAL (150 mg/kg) with Cr contents of 177 and 486 mg/kg, in Acerra and Casoria, respectively. In groundwater Cr content ranges from 0.25 to 28.4 μg/l with a median of 0.25 μg/l, which is above that the Italian groundwater value of 0.17 μg/l (Cicchella et al., 2010) but lower than the median (13.6 μg/l) determined for the Sarno river basin (Cicchella et al., 2016) (Table 1D). Chromium in hair ranges from 58 to 1650 μg/kg with a median of 223 μg/kg much higher than the one reported by Dongarrà et al. (2011) (70 μg/kg) and lower than the one (247 μg/kg) reported by Cicchella et al. (2016) (Table 1C). The Cr concentrations in corn range from 2.1 to 5 mg/kg with a median value of 3.2 mg/kg (Table 1D).

Copper (Cu)

In topsoil, Cu concentrations range from 4.59 to 1034.3 mg/kg with median of 60 mg/kg (Fig. 3C and Table 2A). About 5% of the analysed samples have concentrations higher than the upper limit of the BCRIN (200 mg/kg) determined by De Vivo et al. (2006); furthermore, 25% of samples are characterized by Cu concentrations exceeding the Italian RAL (120 mg/kg). One sample, within the Casoria municipality administrative area, also exceeds the Italian IAL fixed by law at 600 mg/kg. Copper content in groundwater ranges from values <0.2 up to 46.9 μg/l with a median of 6.6 μg/l. The latter is much higher than the median (0.19 μg/kg) reported by Cicchella et al. (2010) and it is above the median (0.9 μg/l) reported by Cicchella et al. (2016) for the Sarno River basin.

Table 1A
Statistical parameters for toxic metals in the topsoil. RAL = Residential use action limit set by Italian Environmental Law for soil (Legislative Decree 152/06), IAL = Commercial and industrial set by Italian Environmental Law for soil (Legislative Decree 152/06), BCRIN = Background Concentration Reference Interval for Neapolitan soil (De Vivo et al., 2006).

Element	mg/kg	N	Range	Min	Max	Mean	Median	St. Dev.	RAL	IAL	BCRIN**
As	mg/kg	1064	3.4–61	3.4	61	13.9	13.7	4,7	20	50	6–18
Be	mg/kg	627	0.7–12.2	0.7	12.2	4.8	4.9	4.9	2	10	–
Cd	mg/kg	1064	<0.005–10.6	<0.005	10.6	0.4	0.39	0.5	2	15	0.1–0.5
Co	mg/kg	1064	2.6–36.6	2.6	36.6	8.8	8.6	3.4	20	250	3–17
Cr	mg/kg	1064	<0.25–486	<0.25	486	14.4	12	18	150	800	1–16
Cu	mg/kg	1064	4.6–1034.3	4.6	1034.3	83	60	73.5	120	600	4–200
Hg	mg/kg	1064	0.037–6.8	0.004	6.775	0.14	0.07	0.2	1	5	0.01–0.1
Ni	mg/kg	1064	1.9–86.6	1.9	86.6	12.08	12	6.9	120	500	1–19
Pb	mg/kg	1064	6.2–1099	6.2	1099	81.4	63	76	100	1000	20–80
Sb	mg/kg	1064	<0.01–42.8	<0.01	42.8	1,07	0.7	2	10	30	0.2–1.1
Se	mg/kg	1064	<0.05–2	<0.05	2	0.04	0.4	0.2	3	15	0.1–0.4
Sn	mg/kg	627	1–63	1	63	5.1	4.4	3.8	1	350	–
Tl	mg/kg	1064	0.15–3.12	0.15	3.12	1.6	1.6	0.2	1	10	0.5–1.5
V	mg/kg	1064	20–144	20	144	62.8	59	21	90	250	25–125
Zn	mg/kg	1064	32–1765	32	1765	121.5	96.4	111.8	150	1500	35–100

In hair, Cu ranges from 12,900 to 299,000 μg/kg with a median concentration value of 18,500 μg/kg, which is slightly lower than the ones of 19,950 μg/kg and 19,717 reported by Dongarrà et al. (2011) and Cicchella et al. (2016), respectively. The Cu concentrations in corn range from 3.9 to 7.6 mg/kg with a median of 5.1 mg/kg.

Lead (Pb)

Lead in topsoil varies from 6.21 to 1099 mg/kg with a median of 63 mg/kg (Fig. 3D and Table 1A). The highest concentrations (1099 and 1095 mg/kg) occur within the Acerra municipality administrative boundaries. About 7% of sampled topsoils exceed the upper limit of the BCRIN (80 mg/kg) determined by De Vivo et al. (2006). About 21% of the samples have Pb concentrations higher than the Italian RAL (10 mg/kg). Lead in groundwater ranges from values <0.05 to 4 μg/l with a median value of 1.1 μg/l, which is above the median of Italian groundwater (0.007 μg/l) reported by Cicchella et al. (2010). Lead in hair ranges from 312 to 2840 μg/kg with a median of 1030 μg/kg. The latter is higher than the median (780 mg/kg) determined by Dongarrà et al. (2011) but slightly lower than the one set by Cicchella et al. (2016) (1087 μg/kg) (Table 1C). Lead in corn ranges from 0.10 to 0.71 mg/kg with a median of 0.27 mg/kg. About 85% of samples have Pb concentration values above the maximum level permitted in food (European Union, 2006 and FAO/WHO, 2011) (0.20 mg/kg). The highest values (>0.20 mg/kg) were found in the towns of Acerra, Giugliano in Campania and Villa Literno.

