A GEOSTATISTICAL APPROACH IN GEOCHEMICAL SOIL CHARACTERIZATION OF URBAN TERRITORY OF COSENZA - RENDE

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INTRODUCTION

Soil contamination by heavy metals and other hazardous elements is one of the most recognized forms of environmental pollution and their concentrations depend on both anthropogenic activities and natural pedo-geochemical background (Albanese *et al.*, 2007; Cicchella *et al.*, 2008a, 2008b).

It is an undesirable change in the physical, chemical, or biological characteristics of soil which can harmfully affect health, survival or activities of humans or other living organisms.

The occurrence of this phenomenon is correlated with the degree of industrializations, intensities of chemical usage, mining, smelting procedures and agriculture (Suciu *et al.*, 2008). In addition, soil is the "recipient" of large amounts of heavy metals from vehicle emissions. Several studies on the pollution in soil along highways indicate that the roadside soils are polluted by heavy metals. About half of the zinc and copper contribution to the environment from urbanization is from automobiles (Ma *et al.*, 2009).

The concern over soil contamination stems primarily from health risks, from direct contact with the contaminated soil. In urban areas dust from the soil may have toxic effects as a consequence of inhalation or ingestion by humans, particularly children, which poses major health hazards (Manta *et al.*, 2002).

There is a very large set of health consequences from exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of the exposed population. Heavy metals are either beneficial or detrimental to plants and animals. For essential micronutrients such as zinc, manganese, copper and nickel, insufficient uptake leads to deficiency-related health problems while excess uptake could cause toxicity. Roles of some other heavy metals such as cobalt, vanadium, chromium, cadmium and lead are more complicated. At trace level, they may be beneficial to some species; nevertheless, they are generally considered to be toxic at larger concentrations and are carcinogenic to all populations but are especially hazardous to young children, in which group there is a high risk of developmental damage to the brain and nervous system (Xu & Tao, 2004).

In addition, soil contaminants can have significant deleterious consequences for ecosystems. As result of this soil pollution, a microbiological activity disturbance occurs, which is expressed by a significant depletion of bacteria.

Mapping of contaminated soil sites and the resulting cleanup are time consuming and expensive tasks, requiring extensive amounts not only of geology, geochemistry skills, but also of geostatistics. Soil quality data sets typically contain many variables measured at several spatially scattered locations. As the variables are generally correlated, it is natural to presume that they reflect some common underlying factors. The geological characteristics or the type of land use are possible factors which govern variations in soil chemical composition. Some of these factors are likely to have a long-range action whereas other ones operate at shorter spatial scales. As result, variables must be expected to correlate in a way that is scale dependent. The study of the scale-dependent correlation structure of the variables requires statistical methods that combine classical factor analysis and geostatistics: the first one provides tools for exploring

the correlation structure of multivariate data sets whereas geostatistics allows one to take into account the regionalized nature of the variables (Goovaerts *et al.*, 1993).

The objectives of the study were: (1) assessing the environmental geochemical conditions, deriving from natural and anthropogenic agents ratio in urban soils of Cosenza-Rende territory (southern Italy), characterized by high population and high vehicular traffic densities; (2) mapping the spatial distribution and the probability of areas exceeding a given regulatory value by using stochastic simulation.

GEOLOGICAL AND TERRITORIAL SETTING

The study area is in NW sector of Calabria region inside the graben of Crati Basin and covers a territory of 92 km^2 where lives a population of 106.000 inhabitants approximately.

The Crati Basin is the most important of Calabria region for its extension, for its number of springs, and for its artificial lakes; it was imposed during Pliocene and so it is interested by some faults relative to horst-graben system of Sila-Coastal Chain (Lanzafame & Tortorici, 1981).

Cosenza and Rende territories are inside the Crati valley which is the largest flat area within the homonymous basin. It is a tectonic depression N-W oriented and located in axial position respect to Appennine Chain and bounded by faults.

