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Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy)

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Abstract

In this paper are discussed the baseline geochemical maps of elements harmful to human health, using concentration values of 2389 stream sediment samples collected over the Campania region (Southern Italy). Each sample was digested in *aqua regia* and analysed by ICP-MS. For compilation of baseline geochemical maps, a recently developed multifractal inverse distance weighted (IDW) interpolation method and spectral analysis (S-A) was applied, using a new geochemistry dedicated GIS software (GeoDAS). The aim of this study is to discriminate between the geogenic natural content (background) and the anthropogenic contribution in the collected sediments. The definition of background values, in contrast to baseline values, is very important in determining the extent of polluted areas in countries like Italy, where environmental legislation has not yet established intervention limits for stream sediments.

In the Campania region, baseline and background values are often coincident, where the samples represent catchment basins away from urban or industrial areas. Potential polluted areas are often very small in size, except for some sites where the anthropogenic influence on sediments is clearly evident, due to the wide extent of local industrial and agricultural activities (e.g., the Sarno River catchment basin).

R-mode factor analysis has proved very useful in distinguishing geochemical data, clearly dominated by anthropogenic in comparison to geogenic sources.
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Keywords: Background; Baselines; Harmful elements; Stream sediments; Environmental pollution

1. Introduction

In recent years, environmental geochemical mapping has assumed an increasing relevance (Plant et al., 2001), and the separation of values to discriminate between anthropogenic pollution and natural (geogenic) sources is probably even more crucial than the distinction of background from anomalies in geochemical prospecting for mineral exploration.

In the Campania region, 2389 stream sediments samples were collected at a density of 1 sample per 5 km^2 (Fig. 1) for the purpose of compiling an environmental geochemical atlas (De Vivo et al., 2003a). The project was undertaken as part of a more general one, aimed, in the near future, at the compilation of an environmental geochemical atlas covering the whole of Italy, with the same sample density used for the Campania region. In this paper the baseline geochemical maps of the

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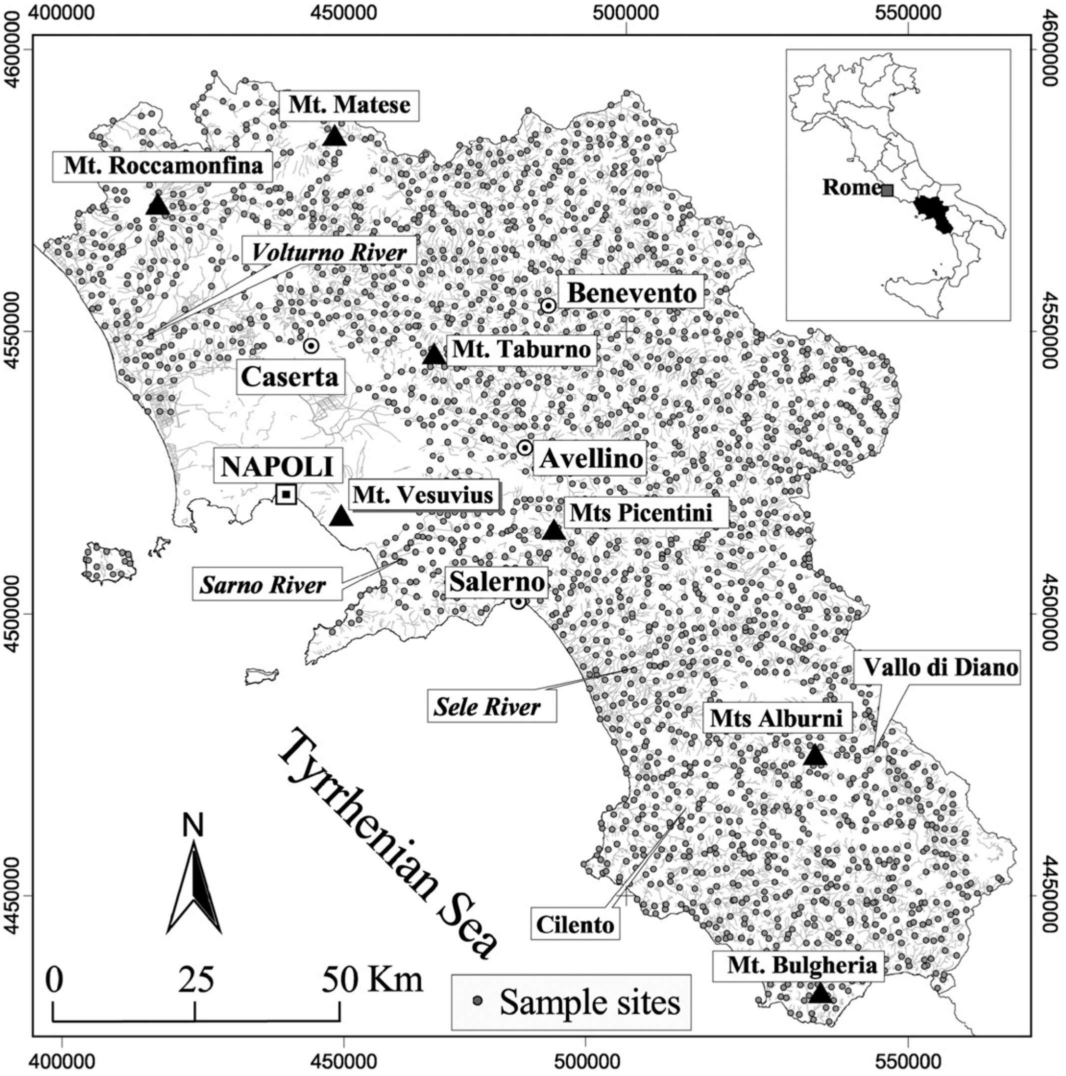

Fig. 1. Stream sediment sample site map.

Campania region for selected elements (considered to be harmful to human health), compiled from stream sediment data, are discussed.

The term geochemical baseline indicates the actual content of an element in the superficial environment at a given point in time, as is defined by Salminen and Gregorauskiene (2000). The geochemical baseline of stream sediments in an area of heavy anthropogenic impact includes the geogenic, natural content (background). The determination of background (geogenic) values, in contrast to baseline values, is very important for defining the extent of pollution in areas where environmental legislation has not yet established intervention limits for all environmental matrices. In 1999, the Italian government established intervention values for some selected toxic elements (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V and Zn) in soil and stream water (Ministero dell'Ambiente, 1999) and, recently, in marine sediments, but not for stream sediment.

Because of the geological complexity and long-term economical development of the Campania region, it is reasonable to presume that elevated concentrations of metals in stream sediment are, in most cases, strongly influenced by anthropogenic contributions.

Studies carried out on soil of the Neapolitan province have already highlighted the influence of human activities on different sample types (Tarzia et al., 2002; Cicchella et al., 2005). Discriminating between geogenic and anthropogenic contributions with respect to total concentrations of toxic elements is fundamental in the quantitative assessment of metal pollution threats to the ecosystem and human health.

The specific aim of this study is to determine geochemical baseline and background levels of potentially harmful elements in stream sediments of the Campania region, using a multifractal approach by means of spectral analysis (S-A) and concentration–area (C-A) fractal methods (Cheng et al., 1996, 2000; Lima et al., 2003) to provide vital information for future developments of environmental legislation.

2. Study area

The Campania region (Fig. 1) covers an area of about 13,600 km^2. It is the second most populated region in Italy (about 6 million inhabitants), with more than 50% being concentrated in the Naples metropolitan area.

