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Murgante · Borruso
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The experience developed by Ian McHarg represents the first attempt to base environmental planning on more objective methods. In particular, he supposed that the real world can be considered as a layer cake and each layer represents a sectoral analysis. This metaphor represents the fundamental of overlay mapping. At the beginning, these principles have been applied only by hand, just considering the degree of darkness, produced by layer transparency, as a negative impact. In the following years, this craftmade approach, has been adopted for data organization in Geographical Information Systems producing analyses with a high level of quality and rigour. Nowadays, great part of studies in environmental planning field have been developed using GIS. The next step relative to the simple use of geographic information in supporting environmental planning is the adoption of spatial simulation models, which can predict the evolution of phenomena. As the use of spatial information has definitely improved the quality of data sets on which basing decision-making process, the use of Geostatistics, spatial simulation and, more generally, geocomputation methods allows the possibility of basing the decision-making process on predicted future scenarios. It is very strange that a discipline such as planning which programs the territory for the future years in great part of cases is not based on simulation models. Sectoral analyses, often based on surveys, are not enough to highlight dynamics of an area. Better knowing urban and environmental changes occurred in the past, it is possible to provide better simulations to predict possible tendencies. The aim of this book is to provide an overview of the main methods and techniques adopted in the field of environmental geocomputation in order to produce a more sustainable development.

Geocomputation, Sustainability and Environmental Planning

ISSN 1860-949X

ISBN 978-3-642-19732-1

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springer.com

Studies in Computational Intelligence 348

Beniamino Murgante
Giuseppe Borruso
Alessandra Lapucci (Eds.)

Geocomputation, Sustainability and Environmental Planning

Springer

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Studies in Computational Intelligence, Volume 348

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ISBN 978-3-642-19732-1

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ISBN 978-3-642-19732-1 e-ISBN 978-3-642-19733-8

DOI 10.1007/978-3-642-19733-8

Studies in Computational Intelligence ISSN 1860-949X

Library of Congress Control Number: 2011923798

Typeset & *Cover Design:* Scientific Publishing Services Pvt. Ltd., Chennai, India.

Printed on acid-free paper

9 8 7 6 5 4 3 2 1

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Contents

Geocomputation, Sustainability and Environmental Planning

Using Environmental Geostatistics for the Geochemical Characterization of Soils from the Polluted Site of National Interest of Tito (PZ – Italy)

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Abstract. The aim of this work was to provide information concerning the distribution of heavy metals in soils of a polluted ecosystem, in order to predict potential environmental risks and to provide a tool for the decision maker. This paper focuses on characterizing the industrial area of Tito (PZ, southern Italy), a site included among national interest sites to decontaminate, according to D.M. 8/7/2002. Soil contamination was monitored by means of a chemical-physical evaluation, coupled with a modelling approach using geostatistic techniques. A multistep sequential acid extraction technique was used to determine partitioning and levels of heavy metals in soil samples. Results showed that concentrations of analyzed elements are high in the whole area and above legislative admissible limits. A high spatial variation of heavy metals was observed in the studied area, with higher levels of heavy metals beside active and abandoned industrial areas. The adopted approach highlighted that anthropogenic industrial pressure may have detrimental repercussions on the surrounding environment and that recovering contaminated areas by implementing decontamination or permanent making safe interventions becomes necessary.

Keywords: Heavy metals, soil contamination, industrial area, geostatistics, kriging.

1 Introduction

The increase in environmental metal concentrations is primarily due to erosion phenomena and anthropogenic activities; since metals are very persistent

B. Murgante et al. (Eds.): Geocomputation, Sustainability & Environ. Planning, SCI 348, pp. 123–144.
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pollutants they accumulate in the soil. One of the most closely monitored areas is the soil ecosystem, where great attention is paid to hazardous elements. Knowledge of the processes driving pollutants migration and availability in the soil is important to evaluate their effect on environment and to forecast their environmental impact. In particular, soil represents one of the matrices receiving many polluting inputs, such as heavy metals. Moreover, soil is a distribution centre towards other environmental compartments due to pollutant flows in different matrices, which may compromise the equilibrium of many ecosystems.

Soil pollution by heavy metals arises strong concerns among developed countries, since it is mainly related to anthropogenic activities performed in industrial zones and in areas with high population density, representing the most important sources of heavy metals.

Decontamination of polluted sites represents one of the most relevant issues in debating environmental themes which particularly interest communities and decision makers. In fact, art. 17 of D. Lgs. 22/97 and D. Lgs. 152/06 regulate decontamination of polluted sites, introducing decisional participation of local agencies, to which most important tasks of human health and environmental safety are demanded. Moreover, decision makers must take into account EU guidelines concerning the analysis of effective or potential risk or different expectations for reusing and controlling abandoned and/or still used areas.

The need of providing a more and more detailed territorial knowledge has led to the development of techniques, which are reaching a broad diffusion thanks to their integration in GIS software (Bailey 1994; Burrough 2001), able to achieve geographic visualization of experimental data.

Spatialization of geochemical data has a great practical relevance in territorial management and may be absolutely necessary to evaluate background levels of polluting species in different investigated matrices. A correct determination of background values is of particular importance in environmental surveys, since law in force fixes intervention limits concerning metal elements noxious for human health (Cicchella *et al.* 2004). If these limits are exceeded, recovering of contaminated areas by means of decontamination or permanent making safe interventions becomes absolutely necessary. Starting from punctually surveyed experimental data, the elaboration of geochemical maps may provide opportune information about numerical models of transport, diffusion and pollutant levels as well as their temporal evolution in analyzed matrices. Defining if a determinate element is present at an anomalous concentration, and therefore it has to be considered a pollutant of that definite matrix, means first knowing its natural background grade, which may significantly vary from zone to zone. The main aim of geochemical survey is the characterization of anomalous areas (*e.g.* due to biotic or abiotic transformations or to anthropogenic pollution). In order to reach this aim, it is necessary to evaluate the values of natural background grades in the study area (Lima *et al*. 2004).

Integration of chemical-physical parameters and geostatistical techniques has been largely applied during the last years, allowing to estimate background values of contaminants in investigated matrices (Liang *et al*. 2003; Aboal *et al.* 2005; Liu *et al*. 2006; El Sebai *et al*. 2006; Rodriguez *et al.* 2008; Wu *et al*. 2008).

In environmental modelling studies, especially for the distribution of xenobiotic molecules in soils, the reconstruction of concentration fields is carried out using simple interpolation procedures. In this way, it is difficult to estimate how measure uncertainty and eventual stochastic characteristics in concentration field due to the small scale complexity of contaminant mobility in soils, affect the reconstructed datum in a point where measures are not available. In order to obtain this kind of results, various geostatistic techniques have been developed and widely applied in the field of mining survey and underground fluxes modeling. These techniques mainly aimed to spatially reproduce a phenomenon above the whole study area, on the basis of a limited number of punctual observations. Particularly, kriging techniques are based on a statistic model of the phenomenon and not on the model of the interpolation function (Chiles *et al.* 1999).

The use of such interpolators, included in the so-called "regionalized variables theory" (Matheron 1965), allows to get an estimate of the characteristics of a stochastic field in the points where it has not been measured (Bocchi *et al.* 2000; Castrignanò *et al.* 2002; Castrignanò *et al.* 2003; Haining 2003; Lloyd *et al.* 2006). In order to perform the geostatistic interpolation, it is necessary to preliminarily carry out the estimate of the so-called variogram, which allows to identify a covariance structure of the stochastic field consistent with the variability of studied data. Once defined a covariance model consistent with the data, it is possible to continue with a reconstruction of the field on a uniform grid (Madeo *et al.* 2005).

