ORIGINAL ARTICLE

Assessment of the topsoil heavy metals pollution in the Sarno River basin, south Italy

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Abstract The Sarno River basin area is one of the most polluted in Europe and it is due to the waste products of the tomato industry, the leather tanneries and the pharmaceutical industry. This area also has been densely populated and urbanized since the Middle Bronze Age, as testified by the presence of numerous archeological sites, including the ancient Pompeii town, and environmental degradation that characterizes the area is absolutely unacceptable. This paper represents a detailed study to assess the potentially harmful element content of topsoils. In total, 283 soil samples were collected and analyzed, after an aqua regia extraction, by a combination of inductively coupled plasma atomic emission and inductively coupled plasma mass spectrometry for 53 elements. Univariate and multivariate analyses were carried out to show the single-element geochemical distribution and the distribution of factor scores of the elemental associations resulting from R-mode factor analysis. Maps showing elements and the association factor score distributions have been obtained using Geo-DAS and ArcGIS software. The assessment of the soil contamination was also carried out using the contamination factor and degree of contamination. The results obtained indicate that soil pollution has different anthropogenic sources. Specifically, Cr pollution derives from tanneries discharging wastewaters in the main water bodies of the basin while Cu contamination seems to depend on widespread agricultural practices. Tin, Pb, Hg, Zn, Cd, Sb anomalies are found mainly in urban and industrial areas, sometimes close to roads with high traffic levels while there is a substantial coincidence with background values for other elements (Co, Ni, Se, Tl and V).

Introduction

Sarno River basin is located to the south of the Somma–Vesuvius volcanic complex in south Italy (Fig. 1a). It covers an area of about 450 km^2 and is drained by the Sarno River (a short watercourse of about 24 km) and its tributaries: Cavaiola and Solofrana. In the south and in the east it is flanked by the Apennine mountain range and in the west opens to the Tyrrhenian Sea. This area is a cultural landscape that is characterized by continuous anthropogenic activity since the Middle Bronze Age. In the last years, it underwent rapid and uncontrolled urban expansion and now is populated by about one million people, concentrated in small towns, that make it one of the most densely populated and urbanized areas in Italy (up to 2,200 inhabitants per km^2 along the coastal zones).

The Sarno is considered the most polluted river in Europe and one of the ten most polluted rivers in the World. Pollution is commonly attributed to the waste products of the tomato industry (108 industries settled mainly along Sarno River), to the chemical processing of animal skin (184 leather tanneries principally along Solofrana tributary) and to the pharmaceutical industry

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Fig. 1 The Sarno River basin:
a industrial sites and roads map;
b geolithological sketch map
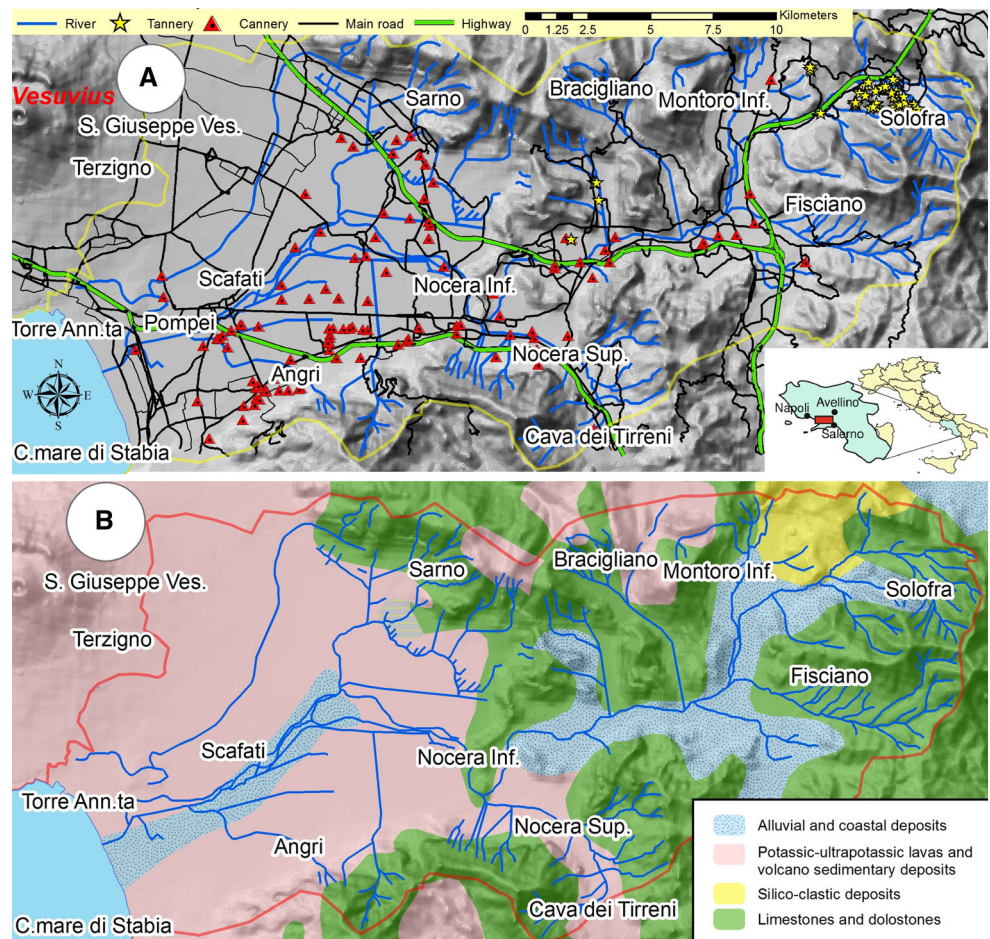
represented principally by Novartis Pharma one of the largest and most important facilities in the World (Fig. 1a). Many other small and medium factories (e.g., producing paints, ceramics and food packaging) are also present in the area.

The situation is worsening by large-scale dumping of untreated agricultural, urban and other industrial wastes into the river (Arienzo et al. 2001). This area is also plagued by frequent flooding and mudslides. In the last 20 years, the banks ruptured two or three times a year, causing spillover polluted waters to the nearby countryside. The man-made drainage canals and the sewers present along the river are also frequently clogged with debris and even cemented in some places, thus increasing the flood risk even more (De Pippo et al. 2006). This area has also been inhabited since antiquity and the past is frequently a hidden source of environmental problems (Albanese and Cicchella 2012).

The combination of high-density population and the presence of highly polluting economic activities has given rise to an extremely precarious environmental situation, which represents an insurmountable obstacle in the way of all prospects of growth. In fact, the serious state of

environmental decline, as well as making necessary redevelopment measures, suffocates the natural and historical-archeological wealth of this area, making social and economic development impossible. It should be taken into account that the ancient city of Pompeii, partially destroyed and buried under 4–6 m of ash and pumice in the eruption of Mount Vesuvius in AD 79, lies in this area. Today, this UNESCO World Heritage Site is one of the most popular tourist attractions of Italy, with approximately 2,500,000 visitors every year and the environmental degradation surrounding it is unacceptable.

The River Sarno decontamination, which began with the Special Project for the reclamation of the entire Bay of Naples in 1973, is a story taking over 40 years, and it did not reach a conclusion yet, despite the ongoing attention it receives from Italian institutions (The Italian Civil Protection Department 2013).