2.1. Geology

Morphologically, Campania is made up of the Apennine Mountains in its eastern sector, oriented roughly NE–SW, and on the west by two coastal plains: Campania and Sele, traversed respectively by the Volturno and Sele Rivers. The Apennine chain consists of a pile of nappes formed during the Miocene, overthrust towards the N-NE, and is made up of several blocks in contact with each other along tectonic discontinuities. The lithology consists mostly of sedimentary and volcanic rocks, spanning from the Triassic to recent times (Bonardi et al., 1998) (Fig. 2).

The sedimentary rocks include limestone, dolostone, siliceous schist and terrigenous sediments (clay, siltstone, sandstone, conglomerate) of Mesozoic age, which characterise mostly the external Apennine domain; the

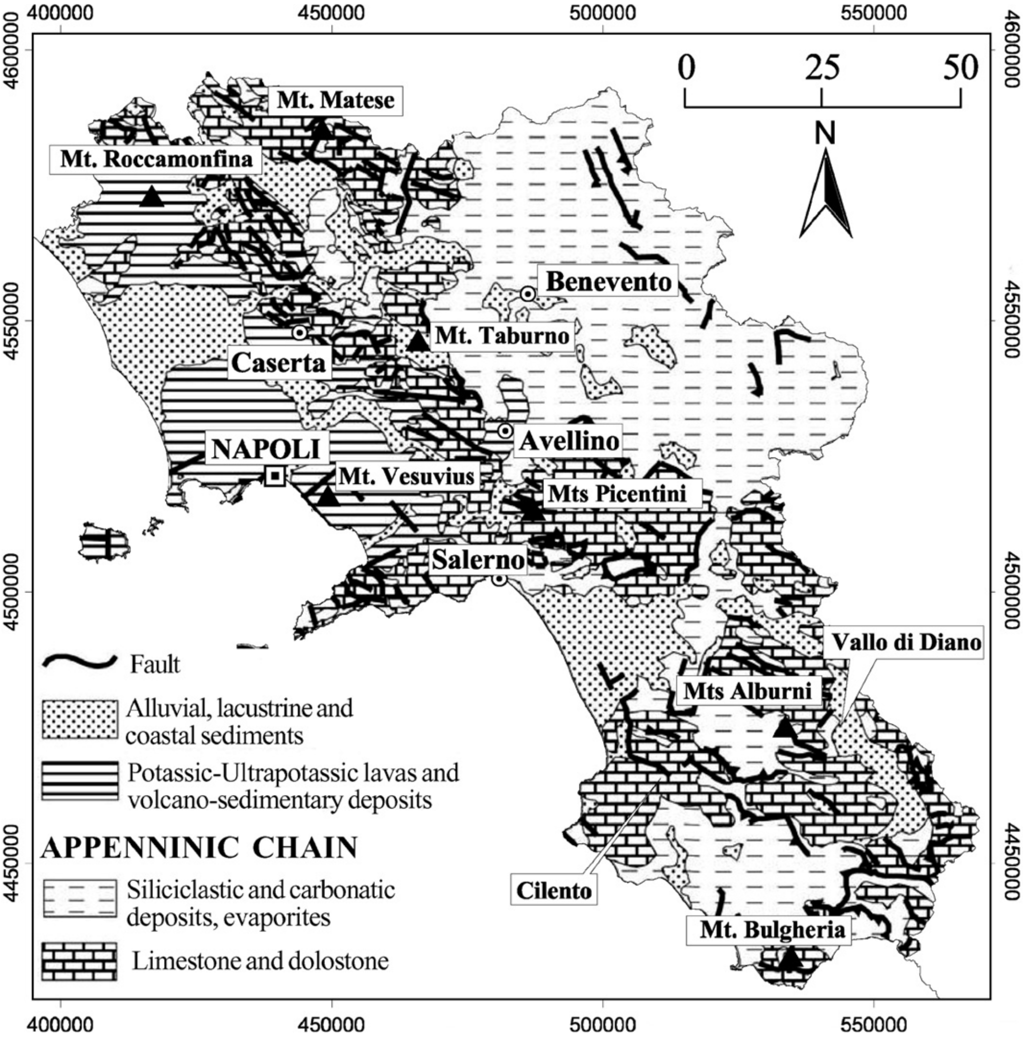

Fig. 2. Simplified geological map of the Campania region (Bonardi et al., 1998).

Neogene units, made up mostly of siliciclastic, carbonate and evaporitic sediments; the Quaternary sediments, which occur mainly in the Campania plains, are made up of lacustrine, alluvial and evaporitic sediments.

The volcanic rocks (dated from about 600 ka to present) are represented by potassic/ultrapotassic rocks (lavas and pyroclastics) of different volcanoes (De Vivo et al., 2001; Rolandi et al., 2003): Roccamonfina, in the north-western sector of the region; Mt. Somma–Vesuvius, Campi Flegrei and Ischia, along the western border of the region; and a fissure activity (Campanian ignimbrite) related to fractures activated in the Campanian plain from >315 to 18 ka. The ignimbrite covers the whole Campanian plain and also occurs on the Apennine Mountains (De Vivo et al., 2001).

2.2. Economy

Agriculture represents one of the most important economic activities of the Campania region (Fig. 3), and in the northern territory, agricultural activities cover more than 50% of the total available land surface. Moving to the south, farming is mostly located around coastal areas, due to the occurrence of mountainous areas, and the lack of significant superficial drainage. Productivity is strongly helped by the extensive presence of pyroclastic deposits that cover the majority of carbonate terrain and flood-plain deposits located along the coastal belt. Tomatoes, potatoes, aubergines, peppers, peas, tobacco and citrus fruits are mainly cultivated in the plain areas, while hilly parts are dominated by