Mercury (Hg)

Mercury concentrations in topsoil range from 0.004 to 6.77 mg/kg (Fig. 3E and Table 1A) with a median value of 0.07. About 37% of analysed topsoils have concentrations exceeding the BCRIN of 0.1 mg/kg (De Vivo et al., 2006). Six samples located in Acerra, Caivano and in the northern part of Naples have Hg concentrations higher than the Italian RAL (1 mg/kg); one sample in Acerra even exceeds the Italian IAL (5 mg/kg). All groundwater samples have concentrations lower than the detection limit (0.1 μg/l). In hair, Hg ranges from 123 to 1560 μg/kg with a median of 622 μg/kg, which is above the median (638 μg/kg) reported by Dongarrà et al. (2011) and is also higher than the one (495 μg/kg) set by Cicchella et al. (2005) for the Sarno River basin. Mercury concentrations in corn range from <0.001 to 0.7015 mg/kg with a median value of 0.005 mg/kg.

Nickel (Ni)

Nickel in topsoil ranges from 1.9 to 86.6 mg/kg with a median of 12 mg/kg (Table 1A). Highest concentrations of 86.6 and 70.2 mg/kg occur in Caivano and Casoria municipality respectively. About 8% of samples exceed the upper value of the BCRIN (19 mg/kg) set by De Vivo et al. (2006). Nickel content in groundwater ranges from 0.1 to 9.9 μg/l with a median of 0.1 μg/l; the latter is lower than Italian median (0.13 μg/l) established by Cicchella et al. (2010). Nickel in hair ranges from 150 to 10,500 μg/kg with a median of 665 μg/kg, higher than the median of 374 mg/kg calculated by Cicchella et al. (2016) for the

Table 1B
Statistical parameters for toxic metals in the groundwater. D^a is a median concentration of Italian groundwater (Cicchella et al., 2010), D^b = median concentration of Sarno area groundwater (Cicchella et al., 2016).

Element	μg/l	N	Range	Min	Max	Mean	Median	St. Dev.	D^a	D^b
As	μg/l	26	<0.025–57.8	<0.25	57.8	6.3	3.8	10.8	0.25	2.2
Be	μg/l	26	<0.025–0.3	<0.025	0.3	0.08	0.03	0.08	0.0013	<0.02
Cd	μg/l	26	<0.025–0.3	<0.025	0.3	0.04	0.03	0.06	0.003	0.02
Co	μg/l	26	<0.01–5.04	<0.01	5.04	0.47	0.04	1.2	0.017	<0.02
Cr	μg/l	26	0.25–28.4	0.25	28.4	2.3	0.25	5.6	0.17	13.6
Cu	μg/l	26	0.2–46.9	0.2	46.9	10.8	6.6	12	0.19	0.9
Hg	μg/l	26	<0.05–0.05	<0.05	<0.05	–	–	–	–	–
Ni	μg/l	26	0.1–9.9	0.1	9.9	1.2	0.10	2.5	0.13	<0.2
Pb	μg/l	26	0.05–4	0.05	4	1.3	1.1	0.95	0.007	<0.05
Sb	μg/l	26	<0.025–1.42	<0.025	1.42	0.24	0.14	0.29	0.302	0.135
Se	μg/l	26	<0.25–8.4	<0.25	8.4	2.8	2.4	2	0.16	1
Sn	μg/l	26	<0.025–0.43	<0.025	0.43	0.05	0.03	0.09	0.006	<0.2
Tl	μg/l	26	<0.005–0.3	<0.005	0.3	0.10	0.10	0.08	0.0053	0.085
V	μg/l	26	0.6–52	0.6	52	12	12	11	0.3	4.6
Zn	μg/l	26	0.25–516	0.25	516	97	27	153	0.31	13.7

Table 1C
Statistical parameters for toxic metals in the hair, C^a is the median concentration of Heavy metals in hair (Dongarrà et al., 2011; Diez et al., 2008), C^b is the median concentration of Heavy metals in hair (Cicchella et al., 2016).

Element	μg/kg	N	Range	Min	Max	Mean	Median	St. Dev.	C^b	C^a
As	μg/kg	23*	5–73	<5	73	36	35	22.4	30.5	0
Be	μg/kg	23*	–	–	–	–	–	–	3	
Cd	μg/kg	23*	5–176	<5	176	36.9	26.9	39.8	16	30
Co	μg/kg	23*	24–1000	24	1000	278,8	75	393	41.5	80
Cr	μg/kg	23*	58–1650	58	1650	388.9	223	446.8	247	70
Cu	μg/kg	23*	13,100–299,000	12,900	299,000	50,274	18,500	73,945	19,717	19,950
Hg	μg/kg	23*	123–1560	123	1560	662	584	403	495	638
Ni	μg/kg	23*	150–10,500	150	10,500	1096	650	2089	374	420
Pb	μg/kg	23*	312–2840	312	2840	1229	1030	756	1087	780
Sb	μg/kg	23*	–	–	–	–	–	–	49	20
Se	μg/kg	23*	–	–	–	–		–	596	–
Sn	μg/kg	23*	–	–	–	–	–	–	436	–
Tl	μg/kg	23*	–	–	–	–	–	–	2	10
V	μg/kg	23*	–	–	–	–	–	–	130	80
Zn	μg/kg	23*	163,000–520,000	163,000	520,000	25,0783	225,000	77,634	167,107	179,200

* One sample with high concentration of Cr was excluded from statistical analysis.

