UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

DIPARTIMENTO DI SCIENZE DELLA TERRA, DELL'AMBIENTE E DELLE RISORSE

DOTTORATO IN
Scienze della Terra, dell'Ambiente e delle Risorse

PH.D. IN
EARTH SCIENCE, ENVIRONMENT AND RESOURCES
XXIX CICLO
PH.D THESIS

MULTIMEDIA ENVIRONMENTAL GEOCHEMICAL CHARACTERIZATION OF DOMIZIO FLEGREO AND AGRO AVERSANO AREA (CAMPANIA REGION, ITALY). BASELINES, ISOTOPIC RATIOS AND ADVANCED HEALTH RISK ASSESSMENT

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Aims and structure of the thesis

This thesis introduces the research activities and results of the environmental studies on different areas of Campania region during my PhD programme from 2013 to 2016 at the Department of Earth, Environmental and Resources Science of University of Naples 'Federico II' under the supervision of Prof. S. Albanese, Prof. A. Lima and Prof. B. De Vivo.

The PhD project is focused on Domizio- Flegreo Littoral and Agro Aversano area, which are of continuous environmental concern due to documented illegal dumping and burning of waste since the early 1990s. This area is also characterised by a high degree of urbanization and by a continuously changing land-use patterns (Rezza et al., 2017).

The aim of this study is the geochemical characterisation of the study area even trough an isotopic approach to define the actual degree of the environmental contamination, the sources that have caused it, and to improve the knowledge of the main pathways followed by contaminants to diffuse throughout the different environmental media. The ^{206}Pb/^{207}Pb ratio is the most common used method to trace the environmental pollution sources (Chen et al., 2016, Ayuso et al., 2013, Grezzi et al, 2011, Bove et al., 2011). Thus, in the present research a detailed study of Pb isotope ratios was used to discriminate and apportion the contribution of various sources (antropogenic or geogenic). (Rezza et al., 2017)

The area has been chosen as a reference for this environmental geochemistry study since:

- it was recently involved in a waste emergency caused by an inadequate management of solid waste;
- it is a highly urbanized and populated area, including main cities as Acerra, Giugliano in Campania, Aversa and Casoria;
- the road network inadequate to traffic load;
- the presence of area of industrial development that are potentially susceptible to pollution in Campania, especially in Acerra, Giugliano, Qualiano, Caivano, Casoria, Marigliano, Nola, Pomigliano and Marcianise municipalities.

The whole project activities has been divided in two main phases:

- The first phase aimed at the collection of different media sampling (soil, groundwater, vegetables and hair) and to the selection of the areas where concentrate the Pb isotopic studies.

- The second part is focused on risk assessment of the study area related to high concentrations of potentially toxic element (PTEs): mostly Pb, Zn, Cu, As and Be.

Regarding the first phase activities, 1064 surface soils (0-15 cm), 27 groundwater, 12 corn and 24 hair samples, has been collected across the whole study area. The field activity was realized based on a sampling grid, following strictly FOREGS sampling procedures (Plant et al., 1996; Salminen et al., 1998). The sampling density was one sample for approximately 5 km^2. All samples has been prepared Environmental Geochemistry Lab (LGA) of DiSTAR at the University of Naples Federico II. Sampling soil were dried at the temperature below 35° C and sifted to a fraction <100 mesh. Then were analysed to determine the concentrations of 53 elements, by using the ICP-MS technique at Bureau Veritas Lab (Vancouver, Canada).The obtained data were statistically and cartographically processed by ArcGIS 10.3 and GeoDAS softwares. Selected surface soil samples along with groundwater, corn and hair samples were prepared and analysed during the second year at the USGS Laboratories in Reston (VA, USA), for isotopic analysis, under the supervision of Dr. Robert A. Ayuso.

Results show that soil sampling sites are characterized by As, Cd, Co, Cr, Cu, Hg, Pb, Se, and Zn contents exceeding the action limits established for residential land use (RAL) and, in some cases, also the action limits for industrial land use (IAL) as established by Legislative Decree 152/06. To interpret the isotopic data and roughly estimate proportion of Pb from an anthropogenic source has been defined possible natural and anthropogenic Pb end-member fields based on literature data. Topsoil, groundwater, human hair and corn samples show a greater contribution from geogenic sources like the Yellow Tuff (from Campi Flegrei) and volcanic rocks from Mt. Vesuvius. Aerosols, fly ash and gasoline (anthropogenic sources) have also been contributors. The detail of results of these activities are reported in Rezza et al. (2017) and in the Chapter 1 of this thesis.

The chapter 2 shows the results of the geochemical characterization of these areas contributed to the realization of the Domizio Flegreo and Agro Aversano Environmental Geochemical Atlas (*Lima et al. 2017. Distribuzione geochimica degli elementi inorganici nei suoli del Sito di Interesse Nazionale Litorale Domizio-Flegreo e Agro Aversano, Aracne editrice).*

967 soil samples were collected in the area of 1555 Km^2, analysed with a methodology which combines the ICP-MS (mass spectrometry Inductively Coupled Plasma) and ICP-ES (Emission Spectrometry coupled plasma inductively).