The aim of the present study was to investigate the distribution of selected heavy metals for the geochemical characterization of the national interest polluted site of Tito (PZ, southern Italy) by applying geostatistical techniques to heavy metal concentration data in different fractions of sampled soils. The area is of considerable ecological relevance, and a detailed knowledge of heavy metals distribution in soils sampled in this ecosystem it is necessary to predict the potential environmental risks and to provide a tool for the decision maker. The evaluation of heavy metal distribution in different soil fractions has been performed both by *multistep* sequential extraction, in order to evaluate leaching processes, and by total mineralization with acid attack for the geochemical characterization. Starting from the initial dataset, we identified the presence of outliers, in order to separate data representative of the natural background by those representative of populations whose values have been determined, and successively we interpolated them.

2 Materials and Methods

2.1 Study Area

The experiment was carried out during summer 2005, and soils were collected in 70 sampling stations at 0-40 cm depth. UTM (Universal Transverse Mercator) coordinates were determined for each position of sampling stations (their locations are shown in Figure 1) by using GPS map (Garmin, Taiwan). The sampling was carried out in stations located on a regular grid with a 200 m side, within the perimeter of the industrial area pertaining to ASI Consortium in Tito municipality

(Potenza, Italy, 40°36'11" N, 15°42'54" E), located at 763 m a.s.l. and 4.5 km distant from the built-up area. Soils were classified as clay loam (sand 432.2 ± 22.2, silt 245.0 ± 25.7, clay 322.8 ± 27.1, g kg^{-1} ± SD). The study area lays along slopes with precarious stability due to the presence of mainly clay soils, strongly eroded by exogenetic agents. Outcropping formations are clay marl, sandstone, siliceous schist and limestone. Drillings highlighted the presence of slimy soils tending to clay, with very low permeability up to 26 m depth. The water table has an average level of about 8 m, which reaches maximum levels of 2-3 m below the pattering plane in winter.

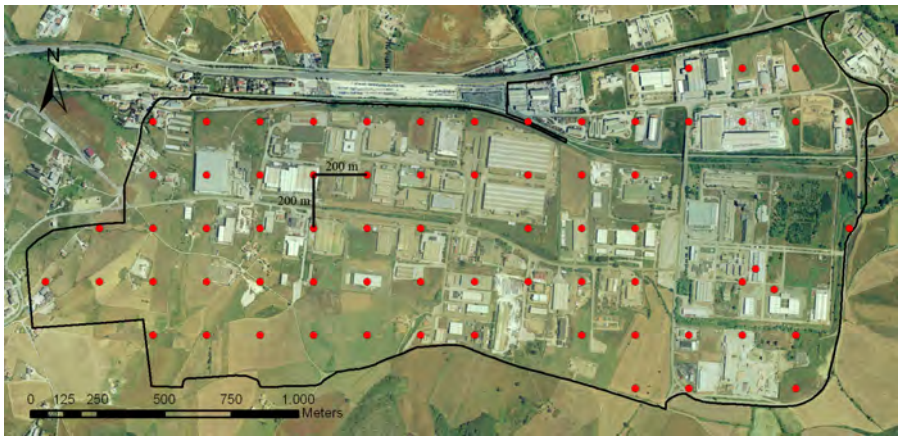

Fig. 1. Map of the Industrial Area of Tito (PZ, Italy). Locations of sampling stations are shown.

Studies carried in this area are among those provided by the national decontamination and environmental restoration program, drawn up according to art. 1, comma 3 of 426/98 law for industrial sites of national interest. According to such rules, Basilicata Region proposed to the Ministry of Environment to delimitate the national interest site. Partly demolished or evidently abandoned buildings and plants, silos and crumbling tanks, vats containing refluing waters and depuration mud, scattered piles of waste products are present in the area.

2.2 Chemical Analysis

All reagents used were of analytical grade (Carlo Erba, Italy), while extra pure grade acids (Merck, Darmstadt, Germany) were used to dissolve solid samples. Chemicals used for preparation of calibrating standard solutions were at heavy metals grade (Merck, Darmstadt, Germany). All solutions were prepared with ultrapure water at 18MΩ supplied by a Milli-Q RG unit (Millipore, Bedford, MA, USA). All plastic bottles, Teflon vessels and glassware materials were cleaned thoroughly with detergent solution, soaked in HNO_3 20% (v/v), rinsed with deionised water and dried.

The selective chemical *multistep* extraction was in accord with the sequential extraction procedure proposed by Tessier *et al.* (1979). The microwave-digestible residual concentration of heavy metals was determined utilizing a Teflon digestion vessel (1 g) and the residual was digested in 3 ml of HNO_3 70%, 4 ml of HF 40% and 1 ml of $HClO_4$ 70%. Samples were first heated from room temperature to 200 °C for 10 min and kept at this temperature for 15 min in a closed high-pressure microwave system Ethos SEL (Milestone, Italy). The instrument was equipped with a 10-vessel position carousel and a temperature controller. After digestion, vessels were allowed to cool to ambient temperature. Another microwave digestion system ETHOS TC (Milestone, Italy) equipped with VAC-4000 was utilized, and samples were boiled to near dryness in order to evaporate the exceeding acids of HF and $HClO_4$. Operating parameters and power of microwave digestion systems were set according to the procedures reported in the instrumentation manual. The residual solution was subsequently transferred into a 25 ml volumetric flask, and 5 ml of 50% HNO_3 (trace metal grade) were added to preserve the sample for trace metal analyses. Samples were kept at –18 ºC until analyses were carried out.

Determination of Al, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn was achieved with inductively coupled plasma mass spectrometer ICP-MS ELAN 6000 DRCe with a cross flow nebulizer (Perkin Elmer, USA). ^{103}Rh and ^{187}Re at the concentration 10 μg l^{-1} were used as internal standards. Blank solutions were prepared to correct for contaminants contained in reagents used during sample dissolution. Calibrating standard solutions were used for the calibration of the ICP/MS instrument at different concentrations of heavy metals. The calibration curves were linear in the whole calibrating range ($r \geq 0.9996$). Measures have been replicated thrice and recoveries have been determined using certified soils.

2.3 Statistical and Geostatistical Analyses

Both spatial and numerical statistical analyses have been applied in order to identify and to handle possible outliers and data distribution, and to obtain indications about population behavior. Identification of outliers has been performed according to EPA (2006), while background values of single metals have been calculated according to APAT-ISS (2006). Graphical representation, used to search for outliers, has been performed using box-plot and normal QQ plots. The presence of anomalous data has been verified by means of Grubbs test (maximum normalized residual test). Probability distribution better approximating the whole of available data has been checked for applying Lilliefors (Kolmogorov-Smirnov) test. All statistical analyses have been carried out using opensource "R" software (Ihaka *et al.* 1996; Ribeiro *et al.* 2001a; Iacus *et al.* 2003; R Development Core Team 2006).

Spatial variability, which interpolates semivariance of observed values in pairs of points at definite distances (lag) along a certain direction through the semivariogram function, described the structure of a regional variable of known value in a discrete number on points (Journel *et al.* 1978). We used a statistical interpolation method of kriging, which allowed to measure the average error and the standardized error variance through cross-validation. Compatibility between the set of

experimental data and their structural model has been evaluated by the vicinity of previous statistics, at values of 0 and 1, respectively. All geostatistical analyses have been performed using “geoR”, a spatial extension of “R” statistical software (Ribeiro *et al.* 2001b; Reimann *et al.* 2008; Bivand *et al.* 2008).