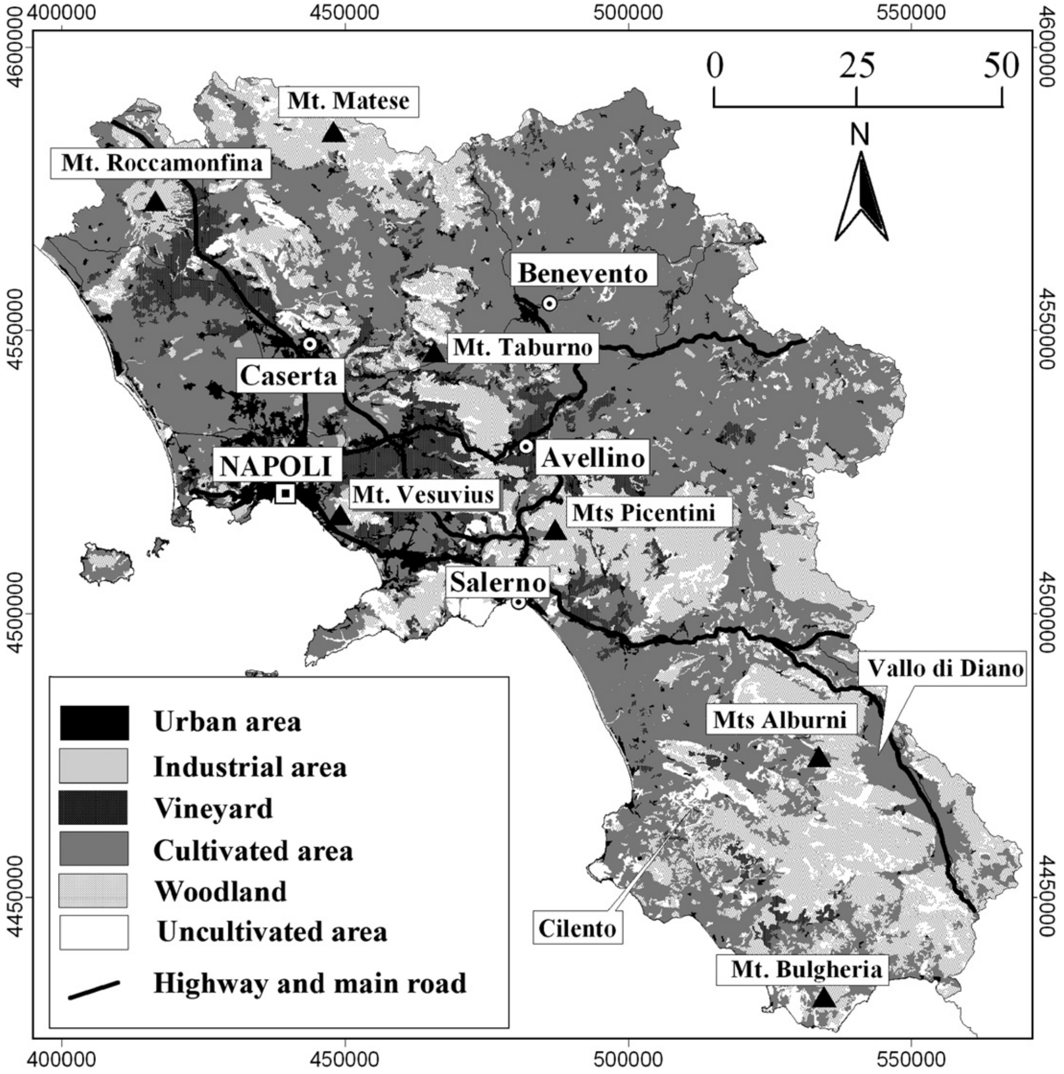

Fig. 3. Campania region land use map after Corine Land Cover 2000 (V.A., 2004).

olive trees and vineyards. Campania is the foremost consumer of fertilisers in southern Italy and azotic fertilisers represent 50% of the regional consumption per year. Non-rational use of nutritive (P- and N-based) fertilisers can produce stream water enrichments phenomena that develop eutrophication processes and co-precipitation of metallic elements.

Poisoning of superficial water can be related also to the use of anticryptogamics, as well as to the presence of fungicides, and biological fertilisers, produced from organic wastes (i.e., compost). Metallic impurities in P-based fertilisers, containing Cd as a natural pollutant, can also impact on sediment contamination.

Industries present a scattered spatial distribution and are mainly concentrated in the northern half of the regional territory. The majority of industries have been developed next to main cities and around agricultural areas. Industries are mainly devoted to vegetable preserving processes, textile-apparel, clothes production and tannery. While textile industries have a low environmental impact (raw materials are produced and imported from foreign countries), non-fitness of purification systems in the tannery and vegetable preserving industries can produce considerable pollution phenomena in stream waters and sediments.

Transport communication networks are strongly developed in coastal areas and in the central-northern part of the region, due to the strong economic development. Highways cross the whole territory but, especially during the summer, highway A3 in the southern sector (Vallo di Diano) is not able to sustain intense traffic that moves to southern regions of Italy (Calabria and Sicily).

No economic mineral deposits occur in Campania; only a few minor bauxite mineral occurrences–of no economic relevance–are situated in the Mesozoic rocks of Mt. Matese in the Apennine Mountains.

3. Sampling methods

During 1998 to 2000, 2389 stream sediment samples were collected from the study area (13,600 km^2) with a nominal density of one sample per 5 km^2. Finer grain size material was collected from the centre of the streams, avoiding, wherever possible, the collection of organic matter. Each sample represents composite material taken from five points over a stream stretch of 200–500 m. The sample collection protocols are described in detail by Salminen and Tarvainen et al. (1998). At each sample site pH and conductivity of stream water were measured, together with partial and total radioactivity using a portable Scintrex GRS-500.

4. Chemical analyses and quality control

All air-dried sediment samples were sieved and 30 g of the <150 μm fraction was retained for analysis of 37 elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W and Zn).

Analyses were carried out by Acme Analytical Laboratories Ltd. (Vancouver, Canada) through its Italian affiliate (ERS Srl, Napoli). Each sample was digested in a modified *aqua regia* solution and analysed by inductively coupled plasma–mass spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES). Specifically, a 15-g split of the pulp was digested in 45 ml of the *aqua regia*

Table 1
Detection limits, accuracy and precision

Elements	Unit	Detection limit (DL)	Accuracy (%)	Precision (%RPD)
Al	%	0.01	0	1.8
Ca	%	0.01	3.9	2.2
Fe	%	0.01	0.7	1.3
K	%	0.01	6.3	5.3
Mg	%	0.01	0	1.5
Na	%	0.001	3.6	2.9
P	%	0.001	0	3.6
S	%	0.02	30	11.9
Ti	%	0.001	0	5.7
As	mg/kg	0.1	0.3	3
B	mg/kg	1	0	11
Ba	mg/kg	0.5	0.3	1.5
Bi	mg/kg	0.02	1.8	3.2
Cd	mg/kg	0.01	1.4	5.6
Co	mg/kg	0.1	0	2.7
Cr	mg/kg	0.5	1.5	3.2
Cu	mg/kg	0.01	1.6	3.7
Ga	mg/kg	0.1	3.2	2.2
La	mg/kg	0.5	3.5	3.4
Mn	mg/kg	1	0.5	1.9
Mo	mg/kg	0.01	1.2	3.1
Ni	mg/kg	0.1	0.6	1.7
Pb	mg/kg	0.01	0.6	3.5
Sb	mg/kg	0.02	1.2	3.1
Sc	mg/kg	0.1	0	4.4
Se	mg/kg	0.1	0	28
Sr	mg/kg	0.5	5.3	2.4
Te	mg/kg	0.02	0.9	8.4
Th	mg/kg	0.1	5.1	3.6
Tl	mg/kg	0.02	1	3.6
U	mg/kg	0.1	1.6	3.7
V	mg/kg	2	1.3	2.4
W	mg/kg	0.2	2.7	4.4
Zn	mg/kg	0.1	0.5	2.6
Ag	mg/kg	2	0.4	7.9
Au	μg/kg	0.2	4.8	28.9
Hg	μg/kg	5	0	8

RPD = relative percent difference.

mixture (1 part concentrated hydrochloric acid to 1 part nitric acid to 1 part deionised water) at 90 °C for 1 h. The solution was taken to a final volume of 300 ml with 5% HCl. Aliquots of sample solution were aspirated into a Jarrel Ash Atomcomp 975 ICP-Emission Spectrometer and a Perkin Elmer Elan 6000 ICP-Mass Spectrometer.

The digestion by modified *aqua regia* is considered to give "pseudo-total" concentrations of metals bound as water-soluble salts, in cation-exchange sites, statically bound to clay particles, in organic chelates, in amorphous oxides and hydroxides of Mn and Fe, in carbonates, in sulphides and some sulphates. It also partially solubilises metals in silicates (generally the darker coloured ferromagnesian-rich silicates), and some crystalline oxides of Fe, Ti and Cr. Refractory minerals of Ta, Hf, Zr, Nb (zircon and some oxides) and Ba sulphates are most resistant to attack.

Precision of the analysis was calculated using three in-house replicates, and two blind duplicates submitted by the authors. Accuracy was determined using ACME's in-house reference material, DS2 (HMTRI, 1997) (Table 1).