It shows the properties of each chemical element, applications, health effects, as well as its distribution in soils geochemistry of Campania.

In order to process only those data that have a good analytical value, quality controls on the laboratories data have been applied. A univariate and multivariate statistical analysis of the analytical data of the soils has been performed. The compiled geochemical maps are: dot map, interpolated and background /baseline of all the 47 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr). Interpretation and evaluation of geochemical concentrations of different elements have been performed, both for geo-mining and environmental purposes. For this information it is very useful the use of multivariate statistical techniques such as factor analysis in R-mode. Through the distribution of factorial associations, it is possible to assess the impact of each association of elements in each site. The detail of results of these activities are reported in Chapter 2 of this thesis.

Chapter 3 reports the main result related to PHEs (potentially harmful metals) and PAHs (polycyclic aromatic hydrocarbons) concentrations in soils of the Acerra - Marigliano - Pomigliano conurbation. This study aimed at supporting epidemiological researches and at establishing a record of the actual environmental conditions to evaluate the future impact of the incinerator on both the Acerra territory and the public health.

In this area, the total population is about 160,000 and the average population density is about 1600 inhabitants/sqkm. A total of 121 samples were collected to analyse potentially harmful elements PHEs :As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, Zn. 33 samples were collected for analysis of PAHs. A univariate statistical analysis was performed on the chemical data which were, subsequently, georeferenced and mapped by means of a geochemistry-dedicated GIS software named GEODAS. Environmental risk assessment for PHEs has been performed by means of three different methods (Potential Hazard, Contamination Degree and Pollution Load Index).

Results show that 1) the most urbanized areas of the conurbation are characterized by concentrations of Pb, Zn and V exceeding the trigger limits established by the Italian Environmental law (D.Lgs. 152/2006); 2) agricultural soils, in the surroundings of the urbanized areas, are enriched in Cu, Co, Cd, Be and Ni, 3) in the incinerator area Se, Hg, Cu, Cd and Sb baselines are generally higher than in the rest of the territory. Furthermore, the PAHs distribution pattern and their diagnostic ratios suggested that the agricultural waste burning in the rural sector of the study area could be a relevant source of pollution. The detail of results are reported in Albanese et al., 2017 (in progress) and Chapter 3.

The second part of the research is described in Chapter 4. This part is finalized to the analysis of risk assessment on the human health of Acerra's area with the following goals:

- investigate the levels of enrichment factor and pollution index of the critical PTEs in the soil and vegetables:
- establish the bio-concentration factor of critic toxic metals;
- Evaluate the health risk associated with these metals by some primary human exposure pathways.

These research activities have been carried out at Aalto University (Finland) with the supervision of Prof. Jaana Sorvari..

Regarding this part of research, 178 topsoil samples and 10 food samples (corn and Chicorium endive) were taken in Acerra's area. All samples were analysed for 15 elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn) at Bureau Veritas Analytical Laboratories (Vancouver, Canada) by ICP-MS and ICP-ES after an aqua-regia digestion. Enrichment factors and pollution indexes of the PTEs in soil were calculated to compare their concentrations with the regional background level and trigger and action values for residential/recreational and industrial/commercial land use set in the Italian Environmental Law (152/06). A conceptual model to describe the formation of human health risks in the study area and divided it into agricultural, urban and industrial subareas was created. Considering the land use and environmental conditions, the following exposure routes are relevant in the formation of human health risks: ingestion of soil, dermal intake from soil particles, food consumption (corn and vegetables), and inhalation of soil particles. We used the generic exposure models presented by the United States Environmental Protection Agency (US EPA) to determine the potential average daily dose (ADD) of each critical element. A probabilistic risk assessment to find out the probability of these hazards was conducted. The results show that observed that there is a slight contamination for these metals according to the Italian soil quality standards (D.lgs 152/06), and the element Pb is the most important contaminant in this area.

The HQ (hazard quotient) is the ratio of the potential exposure to a substance and the level at which no adverse effects are expected.The sum of HQ is the Hazard Index (HI), if the Hazard Index is calculated to be less than 1, then no adverse health effects are expected as a result of exposure in the urban area is >1 only in the case of lead exposure of both children and adults. In this area HI is > 1 in the case of lead exposure of both children and adults.The detail of this study are reported in Chapter 4 and Rezza et al.2017 (submitted).

At the same time of the implementation of my PhD project, I had the opportunity to give my contribution to other Prof. De Vivo group research projects. These activities and their results have been described in detail in Chapters 5 and 6.

The Chapter 5 describes the research activities related to the geochemical characterization of Campania region's soils, which led to the compilation of the Environmental Geochemical Atlas of the soils of Campania Region (*De Vivo et al., 2016.* Atlante geochimico-ambientale dei suoli della Campania*, Aracne Editrice, Roma, pp.400*).