3 Results and Discussion

Characteristics and utilization of contaminated sites, character of environmental impact and target-oriented protection objectives determine different criteria and methods for site investigation, evaluation and remedial concepts. Knowledge regarding physical, chemical, and biological characteristics of the soil is important for assessing its capacity to act as sink and source of heavy metals. In particular, remobilization processes may reintroduce heavy metals in a natural or terrestrial system in different chemical forms or can be strongly retained in function of soil parameters, such as pH, redox potential, and ionic strength. In the present study, organic matter content has not been examined, according to D.M. 471/99 and D.Lgs. 152/2006. Nevertheless, it is well known that availability of heavy metals in soils is strongly affected by organic matter content and quality. Many studies have highlighted the importance of microbial biomass, an important fraction of soil organic matter, in metal mobilization equilibriums. The determination of heavy metals total concentrations is not sufficient for predicting the potential toxicity or their behaviour in the soil.

Soil contamination with heavy metals is often neglected or underestimated, both for the slowness of progression of the phenomenon and for the difficulty of measuring (Capri *et al.* 2002). Evaluating the level of heavy metals and metalloids in soils is extremely important since they are potentially toxic for life forms, as assessed by organizations such as U.S. EPA (*Environment Protection Agency* of USA) and World Health Organization.

The most used method for determining soil metal concentration is the mineralization in turpentine oil, which is not able to solubilize the silicate component (Gupta *et al.* 1996). Many authors studied fractioning of soil constituents with different reagents and operative conditions. Currently, different chemical extracting methods are used to study the distribution of metals in soils, based on partition techniques using selective chemical solutions able to remove heavy metals, according to their bond strength (Leita *et al.* 2000). Selective sequential extraction techniques provide indications on mobility and availability of different chemical forms of the metals in the soil. The basic principle is that various soil constituents are attacked by different solutions in a selective way, so that the different phases are separately solubilized and it is possible to determine the amount of heavy metal adsorbed on them. The experimental work allowed to consolidate and define operative modalities and the best experimental conditions (Hlavay *et al.* 2004). Geochemical characterization has been performed on fine ground, in order to ensure an effective contact of extracting solutions. Furthermore, granulometry has been determined and cluster analysis performed (data not shown).

ICP-MS allowed to simultaneously determine elements with few spectral interferences. Disadvantages due to overlapping of isotopes or polyatomic species have been eliminated by the use of DRC (*Dynamic Cell Reaction*), located between the ion source and the spectrometer. This consists of a quadrupole enclosed in a reaction chamber.

Determined elements were present in soils with amounts in a wide order of magnitude. Normally, Al and Mn are held in soils in the order of some g kg^{-1}, whilst concentration of most of the other elements is in the order of mg kg^{-1}. Hg, Cd, Tl, Sb and others generally reach concentrations of μg kg^{-1}. Therefore, it has not been possible to determine all elements by operating with a single dilution. Elements in great amounts tend to saturate the spectrometric detector and to compromise its regular functioning; therefore, it has been necessary to operate opportune dilutions. As for trace elements, dilution has been reduced to the minimum in order to maintain a good signal/noise ratio. Isotopes of more abundant elements, or alternatively the less interfered ones (^{27}Al, ^{9}Be, ^{114}Cd, ^{202}Hg, ^{205}Tl, ^{75}As, ^{52}Cr ^{59}Co, ^{63}Cu, ^{60}Ni, ^{51}V, ^{208}Pb, ^{64}Zn, ^{121}Sb, ^{120}Sn, ^{55}Mn, ^{80}Se) have been used. Detectability limits have been calculated on the basis of blank standard deviation, of instrumental variability and of volumes of reagents used to treat samples. Distribution of individual metals is shown in Fig. 5 and 6.

The study of background values and distribution has been carried out on elements with legally fixed limits (except for Al and Mn). Mercury has been analyzed as well, since it was detected in two samples only. Nevertheless, in our samples this element showed concentration values strongly below law limits.

In order to identify anomalous points corresponding to much higher or lower values relative to the others, box plots (Figure 2) and normal Q-Q plots (Figure 3) have been used as data graphical representations. Box plots support table presentation, aiming to simplify analysis and reasoning. They summarize the main aspects of a value distribution: lower and upper bases of the rectangle represent 25^{th} and 75^{th} percentile, respectively; the internal line reproduces the median. Nearby these parameters, the box plot identifies two limits (*upper* e *lower fence*), corresponding to 75^{th} percentile + 1.5 times interquartile difference and to 25^{th} percentile – 1.5 interquartile difference, respectively. Values beyond these limits might be outliers. Normal Q-Q plots can discriminate the presence of gaps or "jumps", as well as slope variations in the obtained curve of a dataset, which may be considered as threshold values for identifying two or more populations. They compare quantiles of a (standardized) dataset to quantiles of a standard normal distribution (average 0 and variance 1). If the distribution is normal, all points would fall along the straight line, while points deviating from it are possible outliers.

Nevertheless, the presence of anomalous data has been confirmed by the Grubbs test (Table 1). Outliers have been excluded from the geostatistical analysis since they were probably due to punctual anthropogenic inputs (analyzed data refer to surface sampling) deriving either from contaminant substances pouring or from landfill unrelated to the study area (e.g. ST72 site proved to be an outlier for Cd, Co, Cu, Se and Zn). Outlier number kept around a value ≤ 3 of 70 analyzed samples.