This situation puts the local population to a serious health threat (Motta et al. 2008). The health situation is precarious as the basin's inhabitants feed on agricultural and animal products, and use polluted water directly or indirectly. The hazard of contracting degenerative illnesses of the digestive or respiratory apparatus, bacterial

infections, tumors and cancers has gradually increased, especially in the last 5 years. Moreover, polluted basin waters flowing into the Bay of Naples increase sea water contamination, thereby damaging tourism, public health and degrading the local coastline quality (De Pippo et al. 2006).

In this paper, we have determined the concentrations of all the elements considered as 'pollutants' by Italian legislation (D.L. 152/2006), monitoring an important aspect related to the health of the environment. Italian legislation sets trigger and action levels, in addition to organic substances and compounds, for only a restricted number of inorganic elements. However, a geochemical survey cannot ignore other elements, even if national legislation does not consider them to be harmful. Hence, we analyzed a much wider set of inorganic elements to properly assess and monitor the quality of the environment.

Carrying out this survey, mapping of contaminant distribution was used to allow immediate appraisal of the variability of potentially harmful elements (PHE) and to enable rapid identification of areas that may contain hazardous concentrations. This methodology is essential for site and subsequent risk assessment.

Features of the study area

The Sarno River basin has a Mediterranean climate regime, with average annual temperature of 17.2 °C and average annual rainfall of 1,203 mm, often intense and concentrated at the end of the summer.

The small size of the basin and the steep slopes of the secondary basins together with the widespread inadequacy of sections along the watercourse, due to intense human impact along the banks, lead to continuous overbank in response to exceptional heavy rainfall of short duration (De Pippo et al. 2008).

Geologically, the basin is part of the great graben structure of the Campanian plain that is filled with volcanic, marine and alluvial deposits (Fig. 1b). The main reliefs are constituted by Triassic dolomite, by dolomitic limestone of the lower Jurassic–Cretaceous as well as by Cretaceous fractured and karstified limestone (De Pippo et al. 2006). Pyroclastic deposits and reworked volcanic ashes related to the Mt. Somma–Vesuvius activity (on the N–W sector of the basin) generally cover the calcareous-dolomitic rock of the Sarno Mts. and are widely spread around the Sarno River plain (Cinque et al. 1997).

Soils are young volcanic soils, mainly formed by both colluviums material (from upslope relieves covered by well-developed andosols) and alluvial sediments (Adamo et al. 2006). De Pippo et al. (2008) identify in the Sarno area approximately three different soil systems:

- Soils consisting of Phlegrean and Somma–Vesuvius pyroclastic deposits interlayered with calcareous deposits, moderately coarse texture and moderately acid;
- Soils of the alluvial plain of the rivers Sarno and Solofrana, consisting of alluvial deposits mixed with pyroclastic material, at times terraced, of moderately fine texture, non-limestone on the surface and limestone at depth, neutral pH;
- Soils of the coastal plain of the River Sarno, consisting of deposits from rivers, marine and river lakes and interdunal lagoons, at times terraced, mixed with pyroclastic material of moderately coarse texture, moderately alkaline limestone.

It must be considered that much of the basin is occupied by densely industrialized and urbanized areas, chiefly concentrated along the coastal belt, the mouth of the Sarno River and the plains of the Solofrana and Cavaiola. Soils in urban and industrial areas and those of active or disused quarries consist of disturbed soil and often illegal landfills. The Sarno valley is used for very intensive agriculture, mainly consisting of field horticulture, orchards, vineyards, chestnuts and greenhouse horticulture and floriculture and crop production.

Materials and methods

Sampling and sample preparation

Sampling took place from spring to early summer 2011 all over the Sarno River basin. In total, 283 soil samples were collected at an average sampling density of approximately one sample per 1.5 km². Soil samples were taken as composites from five pits within an area of ∼100 m² in accordance with internationally adopted methods (Salminen et al. 1998; EGS 2008). Approximately 3 kg of soil was collected between 0 and 20 cm below the surface, and stored in inert plastic bags. All samples were air-dried to prevent the volatilization of Hg and sieved to collect 30 g of the <2 mm fraction for chemical analysis.

Chemical analysis

Analyses were carried out at Acme Analytical Laboratories Ltd (Vancouver, Canada), accredited under ISO 9002 within a time span of 20 days from receiving the samples to final delivery of analytical results. The samples were analyzed, after an aqua regia extraction, by a combination of inductively coupled plasma atomic emission (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) 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) using Acme's Group 1F-MS package.

A weight of 15 g of the sieved mineral soil samples (<2 mm) was digested in 90-ml aqua regia and leached for 1 h in a hot (95 °C) water bath. After cooling, the solution was made up to a final volume of 300 ml with 5 % HCl. The sample weight to solution volume ratio is 1 g per 20 ml. The solutions were analyzed using a Spectro Ciros Vision emission spectrometer (ICP-AES) and a Perkin Elmer Elan 6,000/9,000 inductively coupled plasma emission mass spectrometer (ICP-MS).

The quality of all data was assessed by estimations of accuracy and precision. Calibration solutions were included at the beginning and end of each analytical run (40 solutions). Spiking of the digestion solution with a tracer element controls internal standardization. Precision is ±100 % at the detection limit and improves to better than ±10 % at concentrations of 50 times the detection limit or higher.

Data analysis and mapping

Univariate and multivariate analyses were carried out to show the single-element geochemical distribution and the distribution of factor scores of the elemental associations resulting from R-mode factor analysis. The statistical parameters of the univariate analysis are reported in Tables 1, 2, 3 and 4.

For statistical computation, the data below the instrumental detection limit (IDL) were assigned a value corresponding to 50 % of the detection limit.

Factor analysis was used to investigate the complex multivariate relationships among variables, which are not normally clear by simple correlation analysis. Factor analysis basically served to identify different groups of chemical elements with approximately the same geochemical pattern. The abundant literature on multivariate statistical methods and on their application to Earth sciences is available (e.g., Davis 1984; Morrison 2005).

The different factors obtained were studied and interpreted in accordance with their hypothetical origin (natural, anthropogenic or mixed).

Maps showing elements and the association factor score distributions have been obtained using GeoDAS and ArcGIS software. Multifractal inverse distance weighted (IDW) is the interpolation method used with a search distance of 1.5 km. The pixel values of geochemical maps (Fig. 4) have been classified using the concentration–area fractal method (C-A). This method allows images to be subdivided into components for symbolizing distinct image zones representing specific features on the ground (for more details on this methodology, see Lima et al. 2003; Cicchella et al. 2005).

The assessment of the soil contamination was also carried out using the contamination factor and degree of contamination. The contamination factor was calculated using the relation described by Hakanson (1980):

$$C_f^i = C_m^i / C_b^i$$

where, C_m^i is the mean content of metals and C_b^i is the background concentration of individual metal. In this study, the upper limit of background value set by Cicchella et al. (2008a) for Neapolitan volcanic soils is used as a reference value. As shown in Fig. 2, we define four categories of contamination factors (CFs).