In this study, the objective is environmental investigations on a territory to assess the "health" of an area, environmental geochemistry helps. The outcome of result of this research is useful to identify hazards, the presence of substances harmful to human health and ecosystems. The origin of contamination can be attributed to different factors both natural and anthropogenic. Toxic metals such as Pb, Hg, Cd, Zn and Cu are very dangerous, and they have increased significantly within the environment as a result of human activities.

This geochemical and environmental atlas reports the results obtained from the surveys about the surface soils of Campania. In an area of around 13,595 km^2, 3535 soil samples were collected, analysed with a methodology which combines the ICP-MS (mass spectrometry Inductively Coupled Plasma) and ICP-ES (Emission Spectrometry coupled plasma inductively). It shows the properties of each chemical element, applications, health effects, as well as its distribution in soils geochemistry of Campania. The compiled geochemical maps are: dot map, interpolated and background /baseline. Interpretation and evaluation of geochemical concentrations of different elements have been performed by the use of univariate and multivariate statistical techniques such as factor analysis in R-mode.

Chapter 6 reports the research activities related to the geochemical characterization of Basilicata region stream sediments which led to the compilation of the Environmental Geochemical Atlas of the Basilicata Region stream sediments (*Lima et al., 2015.* Atlante geochimico-ambientale dei sedimenti fluviali della Basilicata*, Aracne Editrice, Roma, pp. 257).*

A sampling of active river sediments was carried out for the realization of environmental geochemical Atlas of Basilicata region. An amount of 801 fluvial sediments were picked up, from 2012 to 2014, and considering that the whole territory has a surface of 9992 km^2, the nominal density is about 12 samples for km. The chemical analyzes, performed at Bureau Veritas (Vancouver, Canada), have affected 39 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, Zn. They were determined through an analytical methodology that combines the ICP-MS (mass spectrometry inductively coupled plasma) and plasma ICP-ES (Inductively Coupled Emission Spectrometry). A univariate and multivariate statistical analysis of the stream sediment analytical data, has been performed. The distribution of the elemental concentrations for every stream sediment sample (999) has been plotted using histograms and cumulative frequency curves. As well as Environmental Geochemical Atlas of the soils of Campania Region. has been generated dot. interpolated and background-baseline map related to the elements analysed.

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CHAPTER I

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

Introduction

This chapter presents the results of a comprehensive geochemical study of the Domizio Littoral and Agro Aversano area (Southern Italy) based on analyses of topsoil, groundwater, vegetable (corn) and human hair samples, conducted in order to determine the impact of human activities on the environment. Preceding studies have documented the heavy metal pollution of topsoils across this area (Albanese et al., 2011; Bove et al., 2011; Grezzi et al., 2011; Lima et al., 2012) as well as an increased rate of cancer mortality compared to the regional average (Senior and Mazza, 2004). Many studies in recent years have focused on environmental issues using isotope ratios of lead. (Ayuso et al., 2013, 2016; Chen et al., 2016; Galuskovà et al., 2014; Jiao et al., 2015; Kumar et al., 2013). The ^{206}Pb/^{207}Pb ratio is the most commonly used as tracer of environmental pollution sources because it can be precisely determined (Komarek et al., 2008). A detailed study of Pb isotope ratios was used as a key method to discriminate and apportion the contribution of various sources (Duzgoren-Aydin et al., 2008). This is possible because the composition of lead resulting from burning of fossil fuels, lead emanating from industrial sources and lead contributed by the use of pesticides (Ayuso et al., 2004; Cheng et al., 2010) can be estimated for comparison,

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

The isotopic compositions have proven very useful to improve geo-environmental characterization throughout the region and to discriminate different sources of pollution in different media.

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

1. *Study area*

The Domizio Flegreo Littoral and Agro Aversano areas cover about 1287 Km^2 and include 90 municipalities. The total population is about 1,300,000. Morphologically, the areas include part of the Campania Plain. The region is surrounded by Mesozoic limestone of the Southern Apennines (N and E), Roccamonfina volcano (N), Somma-Vesuvius volcano (SE), the Phlegrean Fields (Campi Flegrei) volcanic area (SW) and the Tyrrhenian Sea (S and W). The Domizio Flegreo Littoral has three different lithologies: loose pyroclastic materials, lithoide tuffs (Campanian Ignimbrite, Yellow tuff) and lava with composition that is mostly trachytic and phonolitic (De Vivo et al., 2006; Grezzi et al., 2011). The Agro Aversano area contains abundant limestone and dolomite; the Caserta Mts. occur to the north, the Avella Mts. are in the NE part of the area, and the Lattari Mts. are found in the south. The entire region is also characterized by alluvial and volcanic deposits where the older sediments derived from the Volturno river are silty and clayey-sandy; the most recent sediments are derived from tuffs and lapilli originating from volcanic activity from Campi Flegrei (Fig.1A) (Bove et al., 2011). On the basis of its hydrogeological features the study area can be divided into two interconnected groundwater bodies related to the Volturno river plain and the Phlegrean Fields pyroclastic hills. (Corniello et al., 2014).