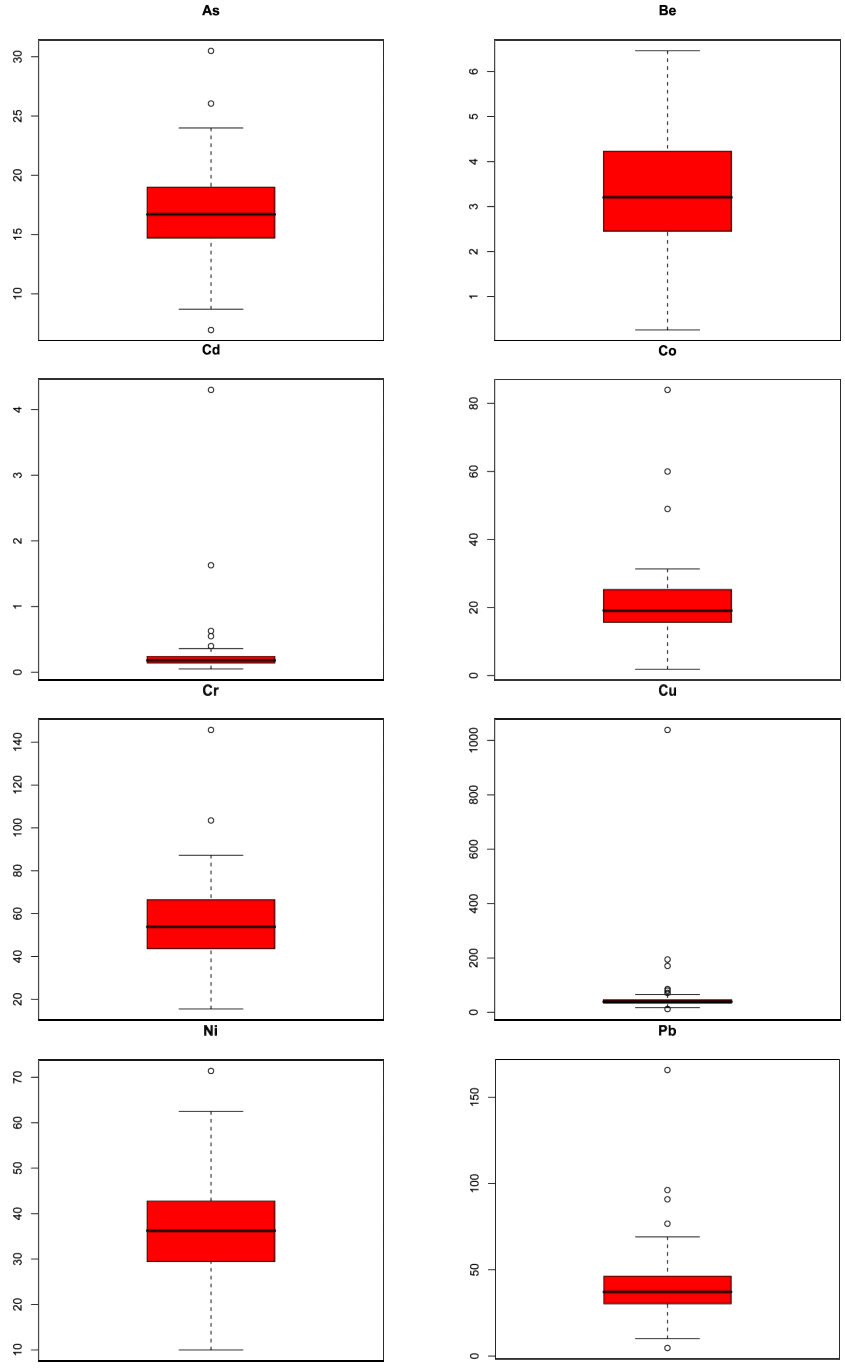

Fig. 2. Box plots

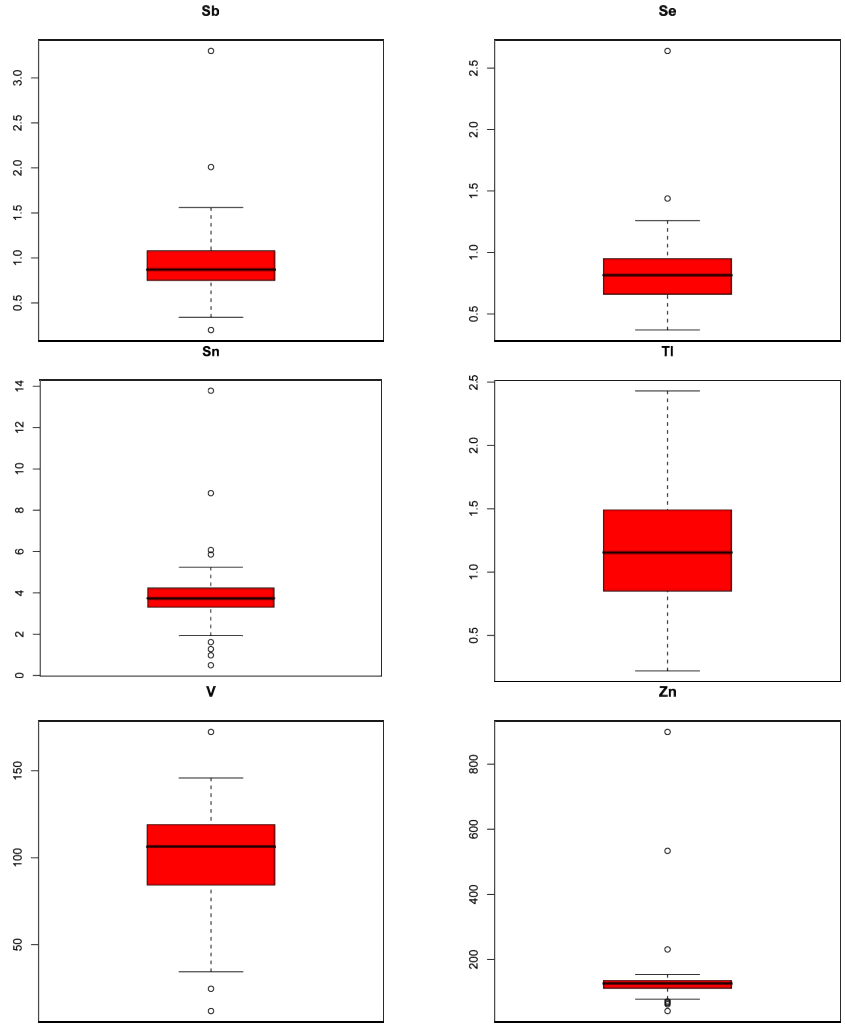

Fig. 2. (*continued*)