Sarno River basin. About 58% of hair samples have Ni contents higher than the median value (420 mg/kg) provided by Dongarrà et al. (2011). Nickel concentrations in corn range from 0.1 to 1.1 mg/kg with a median of 0.3 mg/kg.

Selenium (Se)

Selenium in topsoils ranges from values <0.05 up to 2 mg/kg with median of 0.4 mg/kg (Table 1A). About 38% of analysed samples have Se contents higher than the upper limit of the BCRIN (0.4 mg/kg) (De Vivo et al., 2006) (Table 1A). Selenium contents in groundwater range from values <0.25 up to 8.4 μg/l with a median of 2.4 μg/l, which is higher than median value shown by Cicchella et al. (2010) for Italy (0.16 μg/l) and by Cicchella et al. (2016) for the Sarno river basin (1 μg/l). The Se concentrations in corn range from 0.10 to 1.2 mg/kg with a median of 0.5 mg/kg.

Thallium (Tl)

Thallium concentrations in topsoil range from 0.15 to 3.12 mg/kg with a median of 1.6 mg/kg (Table 1A). About 81% of the samples exceed the upper value of the BCRIN (1.5 mg/kg) (De Vivo et al., 2006). Thallium in groundwater ranges from values <0.005 up to 0.3 μg/l with a median of 0.10 μg/l, which is higher than the corresponding value for Italian groundwater (0.0053 μg/l) (Cicchella et al., 2010) and for Sarno River basin (0.085 μg/l) (Cicchella et al., 2016). Thallium in the corn ranges from 0.01 to 0.04 mg/kg with a median of 0.30 mg/kg.

Vanadium (V)

Vanadium in topsoils ranges from 20 to 144 mg/kg with a median of 0.4 mg/kg. About 1% of analysed samples show concentrations exceeding the upper limit of the BCRIN set by De Vivo et al. (2006) at 125 mg/kg (Table 1A). Vanadium in groundwater ranges from 0.6 to 52 μg/l with a median of 12 μg/l; the local median is much higher than the Italian median (0.3 μg/l) established by Cicchella et al. (2010) and is also higher than the one set for the Sarno River basin (4.6 μg/l) (Cicchella et al., 2016) (Table 1B). Vanadium in corn range from 1 to 5 mg/kg with a median value of 2 mg/kg (Table 1D).

Zinc (Zn)

Zinc concentrations in topsoil vary from 32 to 1765 mg/kg, with a median of 96.4 mg/kg (Fig. 3F and Table 1A). About 48% of the samples exceed the local background of 400 mg/kg and about 2% of samples exceed the uppermost limit of the BCRIN (100 mg/kg) established by De Vivo et al. (2006). The same 2% of samples exceed the Italian RAL (100 mg/kg) and only one sample in Casoria municipality exceeds the Italian IAL (1500 mg/kg) (Table 1A). Zinc contents in groundwater range from values <0.25 up to 516 μg/l with a median of 27 μg/l; the median is well above the median established by Cicchella et al. (2010) for Italian groundwater (0.31 μg/l). The local median is also higher than the Sarno River basin groundwater median value of 13.7 μg/l (Cicchella et al., 2016) (Table 1B). In the hair samples, Zn ranges from 163,000 to 520,000 μg/kg. The median of 224,000 μg/kg exceeds both

Table 1D
Statistical parameters for toxic metals in the corn. F^a = reference value of HM in vegetables (European Union, 2006), F^b = reference value of HM in vegetables (FAO/WHO, 2011).

Element	mg/kg	N	Range	Min	Max	Mean	Median	St. Dev.	Fa	Fb
As	mg/kg	13	<0.050–0.50	<0.050	0.50	0.169	0.10	0.41	–	–
Be	mg/kg	13	<0.050–0.050	<0.050	0.050	0.050	0.050	–	–	–
Cd	mg/kg	13	0.005–0.060	0.005	0.060	0.027	0.020	0.015	0.20	0.20
Co	mg/kg	13	0.020–0.070	0.020	0.070	0.045	0.040	0.018	–	–
Cr	mg/kg	13	2.1–5	2.100	5	3.3	3.2	0.711	–	–
Cu	mg/kg	13	3.9–7.6	3.9	7.6	5.4	5.1	1.1	–	–
Hg	mg/kg	13	<0.001–0.015	<0.001	0.015	0.006	0.005	0.004	–	–
Ni	mg/kg	13	0.10–1.1	0.10	1.10	0.400	0.30	0.27	–	–
Pb	mg/kg	13	0.100–0.71	0.10	0.71	0.305	0.27	0.16	0.20	0.20
Sb	mg/kg	13	<0.010–0.03	<0.010	0.03	0.016	0.010	0.008	–	–
Se	mg/kg	13	0.100–1.2	0.100	1.2	0.0447	0.50	0.29		–
Sn	mg/kg	13	<0.010–0.1	<0.010	0.1	0.045	0.040	0.023	–	–
Tl	mg/kg	13	<0.010–0.04	<0.010	0.04	0.015	0.010	0.009	–	–
V	mg/kg	13	1–5	1	5	2.4	2	1.5	–	–
Zn	mg/kg	13	10.9–35.4	10.9	35.4	24.5	24.3	9.1	–	–

F^a = reference value of HM in vegetables (European Union, 2006).
F^b = reference value of HM in vegetables (FAO/WHO, 2011).

Table 2
Isotopic values and related anthropogenic estimates in the analysed media.