5. Statistical analyses

Univariate and multivariate statistical analyses were performed in order to show the single element geochemical distribution, and the distribution of elemental association factor scores resulting from *R*-mode factor analysis. The main descriptive statistics for multi

Table 2
Statistical parameters of 2389 stream sediment samples from the Campania region

Element	Unit	Number of samples	Minimum	Maximum	Mean	Median	Geometric mean	Standard deviation	Skewness	Kurtosis
Al	%	2389	0.29	8.59	2.03	1.53	1.69	1.34	1.41	1.37
Ca	%	2389	0.10	26.73	6.68	6.43	5.16	4.09	0.91	1.70
Fe	%	2389	0.33	7.66	2.21	2.11	2.07	0.83	1.09	2.97
K	%	2389	0.03	4.21	0.42	0.25	0.28	0.51	3.39	14.45
Mg	%	2389	0.05	8.81	1.00	0.60	0.69	1.18	3.02	9.61
Na	%	2389	0.00	2.02	0.09	0.03	0.04	0.18	4.58	27.68
P	%	2389	0.01	0.67	0.08	0.07	0.07	0.05	3.39	20.49
S	%	1577	0.00	1.43	0.07	0.06	0.05	0.08	7.06	85.09
Ti	%	2389	0.00	0.48	0.06	0.02	0.02	0.07	1.78	3.05
As	mg/kg	2389	0.08	126.20	7.18	5.70	5.66	5.84	5.94	90.30
B	mg/kg	2389	0.80	65.00	7.74	7.00	6.21	5.48	2.29	10.15
Ba	mg/kg	2389	16.30	1429.20	193.31	152.10	157.41	138.18	2.13	6.99
Bi	mg/kg	2389	0.03	1.40	0.30	0.26	0.26	0.18	1.71	4.00
Cd	mg/kg	2389	0.02	4.25	0.30	0.21	0.23	0.36	5.40	38.96
Co	mg/kg	2389	1.50	22.50	11.18	10.50	10.36	4.54	1.84	9.54
Cr	mg/kg	2389	1.60	1117.90	24.18	19.90	19.63	42.40	18.04	397.61
Cu	mg/kg	2389	3.61	4699.48	38.90	30.30	30.44	101.24	41.21	1884.05
Ga	mg/kg	2389	0.90	18.90	5.42	4.50	4.78	2.83	1.15	0.88
La	mg/kg	2389	1.20	124.20	22.64	15.80	16.97	18.33	1.61	2.64
Mn	mg/kg	2389	100.00	7118.00	903.86	811.00	803.40	543.69	4.42	34.09
Mo	mg/kg	2389	0.11	29.07	1.01	0.80	0.82	1.15	11.33	203.96
Ni	mg/kg	2389	1.60	352.00	23.21	21.20	20.65	12.87	7.76	179.52
Pb	mg/kg	2389	3.29	546.30	31.69	22.40	24.45	31.85	5.86	59.39
Sb	mg/kg	2389	0.04	5.82	0.47	0.34	0.38	0.41	4.57	36.12
Sc	mg/kg	1222	0.40	12.60	2.63	2.40	2.41	1.13	1.28	5.11
Se	mg/kg	2389	0.08	3.10	0.44	0.40	0.38	0.27	2.97	17.71
Sr	mg/kg	2389	8.80	924.40	159.74	152.30	134.85	90.21	1.75	7.07
Te	mg/kg	2389	0.02	0.46	0.05	0.05	0.05	0.03	3.11	24.69
Th	mg/kg	2389	0.70	43.50	7.83	5.60	6.03	6.46	2.04	4.77
TI	mg/kg	2389	0.05	2.98	0.52	0.27	0.33	0.54	1.60	2.05
U	mg/kg	2389	0.10	22.50	1.58	0.90	1.11	1.56	3.30	25.85
V	mg/kg	2389	6.00	299.00	47.61	35.00	39.26	33.72	2.11	6.45
W	mg/kg	2389	0.10	5.50	0.43	0.20	0.29	0.44	2.59	13.81
Zn	mg/kg	2389	8.10	2074.70	89.27	70.80	73.31	106.18	9.52	121.94
Ag	mg/kg	2389	1.80	17,459.00	105.93	54.00	57.99	519.19	23.84	668.25
Au	μg/kg	2389	0.15	668.80	11.67	4.00	4.75	33.68	9.99	137.21
Hg	μg/kg	2389	3.80	6286.00	84.66	43.00	47.27	244.08	12.99	235.33

elemental concentrations in the 2389 stream sediment samples are shown in Table 2.

For statistical computation, data below the instrumental detection limit (IDL) have been assigned in this case a value corresponding to 80% of the detection limit; normally a value of 50% the detection limit is assigned. The data distribution is generally positively skewed, so data were normalised by conversion into their logarithms (the natural log). The geochemical data were statistically treated by means of the GeoDAS software (Cheng, 2001; Cheng et al., 2001; GeoDAS, 2001) for plotting individual distribution maps for the purpose of compiling an environmental geochemical atlas for the Campania region (De Vivo et al., 2003b; Lima et al., 2003). *R*-mode factor analysis was also performed using G-RFAC (Miesch Programs, 1990) software on a matrix containing 37 elements.

Factor analysis is a statistical method that characterises different groups of chemical elements with approximately similar geochemical patterns. It extracts the most important information from the data, because it is based on the concept of communality (for each variable, communality is defined as the common variance explained by the factors). In order to facilitate the interpretation of results, varimax rotation was used, since it is an orthogonal rotation that minimises the number of variables that have high loadings on each factor, simplifying the transformed data matrix and assisting interpretation. The different factors obtained were studied and interpreted in accordance with their presumed origin (natural, anthropogenic or mixed).

The five-factor model, accounting for 73.45% of data variability, deemed appropriate for stream sediments of the Campania region, is shown in Table 3.

Elements with loadings over 10.51 are considered to describe quite effectively the composition of each factor.

The associations of the five-factor model are F1: Tl–La–Th–W–Ti–Al–U–V–K–Ga–Ba–Ba–As–Na–Pb–Bi–Sb–P–Mo–Fe; F2: Co–Ni–Sc–Te–Cr–Mn–Fe; F3: Ag–Au–Zn–Hg–Cu–Pb–Sb; F4: Sr–B–Ca–S–Na–P–K; and F5: Mg–Cd–Ca–Se.

6. Method to generate geochemical maps

In this paper, the production of geochemical maps for Campania stream sediment results, using a new software technique, GeoDAS (Cheng et al., 2001), is described by presenting, as an example, a complete set of geochemical maps produced for Zn (Fig. 4). The usefulness of this technique in environmental studies has already been demonstrated by Lima et al. (2003) and Cicchella et al. (2005).