The contamination factor described above is a single element index. The sum of contamination factors for all

Table 1 Statistical parameters for major elements in the topsoils of the Sarno River basin

	DL	% <DL	Min	Q10	Q25	Q50	G. mean	Mean	Q75	Q90	Max	MAD
Al	0.01	0	2.24	4.63	5.31	5.78	5.73	5.82	6.48	7.03	9.47	0.57
Ca	0.01	0	0.43	1.59	2.15	2.98	3.21	3.87	4.94	7.38	12.77	1.17
Fe	0.01	0	1.57	2.41	2.74	3.04	2.96	2.99	3.3	3.5	4.12	0.27
K	0.01	0	0.4	0.97	1.45	2.49	2.13	2.42	3.38	3.85	4.76	0.94
Mg	0.01	0	0.33	0.62	0.74	0.85	0.92	1.01	1.04	1.56	4.69	0.14
Na	0.001	0	0.05	0.15	0.30	0.70	0.51	0.65	0.97	1.08	1.54	0.31
P	0.001	0	0.05	0.12	0.19	0.28	0.25	0.28	0.36	0.43	0.62	0.08
S	0.02	0.05	<0.02	0.03	0.04	0.05	0.05	0.06	0.07	0.08	0.21	0.01
Ti	0.001	0	0.06	0.12	0.14	0.16	0.16	0.16	0.18	0.20	0.27	0.02

All values are in %

DL Laboratory detection limit, % <DL percent of samples with concentration <DL, Q quantiles, G. mean geometric mean, MAD median absolute deviation

Table 2 Statistical parameters for potentially harmful elements in the topsoils of the Sarno River basin

	DL	% <DL	Min	Q10	Q25	Q50	G. mean	Mean	Q75	Q90	Max	MAD
As	0.1	0	5.8	10.7	12	13.4	14.1	15.0	15.9	19.9	111.5	1.9
Be	0.1	0	2	4.1	4.8	5.8	5.9	6.2	7.1	8.9	16.9	1.1
Cd	0.01	0	0.15	0.32	0.43	0.56	0.54	0.64	0.68	0.83	11.06	0.13
Co	0.1	0	6	9.1	10.7	12.4	12	12.2	13.9	14.9	16.6	1.6
Cr	0.5	0	5.3	10.7	13	15.9	18.3	27.3	22.2	33.8	808.4	4.1
Cu	0.01	0	25.3	62.0	111.1	187.4	174.3	225.1	273	409	1,555.9	82
Hg	0.005	0	0.008	0.032	0.043	0.065	0.069	0.088	0.11	0.17	0.61	0.027
Ni	0.1	0	8.5	12.7	14	15.4	15.5	15.7	16.8	18.6	29.4	1.4
Pb	0.01	0	27.0	43.7	54.2	65.6	67.7	73.4	81.9	104.8	585.2	13.5
Sb	0.02	0	0.29	0.46	0.61	0.8	0.85	1.04	1.06	1.49	15.79	0.21
Se	0.1	0.01	<0.1	0.3	0.5	0.6	0.55	0.59	0.7	0.8	2.1	0.1
Sn	0.1	0	1.5	3.1	3.6	4.7	5.1	5.7	6.3	9.9	20.8	1.3
Tl	0.02	0	0.67	1.47	1.78	2.03	1.97	2.02	2.32	2.57	3.13	0.26
V	2	0	43	70	80	91	90	91.7	105	114	131	12
Zn	0.1	0	60.5	84.9	103.2	146.3	147.7	165.6	198.3	264.8	1,115.5	47.4

All values are in mg/kg

DL Laboratory detection limit, *% <DL* percent of samples with concentration <DL, *Q* quantiles, *G. mean* geometric mean, *MAD* median absolute deviation

Table 3 Statistical parameters for ultra-trace elements in the topsoils of the Sarno River basin

	DL	% < DL	Min	Q10	Q25	Q50	G. mean	Mean	Q75	Q90	Max	MAD
Ag	2	0	25	64	91	120	121	140	164	231	626	37
Au	0.2	0	0.4	2.8	4.1	7.2	7.3	11	11.6	23.4	212.9	3.3
Pd	10	66.8	<10	<10	<10	<10	<10	<10	11.5	21	66	0
Pt	2	41.2	<2	<2	<2	3	2.5	3.3	4	6	45	2
Re	1	73	<1	<1	<1	<1	<1	<1	1	2	5	0

All values are in µg/kg

DL Laboratory detection limit, *% <DL* percent of samples with concentration <DL, *Q* quantiles, *G. mean* geometric mean, *MAD* median absolute deviation

elements examined represents the contamination degrees (CDs) of the environment.

The map of the spatial distribution of the contamination degrees (CDs) (Fig. 3) was compiled interpolating data obtained by adding together, for each sampled site, the contamination factors of the single fifteen potentially harmful elements.

The grid of CDs was reclassified as follows

$CD \leq 15 =$ No contamination

$15 < CD \leq 18 =$ Low degree of contamination;

$18 < CD \leq 22 =$ Moderate degree of contamination;

$22 < CD \leq 35 =$ High degree of contamination;

$CD > 35 =$ Very high contamination factor.

Results and discussion

To be concise, only distribution maps (Fig. 4) of PHEs with CF values >3 (high) (see Fig. 2) at several sampled sites and the factor scores for the four element associations (Fig. 5), obtained by R-mode factor analysis, are presented here.

Single element distribution

Antimony (Sb)

Sb median concentration value (0.8 mg/kg) in soils of the Sarno River basin (Table 2) is about four times higher than the one (0.23 mg/kg) found by Reimann et al. (2013) in

Table 4 Statistical parameters for trace elements in the topsoil of the Sarno River basin

	DL	% <DL	Min	Q10	Q25	Q50	G. mean	Mean	Q75	Q90	Max	MAD
B	1	0	5	12	16	23	21	22.4	28	32	46	6
Ba	0.5	0	295	445	546	651	633	652	764	849	1,035	108
Bi	0.02	0	0.2	0.3	0.4	0.5	0.5	0.5	0.5	0.6	1.0	0.1
Ce	0.1	0	39.5	66.5	75.7	89	89.5	92.6	107.6	125.8	175.2	15.4
Cs	0.02	0	5.6	11.1	13.3	14.5	14.3	14.5	16.2	17.5	25	1.4
Ga	0.1	0	4.4	8.1	9.2	10.1	10.3	10.5	11.9	13.5	21.3	1.2
Ge	0.1	26.5	<0.1	<0.1	<0.1	0.1	0.1	0.12	0.2	0.2	0.3	0.05
Hf	0.02	0	0.09	0.2	0.24	0.31	0.34	0.41	0.43	0.7	3.32	0.09
In	0.02	33.2	<0.02	<0.02	<0.02	0.02	0.02	0.025	0.03	0.04	0.09	0.01
La	0.5	0	19.7	33.6	38.5	45.3	45.1	46.6	53.6	63.4	86.7	7.1
Li	0.1	0	8.4	13.2	15.4	19.6	19.9	21	26	31.2	45.5	4.8
Mn	1	0	410	669	737	840	847	873	951	1,115	2,741	105
Mo	0.01	0	0.91	1.3	1.58	1.89	1.954	2.076	2.46	2.81	14.06	0.41
Nb	0.02	0	1.9	5.8	7.4	9.3	9.3	10.1	12.4	15.5	22.8	2.5
Rb	0.1	0	51.2	103.4	134.9	182.3	166.1	174.6	219.7	233.8	259.4	39.9
Sc	0.1	0	1.1	1.7	2	2.3	2.4	2.5	2.8	3.5	5.9	0.3
Sr	0.5	0	60.2	142.8	183.9	278.8	255.2	276.2	359.9	408.2	509.7	88.1
Ta	0.05	100	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0
Te	0.02	21.2	<0.02	<0.02	0.02	0.05	0.04	0.05	0.07	0.09	0.18	0.02
Th	0.1	0	3.6	9	10.9	13.3	13.5	14.3	16.7	20.8	47.8	2.9
U	0.1	0	1.8	3	3.8	4.8	4.8	5.1	6	7.2	23.7	1
W	0.1	0	0.7	1	1.2	1.4	1.4	1.5	1.7	2	4.3	0.3
Y	0.01	0	7.1	12.4	14.1	16.5	16.7	17.2	19.9	23.5	34.0	2.7
Zr	0.1	0	7.4	18.4	22	28.8	31.9	38.0	41	69.2	269.8	8.1