	Soil residues $^{206}Pb/^{207}Pb$	Soil residues $^{207}Pb/^{208}Pb$	% Pb anthropogenic*	Soil leached $^{206}Pb/^{207}Pb$	Soil leached $^{207}Pb/^{208}Pb$	% Pb anthropogenic	Pb (mg/kg)	Zn (mg/kg)
ACE 24	1.1839	2.4624	49	1.1680	2.4629	58	102.7	103.4
ACE 29	1.1795	2.4567	56	1.1536	2.4199	91	111.6	158.6
ACE 10a	1.1790	2.4542	41	1.1743	2.4437	29	69.6	114.5
ACE 13	1.1906	2.4727	36	1.1797	2.4538	58	69.1	109.6
ACE 4	1.1960	2.4740	31	1.1766	2.4509	63	101.2	85.8
ACE 56d	1.1642	2.4498	73	1.1769	2.4495	64	1099.1	627.9
ACE 66a	1.1663	2.4505	71	1.1622	2.4437	79	1095.4	496.7
NOL-B 35	1.1864	2.4595	49	1.1691	2.4515	68	162.7	173.0
ACE 61	1.2046	2.4749	23	1.1828	2.4599	52	88.4	117.1
NOL-B 16	1.1866	2.4578	50	1.1692	2.4548	65	107.8	175.8
AV119T1	1.1972	2.4668	35	1.1758	2.4578	58	108.5	175.0
LIFE 01	1.1928	2.4629	41	1.1568	2.4371	88	97.2	176.0
LIFE 02	1.2041	2.4765	23	1.1804	2.4562	56	68.1	121.0
LIFE 04	1.1998	2.4797	23	1.1831	2.4562	54	26.0	59.3
LIFE 05	1.1707	2.4405	75	1.1616	2.4421	81	186.9	45.2
LIFE 06	1.1999	2.4705	30	1.1692	2.4548	65	57.7	87.0
LD 4	1.2120	2.4823	12	1.1982	2.4728	30	53.2	58.0
LD 15	1.1963	2.4695	34	1.1786	2.4634	52	159.7	114.3
LD 42	1.1627	2.4284	87	1.1474	2.4244	94	157.1	207.3
LD 62	1.1603	2.4308	89	1.1470	2.4225	93	166.9	243.9
LD 41	1.1707	2.4456	72	1.1616	2.4417	81	225.6	222.1
LD 49	1.1588	2.4287	91	1.1470	2.4231	93	250.6	153.5
LD 50	1.1613	2.4325	88	1.1503	2.4257	97	327.9	153.0
LD 52	1.1645	2.4385	82	1.1323	2.4098	72	265.4	108.1
	GW $^{206}Pb/^{207}Pb$	GW $^{207}Pb/^{208}Pb$					Pb (μg/l)	Zn (μg/l)
GW 02	1.1977	2.4569	41				4	20.7
GW 06	1.1742	2.4444	69				1.6	463.4
GW 11	1.1771	2.4482	65				1.1	89.2
GW 12	1.1702	2.4288	79				0.9	17.7
GW 13	1.1565	2.4305	93				1.4	8.2
GW 15	1.1622	2.4368	85				1.4	40.9
GW 25	1.1571	2.4369	88				2.9	265.9
GW 26	1.1587	2.4360	88				1.1	28.6
GW 27	1.1659	2.4354	82				0.8	17.2
	Hair $^{206}Pb/^{207}Pb$	Hair $^{207}Pb/^{208}Pb$					Pb (μg/kg)	Zn (μg/kg)
ACE-HF-01	1.1597	2.4383	85				1120	214,000
ACE-HF-02	1.1589	2.4428	82				849	223,000
ACE-HF-04	1.1598	2.4460	78				1190	163,000
ACE-HF-05	1.1790	2.4303	70				2840	198,000
MR-HF-01	1.1698	2.4371	77				1590	208,000
PM-HF-01	1.1871	2.4295	61				1090	256,000
CAS-HF-02	1.1633	2.4353	85				2150	289,000
CAS-HF-03	1.1704	2.4394	76				598	244,000
CAS-HF-04	1.1620	2.4208	86				322	220,000
	Corn $^{206}Pb/^{207}Pb$	Hair $^{207}Pb/^{208}Pb$					Pb (mg/kg)	Zn (mg/kg)
C-01	1.1909	2.4459	72				0.3	29.7
C-03	1.1897	2.4604	45				0.7	34.6
C-05	1.1700	2.4605	46				0.3	35.4
C-09	1.1844	2.5011	14				0.1	19.3

the one calculated by Dongarrà et al. (2011) of 17,200 μg/kg and the one calculated by Cicchella et al. (2016) of 167,107 μg/kg (Table 1C). The Zn concentrations in the corn range from 10.9 to 35.4 mg/kg with median of 24.3 mg/kg (Table 1D).

5. Discussion

5.1. Contamination factor (CF) and degree of contamination

According to Hakanson (1980), Albanese et al. (2013) and Cicchella et al. (2014), grids of Concentration Factor (CF), for each element can be reclassified as follows:

- CF < 1 Low contamination
- 1 ≤ CF ≥ 3 Moderate contamination
- 3 ≤ CF ≥ 6 High contamination
- CF ≥ 6 Very High contamination

Fig. 4 shows selected CF maps for Pb, Hg and Sb. Thallium and vanadium were excluded from the evaluation of degree of contamination because their concentrations are attributed to a geological source (Cicchella et al., 2005; Lima et al., 2012). The CF map for As shows that 97% of the study area has CF < 1, and the rest (3%) has a CF between 1 and 3, confirming the mostly geogenic nature of As in the environmental media and suggesting that it can be related to the volcanic origin of soils in this area. For Cd, the CF map shows that 75% of the study area has CF < 1 and the rest (25%) has a CF between 1 and 3 (moderate contamination). The CF map for Cr shows that 59% of the study area has CF <1 and the 41% has a CF between 1 and 3; we speculate that this moderate pollution may be related in some cases to anthropogenic activities. The comparable trend of Co and Cu, where the percentage of CF >1 is 99% and 98% respectively, demonstrate that the distribution of concentrations is for the most part geogenic, while the remaining samples (only 1% for Co and 2% for Cu), with CF between 1 and 3, are associated with agricultural practices, as perhaps in the use of fertilizers. It is