Table 3
Varimax-rotated factor (five-factor model) for 2389 stream sediment samples from the Campania region

Element	Factors				
	F1	F2	F3	F4	F5
Al	0.870	0.265	0.292	−0.046	0.010
Ca	−0.394	−0.143	−0.154	0.572	0.525
Fe	0.531	0.618	0.270	−0.125	−0.112
K	0.828	0.028	0.201	0.368	−0.078
Mg	−0.018	−0.204	0.021	0.038	0.654
Na	0.755	−0.227	0.154	0.465	−0.086
P	0.565	0.058	0.384	0.449	0.177
S	−0.217	0.052	0.349	0.503	0.163
Ti	0.870	−0.336	0.090	0.014	0.013
As	0.773	0.211	0.053	−0.088	0.048
B	0.482	0.167	0.147	0.678	−0.015
Ba	0.777	0.190	0.262	0.199	−0.037
Bi	0.621	0.415	0.399	−0.318	−0.036
Cd	0.471	0.243	0.283	−0.180	0.579
Co	0.191	0.885	0.086	0.045	−0.108
Cr	−0.220	0.679	0.345	−0.060	0.192
Cu	0.403	0.327	0.644	0.134	0.005
Ga	0.816	0.380	0.301	−0.129	−0.049
La	0.914	0.047	0.112	−0.042	−0.030
Mn	0.205	0.654	−0.103	0.058	−0.110
Mo	0.545	0.196	0.235	−0.080	0.437
Ni	−0.266	0.883	0.123	0.005	0.066
Pb	0.701	0.029	0.575	−0.090	0.070
Sb	0.567	−0.018	0.575	−0.305	0.200
Sc	−0.005	0.748	0.006	−0.102	−0.095
Se	−0.059	0.091	0.181	0.159	0.514
Sr	0.018	−0.045	−0.088	0.892	0.039
Te	0.089	0.684	−0.062	0.102	0.143
Th	0.896	0.172	0.114	−0.079	−0.202
Tl	0.948	−0.037	0.192	−0.013	0.032
U	0.862	−0.247	0.130	0.030	0.176
V	0.856	0.205	0.188	−0.008	0.004
W	0.889	−0.170	0.210	0.059	−0.004
Zn	0.350	0.255	0.723	0.031	0.042
Ag	0.222	0.020	0.775	0.168	0.104
Au	0.155	−0.133	0.765	0.097	0.117
Hg	0.240	0.037	0.694	−0.082	0.054
Variance % (total data)	47.1	18.6	17	10.6	6.7

All the geochemical maps were generated using the Multifractal Inverse Distance Weighted (IDW) algorithm as an interpolation method (Cheng, 1999a). Fig. 4A shows an example of the interpolated map for Zn on which grid pixels were classified with a colour scale using the fractal concentration–area plot (C-A method) that characterises image patterns and classifies them into components based on a C-A plot (Fig. 4B) (Cheng et al., 1994; Cheng, 1999a,b). In this plot, the vertical axis represents cumulative pixel areas $A(\rho)$, with element concentration values greater than p, and the horizontal axis the values themselves (ρ). Breaks between straight-line segments and corresponding values of ρ were used

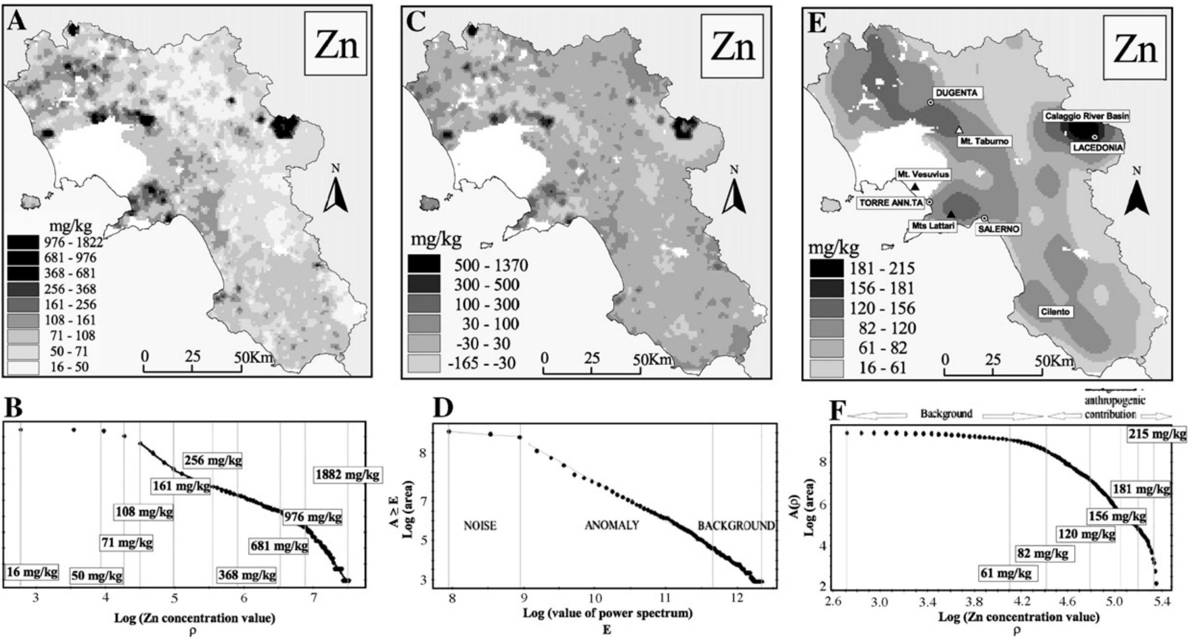

Fig. 4. (A) Zn interpolated map. (B) Fractal Concentration–Area (C-A method) plot for Zn interpolated data. (C) Zn anomaly map. (D) Spectrum-Area plot for Zn data: the vertical axis represents log $A(\geq E)$ and the horizontal axis the log-transformed power spectrum value itself; the cut-off indicated by the vertical line was applied to generate the corresponding filter used for geochemical baseline and anomaly separation. (E) Zn baseline map. (F) Zn baseline C-A plot.

as a cut-off to group pixel values in the multifractal-IDW interpolated map (Fig. 4A).

Maps showing the distribution of geochemical baselines (Fig 4E) and anomalies (Fig. 4C) were obtained by the S-A method.

The S-A method, based on a Fourier spectral analysis, is a fractal filtering technique used to separate the anomalies of an element from its baseline values. The baseline Zn map generated from geochemical data was transformed into the frequency domain in which a spatial concentration–area fractal method was applied to distinguish the patterns on the basis of the power-spectrum distribution.

A log–log plot (Fig. 4D) shows the relationship between the area and the power spectrum values on the Fourier transformed map of the power spectrum. The values on the log–log plot were modelled by fitting straight lines using least-squares. Distinct classes can be generated, such as lower, intermediate, and high power-spectrum values, approximately corresponding to baseline values, anomalies and noise of geochemical values in the spatial domain. An irregular filter was applied on these distinct patterns to remove the anomalies and noise related to intermediate and high power-spectrum values. The image, converted back to a spatial domain with the filter applied, shows patterns that, after the removal of anomalies and noise, indicate an area that represents Zn baseline geochemical patterns (Fig. 4E) (Cheng et al., 1994, 1996; Cheng, 1999a; Cheng et al., 2000). In the same way, the Zn anomaly map (Fig. 4C) was obtained by applying a band-type filter (selecting the second and third break as the cut-off on the S-A plot) that remove noise and baseline, related to lower and high power spectrum values.

The pixel values of baseline and anomaly geochemical maps were classified by using the concentration–area fractal method (C-A) (Fig. 4F), as discussed above.

In this paper only baseline maps (Fig. 5) for potentially harmful elements (As, Cd, Cr, Cu, Pb, Hg and Zn) are presented, together with the interpolated five maps of elements association (factor scores distribution) resulting from *R*-mode factor analysis (Fig. 6).