All values are in mg/kg

DL Laboratory detection limit, *% <DL* percent of samples with concentration <DL, *Q* quantiles, *G. mean* geometric mean, *MAD* median absolute deviation

agricultural soils of Europe (Table 5). Antimony content in soils (Table 2) ranges from 0.29 to 15.79 mg/kg with 67 % of the samples characterized by values below 1 mg/kg (Fig. 6) that represent the upper limit of natural background in this area as stated by Cicchella et al. (2008a). The antimony interpolated data distribution (Fig. 4) show the highest values (>5 mg/kg) in correspondence to the most urbanized areas of Sarno River basin and has clearly an anthropogenic origin due to motor vehicle traffic. The occurrence of Sb anomalous value (15.79 mg/kg) might represent the presence of illegal waste disposal close to Nocera Superiore where Sb is associated with Sn and Zn (Fig. 3). In this area, antimony, highly toxic for humans, exceeds the trigger and action levels (10 mg/kg) set by Italian environmental law (D.L. 152/2006). Here, the CDs map (Fig. 3) shows a high degree of contamination.

Arsenic (As)

The volcanic soils of the entire Sarno River basin are characterized by quite elevated As concentration with a

median value of 13.4 mg/kg well beyond the median (5.5 mg/kg) of European soils. The mean values are 15 mg/kg with a range from a minimum of 5.8 mg/kg up to a maximum of 111.5 mg/kg (Table 2). These high concentrations coincide at 82 % with natural background values (Fig. 6) set by Cicchella et al. (2008a) for Neapolitan volcanic soils. The 9 % of samples exceed the residential/recreational intervention limit (20 mg/kg) and 1 % shows concentration higher than the commercial/industrial intervention limit (50 mg/kg). The anomalous values (>18 mg/kg) between Bracigliano and Mercato S. Severino and between Sarno and Nocera Superiore are probably due to As tendency to be sorbed strongly by secondary iron oxyhydroxides, as well as by clay and organic matter. In these periodically flooded areas, the oxidation/reduction reactions strongly govern the mobility of As in soil. The another cause of soil enrichment might be related to agricultural activities and the ability of As^{5+} to replace P^{5+} in phosphate minerals, such as apatite, which are often used as mineral fertilizers. The CDs map (Fig. 3) shows a very high degree of contamination close
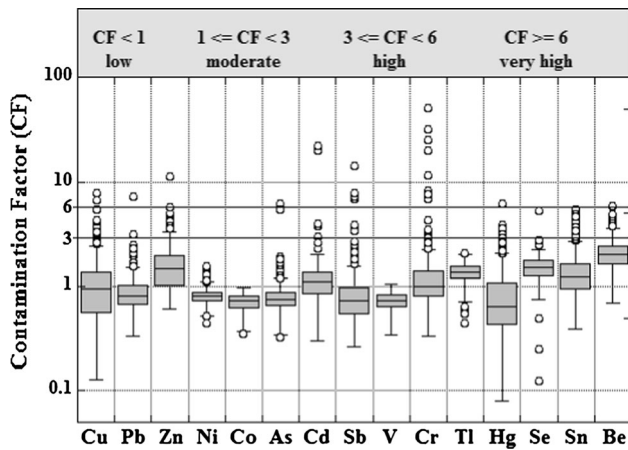
Fig. 2 Box-plots of contamination factors

to Bracigliano (Cr and As) and M. S. Severino (Cr, As, Zn and Hg).

Beryllium (Be)

Be median concentration in an aqua regia extraction of the Sarno River basin soil is 5.8 mg/kg much higher (11 times) than the median concentration of the European soil (0.52 mg/kg) (Table 5). The unusually high Be concentrations arise from natural sources; they are certainly caused by the presence in the soil of clay minerals weathered from alkaline igneous rocks representing the parent rock from which the soils resulting. When released during weathering, Be binds to clay or humic material or co-precipitates with Fe–Mn hydroxides. The maps of Be (Fig. 4) show a clear difference between eastern area of the Basin with predominantly relative low concentrations (mostly <5.3 mg/kg), and central area with distinctly higher values (up to 16.9 mg/kg). The clear break in concentrations marks well a slight variation in the soil pH; in

facts Be mobility is strongly pH dependent and can be quite high at an acid pH. As shown in Fig. 6, all analyzed soils show concentration values higher than the residential/recreational intervention limit (2 mg/kg) and 1 % exceeds the commercial/industrial intervention limit (10 mg/kg).

Cadmium (Cd)

Cd median concentration is 0.56 mg/kg three times greater than the median of aqua regia extractable Cd (0.18 mg/kg) in the European agricultural soils (Table 5). The 65 % of the analyzed samples show concentration above 0.5 mg/kg (Fig. 6) that represents the upper limit of background value set by Cicchella et al. (2008a) for Neapolitan volcanic soils. In two samples between Poggiomarino and San Valentino T. (Fig. 4), Cd concentration exceeds action level (2 mg/kg) set by Italian environmental law (D.L. 152/2006). As for Sb, the anomalous values have an anthropogenic origin and they are related to the high urbanization of the area rather than to the agricultural activities. The CDs map (Fig. 3) shows that Cd is the main responsible for the high degree of contamination in the area between the municipalities of Scafati and Striano.

Chromium (Cr)

The Sarno basin soil median for Cr in an aqua regia extraction is 15.9 mg/kg lower than the Cr median concentration (20 mg/kg) in European agricultural soils (Table 5). The 49 % of the analyzed samples show concentration above 16 mg/kg (Fig. 6) that represents the upper limit of background value set by Cicchella et al. (2008a) for Neapolitan volcanic soils and 2 % of samples have a Cr concentration that exceed action level (150 mg/kg) set by Italian environmental law (D.L. 152/2006). Observation of interpolated data shows that most of the