The Regi Lagni, a system of artificial canals running for about 56 km with a basin covering an area of 1,300 km across the provinces of Caserta, Naples and Benevento, is also included in the Agro Aversano area. In the past, the system was used as a source of irrigation water, but now it mostly collects sewage from factories of Nola, Naples, and from Marcianise and Acerra.

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

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

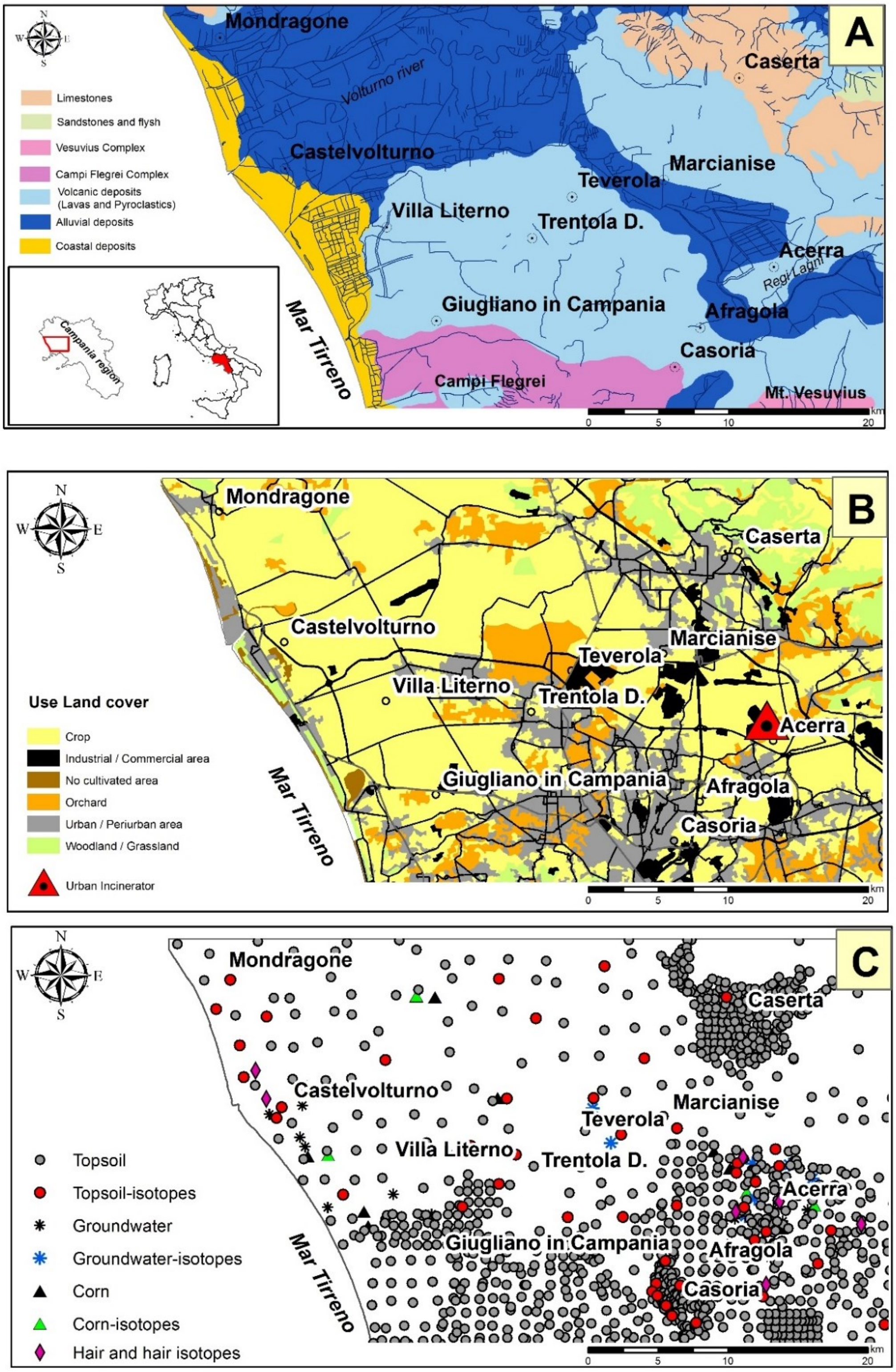

Figure 1 Study area

2. Sample preparation and chemical analysis

2.1 Topsoil

Geochemical data for 1064 topsoil samples were retrieved from former studies focused on the area (Lima et al., 2012, Grezzi et al., 2011, Bove et al., 2011). The sampling density was one sample for approximately 5 km^2 (Fig.1c). Topsoil samples were collected in accordance with international methods described in Salminem et al. (1998). Each sample consisted of 1 kg of material taken from the depth of 0-20 cm. All samples were dried at the temperature below 35° C and sifted to a fraction <100 mesh. Samples were sent to Bureau Veritas (Vancouver, Canada), where they were analysed by inductively coupled plasma mass spectroscopy (ICP-MS) after digestion with aqua regia (Cicchella et al., 2008, Bove et al., 2011, Grezzi et al., 2011). The analyses included the following 53 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr.