Geologically this area is characterized by a powerful succession of pliocenic sediments such as light brown and red sands and gravels, blue gray silty clays and silt interlayers (Dell'Anna *et al.*, 1981), overlapped on paleozoic intrusive-metamorphic complex formed by paragneiss, biotite schists, gray phyllitic schists with quarze, chlorite and muscovite which, in some cases, are in weathering process (Critelli *et al.*, 1990; Le Pera & Sorriso-Valvo, 2000; Le Pera e*t al.*, 2001) (Fig. 1).

Considering territorial setting, the whole area is characterized by high population and high automobile traffic densities: for these reasons there are numerous sources of pollution which contaminate urban soils. Conversely there is a limited presence of industrial activities.

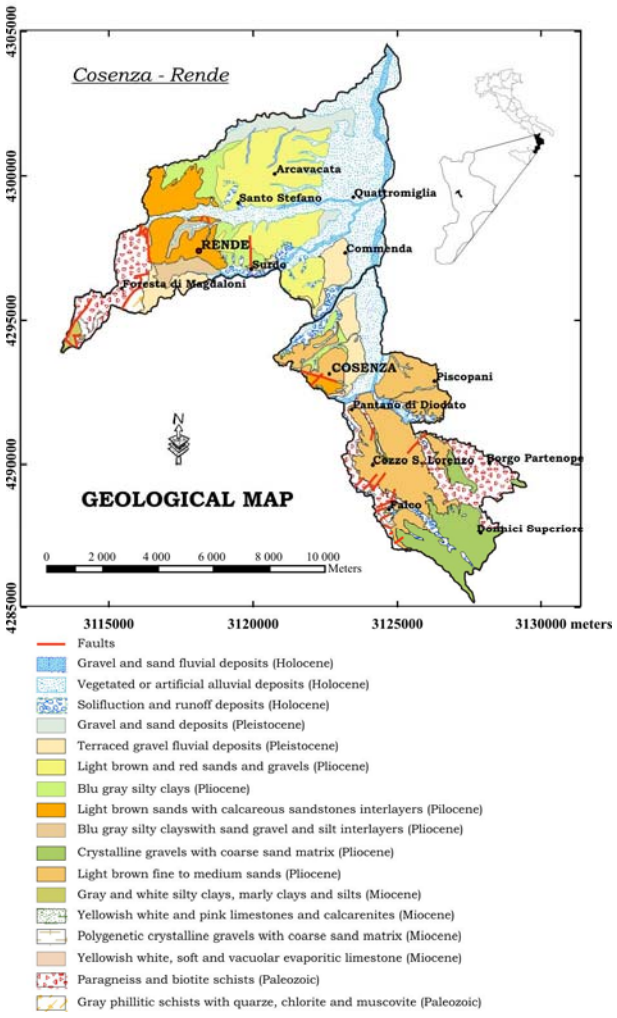

Fig. 1 - Geological map of Cosenza-Rende territory.

The investigation area comprises typical urban land use types such as housing, traffic, industry, commerce, parks and gardens of the Cosenza-Rende territory.

SAMPLING AND ANALYTICAL METHODS

Procedures for regional geochemical mapping, which are now well established (Johnson & Ander, 2008), were adopted to provide a sampling programme over the entire territory.

Samples were collected at 149 points of residual and non-residual topsoil (0-15 cm) (Fig. 2).

The whole area was divided into cells of 1 km × 1 km in size, in suburban areas and into cells of 0.5 km × 0.5 km in size in urban centre.

Each of the soil samples consisted of 5 sub-samples obtained in a 2 m × 2 m grid using a stainless steel hand auger: it is to create representative samples for each grid. The collected soil samples were stored in polyethylene bags for transport and storage.