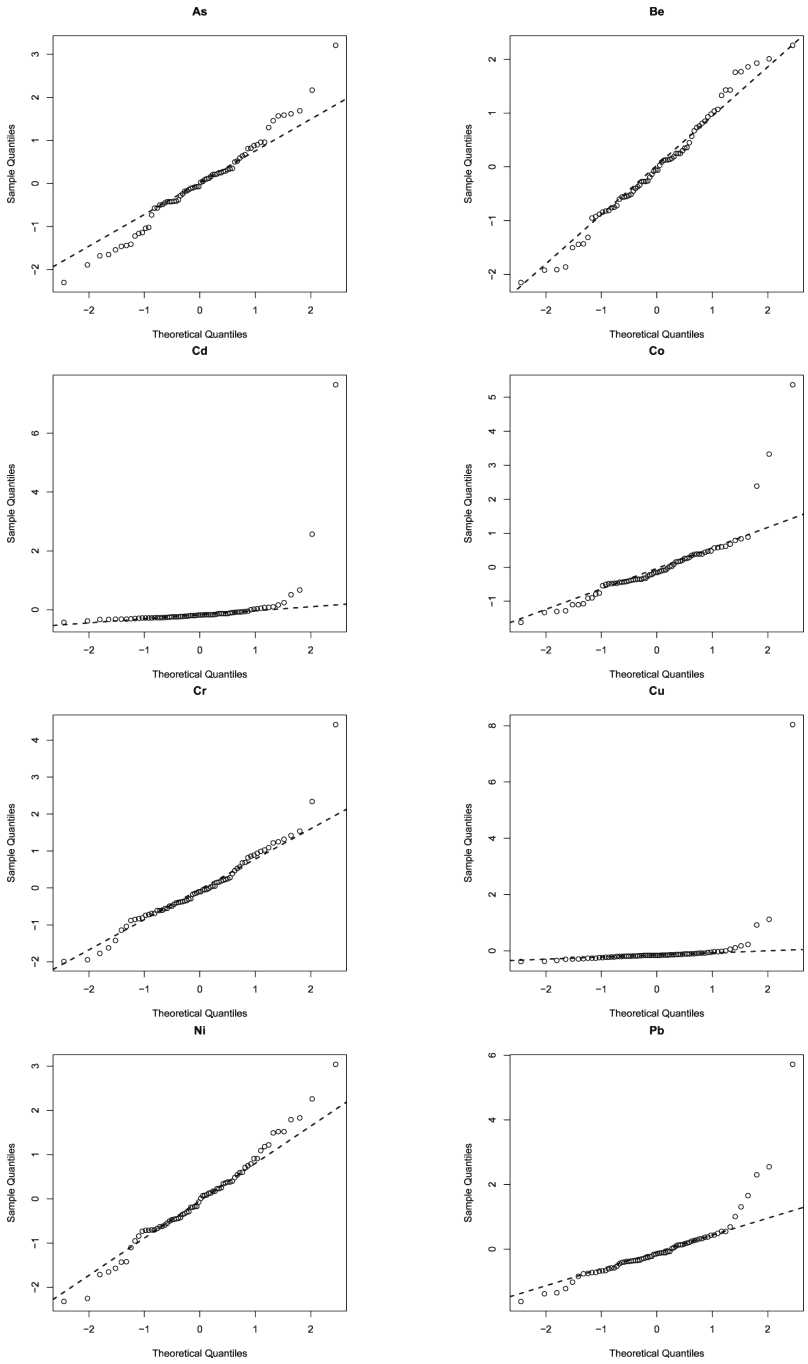

Fig. 3. Normal Q-Q plots

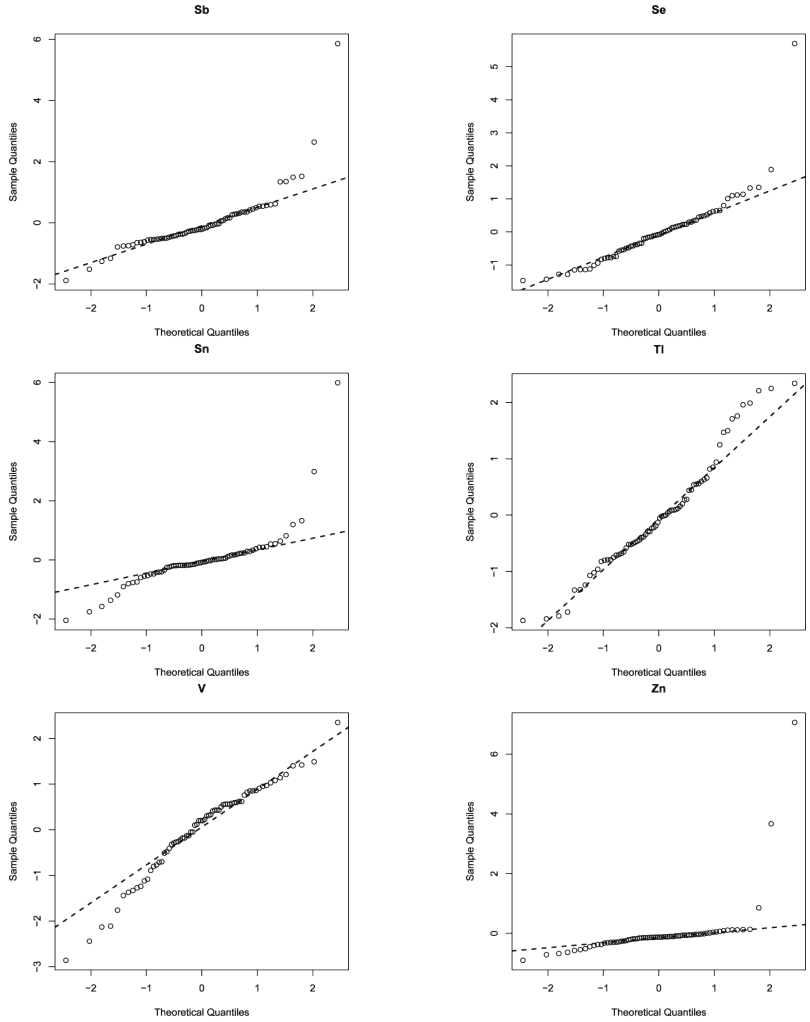

Fig. 3. (*continued*)

Data population without outliers has been considered as a background representation and the 95th percentile has been calculated on the basis of this value as an indication of the background value. As indicated by APAT-ISS document, we suggest that concentrations of samples collected within the enclosed area might be used, once provided that they are external to areas occupied by industrial plants, dumps or, in general, by zones where actual or past contamination sources are located. Nevertheless, our data indicate that, for many metals, values exceeded threshold levels listed in Table A of D.Lgs. 152/2006 and, in some cases, those reported in Table B (Table 2) as well.

Table 1. Grubbs test, for each element G statistic and *p*-value for the most extreme element are shown, the test has been repeated several times till the identification of outlier number

Heavy metals	As	Be	Cd	Co	Cr	Cu	Ni
G	3.2127	2.2555	7.6516	5.3649	4.4217	8.0374	3.0380
p-value	0.03004	0.769	2.2e-16	3.821e-08	6.026e-05	2.2e-16	0.05961
n. outliers	0	0	2	3	2	3	0
Heavy metals	Pb	Sb	Se	Sn	Tl	V	Zn
G	5.7168	5.8591	5.6967	5.9886	2.3337	2.8590	7.0601
p-value	1.024e-09	1.974e-10	1.281e-09	3.96e-11	0.6165	0.1149	2.2e-16
n. outliers	2	3	2	1	0	0	3

Table 2. Provided limits by D.Lgs 152/2006 for public, private and residential green zones (Tab A), for commercial and industrial zones (Tab B) and calculated background value

D.lgs. 152/2006	As	Be	Cd	Co	Cr	Cu	Ni
Tab A	20	2	2	20	150	120	120
Tab B	50	10	15	250	800	600	500
Background	20.52	4.60	0.35	28.69	81.07	54.04	55.72
D.lgs. 152/2006	Pb	Sb	Se	Sn	Tl	V	Zn
Tab A	100	10	3	1	1	90	150
Tab B	1000	30	15	350	10	250	1500
Background	49.93	1.17	1.19	4.61	1.55	140.69	151.39

Therefore, we need to discriminate if calculated values should be considered mostly as a “current background tenor” (baseline), so also including the presence of anthropogenic elements (contamination) in soils, than as a “natural background tenor” (background), which is a natural background value the presence of mineralization (Lima *et al.* 2004).

The population representing the background shows with good approximation a normal distribution for all elements, as showed by the istograms (Figure 4), where the class number has been calculated with Sturges method and confirmed with Lilliefors (Kolmogorov-Smirnov) test (Table 3). Descriptive statistics are reported in Table 4.