2.2 Groundwater

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

2.3 Hair and corn

Human hair samples were collected at local barber and hairdresser shops. The samples were stored in plastic bags. Each hair sample, weighing 50 g, was a composite from five adults of the same gender, and coming from the same municipality. A total of 24 samples were collected. The samples were cleaned using methanol and purified water, and dried prior to analysis. After this, they were dissolved using a microwave digestion with ultrapure nitric acid and hydrogen peroxide. All samples were further dried in the laboratory of DISTAR (University of Naples, Federico II), and shipped to Act Labs laboratories (Toronto, Canada) for the determination of the following 16 elements by inductively coupled plasma mass spectroscopy (ICP-MS) technique: Al, As, Cd, Co, Cr, Cu Hg, Mn Mo, Ni, Pb, Th, U, Sc, Ni, V.A total of 13 corn (*Zea mays*) samples were collected at different farms in this area. After collection, 100 g of each sample was dried in a temperature of 60 °C and ground to a powder. Then 20 g of each sample was shipped to Bureau Veritas for analysing 53 elements (Ag, Al, As, Au, B, Ba, Be, Bi, ca, Vd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re,S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, U, V, W, Y, Zn, Zr) by inductively coupled plasma mass spectroscopy (ICP-MS) technique. Before the analysis, the samples were dissolved with nitric acid and digested in a hot water bath. After cooling a modified aqua regia solution consisting of equal parts of concentrated HCl, HNO_3 and DI H_2O was added to each sample to dissolve it in a heating block within a hot water bath. Sample was further diluted with HCl and filtered. Finally, 5 g of each sample was taken for the analysis.

2.4 Pb isotopes.

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

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

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

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

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

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

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

Table 2-B Statistical parameters for toxic metals in the groundwater. Da is a median concentration of Italian groundwater (Cicchella et al., 2010), Db = median concentration of Sarno area groundwater (Cicchella et al., 2016)

Element	µg/kg	N	Range	Min	Max	Mean	Median	St. Dev.	C^b	C^a
As	µg/kg	23*	5-73	<5	73	36	35	22.4	30.5	0
Be	µg/kg	23*	-	-	-	-	-	-	3	
Cd	µg/kg	23*	5-176	<5	176	36.9	26.9	39.8	16	30
Co	µg/kg	23*	24-1,000	24	1,000	278,8	75	393	41.5	80
Cr	µg/kg	23*	58-1650	58	1650	388.9	223	446.8	247	70
Cu	µg/kg	23*	13,100- 299,000	12,900	299,000	50,274	18,500	73,945	19,717	19,950
Hg	µg/kg	23*	123-1,560	123	1,560	662	584	403	495	638
Ni	µg/kg	23*	150-10,500	150	10,500	1,096	650	2,089	374	420
Pb	µg/kg	23*	312-2,840	312	2,840	1,229	1,030	756	1087	780
Sb	µg/kg	23*	-	-	-	-	-	-	49	20
Se	µg/kg	23*	-	-	-	-		-	596	-
Sn	µg/kg	23*	-	-	-	-	-	-	436	-
Tl	µg/kg	23*	-	-	-	-	-	-	2	10
V	µg/kg	23*	-	-	-	-	-	-	130	80
Zn	µg/kg	23*	163,000-520,000	163,000	520,000	25,0783	225,000	77,634	167,107	179,200

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

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

Table 1-D Statistical parameters for toxic metals in the corn. Fa = reference value of HM in vegetables (European Union 2006), Fb = reference value of HM in vegetables (FAO 2011)

3. *Results*

3.1 Data analysis and mapping

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

$$CF = C_i / C_b$$

Where:

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

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

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

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

3.2 Geochemical distribution of toxic elements

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

Antimony (Sb)

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

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

Arsenic (As)

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

Arsenic content in groundwater ranges from 0.25 to 57.8 µg/l, with a median of 3.8 µg/l. The latter is much higher than the Italian groundwater concentration median of 2.2 µg/l (Cicchella et al., 2010) (Table 1B). In hair, As ranges from 5 to 73 µg/kg, with a median of 35 µg/kg (table 1C), very close to median value of 31 µg/kg reported by Cicchella et al. (2015) in the Sarno river basin. The As concentrations in corn range from values <0.050 up to 0.50 mg/kg with a median of 0.10 mg/kg (Table 1D).

Cadmium (Cd)

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

Cobalt (Co)

In topsoil, Co ranges from 2.6 to 35.6 mg/kg with a median of 8.6 mg/kg (Table 1A). About 1 % of samples exceed the uppermost value of the BCRIN (17 mg/kg) (De Vivo et al., 2006) (Table 1A). Three samples located in Giugliano and Casoria municipalities exceed the Italian RAL (20 mg/kg). Cobalt content in groundwater ranges from values <0.01 up to 5.04 µg/l with a median of 0.04 µg/l, which is well below the Italian groundwater reference value of 0.17 µg/l (Cicchella et al., 2010). Cobalt in hair varies from 24 to 1,000 µg/kg with a median of 75 µg/kg. The latter value is lower than the median (80 µg/kg) reported by Dongarrà et al. (2011) and higher than the one (41.5 µg/kg) reported by Cicchella et al. (2016). Cobalt concentrations in corn range from 0.020 to 0.070 mg/kg with a median value of 0.040 mg/kg.