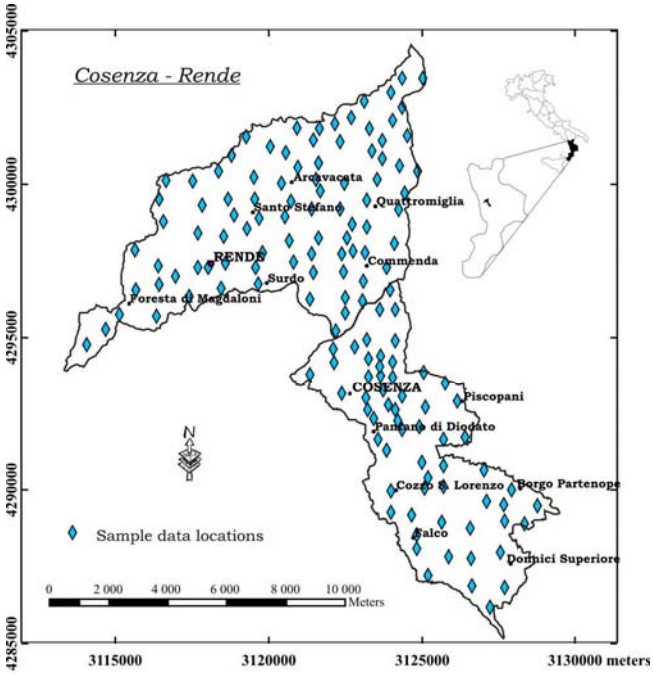

Fig. 2 - Soil sample sites map.

Each fine fraction (< 2 mm) of soil sample was analyzed for 25 elements by X-ray fluorescence spectrometry (XRF) (Al_2O_3, As, Ba, CaO, Ce, Co, Cr, Fe_2O_3, P_2O_5, Y, La, MgO, MnO, Ni, Nb, Pb, K_2O, Rb, SiO_2, Na_2O, Sr, TiO_2, V, Zn, Zr) and for 19 elements by inductively coupled plasma mass spectrometry (ICP-MS) (Ag, As, Be, Bi, B, Cd, Co, Cr, Hg, Mo, Ni, Pb, Cu, Se, Sr, Te, Tl, V, Zn). In the ICP-MS method the metals were extracted by digestion with a dilution of 6 ml of $HClO_4$, 5 ml of HF and 3 ml of HNO_3.

In addition, were collected also 18 samples of rocks, one for each lithological type present in the study area.

ANALYSIS OF DATA BY GEOSTATISTICS: SPATIAL INTERPOLATION, UNCERTAINTY ASSESSMENT AND RISK ANALYSIS

A characterisation of the spatial distribution of pollutants in contaminated soils is important for soil remediation, uncertainty assessment and risk analysis.

It is essential to illustrate the data and assess potential environmental hazard in the form of raster maps depicting the regional geochemical distribution of pollutants by spatial interpolation (Zheng *et al.*, 2008). Geostatistical methods were used to analyze and mapping the environmental geochemical levels of these elements.

Variographic analysis, using the simple variogram function, is the starting point for all geostatistical applications and is the basis for the study of the spatial behaviour of each geochemical element (Jimenez-Espinosa *et al.*, 1993).

The process of semivariogram model fitting was performed using the software Isatis® version 10 and experimental semivariogram of soil heavy metal concentrations was fitted with spherical and exponential models. The spatial distribution was fulfilled with multi-Gaussian kriging, an approach used to reduce the influence of skewed distribution of data (Buttafuoco *et al.*, 2007).

In addition, multivariate statistical methods were exploited to detect similarities between variables and therefore allow profound interpretation of data (Gallego *et al.*, 2002).

The multivariate and regionalized character of geochemical variables makes them an interesting candidate for numerical analysis using both geostatistics and data analysis methods in order to identify geochemical anomalies (Jimenez-Espinosa *et al.*, 1993).

Initially, for multivariate statistical approach, principal component analysis was used. It seems an appropriate method for establishing element associations (Jimenez-Espinosa *et al.*, 1993). The intention underlying the use of principal components in exploration geochemistry has generally been to separate the element associations inherent in the structure of the correlation matrix into a number of groups of elements that, together, account for the greater part of the observed variability in the original data.

The small number of components, identified by principal component analysis, was applied in factorial kriging analysis, which is a geostatistical method, developed by Matheron (1982), allowing the decomposition of a regionalized variable into different components that may be mapped separately for analysis (Jaquet, 1989).

The geostatistical approach increases the exploratory power of this method by taking into account the regionalized nature of information, making it possible to distinguish between factors according to the spatial scale at which they operate (Goovaerts *et al.*, 1993). It leads to modelling the variability of the variable under study as a sum of several elemental structures of covariance. All simple and cross model variograms were calculated by fitting a linear model of coregionalization including the nugget effect and two spatial structures at shorter (2500 m) and longer range (6000 m).