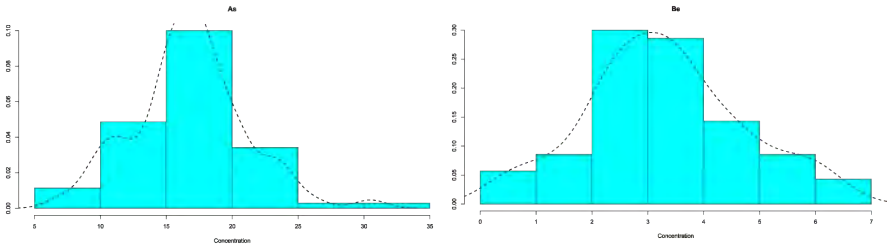

Fig. 4. Istograms

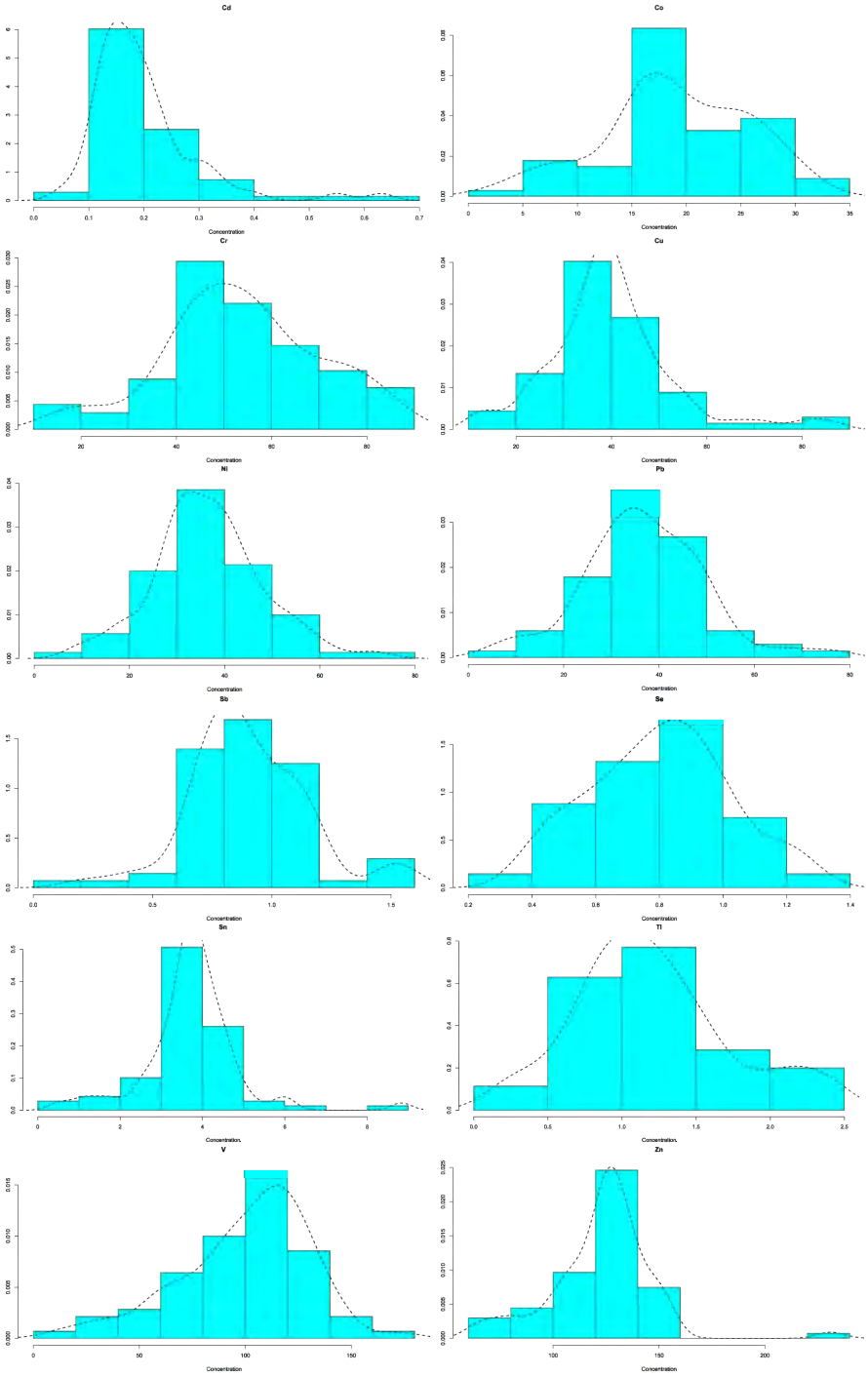

Fig. 4. (*continued*)

Table 3. Lilliefors (Kolmogorov-Smirnov) test's results

Heavy metals	Sample number	D	p-value
As	70	0.09	0.18
Be	70	0.07	0.48
Cd	68	0.08	0.28
Co	67	0.10	0.07
Cr	68	0.06	0.76
Cu	67	0.12	0.02
Ni	70	0.09	0.16
Pb	67	0.07	0.60
Sb	68	0.09	0.18
Se	68	0.05	0.93
Sn	69	0.13	0.01
Tl	70	0.09	0.13
V	70	0.11	0.05
Zn	67	0.13	0.01

Table 4. Statistical descriptors of data population (mg kg^{-1})

	As	Be	Cd	Co	Cr	Cu	Ni
Count	70	70	68	67	68	67	70
Min	6.95	0.26	0.05	1.86	15.47	12.42	9.98
Max	30.50	6.46	0.63	31.34	87.22	85.77	71.42
Mean	16.78	3.29	0.20	18.93	53.82	39.87	36.57
Std.Dev.	4.27	1.41	0.10	6.73	16.34	13.26	11.47
Skewness	0.33	0.16	2.21	-0.34	-0.09	0.98	0.31
Kurtosis	0.84	-0.19	6.89	-0.25	-0.11	2.59	0.76
1-st quartile	14.73	2.46	0.14	15.51	43.57	33.59	29.54
Median	16.69	3.21	0.18	18.87	53.47	39.12	36.25
3-rd Quartile	18.98	4.20	0.22	24.07	64.18	44.71	42.60
	Pb	Sb	Se	Sn	Tl	V	Zn
Count	67	68	68	69	70	70	67
Min	4.74	0.20	0.37	0.50	0.22	11.87	41.70
Max	76.82	1.56	1.26	8.83	2.43	172.44	153.85
Mean	36.82	0.90	0.80	3.73	1.20	100.05	120.21
Std.Dev.	12.92	0.25	0.22	1.15	0.53	30.84	22.85
Skewness	0.27	0.30	0.04	0.73	0.52	-0.67	-1.20
Kurtosis	1.17	1.26	-0.49	5.98	0.04	0.48	1.71
1-st quartile	29.47	0.75	0.66	3.31	0.85	84.61	109.69
Median	36.87	0.87	0.81	3.73	1.16	106.30	125.72
3-rd Quartile	44.59	1.06	0.94	4.19	1.49	118.88	133.41

Spatial variability for all the analyzed elements has been evaluated by interpolating the spherical model with experimental semivariograms (Table 5). Parameters deduced from the semivariogram (nugget, partial sill, range and Q index), concerning the distribution of the analyzed metals, showed a spatial dependence up to a distance between 600 m and 900 m. The Q index for almost all the metals gave evidence for an average spatial structure, so allowing to explain great part of the variance with the adopted model. The Q values were definitely low for Cu, Pb and Sb, indicating the permanence of a significant residual variance at distance zero. This suggests to thicken sampling points around some sites in order to deepen the study of the small scale variability.

Figg. 5 and 6 show the experimental semivariograms with their interpolates model and the maps obtained by kriging. Results of cross validation (Table 6) indicate the compatibility between the experimental dataset and the adopted structural model. In fact, the average of errors and standardized errors was close to zero for all elements, whilst standard deviation of standardized errors was close to 1.

Table 5. Parameters of adepte semivariograms models

	Model	Nugget	Partial Sill	Range	Q
As	spherical	8.33	11.40	890.90	0.58
Be	spherical	0.96	1.11	583.04	0.54
Cd	spherical	0.08	0.17	643.10	0.68
Co	spherical	25.87	21.76	724.54	0.46
Cr	spherical	131.64	156.72	737.35	0.54
Cu	spherical	132.73	19.43	837.61	0.13
Ni	spherical	79.29	53.32	993.09	0.40
Pb	spherical	102.66	56.05	856.65	0.35
Sb	spherical	0.05	0.01	900.00	0.19
Se	spherical	0.02	0.04	900.00	0.66
Sn	spherical	0.75	0.51	800.00	0.40
Tl	spherical	0.13	0.15	583.20	0.54
V	spherical	338.65	653.49	626.34	0.66
Zn	spherical	210.32	279.41	942.70	0.57