Chromium (Cr)

In topsoil, Cr concentrations range from 0.25 to 486 mg/kg with a median of 12 mg/kg (Table 1A). About 30 % of samples exceed the uppermost value of the BCRIN (16 mg/kg) reported by De Vivo et al. (2006) (Table 1A). Two samples exceed the Italian RAL (150 mg/kg) with Cr contents of 177 and 486 mg/kg, in Acerra and Casoria, respectively. In groundwater Cr content ranges from 0.25 to 28.4 µg/l with a median of 0.25 µg/l, which is above that the Italian groundwater value of 0.17 µg/l (Cicchella et al., 2010) but lower than the median (13.6µg/l) determined for the Sarno river basin

(Cicchella et al., 2016) (Table 1D). Chromium in hair ranges from 58 to 1650 µg/kg with a median of 223 µg/kg much higher than the one reported by Dongarrà et al. (2011) (70 µg/kg) and lower than the one (247 µg/kg) reported by Cicchella et al. (2016) (Table 1C). The Cr concentrations in corn range from 2.1 to 5 mg/kg with a median value of 3.2 mg/kg (Table 1D).

Copper (Cu)

In topsoil, Cu concentrations range from 4.59 to 1034.3 mg/kg with median of 60 mg/kg (Fig. 3C and Table 2A). About 5% of the analysed samples have concentrations higher than the upper limit of the BCRIN (200 mg/kg) determined by De Vivo et al. (2006); furthermore, 25 % of samples are characterized by Cu concentrations exceeding the Italian RAL (120 mg/kg). One sample, within the Casoria municipality administrative area, also exceeds the Italian IAL fixed by law at 600 mg/kg. Copper content in groundwater ranges from values < 0.2 up to 46.9 µg/l with a median of 6.6 µg/l. The latter is much higher than the median (0.19 µg/kg) reported by Cicchella et al. (2010) and it is above the median (0.9 µg/l) reported by Cicchella et al. (2016) for the Sarno River basin. In hair, Cu ranges from 12,900 to 299,000 µg/kg with a median concentration value of 18,500 µg/kg, which is slightly lower than the ones of 19,950 µg/kg and 19,717 reported by Dongarrà et al. (2011) and Cicchella et al. (2016), respectively. The Cu concentrations in corn range from 3.9 to 7.6 mg/kg with a median of 5.1 mg/kg.

Lead (Pb)

Lead in topsoil varies from 6.21 to 1,099 mg/kg with a median of 63 mg/kg (Fig. 3D and Table 1A). The highest concentrations (1,099 and 1,095 mg/kg) occur within the Acerra municipality administrative boundaries. About 7% of sampled topsoils exceed the upper limit of the BCRIN (80 mg/kg) determined by De Vivo et al (2006). About 21 % of the samples have Pb concentrations higher than the Italian RAL (10 mg/kg). Lead in groundwater ranges from values < 0.05 to 4 µg/l with a median value of 1.1 µg/l, which is above the median of Italian groundwater (0.007 µg/l) reported by Cicchella et al. (2010). Lead in hair ranges from 312 to 2,840 µg/kg with a median of 1030 µg/kg. The latter is higher than the median (780 mg/kg) determined by Dongarrà et al. (2011) but slightly lower than the one set by Cicchella et al. (2016) (1087 µg/kg.) (Table 1C). Lead in corn ranges from 0.10 to 0.71 mg/kg with a median of 0.27 mg/kg. About 85 % of samples have Pb concentration values above the maximum level permitted in food (European Union, 2006 and FAO 2011) (0.20 mg/kg). The highest values (> 0.20 mg/kg) were found in the towns of Acerra, Giugliano in Campania and Villa Literno.