Furthermore, another geostatistical application was adopted: the sequential stochastic simulation which was used to estimate the conditional cumulative distribution functions at each location. Statistical information deriving from stochastic simulation allowed to estimate the probability that each pixel exceeds a threshold value and to produce the probability map of areas exceeding given regulatory values.

GEOCHEMICAL ANALYSIS SOIL/ROCK

Too often the lack of information on geochemical composition of bedrock leads to adopt elemental concentrations internationally determined, typical of analyzed rocks, but from other studies, for the identification of natural background.

This causes a high degree of imprecision in the definition of the background, resulting in negative consequences on the correct estimation of geochemical anomalies. For this reason, in the present study, were collected also 18 rock samples.

The majority of soil samples fell within the compositional field defined by the local content of marbles, sandstones and gneisses, suggesting a strong control of outcropping lithologies on elemental concentration analyzed. This was the case of CaO, Fe_2O_3, NaO_2, K_2O, TiO_2, Ba, Ce, Co, La, Rb and Sr, which proved to be of undoubted natural origin. The case of MnO, P_2O_5, Ni, Pb and Zn was different.

They were outside of the rocks compositional filed of study area and therefore their origin was anthropogenic.

RADIOACTIVITY: GAMMA RAYS SURVEY

In this study also a mapping of environmental radioactivity from *in-situ* γ-ray spectrometry was carried out. It is a valuable tool for understanding and interpreting lithologic control of naturally occurring radioactivity (Lima *et al.*, 2005; Buccianti *et al.*, 2009). The activities of naturally occurring radionuclides were measured at 181 locations by *in-situ* measurements of ^{40}K, ^{238}U, ^{232}Th and total radioactivity by using gamma-ray spectrometry in two periods, summer and winter, to compare measurements in different climatic conditions and establish the influence of climate, rainfall, moisture and atmospheric pressure on the radioactivity emission.

Table 1 - Summary statistics of multi-elemental concentrations.

	Count	Min (ppm)	Max (ppm)	Mean (ppm)	Median (ppm)	Lower quartile (ppm)	Upper quartile (ppm)
Al	149	11.19	23.79	15.89	15.38	13.65	17.48
Ca	149	1.45	6.47	2.81	2.74	2.32	3.06
Fe	149	3.11	10.58	5.47	5.13	4.42	6.16
P	149	0.1	0.64	0.29	0.26	0.19	0.36
Mg	149	1.45	6.47	2.81	2.74	2.32	3.06
Mn	149	0.05	0.54	0.13	0.1	0.09	0.14
K	149	1.32	3.45	2.41	2.4	2.22	2.6
Si	149	33.45	68.98	55.72	56.31	51.98	59.46
Na	149	0.44	2.08	1.23	1.23	1.02	1.46
Ti	149	0.45	1.18	0.73	0.71	0.61	0.83
Ag	50	0.16	1.18	0.41	0.34	0.26	0.47
As	149	3	22	7.48	7	5	9
Ba	149	335	2000	603.05	592	530	643
Be	50	1.51	5.64	2.67	2.5	2.26	2.93
Bi	50	0.03	1.35	0.22	0.15	0.13	0.27
B	50	3.17	44.65	10.21	7.64	5.53	11.14
Cd	50	0.13	2.44	0.4	0.3	0.23	0.45
Ce	149	34	127	72.66	70	60	82
Co	149	6	40	17.05	16	13	20
Cr	149	46	309	90.54	86	73	103
Y	149	0	55	24.99	26	19	30
La	149	13	80	37.71	37	31	42
Hg	50	0.09	0.45	0.19	0.18	0.13	0.25
Mo	50	0.35	12.2	1.9	1.3	0.9	2.24
Ni	149	18	82	34.67	33	28	40
Nb	149	6	35	14.49	14	11	15
Pb	149	8	708	63.67	31	20	69
Cu	50	11.59	249.97	44.36	30.38	20.92	38.26
Rb	149	62	154	104.66	105	92	114
Sr	149	109	514	234.25	233	194	271
Tl	50	0.03	2.03	0.64	0.29	0.17	1.33
V	149	54	239	107.36	102	87	123
Zn	149	38	871	166.73	127	93	189
Zr	149	121	383	209.36	209	186	233

Table 1 - (continued).