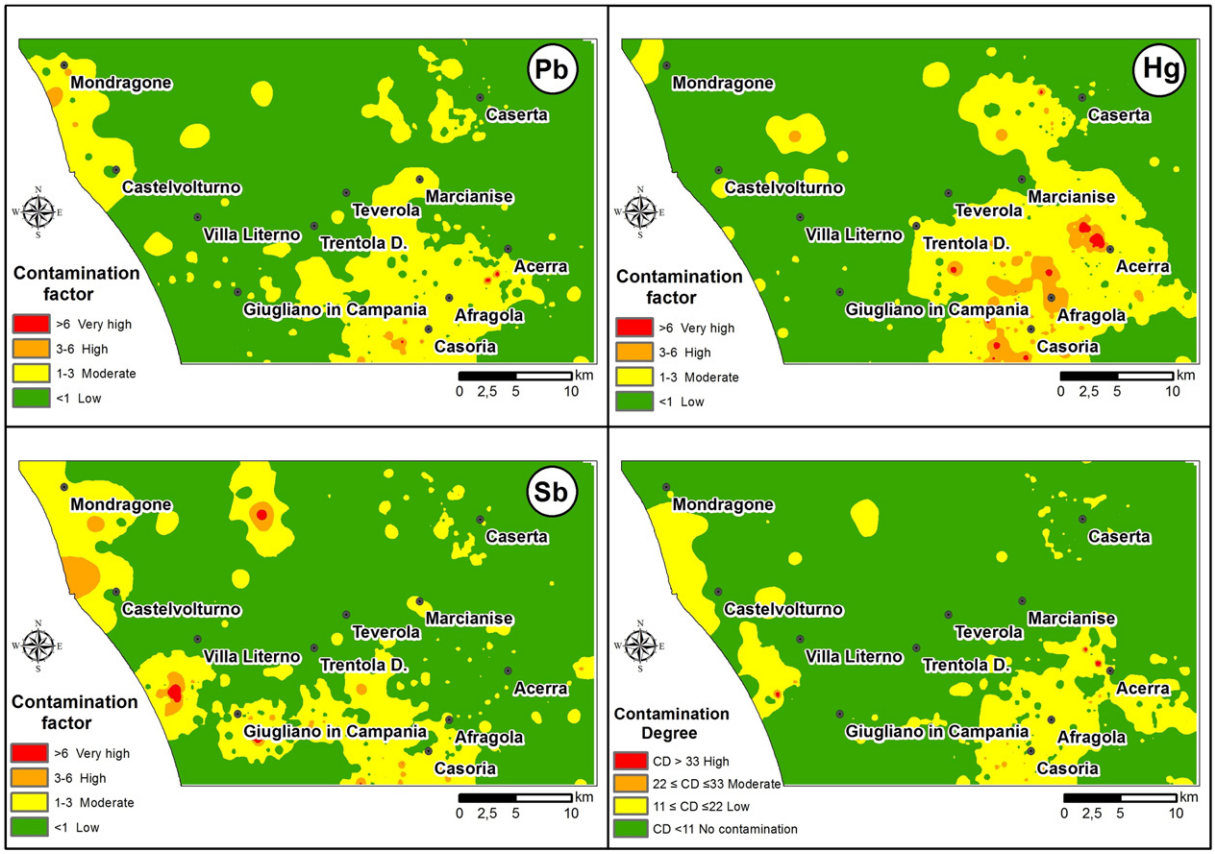

Fig. 4. Contamination factor maps for Pb. Hg, Sb and contamination degree map in topsoil.

possible that the trends of Pb, Hg, Sb, are different from the others. Hg and Sb (Fig. 4) show similar trends with values of 70% and 74% and CF <1 (no contamination); the rest of the samples for Hg and Sb have values of 27% and 23%, respectively, and CF between 1 and 3 (moderate contamination). Perhaps 2–3% of the total area has CF values between 3 and 6 (high contamination) and some samples exceed values of CF ≥6 (very high contamination). The occurrence of several anomalous values might represent the presence of illegal landfill close these cities.

The CF map for Pb (Fig. 4) shows that 75% of the study area has CF < 1 (no contamination), and that 24% of the area has a CF between 1 and 3 (moderate contamination) and 1% has a CF between 3 and 6 (high contamination). Lead contamination is related to the high anthropic impact from heavy vehicular traffic; leaded gasoline was allowed in fuel until 2002.

The CF map for Zn (not shown) shows that 45% of the study area has CF < 1 and the rest (55%) has a CF value between 1 and 3 (moderate contamination). The latter corresponds to areas densely urbanized, close to Acerra, Casoria and Caserta where vehicular traffic is very intense. The CF map for Ni shows that the 84% of the study area has CF < 1, and the rest (15%) has a CF between 1 and 3 (moderate contamination).