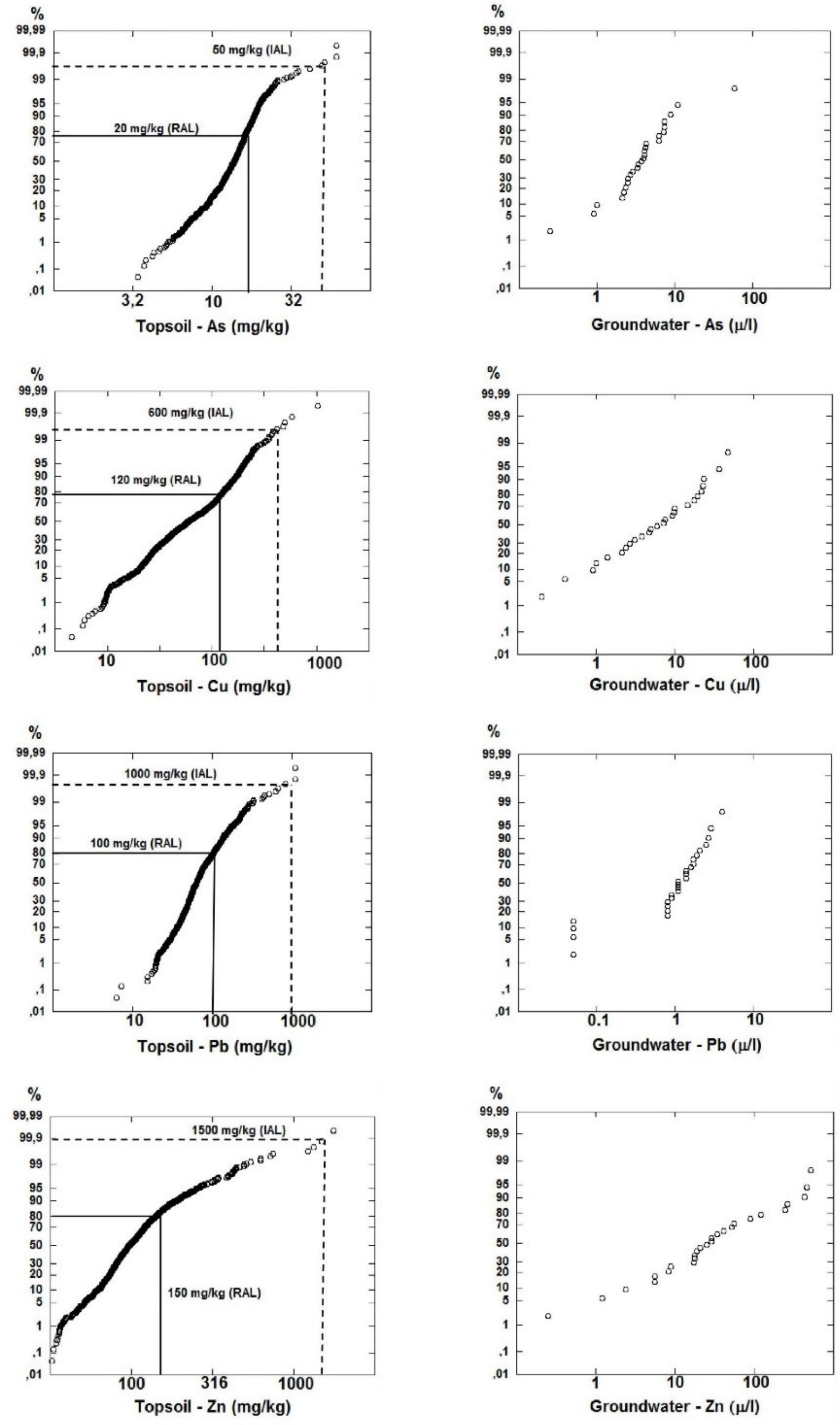

Figure 2 Cumulative frequency curves for As, Cu, Pb, Zn in the topsoil and groundwater samples.

Mercury (Hg)

Mercury concentrations in topsoil range from 0.004 to 6.77 mg/kg (Fig. 3E and Table 1A) with a median value of 0.07. About 37 % of analysed topsoils have concentrations exceeding the BCRIN of 0.1 mg/kg (De Vivo et al., 2006). Six samples located in Acerra, Caivano and in the northern part of Naples have Hg concentrations higher than the Italian RAL (1 mg/kg); one sample in Acerra even exceeds the Italian IAL (5 mg/kg). All groundwater samples have concentrations lower than the detection limit (0.1µg/l). In hair, Hg ranges from 123 to 1,560 µg/kg with a median of 622 µg/kg, which is above the median (638 µg/kg) reported by Dongarrà et al. (2011) and is also higher than the one (495 µg/kg) set by Cicchella et al. (2005) for the Sarno River basin. Mercury concentrations in corn range from <0.001 to 0.7015 mg/kg with a median value of 0.005 mg/kg.

Nickel (Ni)

Nickel in topsoil ranges from 1.9 to 86.6 mg/kg with a median of 12 mg/kg (Table 1A). Highest concentrations of 86.6 and 70.2 mg/kg occur in Caivano and Casoria municipality respectively. About 8% of samples exceed the upper value of the BCRIN (19 mg/kg) set by De Vivo et al. (2006). Nickel content in groundwater ranges from 0.1 to 9.9 µg/l with a median of 0.1 µg/l; the latter is lower than Italian median (0.13 µg/l) established by Cicchella et al. (2010). Nickel in hair ranges from 150 to 10,500 µg/kg with a median of 665 µg/kg, higher than the median of 374 mg/kg calculated by Cicchella et al. (2016) for the Sarno River basin. About 58 % of hair samples have Ni contents higher than the median value (420 mg/kg) provided by Dongarrà et al. (2011). Nickel concentrations in corn range from 0.1 to 1.1 mg/kg with a median of 0.3 mg/kg.