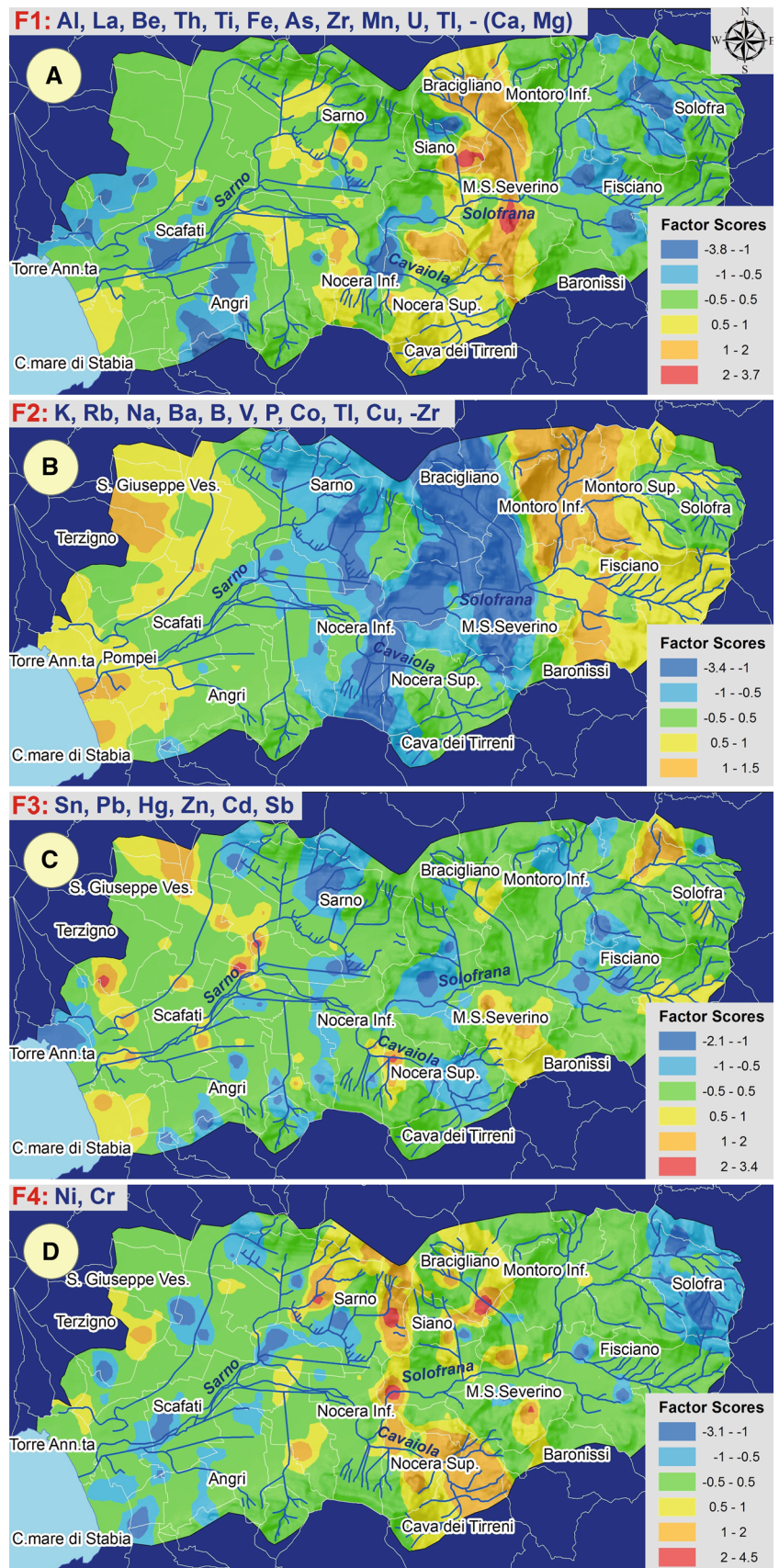Fig. 3 Map of the contamination degree (CDs) distribution
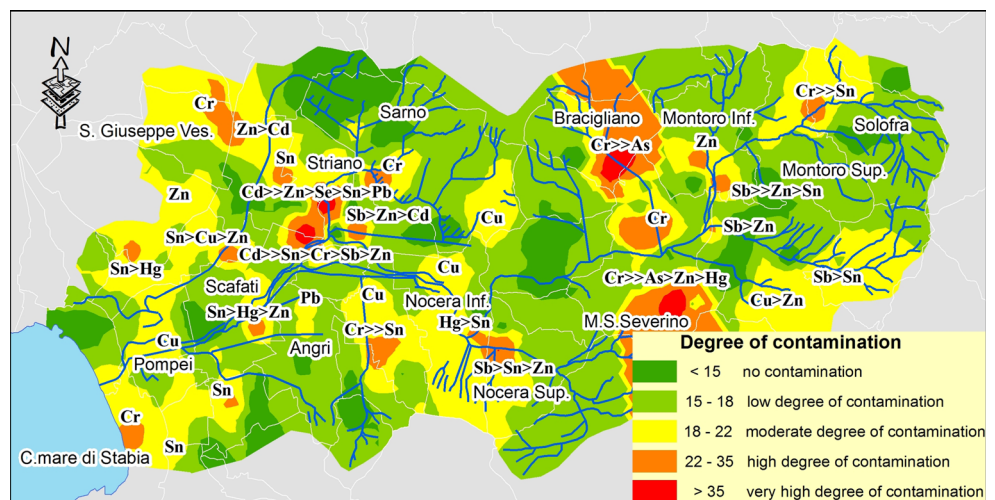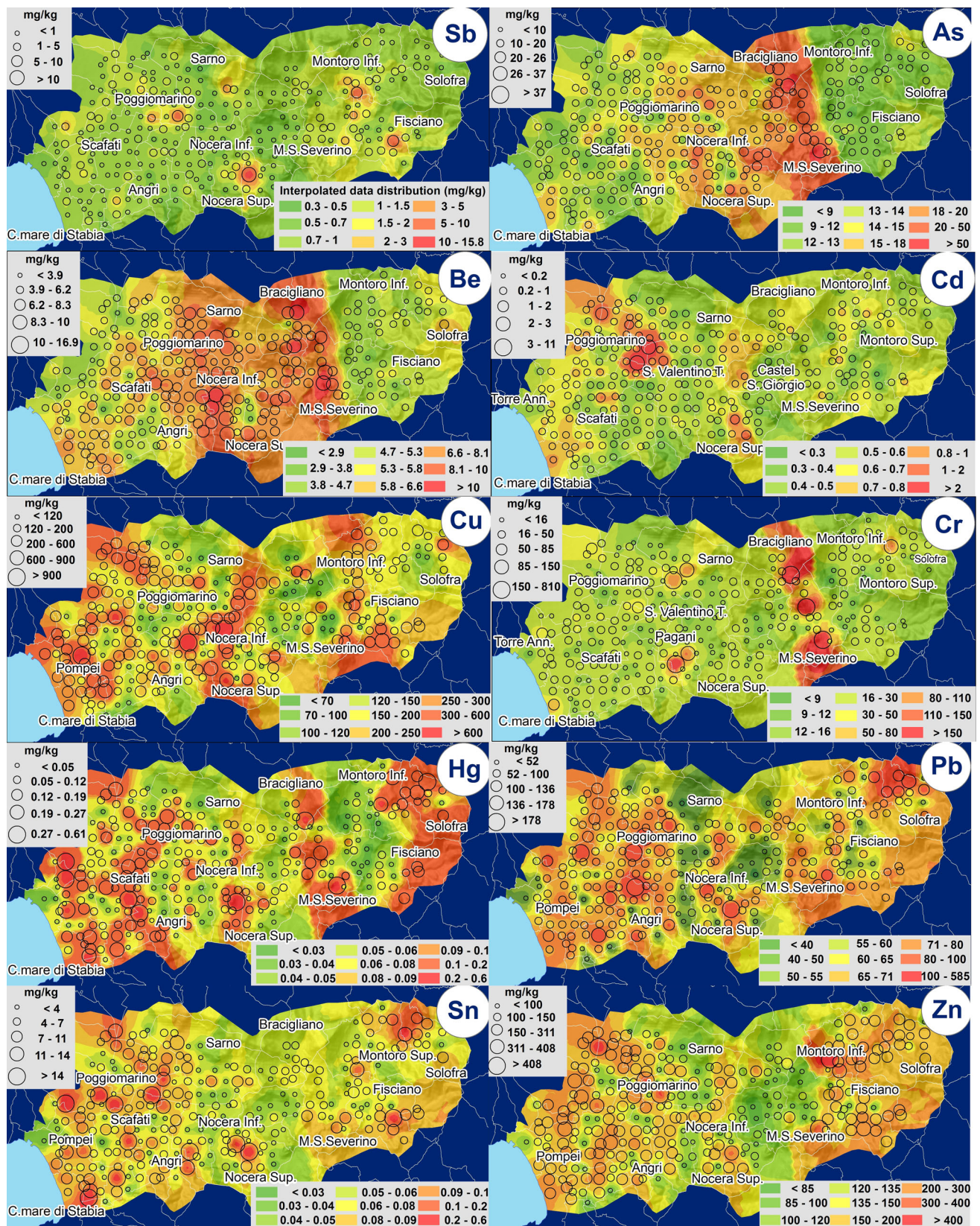
Fig. 4 Potentially harmful elements (PHEs) geochemical maps