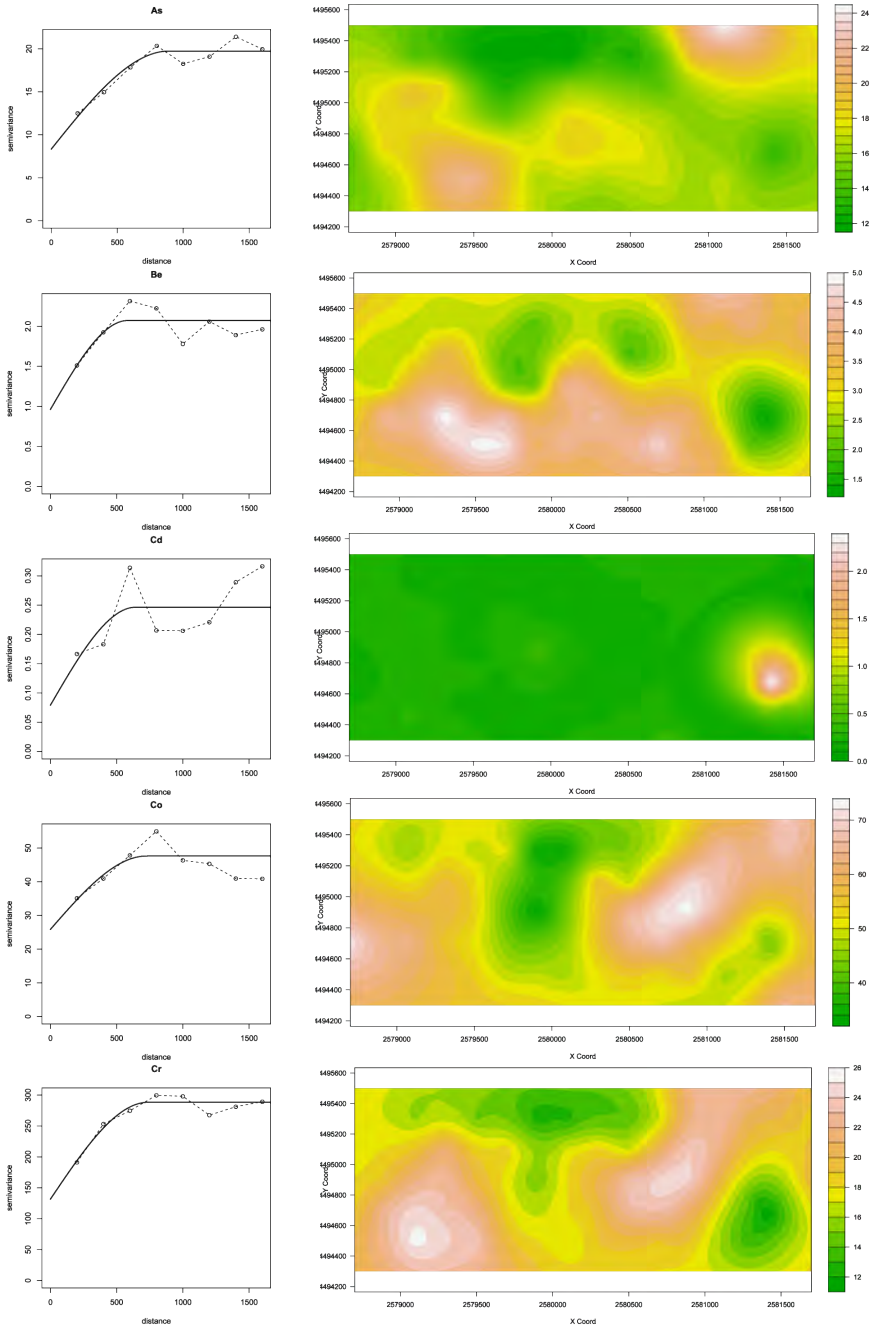

Fig. 5. Experimental semivariogram,background value model and map of elements As, Be, Cd, Co, Cr, Cu and Ni

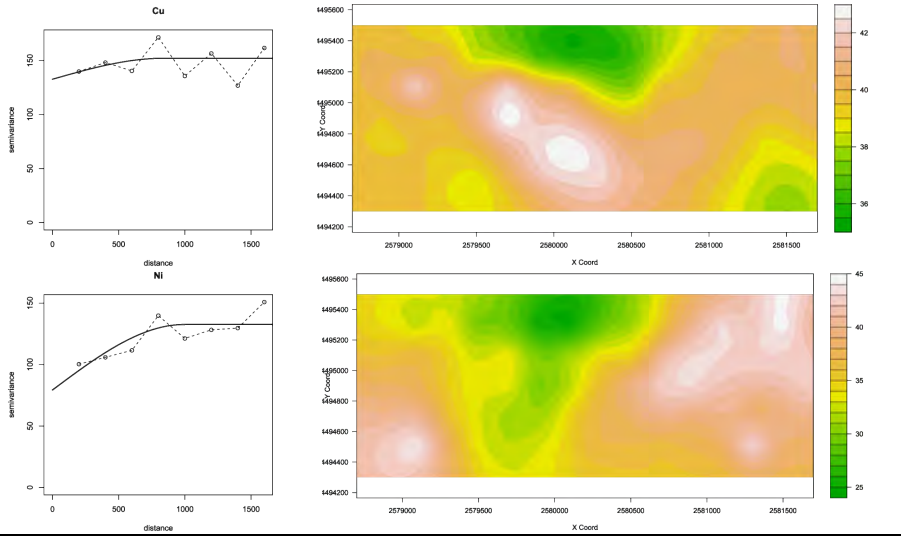

Fig. 5. (*continued*)

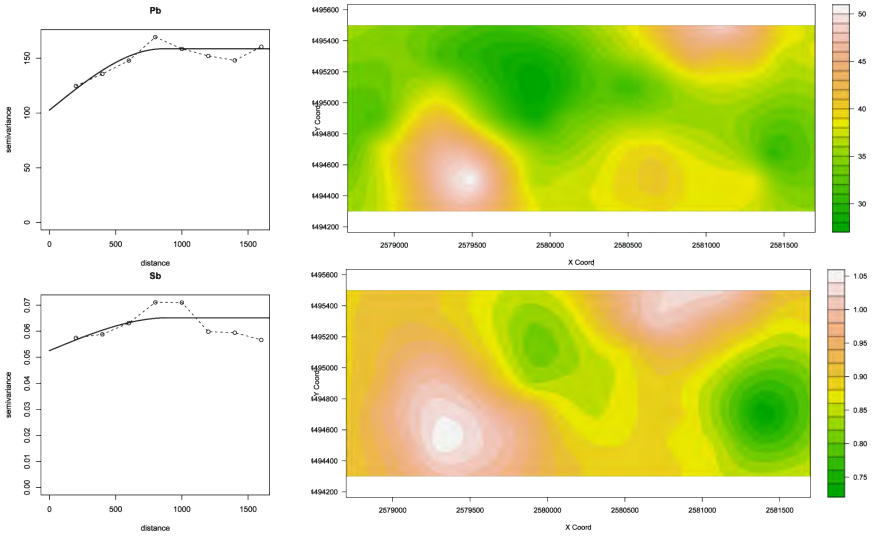

Fig. 6. Experimental semivariogram, background value model and map of elements Pb, Sb, Se, Sn, Tl, V, Zn