	SD (ppm)	Asymmetry (-)	Kurtosis (-)	DL (ppm)	Accuracy (%)	Precision (%)
Al	2.8	0.69	0.04	0.03	3.5	0.9
Ca	0.81	1.45	3.27	0.01	1.5	1.9
Fe	1.47	1.03	1.01	0.04	3.9	1.8
P	0.12	1	0.72	0.01	3.2	2.5
Mg	0.81	1.45	3.27	0.01	1.5	1.9
Mn	0.08	2.67	8.4	0.01	6.1	3.5
K	0.34	0.06	1.28	0.04	1	1.3
Si	5.89	0.52	0.87	0.02	2.1	0.6
Na	0.34	0.03	0.31	0.01	3.8	1.6
Ti	0.15	0.47	0.2	0.01	4.6	2.5
Ag	0.23	1.89	3.97	0.002	0.4	1.6
As	3.03	1.53	3.47	0.01	4.3	7.6
Ba	153.08	5.36	46.74	0.05	6.7	2.7
Be	0.66	2.09	7.25	0.18	1.3	2
Bi	0.02	3.96	20.43	0.05	1.8	11.4
B	8.31	2.71	8.29	0.92	10.4	6.6
Cd	0.37	3.94	19.5	0.01	1.4	8
Ce	18.77	0.82	0.57	0.05	8.2	11.9
Co	5.91	1.21	2.02	0.05	8.6	10
Cr	31.9	2.9	15.44	0.02	1.2	5.4
Y	8.15	0.35	1.08	0.01	6.9	4.7
La	11.24	0.92	1.91	0.05	9.6	17.9
Hg	0.09	1.18	1.41	0.01	1.3	1.2
Mo	2.06	3.69	15.5	0.42	6.9	3.2
Ni	9.93	1.16	2.95	0.01	8.1	3.8
Nb	5.13	1.67	3.87	0.05	7.5	2.3
Pb	85	3.89	22.56	0.02	6.3	12.6
Cu	45.75	2.96	9.75	0.27	5.9	9.7
Rb	18.15	0.33	0.2	0.05	5.4	1.6
Sr	63.73	0.63	1.66	0.05	4.2	1.4
Tl	0.62	0.87	0.84	0.61	1.1	3.5
V	30.89	1.28	2.46	0.05	5.7	3
Zn	130.53	2.68	8.7	0.01	5.4	2.8
Zr	41.33	0.44	1.74	0.05	4.6	6.1

Then a multi-Gaussian approach was used to explore and map the activity of naturally occurring radionuclides (^{40}K, ^{238}U, ^{232}Th) and total radioactivity.

RESULTS AND DISCUSSION

Main descriptive statistics for multielemental concentrations are shown in Table 1. Note that there were some high values (see max. levels of Zn, Pb and others) which are not typical in natural soils. This situation suggests a strong spatial variability due to the presence of anthropogenic sources.

Concentrations of the heavy metal and the other hazardous elements (mg kg^{-1}, dry weight basis) in soils ranged from 3.0 to 22.0 for As, 1.51 to 5.64 for Be, 0.13 to 2.44 for Cd, 6.0 to 40.0 for Co, 46.0 to 309.0 for Cr, 11.59 to 249.97 for Cu, 0.09 to 0.45 for Hg, 18.0 to 82.0 for Ni, 8.0 to 708.0 for Pb, 0.03 to 2.03 for Tl, 54.0 to 239.0 for V and 38.0 to 871.0 for Zn.

For simplicity, only the interpolated data distribution and the simulated map of the topsoil Zn concentrations are shown, respectively in Figs. 3 and 4.