Fig. 5 Factor scores
association maps

Table 5 Average distribution of selected elements harmful to human health

Elements	A	B	C	D	E	F	G
As	13.4	12.4	7	11.7	5.4	7.65	2
Be	5.8	3.8	–	–	0.52	–	–
Cd	0.56	0.5	0.1	–	0.18	0.53	0.102
Co	12.4	9.3	3	19.3	7.4	7.9	11.6
Cr	15.9	12.5	5	42.5	20	54	35
Cu	187.4	163	39	72.5	14	19.8	14.3
Hg	0.065	0.19	–	–	0.03	0.03	0.056
Ni	15.4	11.8	5	22.4	15	22	18.6
Pb	65.6	100	48.5	42.5	16	28.6	17
Sb	0.8	1.4	0.5	0.53	0.23	5	0.31
Se	0.6	0.3	–	0.6	0.35	0.33	0.083
Sn	4.7	4.6	–	–	0.72	–	–
Tl	2.03	1.5	1	0.5	0.12	0.1	0.75
V	91	71	26	94	25	70.8	53
Zn	146.3	142	66	84.4	45	64	52

A Sarno River basin soils, *B* Neapolitan volcanic soils (Cicchella et al. 2008a), *C* Ischia island volcanic soils (Frattini et al. 2006), *D* representative Vesuvius eruptive formations (Paone et al. 2001), *E* agricultural soils of Europe (Reimann et al. 2013), *F* upper continental crust (Wedepohl 1995), *G* earth's soils (Kabata-Pendias and Pendias 2001)

area has a Cr concentration ranging between 12 and 30 mg/kg while concentrations increase remarkably reaching values higher than 110 mg/kg up to maximum of 810 mg/kg between Bracigliano and Mercato San Severino, south of Pagani and in the municipalities of Sarno and Solofra.

As demonstrated in previous paper (Adamo et al. 2003, 2006; Albanese and Cicchella 2012; Arienzo et al. 2001), the increase of Cr values in the Sarno River basin can be related to the activity of numerous tannery plants located along the banks of the Solofrana river (Fig. 1a) which caused, in the past, a Cr-enrichment of the Solofrana waters. Adamo et al. (2003) emphasize how the extensive use of river water for irrigation (prohibited since 1990) and the frequent river overflowing events produced a widespread and well-documented pollution of the valley soils. In recent years, the concentration of Cr in river waters has decreased as a result of the tendency to import already tanned raw materials (Manzo 1999) and improved wastewater control from the tanning plants. Nevertheless, as is evident by observing the Cr interpolated data distribution map (Fig. 4), the valley soils still retain Cr whose concentrations are well above background values. Adamo et al. (2003) states that the dominance of the relatively insoluble and less mobile Cr(III) form over the more soluble and less strongly adsorbed to soil particles Cr(VI) attests to the low hazard associated with the Cr contamination of the soil.

Copper (Cu)

The distribution of Cu concentration values shows the highest values (250–1,556 mg/kg) in the western area along the Mt. Vesuvius slopes in the vicinity of flourishing vineyard crops and in the most urbanized areas between Pompei and C.mare di Stabia (Fig. 4). These anomalous values are certainly influenced by anthropogenic pollution, and are well above the intervention level established by the environmental Law 152/2006 (Fig. 6) for both recreational/residential areas (120 mg/kg) and industrial/commercial land use (600 mg/kg). Only 50 % of analyzed samples (Fig. 6) show concentration values <200 mg/kg which represents the upper limit of background value set by Cicchella et al. (2008a). The anthropogenic factor influencing the high baseline values is well evident from Table 6, which shows a very high enrichment of Cu in Sarno River basin soils compared to the average concentrations in European agricultural soils, upper continental crust, in Mt. Somma–Vesuvius rocks and in Earth's soils. The CDs map (Fig. 3) shows that, in several areas of the basin, Cu contributes to confer a moderate degree of contamination almost always as a single element.

Lead (Pb)