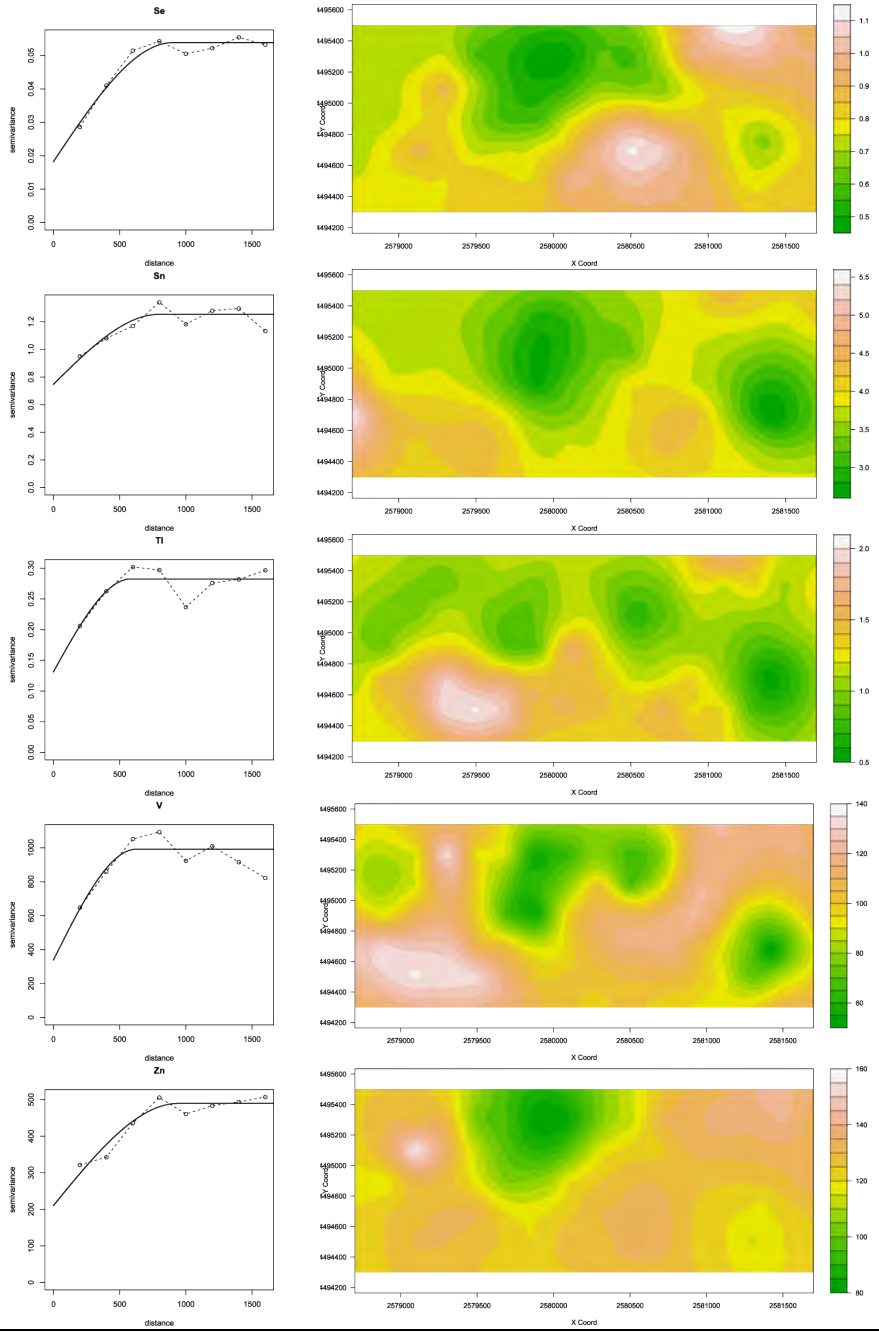

Fig. 6. (*continued*)

Table 6. Cross validation results

		Min	1st Qu.	Median	Mean	3rd Qu.	Max	sd
As	errors	-7.87	-2.54	0.44	-0.02	1.96	1067	3.77
	std.error	-2.03	-0.70	0.12	0.00	0.53	2.89	1.02
Be	errors	-2.67	-0.88	-0.06	0.00	0.68	3.03	1.28
	std.error	-2.11	-0.68	-0.04	0.00	0.52	2.36	0.99
Cd	errors	-1.10	-0.08	-0.03	-0.01	0.03	3.60	0.50
	std.error	-2.64	-0.19	-0.06	-0.01	0.08	9.31	1.28
Co	errors	-13.47	-4.42	0.74	0.01	3.75	12.84	6.18
	std.error	-2.22	-0.72	0.12	0.00	0.61	2.11	1.00
Cr	errors	-39.54	-7.35	-1.70	0.13	7.97	39.87	15.29
	std.error	-2.76	-0.50	-0.12	0.00	0.54	2.76	1.04
Cu	errors	-27.02	-6.72	-1.42	-0.02	5.85	49.16	13.77
	std.error	-2.21	-0.55	-0.12	0.00	0.48	4.03	1.13
Ni	errors	-23.37	-6.70	-1.01	-0.02	5.45	37.09	11.46
	std.error	-2.31	-0.65	-0.10	0.00	0.53	3.64	1.11
Pb	errors	-33.94	-4.71	0.66	-0.01	6.67	34.75	12.48
	std.error	-2.92	-0.40	0.06	0.00	0.58	2.98	1.07
Sb	errors	-0.62	-0.15	-0.01	0.00	0.11	0.69	0.24
	std.error	-2.50	-0.59	-0.06	0.00	0.44	2.80	0.98
Se	errors	-0.34	-0.13	0.01	0.00	0.11	0.39	0.17
	std.error	-1.91	-0.71	0.08	0.00	0.62	2.20	0.93
Sn	Errors	-2.82	-0.44	-0.05	0.01	0.45	5.24	1.13
	std.error	-2.82	-0.44	-0.04	0.00	0.44	4.85	1.09
Tl	Errors	-1.01	-0.35	-0.03	0.00	0.29	1.33	0.47
	std.error	-2.15	-0.72	-0.05	0.00	0.62	2.79	1.00
V	Errors	-70.12	-13.33	5.60	0.22	17.23	81.35	26.92
	std.error	-2.81	-0.50	0.21	0.00	0.62	3.04	1.02
Zn	Errors	-61.25	-12.07	1.58	-0.05	10.09	116.30	24.19
	std.error	-3.29	-0.65	0.09	0.00	0.56	6.41	1.32

4 Conclusions

The role of geostatistics in soil science and its future perspectives have been widely studied. The use of geostatistical techniques in soil geochemical characterization has proved to be very useful for at least two main reasons. The former is due to the possibility of distinguishing pollution double nature: “natural”, related to intrinsic qualitative characteristics of rocks (weathering), and “anthropogenic”, deriving from industrial activities. The latter, since these techniques allow to produce distribution maps of background values, which may represent an efficient

decisional tool for natural resources managers and planners, since they allow to identify risk areas and to plan the most effective recovery actions.

If the geostatistical approach fits to reproduce a spatial structure (correlation) of pollutant data, the interest of such approach remains unaltered even when this correlation is low (e.g. Cu and Sb where the Q index is low).

Nevertheless, the detection of no spatial continuity in concentrations is an important result and suggests that the whole predictive model will be uncertain concerning pollutant species positioning. The knowledge of a heavy metal chemical form is important for future recovery actions of contaminated soils or for future interventions of contamination attenuation. Evaluation of such parameters, essential for planning a recovery project, represents the necessary preamble to deepen both investigations concerning most salient aspects of this work and studies concerning biological aspects.

Vastness of the study area, danger related to pollutant typology and to presence of waste products disposal, together with side instability, have led to consider as extremely interesting the study of the chemical-physical parameters of the site, which showed high environmental risk characteristics..

Due to the extreme anthropogenic impact, levels of the analyzed elements were high in the whole area, and generally higher than admissible limits and values characteristic of polluted soils. Our study showed a high spatial variation of heavy metals in soils from the industrial area analyzed. Nevertheless, the study of spatial distribution highlighted the highest metal concentrations nearby industrial plants. In fact, these plants are the main pollution sources due to their present productive activity and to the long-period contamination deriving from abandoned enterprises. Heavy metal mobility is a problem to be considered for its noxious environmental repercussion, since migration of heavy metals in the soil compartment may lead to dangerous situations for the surrounding environment.

Acknowledgments. This study was supported by Regione Basilicata, Project "Caratterizzazione Geochimica dei Siti Inquinati di Interesse Nazionale di Tito e della Val Basento finalizzata agli interventi di messa in Sicurezza e di Bonifica".

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