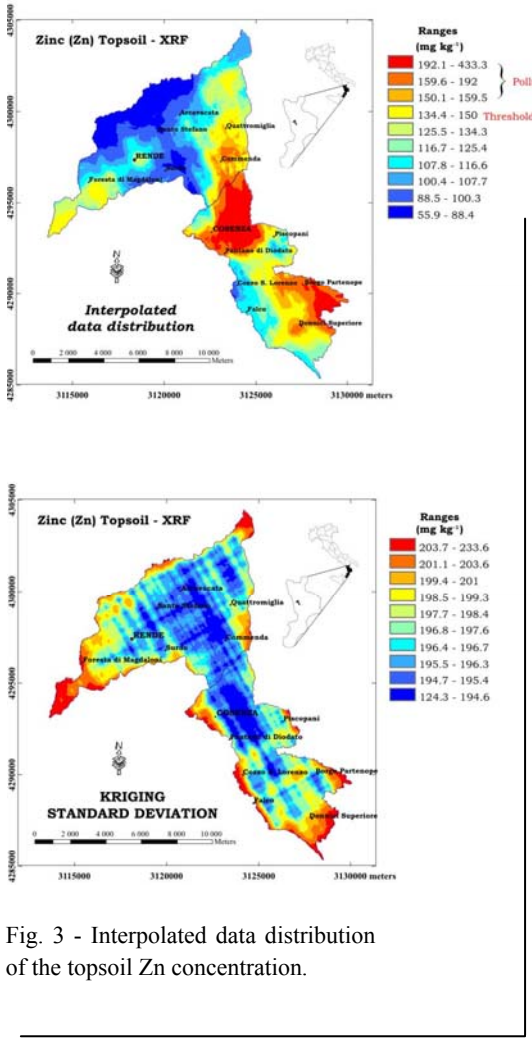

Fig. 3 - Interpolated data distribution of the topsoil Zn concentration.

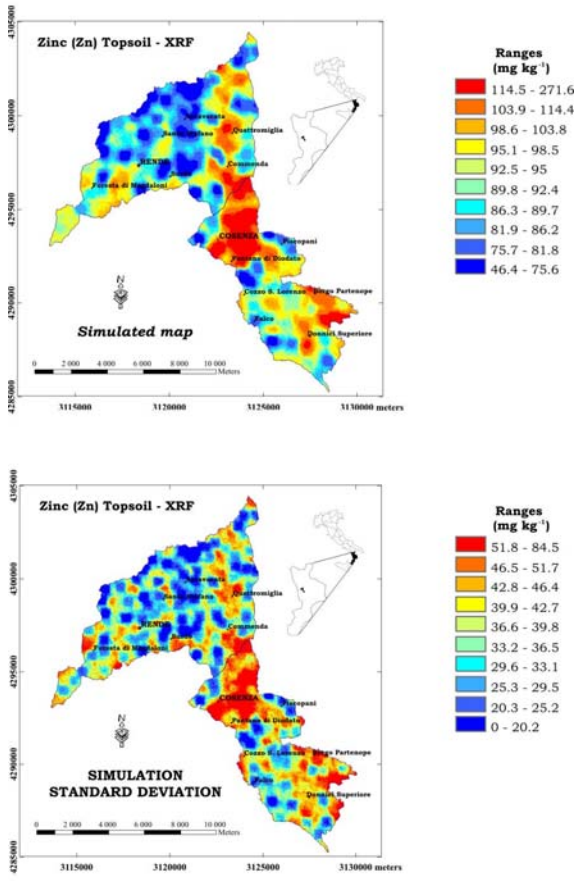

Fig. 4 - Simulated map of the topsoil Zn concentration.

Geochemical analysis and spatial distribution showed that zinc had elevated levels in soils close to major roads, confirming its anthropogenic character.

As can be seen, simulated maps reduce the effects of smoothing present in interpolated distribution, with most regard to spatial variability of elements and therefore the first ones are preferable to study the territory.

From the spatial distributions of heavy metals, it could be establish that the parent material and anthropogenic factors played important roles in soil heavy metal concentrations of Cosenza-Rende, and the effects of these two factors varied with the heavy metals.

Geochemically each of the elemental structures as directly related to the spatial scales of the geochemical phenomenon. Application of factor cokriging allowed us to identify two regionalized factors: short range structures, with strictly local self-correlation and random behaviour, were associated with the anomalous component, long range structures, on the other hand, being continuous in their distribution as well as in their spatial variability, were associated with the geochemical background.