Pb median concentration is 65.6 mg/kg, four times greater than the median of aqua regia extractable Pb (16 mg/kg) in the European agricultural soils (Table 5) (Reimann et al. 2012). The lead interpolated data distribution (Fig. 4) shows the highest values (>80 mg/kg) corresponding to the highly urbanized areas of the investigated territory (Castellammare, Poggiomarino, Pompei, Angri, Nocera). As shown in Figs. 4, 6, most of the volcanic soils (70 %), not anthropogenically influenced, show concentration values in the range 27–80 mg/kg, which represents the upper limit of background value set by Cicchella et al. (2008a). The 15 % of samples have a Pb concentration value above the intervention criteria fixed by Environmental Italian Law (D.L. 152/2006) for Pb in soils for recreational/residential land use (100 mg/kg). The motor vehicle emissions are certainly the major source of Pb, especially in the urban environment. In Italy, the use of Pb gasoline was permitted until January 2002, when catalytic exhausts became mandatory (Cicchella et al. 2008b). Similar to the Hg distribution, the influence of anthropogenic factors on concentration value distribution is clear from Table 6 which shows enrichment of Pb in Sarno River basin soils when compared with average concentrations of Ischia soils, European agricultural soils, upper continental Crust, Mt. Somma–Vesuvius rocks and Earth's soils. The average concentration levels are slightly lower than those of the Naples metropolitan area where recent studies have
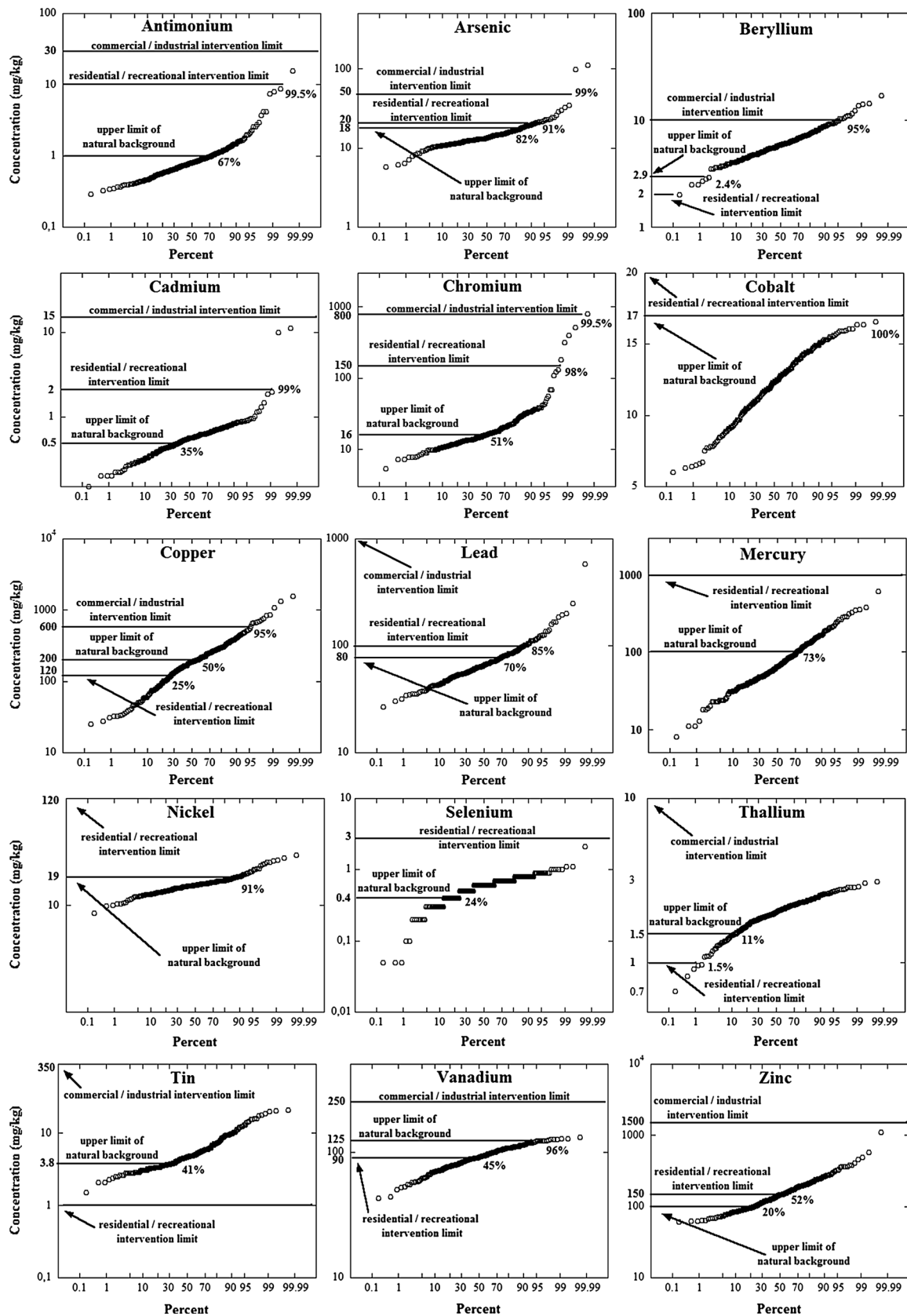
Fig. 6 Cumulative frequency curves for PHEs. The graphs also report the upper limit of natural background values, the residential/recreational and the commercial/industrial intervention limit

Table 6 Varimax-rotated factor (five-factor model) for 283 soil samples from Sarno River basin

Elements	Factors				Communalities
	F1	**F2**	**F3**	**F4**	
Al	**0.90**	0.17	−0.19	0.03	0.94
As	**0.71**	−0.29	0.06	0.29	0.81
B	−0.26	**0.78**	0.20	−0.10	0.83
Ba	0.28	**0.88**	0.10	0.05	0.90
Be	**0.84**	−0.31	−0.11	−0.05	0.89
Ca	**−0.80**	−0.03	0.15	0.04	0.83
Cd	−0.03	0.08	**0.68**	0.29	0.62
Co	0.45	**0.74**	−0.09	0.41	0.94
Cr	−0.02	−0.08	0.41	**0.57**	0.59
Cu	−0.06	**0.51**	0.35	0.18	0.56
Fe	**0.78**	0.39	−0.13	0.36	0.95
Hg	−0.05	−0.06	**0.71**	0.01	0.67
K	−0.17	**0.96**	0.03	−0.10	0.97
La	**0.88**	−0.27	−0.09	0.11	0.93
Mg	**−0.50**	−0.31	−0.02	0.19	0.67
Mn	**0.61**	−0.01	0.02	0.34	0.71
Na	−0.25	**0.89**	0.02	−0.20	0.95
Ni	0.18	0.07	0.22	**0.76**	0.77
P	−0.23	**0.75**	0.44	0.13	0.91
Pb	−0.02	0.13	**0.80**	−0.02	0.66
Rb	0.02	**0.94**	−0.06	−0.04	0.95
Sb	−0.26	−0.08	**0.65**	0.05	0.68
Sn	−0.14	0.06	**0.83**	0.06	0.75
Th	**0.84**	−0.17	−0.30	−0.02	0.93
Ti	**0.81**	0.19	−0.21	0.07	0.89
Tl	**0.57**	**0.72**	−0.12	0.09	0.90
U	**0.59**	0.45	0.10	−0.11	0.70
V	0.47	**0.76**	−0.18	0.24	0.94
Zn	−0.23	0.37	**0.71**	0.20	0.77
Zr	**0.71**	**−0.54**	−0.33	−0.09	0.95
Eigenvalues	8.99	8.06	3.65	1.16	–
%Variance explained	29.95	26.87	12.16	3.88	–
Cumulative % variance	29.95	56.82	68.98	72.86	–

F1 association = Al, La, Be, Th, Ti, Fe, As, Zr, Mn, U, Tl, –(Ca, Mg); F2 association = K, Rb, Na, Ba, B, V, P, Co, Tl, Cu, –Zr; F3 association = Sn, Pb, Hg, Zn, Cd, Sb and F4 association = Ni, Cr. In bold the factor values >|0.5|

demonstrated that Pb contamination affects semen quality in men (Giaccio et al. 2012; Filippelli et al. 2012).

Mercury (Hg)

Hg median in aqua regia extraction in studied soil is 0.065 mg/kg that is two times higher than the median found in European agricultural soil (0.030) mg/kg. Table 6 shows an enrichment of Hg in Sarno River basin soils compared also with average concentration values of upper continental crust and Earth's soils (no comparative data exist for Ischia island and Mt. Somma–Vesuvius rocks) (Table 5).

The Hg interpolated data distribution (Fig. 4) shows the highest values (>0.1 mg/kg) in the mostly urbanized areas in the western part of the basin and between Solofra and Montoro where they could be related to the activity of numerous tannery plants. This is true also for the area between Bracigliano and Mercato San Severino where the anomalies are due to strong Hg tendency to bind to organic material of which the soils of this area are rich. The rest of soils are characterized by concentration values <0.1 mg/kg, which Cicchella et al. (2008a) identify as natural background values of Neapolitan volcanic soils. It is important to note that the extent of these clearly anthropogenic Hg anomalies (that, as shown in Fig. 6, represent the 27 % of the soil samples) poses a potential health risk to a large segment of the population.