7. Results and discussion

7.1. Single element distributions

In order to better distinguish and evaluate geogenic from anthropogenic contribution in the distribution of baseline values obtained, with the S-A fractal technique, Table 4 reports the average distribution of the same elements in the upper continental crust (Wedepohl, 1978),

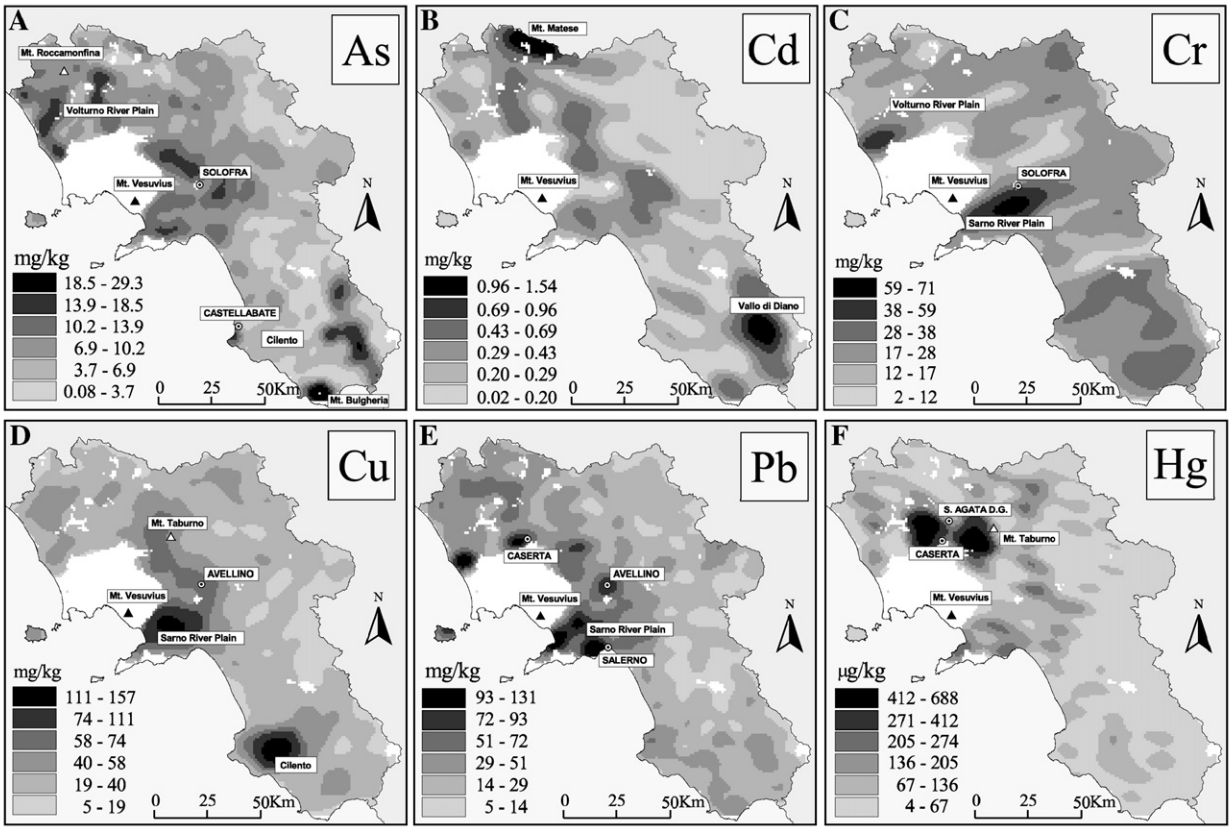

Fig. 5. Campania region: As, Cd, Cr, Cu, Pb and Hg baseline geochemical maps.

in representative Vesuvius eruptive formations (Paone et al., 2001) and in the Earth's shales and limestones (Levinson, 1974).

Table 5 shows intervention limits for stream sediments fixed by Dutch and Canadian law, because environmental legislation in Italy has not yet set up intervention limits for stream sediments.

7.2. Arsenic

Arsenic baseline values (Fig. 5A) range from 0.08 to 29.3 mg kg^{-1}. Highest baseline values (between 10.2 and 29.3 mg kg^{-1}) appear to be highly correlated to pyroclastic deposits that generally cover carbonate rocks outcropping mostly in the NW and SE sectors of the region. The Volturno River plain also has high As values. It is assumed that baseline values (between 3.7 and 10.2 mg kg^{-1}) occur on siliciclastic deposits in the NE and SW sectors of Campania can be considered as the natural background variation for these lithologies.

Although most of the baseline values for As are linked to the underlying volcanoclastic lithologies, agrochemicals in the Volturno River plain and tannery industries in the Solofra district cannot be excluded as potential polluting sources.

A small area along the Cilento coastline, corresponding to the town of Castellabate, shows very high As baseline values (between 13.9 and 29.3 mg kg^{-1}). Due to the absence of industries and agricultural activities, as well as a geogenic source, it is presumed, on the basis of information provided by local environmental authorities, that high As values may be due to an inefficient or malfunctioning local water purification plant.

Table 4 shows clearly that As in Campanian stream sediments is generally enriched in comparison to the average upper continental crust value. On the other hand, areas characterised by the large occurrence of volcanoclastics have average concentrations in the range of values of Neapolitan volcanoes (Paone et al., 2001) (Table 4).

Factor scores distribution of Fl association (Tl–La–Th–W–Ti–Al –U–V–K–Ga–Ba–As–Na–Pb–Bi–Sb–P–Mo–Fe) clearly provides evidence that high As concentrations are related to the presence of pyroclastic deposits (Mt. Roccamonfina in NW and Mt. Vesuvius in Central SW part of the region).

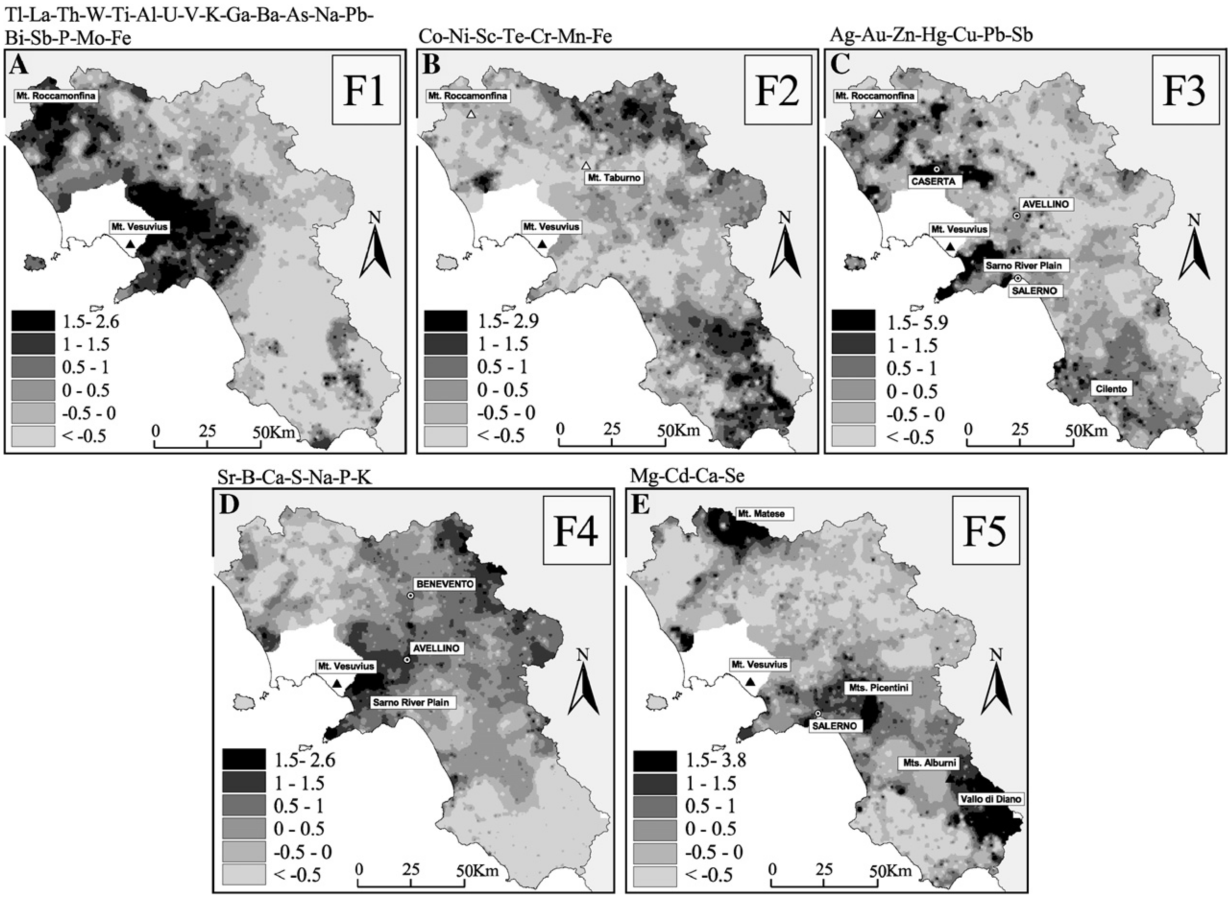

Fig. 6. Campania region: factor score association maps.