We now present the map of contamination degree (CD), which is the result of the sum of all the CF grids:

$$CD = \sum \mathrm{CF}$$

The grid of CDs was reclassified in accordance of elements (11) considered in this study (Zuzolo et al., 2016):

- CD < 11 Low degree of contamination
- 11 ≤ CD ≥ 22 Moderate degree of contamination
- 22 ≤ CD ≥ 33 High degree of contamination
- CD ≥ 33 Very high degree of contamination

The CD map, (Fig. 4) shows that the highest value (CD ≥ 33) is located in the towns of Acerra, and Villa Literno and the moderate value (22 < CD < 33) located in Casoria and Giugliano, where serious anthropogenic pollution occurs, due to a high vehicular traffic, burning toxic waste, illegal waste disposal and sewage.

5.2. Pb isotopic compositions

Anthropogenic contamination by lead in soils is an acute problem particularly in urban and industrial areas (Komarek et al., 2007). Pb isotopic studies provide a way to determine how enrichment of Pb in soil may reflect an interplay of natural and anthropogenic sources. Environmental studies commonly report the isotopic composition of Pb ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$. Table 3 shows Pb isotopic results. The two box plots of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ (Fig. 5e, f) show the range of all environmental media analysed. The samples plot intermediate to the fields for geogenic (volcanic rocks) and anthropogenic (gasoline, fly ash, aerosols) sources.

The dot map (Fig. 5) shows $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ distributions for leached soil (a, b) and soil residues (c, d) for the study area. The dot map also shows Pb isotopic data obtained by Bove et al. 2011, Grezzi et al. 2011, and Civitillo et al. 2016, for leached soil. The $^{206}Pb/^{207}Pb$ isotopic distributions for leached soil (Fig. 5b) demonstrate that values between 1,13 to 1,18 are common in the area. Near the towns of Acerra, Casoria, Teverola, Mondragone and Castelvolturno, such $^{206}Pb/^{207}Pb$ values are linked mostly to anthropogenic sources. The soil residues (Fig. 5d) have values of $^{206}Pb/^{207}Pb$ (1,21–1,23) that are more likely controlled by the natural/geogenic component, in contrast to the compositions of the leached soils which are more closely related to anthropogenic factors.

Plots involving Pb isotopic compositions and heavy metals such as Pb, Sb, Zn (Table 2 and Fig. 6b), show the correlation with soil leaches and residues and suggest mixing. The estimates of anthropogenic contributions are preliminary and represent a first pass at determining