Tin (Sn)

The volcanic soils of the entire Sarno River basin are characterized by elevated Sn concentration. The mean values are 5.7 mg/kg with a range from a minimum of 1.5 mg/kg up to a maximum of 20.8 mg/kg (Table 2). The median concentration of Sn in an aqua regia extraction of European soil is 0.723 mg/kg while in Sarno River basin soils is 6.5 times greater (4.7 mg/kg). The high concentration values are partly due to a high content of natural background and the other part from widespread anthropogenic contamination present in the most populated areas of the basin. The CDs map (Fig. 3) shows that, in several areas of the basin, Sn largely contributes to increase a degree of contamination.

Zinc (Zn)

The distribution of zinc concentration values matches quite well with the Pb distribution. The highest Zn values (200–1,115 mg/kg) correspond to the mostly urbanized territory. The 80 % of the analyzed samples show concentration above 100 mg/kg (Fig. 6) that represents the upper limit of background value set by Cicchella et al. (2008a, b) for Neapolitan volcanic soils and 48 % of samples have a Zn concentration that exceeds action level (150 mg/kg) set by Italian environmental law (D.L. 152/2006). The median of Zn in an aqua regia extraction of European agricultural soil is 45 mg/kg more than three times lower than that of Sarno basin soils (146.3 mg/kg). As also reported in Albanese et al. (2013), in these areas,

where Zn values rise up to 400 mg/kg (Fig. 4), the element accumulation in the environment is mostly related to traffic load and human mobility with special emphasis to the tire consumption process of motor vehicles.

Factor associations

R-mode factor analysis has been performed to determine the possible relationship existing between the distribution of individual elements (and other parameters) and lithology or surface enrichment phenomena related to the weathering, environmental condition or to anthropogenic sources. R-mode factor analysis has been performed on a matrix containing 35 elements. The chemical elements with an elevated percentage (>5 %) of analytical determinations below the instrumental detection limit were not considered for factor analysis. To facilitate the interpretation of results, varimax rotation was used because it is an orthogonal rotation that minimizes the number of variables that have high loading on each factor, simplifying the interpretation (Reimann et al. 2002). Table 6 lists the four factor solutions accepted along with rotated factors' loadings. This solution accounts for 72.9 % of the total variance. Table 6 shows the rotated factors' loadings with variables in alphabetical order, communalities, eigenvalues and percentages of variance accounted for the four factors associations.

Elements with loadings over (0.5) are considered as representative members of each association that results from the chosen factor model. The element association F1 [Al, La, Be, Th, Ti, Fe, As, Zr, Mn, U, Tl, –(Ca, Mg)] accounts for 29.95 % of data variability while the F2 association (K, Rb, Na, Ba, B, V, P, Co, Tl, Cu, –Zr) accounts for 26.87 % of data variability; F3 (Sn, Pb, Hg, Zn, Cd, Sb) and F4 (Ni, Cr) accounts for 12.17 % and 3.88 % of data variability, respectively. In each association, elements are listed with decreasing loadings (Table 6).

Maps of the factor score distributions are very useful to correlate lithologies with physicochemical and pollution processes of the surface environment at each sampled site. Figure 5 shows, for each association identified by the factor model 4, an interpolated distribution map of factor scores. These maps fit well with the distribution of the single elements that have a high loading in this association.

The element association of Factor 1 [Al, La, Be, Th, Ti, Fe, As, Zr, Mn, U, Tl, –(Ca, Mg)] is mostly controlled by the presence of pyroclastics and volcanic soils covering hilly and mountain areas surrounding the Sarno River plain and the Solofrana valley. Specifically, the highest factor score values (ranging from 0.5 to 3.7) characterize the areas between Bracigliano, Siano and Mercato S. Severino.

The elevated concentrations of elements from this association in the Sarno soils are derived from a natural origin and can be explained mostly by the occurrence of Fe and Mn hydroxides which can adsorb and co-precipitate metallic elements.

The association F2 (K, Rb, Na, Ba, B, V, P, Co, Tl, Cu, –Zr) is characterized by elements primarily affected by natural factors (lithological background) and by anthropogenic influence. The highest factor score values (up to 1) are distributed along the southeastern slopes of Vesuvius and in the eastern sector of studied area between Montoro and Baronissi. The elevated values of the factor scores of this association are mainly explained by the presence of volcanic soils, with andic properties, rich in feldspars and micas.

On the other hand, this enrichment, is also justified by the agricultural activity, with large areas cultivated as vineyards, crops and orchards where the use of pesticides and fertilizers is very intense.

The element association F3 (Sn, Pb, Hg, Zn, Cd, Sb) is explained by elements exclusively introduced in the environment by human activities. The factor score distribution is clearly dominated by anthropogenic sources; in fact the very high values (between 0.5 and 3.4) coincide exactly with the most urbanized areas and particularly correspond to roads with heavy daily traffic jams (Fig. 5). The least inhabited areas are practically uncontaminated, being characterized by negative values of the factor scores which indicate a depletion, in the soil sampled, of the elements that constitute this association.

The factor scores association F4 (Ni–Cr) (Fig. 5) shows the highest scores in the central sector of Sarno River basin. These anomalies can be related to the non-effective treatment of the wastewaters from the tannery district of Solofra. As already stated by Albanese et al. (2013) and references therein, chromium salts (particularly Cr sulfate) are the most widely used tanning substances, well in excess from the skin tanning process. Ni is released from additional tanning agents used during the industrial process.

Conclusions

The results obtained indicate that there is a coincidence with background values for some elements (Co, Ni and V), whereas the other investigated toxic elements (Cr, Cu, Hg, Pb, Sb, Zn) show concentration values with an evident anthropogenic control mostly in the soils of the more urbanized areas or in areas characterized by industrial or agricultural activities. The contamination of soils has different anthropogenic sources. Specifically, Cr pollution derives from tanneries in the Solofrana river valley, discharging wastewaters in the main water bodies of the basin while Cu contamination seems to depend by widespread agricultural practices. Tin, Pb, Hg, Zn, Cd, Sb anomalies

are found mainly in urban and industrial areas, sometimes close to roads with high traffic levels, suggesting a direct connection with human presence and activity.

Elemental associations obtained by means of R-mode factor analysis have been very helpful in interpreting and distinguishing spatial data dominated by anthropogenic sources as opposed to those controlled by geogenic sources. F1 [Al, La, Be, Th, Ti, Fe, As, Zr, Mn, U, Tl, –(Ca, Mg)] and F2 (K, Rb, Na, Ba, B, V, P, Co, Tl, Cu, –Zr) are the elemental associations which indicate a geogenic influence whereas F3 (Sn, Pb, Hg, Zn, Cd, Sb) and F4 (Ni–Cr) are the elemental associations which unmistakably reflect anthropogenic control.

The sum of contamination factors for all metals examined indicates widespread degree of contamination in soil. It is inferred that the contamination is from the anthropogenic sources like traffic, discharge of untreated industrial waste, agricultural activities and dumping of solid waste.

While our objective was not to examine the adverse health effect associated with the pollution of the Sarno River basin, the present article has shown that people living in this area may be exposed to high health hazard. The results of this study allow us to evaluate qualitatively and provide information on the presence in surface soils of potentially harmful elements associated with pathogenicity in humans. The human health risk associated with the heavy metal contamination of the soil, and indirectly the food chain, seemed very high. The most important exposure risks is associated with Cr, Cd, Sn, Sb, Cu, As, Hg, Zn and Pb levels in soils and the ingestion of locally grown vegetables could be the predominant exposure pathway.

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