Regulatory authorities require estimates of ambient background concentrations of potentially harmful elements in topsoil. Statistical information deriving from stochastic simulation allowed to estimate the probability that each pixel exceeds a threshold value and to produce the probability map of areas exceeding given Italian regulatory values (D.Lgs. 152/06). Elements exceeding the regulatory values were: As (0.52% of the samples), Be (97.23%), Cd (1.48%), Co (22.31%), Cr (3.72%), Pb (16.37%), Cu (5.37%), Tl (30.08%), V (69.23%), and Zn (37.21%). These results can provide decision-makers with the information to delineate the hazardous areas and evaluate the possible remediation techniques in a heavy metal contaminated site. Fig. 5 showed the probability map of areas exceeding the value of 150 mg kg^{-1} of Zn imposed by D.Lgs. 152/06.

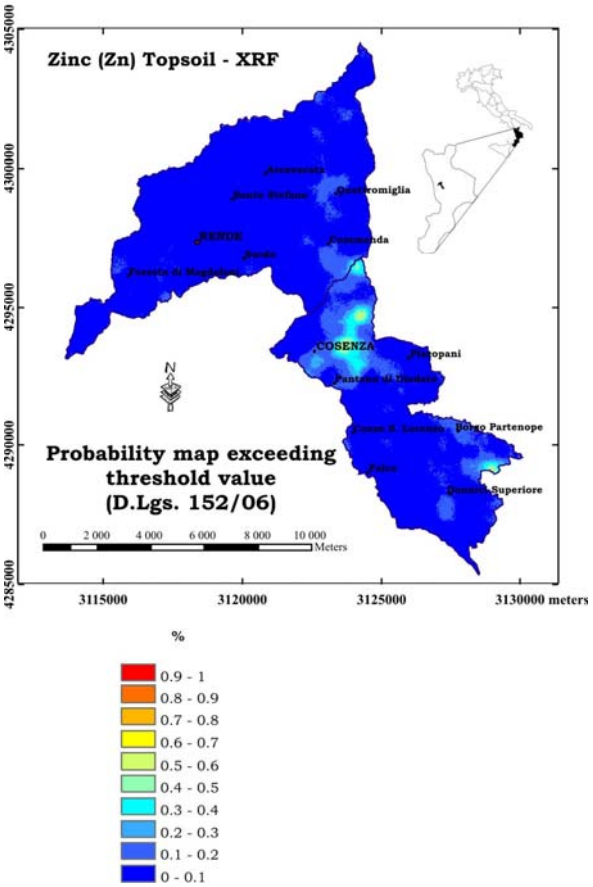

Fig. 5 - Probability map of areas exceeding the threshold value of 150 mg kg^{-1} of Zn imposed by D.Lgs. 152/06 (2006).

In addition, locations and lithological compositions of bedrock appear to be responsible for variations in radioelement activity. From radiometric investigations it has emerged that the natural activity of radionuclides in rocks and soils was not equally distributed, but rather influenced by the different geologic conformations of the various areas examined. As expected, high values of ^{40}K, ^{232}Th and total radioactivity were found in rocks of plutonic origin and low values in sedimentary rocks. Uranium radioactivity behaved in a constant manner, although with some differences in clayey sites particularly rich in this radionuclide.

REFERENCES

Buccianti, A., Apollaro, C., Bloise, A., De Rosa, R., Falcone, G., Scarciglia, F., Tallarico, A., Vecchio, G. (2009): Natural radioactivity levels (K, Yh, U and Rn) in the Cecita Lake area (Sila Massif, Calabria, Southern Italy): An attempt to discover correlations with soil features on a statistical base. *Geoderma*, **152**, 145-156.

Buttafuoco, G., Tallarico, A., Falcone, G. (2007): Mapping soil gas radon concentration: A comparative study of geostatistical methods. *Environ. Monit. Assess.*, **131**, 135-151.