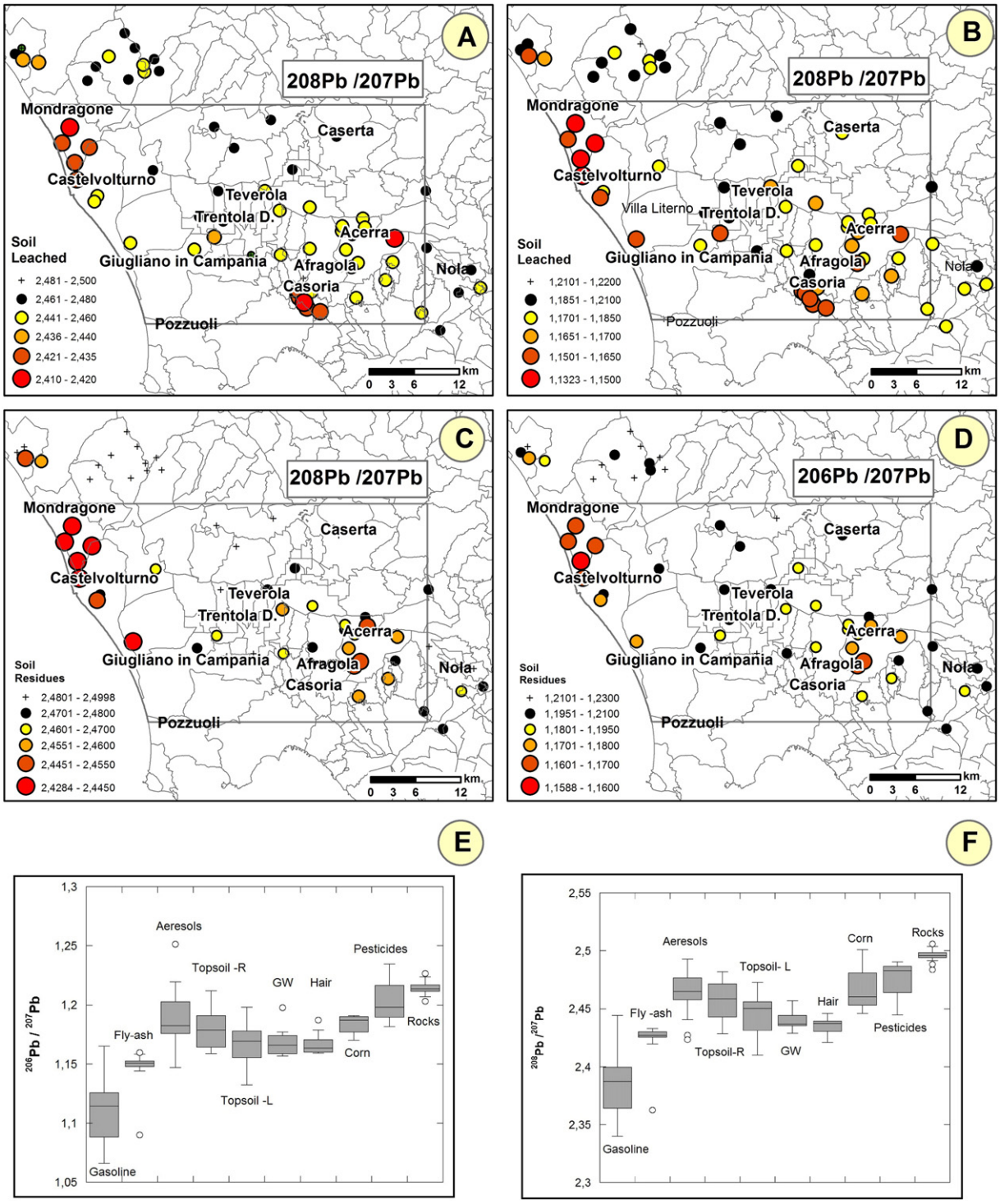

Fig. 5. (A, B, C, D) dot maps showing the concentration of each isotopic ratio $^{206}Pb/^{207}Pb$ and $^{207}Pb/^{208}Pb$. Intervals classified by soil residues and soil leached cumulative frequency graphs; (E, F) $^{206}Pb/^{207}Pb$ and $^{207}Pb/^{208}Pb$ box plots for analysed environmental media (this paper) and for other reference media.

the impact of human activities. This mixing trend can be examined using the value of 1/Pb versus isotopic composition ($^{206}Pb/^{207}Pb$) involving different anthropogenic sources (gasoline and combustion processes). Fig. 6 shows the isotopic ratio $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$ for topsoil, groundwater, human hair and corn. The linear correlation ($R^2 = 0.98$) may represent a mixing scheme, whereby two different end members (geogenic and anthropogenic) are involved, as deduced from statistical analysis. In detail, Fig. 6 shows the regular trend of leached and residue surface samples of this study. Some topsoil samples (LD 41 and LIFE 05) in Castelvolturno and Villa Literno have isotopic values close to the CRITTAM pesticide value, in agreement with results by Grezzi et al. (2011). Leached samples have an isotopic composition close to that of the Pb signature in aerosols (Tommasini et al., 2000), fly ash (Carignan et al., 2005), and urban incinerator products (Geagea et al., 2008). The soil residues, in contrast, plot closer to the compositions of regional volcanic rocks (Ayuso et al., 2008; D'Antonio et al., 1995). Leached samples (LD 42, LD 50 and LD 62) from the city of Castelvolturno and the town of Villa Literno have values closer to the

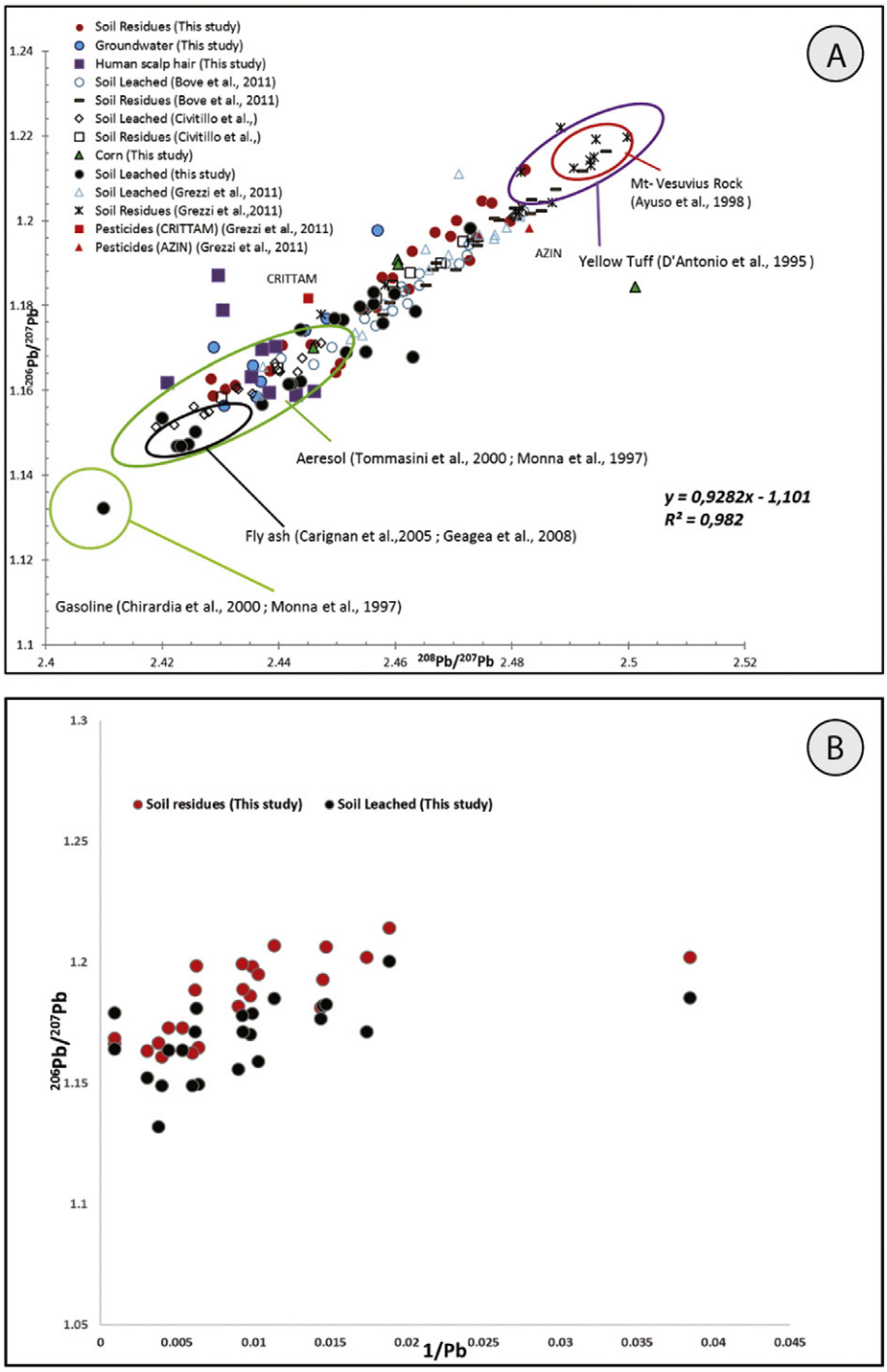

Fig. 6. (A) $^{206}Pb/^{207}Pb$ versus $^{207}Pb/^{208}Pb$ isotopic composition of all sample collected for this study. Also shown data from previous study and field for natural and anthropogenic reference data. (B) $^{206}Pb/^{207}Pb$ versus 1/Pb for soil residues and soil leached.