Some stream sediment samples, collected in the SE sector of the region and along the lower sector of the Volturno River Plain, have As values that are higher than the Dutch intervention limit (>55 mg kg^{-1}).

Only two samples, collected along the Cilento coastline (Mt. Bulgheria and Castellabate areas), exceed the Canadian intervention limit of 13 mg kg^{-1} (Table 5).

7.3. Cadmium

Distribution of Cd baseline values (Fig. 5B) range from 0.02 to 1.54 mg kg^{-1}. Most of the regional territory has moderate Cd baseline values below 0.43 mg kg^{-1}, which can be assumed to represent the natural background for siliciclastic deposits outcropping all over the region. Because of the pyroclastic sediments, covering most of the carbonate mountains, stream sediments collected from rivers draining carbonate rocks generally have average Cd values higher than the rest of the regional territory. Thus, Cd baseline values related to the Mt. Matese area, and to the mountain belt on the western side of the "Vallo di Diano" plain, have values between 0.43 and 1.54 mg kg^{-1}, which according to our interpretation represent the natural background for regional volcanoclastic deposits.

A close relationship between phosphate fertilisers and increasing Cd baseline values cannot be excluded for coastal areas where there is intensive farming.

Cadmium values are generally higher than average values of the upper continental crust (Wedepohl, 1978), as well as shale and limestone (Levinson, 1974).

All the Campania territory has Cd values lower than the Dutch and Canadian intervention limits (Table 5).

7.4. Chromium

The spatial distribution of baseline values for Cr (Fig. 5C), ranging from 2 to 71 mg kg^{-1}, does not highlight any geogenic or lithological control related to the element. It may be very probable that anthropogenic activities play an important role in determining high Cr baseline values, between 28 and 71 mg kg^{-1}, along the

Table 4
Average distribution of selected toxic elements

E1ement	A	B	C(1)	C(2)
As (mg/kg)	2	11.7	15	2.5
Cd (mg/kg)	0.102	–	0.2	0.1
Cr (mg/kg)	35	42.5	100	10
Cu (mg/kg)	14.3	72.5	50	15
Pb (mg/kg)	17	42.5	–	8
Hg (mg/kg)	0.056	–	0.5	0.05
Zn (mg/kg)	52	84.4	100	25

(A) Upper continental crust (Wedepohl, 1978). (B) Representative Vesuvius eruptive formations (Paone et al., 2001). (C) Average shale (1) and limestone (2) (Levinson, 1974).

Sarno River basin (SE of Mt. Vesuvius), and in relation to the Voltumo River outlet. High Cr baseline values occurring in Sarno River stream sediments (between 38 and 71 mg kg^{-1}) are strictly related to tannery industries waste waters that flow into the Solofrana River (one of the main Sarno River tributaries). At regional level, it is assumed that the natural, geogenic background values of Cr are lower than 28 mg kg^{-1}. The southern sector of the Campania region is characterised by Cr baseline values ranging from 12 to 28 mg kg^{-1}, whereas lower values occur on the other parts of the territory.

Chromium in Campania stream sediments is, on average, within the same range of values as the upper continental crust and Neapolitan volcanics, whereas depletion occurs compared with the average values of Cr in shale (Table 4).

Some stream sediment samples collected along the main course of Sarno River has Cr values exceeding both Dutch and Canadian intervention limits. Isolated samples along the Campania region coastline (Volturno River outlet and Cilento area) also have Cr values higher than the Dutch intervention limit (Table 5).

7.5. Copper

Baseline values for Cu (Fig. 5D) range from 5 to 157 mg kg^{-1} with a mean of 38.9 mg kg^{-1}. Copper values between 74 and 157 mg kg^{-1} occur in stream sediments collected along the Sarno River basin (south of Mt. Vesuvius) and in the Cilento area. Lower Cr values, between 58 and 74 kg^{-1}, characterise a large territorial belt from the northern side of Mt. Tabumo to the southern part of the city of Avellino. All these areas are rich in flourishing vineyard crops, and it is assumed that the stream sediment Cu values are certainly influenced by an anthropogenic contribution (Cu-sulphate intensely used in viticulture). Copper values lower than 58 mg kg^{-1}, which characterise regional stream sediment samples, collected in areas with no evident anthropogenic influence, can be assumed to represent natural, geogenic, background values.

Copper values occurring over unpolluted, pristine areas are generally higher than average values found in the upper continental crust (Wedepohl, 1978), whereas they are generally in the same range of average shale and limestone (Levinson, 1974).

Several stream sediments collected along the Sarno River basin, and in the Cilento area, have concentration values higher than intervention limits established by both Dutch and Canadian legislation (Table 5).

7.6. Lead (Pb)

Lead (Fig. 5E) is one of the most important decay products of U and Th. Generally, northern coastline areas have Pb baseline average values in the range between 29 and 51 mg kg^{-1}. The highest Pb baseline values in stream sediment along the Sarno River basin (from 51 to 131 mg kg^{-1}) were found strictly in correspondence to the highly urbanised areas of the Campania region (Caserta, Avellino, Salerno). Comparison with U baselines (Lima et al., 2003; De Vivo et al., 2003a,b) assists in the discrimination between geogenic and anthropogenic contributions, as for example, high baseline values for both Pb and U do not show a spatial correspondence.

The remaining Campania territory, where anthropogenic influence is less important, shows baselines ranging from 5 to 51 mg kg^{-1} Pb. It is assumed that the Pb values ranging from 5 to 29 mg kg^{-1} represent natural, geogenic background for siliciclastic and alluvial deposits, and the values from 29 to 51 mg kg^{-1} Pb are representative of volcanoclastic deposits.

Lead in the Campania stream sediments is on average enriched, when compared with upper continental crust, whereas it is in the same range as the geogenic content of volcanoclastic rocks of the Neapolitan area (Paone et al., 2001). A substantial Pb enrichment is shown in comparison with the general average value of limestone (Table 4).

Table 5
Intervention limits for some toxic elements in stream sediments established by Dutch (VROM, 2000) and Canadian law (CCME, 1995)

Elements	Netherlands	Canada
As (mg/kg)	55	33
Cd (mg/kg)	7.5	10
Cr (mg/kg)	380	111
Cu (mg/kg)	90	114
Pb (mg/kg)	530	250
Hg (mg/kg)	1.6	2
Zn (mg/kg)	720	80

Isolated samples collected along the Campania region coastline (Volturno River outlet, the southern side of Mt. Vesuvius and the Salerno area) have Pb values higher than the Canadian intervention limit (Table 5).