Cicchella, D., De Vivo, B., Lima, A., Albanese, S., Fedele, L. (2008a): Urban geochemical mapping in the Campania region (Italy). *Geochem.*, **8**, 19-29.

Cicchella, D., De Vivo, B., Lima, A., Albanese, S., McGill, R.A.R., Parrish, R.R. (2008b): Heavy metal pollution and Pb isotopes in urban soils of Napoli, Italy. *Geochem.*, **8**, 103-112.

Critelli, S., Gullà, G., Matano, F. (1990): L'alterazione delle rocce cristalline e sua incidenza sulla franosità in Calabria. *In*: "Indagine a scala regionale sul dissesto idrogeologico in Calabria provocato dalle piogge dell'inverno 1990", L. Antronico, S. Critelli, S. Gabriele & P. Versace, eds.. Editoriale BIOS, Cosenza, 51-73.

D. Lgs 152/06 (2006): Decreto Legislativo 3 Aprile 2006, n. 152. Norme in materia ambientale. Gazz. Uff. n. 88 del 14 Aprile 2006, Suppl. Ord. n. 96.

Dell'Anna, L., Rizzo, V., Simone, A. (1981): Composizione mineralogica e granulometrica e alcune caratteristiche geotecniche delle argille infraplioceniche della Media Valle del Fiume Crati. Caratteri distintivi delle argille in frana. *Rend. Soc. It. Mineral. Petrol.*, **37**, 161-178.

Gallego, J.L.R., Ordóñez, A., Loredo, J. (2002): Investigation of trace element sources from an industrialized area (Avilés, northern Spain) using multivariate statistical methods. *Environ. Int.*, **27**, 589-596.

Goovaerts, P., Sonnet, P., Navarre, A. (1993): Factorial kriging analysis of springwater contents in the Dyle River Basin, Belgium. *Water Resources Res.*, **29**, 2115-2125.

Jaquet, O. (1989): Factorial kriging analysis applied to geological data from petroleum exploration. *Mathem. Geol.*, **21**, 683-691.

Jimenez-Espinosa, R., Sousa, A.J., Chica-Olomo, M. (1993): Identification of geochemical anomalies using principal component analysis and factorial kriging analysis. *J. Geochem. Expl.*, **46**, 245-256.

Lanzafame, G. & Tortorici, L. (1981): La tettonica recente della Valle del Fiume Crati (Calabria). *Geogr. Fis. Dinam. Quatern.*, **4**, 11-21.

Le Pera, E. & Sorriso-Valvo, M. (2000): Weathering and morphogenesis in a mediterranean climate, Calabria, Italy. *Geomorphol.*, **34**, 251-270.

Le Pera, E., Critelli, S., Sorriso-Valvo, M. (2001): Weathering of gneiss in Calabria, southern Italy. *Catena*, **42**, 1-15.

Lima, A., Albanese, S., Cicchella, D. (2005): Geochemical baseline for the radioelements K, U and Th in the Campania regione, Italy: a comparison of stream-sediments geochemistry and gamma-ray survey. *Appl. Geochem.*, **20**, 611-625.

Ma, J.-H., Chu, C.-J., Li, J., Song, B. (2009): Heavy Metal Pollution in Soils on Railroad Side of Zhengzhou-Putian Section of Longxi-Haizhou Railroad, China. *Pedosphere*, **19**, 121-128.

Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M. (2002): Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci. Total Environ.*, **300**, 229-243 (2002).

Matheron, G. (1982): Pour une analyse krigeante de données regionalisées. CGMM, ENSMP, Fontainebleau, 22 p.

Suciu, I., Cosma, C., Todică, M., Bolboacă, S.D., Jäntschi, L. (2008): Analysis of soil heavy metal pollution and pattern in Central Transylvania. *Int. J. Mol. Sci.*, **9**, 434-453.

Xu, S. & Tao, S. (2004): Coregionalization analysis of heavy metals in the surface soil of Inner Mongolia. *Sci. Total Environ.*, **320**, 73-87 (2004).

Zheng, Y.M., Chen, T.B., He, J.Z. (2008): Multivariate geostatistical analysis of heavy metals in topsoils from Beijing, China. *J. Soils Sedim.*, **8**, 51-58.