fly ash (Carignan et al., 2005). These results may indicate that the elemental and isotopic variations are related to refuse burning activities in this area. Leached samples CAS 45, CAS 72, CAS 142 and ACE 29 are closer to the urban incinerator concentration reported by Geagea et al. 2008, particularly samples near the towns of Casoria and Acerra.

To estimate the contributions of Pb from two end members (anthropogenic and geogenic) we have used a simple binary model involving values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$. The value used as a possible anthropogenic end member is a mean of the fly ash and aerosol values from Geagea et al. 2008, Carignan et al. 2005 and Tommasini et al. 2000. The estimated anthropogenic fractions (aerosols and fly ash) in Fig. 6 indicate that the Pb-contamination in soils, groundwater, hair and corn from Domizio Flegreo - Agro Aversano area cannot be linked to a single source but that it is connected to several anthropogenic sources.

Table 2 and Fig. 7 show the distribution of anthropogenic contributions as percentage values for the different media analysed. In detail, the maximum value of anthropogenic Pb is >91% for soil (LD 49) in the town of Mondragone. In general, high percentages of anthropogenic Pb in soils are found in the Domizio - Flegreo area and in some samples in and near the town of Acerra. We note that the mild leaches did not remove all the anthropogenic contribution of the leached soils.

Pb isotopic compositions of hair show that three samples from Acerra (ACE-HF-01, ACE-HF-02, ACE-HF-04) plot in the field of aerosol

Fig. 7. Comparison with 'anthropogenic content' (in %) in all analysed media calculated by taking as reference both aerosols and gasoline Pb isotopic contents. In abscissa sample ID.

products (Tommasini et al., 2000). One hair sample in the town of Castelvolturno has a value as high as 86%, suggesting an anthropogenic source (CAS-HF-04). However, we caution that the effects of hair dyes have not been fully examined and that they could have strongly affected the isotopic compositions of the samples. Moreover, Pb in hair analysed in this study cannot be shown to be directly related to a single individual and, although Pb may be anthropogenic in origin, it may not represent the internal Pb isotopic composition (blood composition). Thus, because we used composite hair samples (from hair salons involving hair from several individuals), the results are at best an approximation of the total amount of Pb and point to an average isotopic composition.

The maximum value of Pb anthropogenic for groundwater samples is 93%, registered for the sample GW 13 situated in Acerra. This high correlation with anthropogenic sources could be related to the high rate of illegal waste disposal and sewage in the region as documented by Bove et al. (2011) Other groundwater isotopic values (GW 05 and GW 11) collected near Acerra are very close to the value of pesticides (CRITTAM); this could reflect agricultural activities in this area. The Pb isotopic approach combined with Geographic Information Systems (GIS) evaluation of elemental values indicate that these concentrations are related to the combustion processes derived from toxic burning, and possibly related to the presence of the urban incinerator in Acerra. The high rate of illegal waste disposal and improper sewage treatment may also be additional point sources (Bove et al., 2011). The estimates of anthropogenic contributions are preliminary and represent a first pass at determining the impact of human activities. Better estimates will be done when the actual regional sources contributing to the Acerra region are discerned and their isotopic compositions established precisely.

6. Conclusions

Results of this study for geochemical and isotopic characterization of various media, with support of GIS and GEODAS software, suggest a complex interplay of geogenic and anthropogenic sources. The results of geochemical analyses of topsoil, groundwater, human hair and corn samples show that the presence of Tl and V can be attributed to a geological source. The numerous agricultural practices in this area could have caused the environmental contamination of Cu. Heavy metal pollution is concentrated in specific areas: Acerra, Casoria, Giugliano in Campania municipalities, as indicated by the high concentration values of several elements such as Hg, Ni, Pb, Se, Sb, Zn. Industrial activities and presence of illegal waste management practices may have greatly contributed to the contamination of Sb, Pb, Hg, Zn and Pb as indicated by the variations of the Pb isotopes ratios in topsoil, groundwater, human hair and local vegetables. We suggest that most of the Pb present in our samples comes from anthropogenic activities. Most of the samples imply the contribution of aerosols and fly ash as a source of lead. Topsoil, groundwater, human hair and corn samples show a greater contribution by geogenic sources, such as yellow tuff and Mt. Vesuvius volcanic and aerosols. Overall, 46% of topsoil (corresponding the solid residues), 96% of topsoil (corresponding the leachate), 88% of groundwater, 90% of human scalp hair, and 25% of corn samples show that >50% percent of the lead found in the area is related to anthropogenic sources. We also conclude that groundwater samples and corn samples can be related to pesticides and thus are a natural effect of intense and long lasting agricultural activities in this area. In the next phase, we are going to study in more detail the potential hazards to human health caused by contamination, either anthropogenic or of natural origin, at the study site.

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