7.7. Mercury (Hg)

The highest Hg baseline values (between 205 and 688 g kg^{-1}) occur in the northern sector of the Caserta provincial area (Fig. 5F). There is no apparent correlation between lithologies and Hg distribution trends in stream sediments, suggesting a possible anthropogenic influence, possibly related to the presence of illegal waste disposal in the S. Agata dei Goti industrial district, and to the extensive use of Hg compounds as pesticides, especially in the Mt. Taburno area.

It can be assumed that Hg concentrations between 4 and 205 μg kg^{-1} have a geogenic source, and values between 4 and 67 μg kg^{-1} can be considered as belonging to the natural background for non-volcanic rocks, whereas values in the range 67–205 μg kg^{-1} may be correlated to stream sediments derived from volcanoclastics covering the majority of carbonate rocks, outcropping around the Neapolitan provincial area.

Some stream sediment samples have Hg values exceeding both Dutch and Canadian intervention limits in the northern sector of the Caserta provincial area (S. Agata dei Goti industrial district) and on the southern side of Mt. Taburno (Table 5).

7.8. Zinc (Zn)

Zinc baseline values (Fig. 4E) are generally higher in areas covered by pyroclastics. Values ranging from 156 to 215 mg kg^{-1} characterise areas where baselines may be influenced by both geology and anthropogenic activities. In fact, such a range of values occur between Mt. Taburno and Dugenta, Salerno and Torre Annunziata (across M.ti Lattari) and all over the Calaggio River basin (Lacedonia). Geogenic control on Calaggio River stream sediments can be excluded, because it is evident that enhanced Zn values depend on inefficient or malfunctioning water and dust purification plants of local industries that use Zn to galvanise steel. Stream sediments assume values ranging between 82 and 156 mg kg^{-1} in the remaining territory covered by volcanoclastic deposits, and in the southern sector of the region (Cilento). Baseline values, lower than 82 mg kg^{-1}, can be assumed to represent natural background for the whole Campania region, especially for those areas where siliciclastic and alluvial deposits outcrop.

All the Campania territory presents Zn values that are lower than the Dutch intervention limit, whereas a large part of the territory show values well above the Canadian intervention limit (Table 5).

7.9. R-mode factor analysis

The element association of factor 1 (F1: Tl–La–Th–W–Ti–Al–U–V–K–Ga–Ba–As–Na–Pb–Bi–Sb–P–Mo–Fe) (Fig. 6A) accounts for 47.1% of total data variability; it is strongly controlled by alkalic volcanic rocks and pyroclastics of the Campania region, mainly outcropping in the areas of Mt. Vesuvius and Mt. Roccamonfina and surrounding regions. These areas are usually characterised by factor scores ranging between 1 and 2.6; the values become lower moving away towards E and SE. Other small areas away from the volcanic centres have high F1 factor scores. This is explained by the presence of pyroclastic layers of Ignimbrites of the Campania plain (De Vivo et al., 2001; Rolandi et al., 2003) overlying local bedrock lithologies (mainly limestone). Areas with sedimentary rocks have negative factor score values, giving further evidence that the F1 association is clearly controlled by volcanics.

The factor scores association F2 (Co–Ni–Sc–Te–Cr–Mn–Fe) (Fig. 6B), which accounts for 18.6% of total data variability, clearly marks two sedimentary lithological units outcropping in the north-eastern (sandstone and claystone) and south-eastern sector (limestone and sandstone) of the Campania region, respectively. Higher F2 factor score values (ranging from 1 to 2.9) show a spatial correlation with many of the faults and overthrusts occurring in these areas.

The factor scores association F3 (Ag–Au–Zn–Hg–Cu–Pb–Sb) (Fig. 6C) accounts for 17% of total data variability. This association can be explained by elements introduced into the environment by human activities. Highest F3 factor scores show a scattered distribution along a wide belt to the coastline. This explanation stems

Table 6
Geogenic background value ranges for As, Cd, Cr, Cu, Pb, Hg and Zn in Campania region stream sediments according to lithology

Element	A	B
As (mg/kg)	3.7–10.2	102–13.9
Cd (mg/kg)	0.02–0.43	0.43–0.69
Cr (mg/kg)	12–28	12–28
Cu (mg/kg)	19–40	19–40
Pb (mg/kg)	5–29	29–51
Hg (mg/kg)	4–67	67–205
Zn (mg/kg)	16–82	82–156

(A) Siliciclastic deposits. (B) Volcanoclastic deposits. (Single regional background value ranges were chosen for Cr and Cu.)

from the Sarno River basin, which is one of the most polluted in Italy. Factor 3 values ranging between 1 and 5.9 mark areas next to main road junctions, urban settlements, industrial cultivated areas where vineyards are present.

The factor scores association F4 (Sr–B–Ca–S–Na–P–K) (Fig. 6D), which accounts for 10.6% of total data variability, is lithologically controlled. It has high F4 factor score values (>1) in the area surrounding the Vesuvian plain (mainly in the Sarno River catchment basin), and covers the north-eastern sector of the region (Benevento and Avellino provinces), where there is a clear correlation with the ''Flysch Rosso''.

The factor scores association F5 (Mg–Cd–Ca–Se) (Fig. 7E) accounts for 6.7% of total data variability. This association is again controlled by lithologies. It clearly marks all the carbonate masses outcropping over the Campania region territory. In fact, F5 factor score values higher than 1 characterise the areas where Mt. Matese, Mt. Picentini and Mt. Alburni are located.

8. Concluding remarks

Through application of a recently developed multifractal IDW interpolation and spectral analysis (S-A) technique using a specially dedicated GIS software (GeoDAS) (Cheng et al., 1994, 1996; Cheng, 1999a,b; Cheng et al., 2000; Lima et al., 2003), it was possible to discriminate between baseline and background values for toxic elements (As, Cd, Cr, Cu, Pb, Hg and Zn) in stream sediments of the Campania region (Italy).

This technique is significant since no intervention limits for contaminated stream sediments are established yet in Italy—current environmental legislation establishes such limits only for soil and waters (Ministero dell'Ambiente, 1999). The results obtained for stream sediments over an important Italian region, where there are urban, agricultural and industrial activities, are important, because they may be used by legislators in Italy as a guideline to define action and intervention limits for the studied toxic elements in stream sediments over the entire national territory.

In the Campania region territory, baseline and background values are often coincident where the samples represent areas away from urban settlements or industrial sites. Potentially polluted areas are very small in size, except at some locations, where the anthropogenic influence on stream sediments is clearly evident due to the wide extent of local industrial and agricultural activities; this is specifically the case, for example, throughout the Sarno River catchment basin, south of Mt. Vesuvius.

Elemental associations obtained by means of *R*-mode factor analysis are very useful in distinguishing geochemical data, where anthropogenic sources are dominant (e.g., F3 association) in comparison to geogenic sources (Fl, F2, F4 and F5 associations). The association F3 (Ag–Au–Zn–Hg–Cu–Pb–Sb) clearly marks areas where human activities mostly influence baseline values.

All over the territory, only Cd has concentration values that are always below both Canadian and Dutch intervention limits (Table 5). Whereas, As, Cr, Cu, Pb and Hg exceed these limits in some areas where the anthropogenic influence is clearly evident. On the whole, these intervention limits appear to be applicable to Campania stream sediments, but not for all elements, e.g., Zn. Countries like Canada and the Netherlands have established intervention limits taking into account their local background variation, reflecting their bedrock lithology. In the Italian case, the geochemical baseline definition for the Campania region stream sediments could be an useful tool to assist legislators to establish intervention and action limits in accordance with the local geogenic background values (Table 6).

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