Selenium (Se)

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

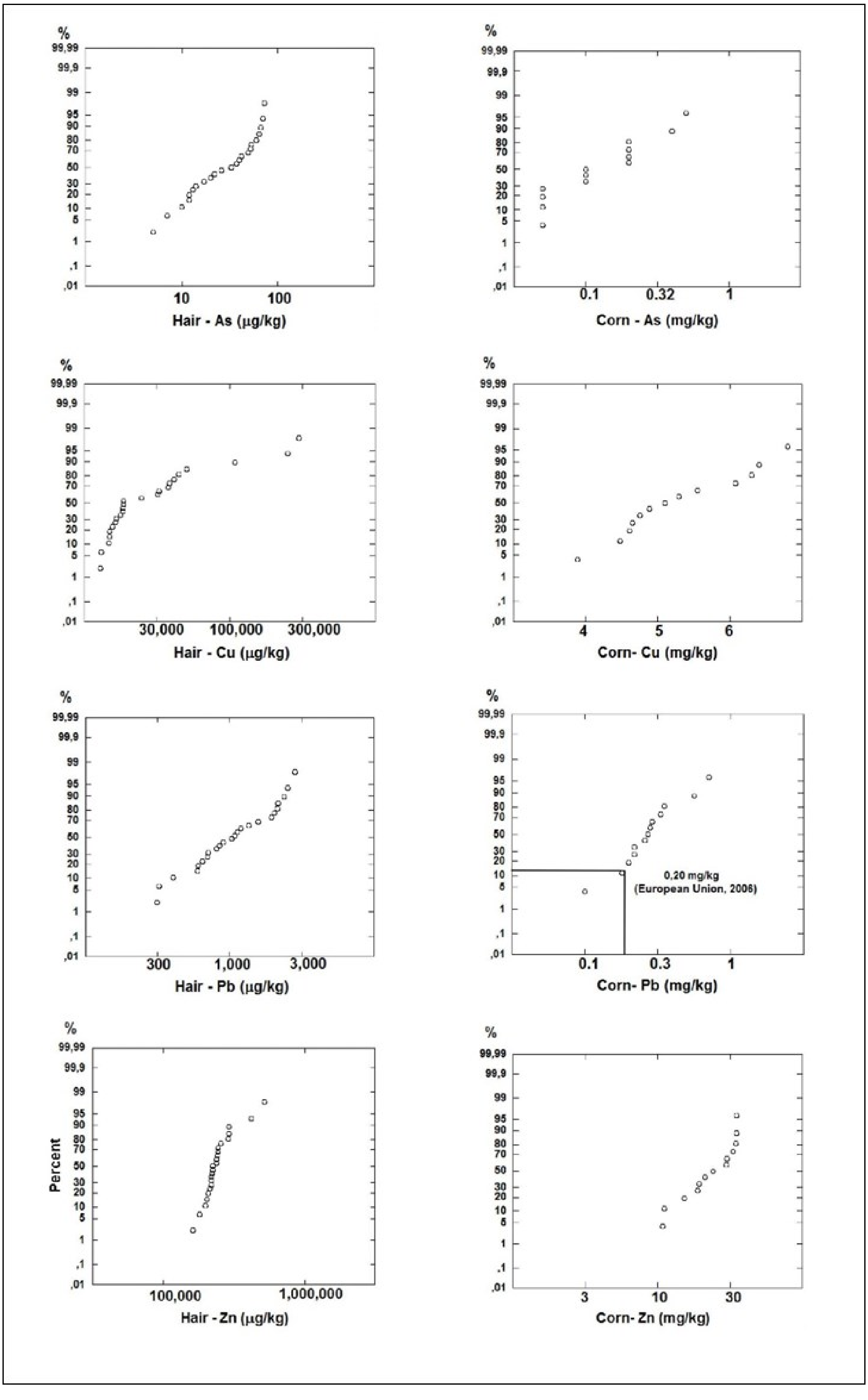

Figure 3 Cumulative frequency curves for As, Cu, Pb, Zn in the human hair and corn samples

Thallium (Tl)

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

Vanadium (V)

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

Zinc (Zn)

Zinc concentrations in topsoil vary from 32 to 1,765 mg/kg, with a median of 96.4 mg/kg (Fig. 3F and Table 1A). About 48 % of the samples exceed the local background of 400 mg/kg and about 2 % of samples exceed the uppermost limit of the BCRIN (100 mg/kg) established by De Vivo et al. (2006). The same 2 % of samples exceed the Italian RAL (100 mg/kg) and only one sample in Casoria municipality exceeds the Italian IAL (1,500 mg/kg) (Table 1A). Zinc contents in groundwater range from values < 0.25 up to 516 µg/l with a median of 27 µg/l; the median is well above the median established by Cicchella et al. (2010) for Italian groundwater (0.31 µg/l). The local median is also higher than the Sarno River basin groundwater median value of 13.7 µg/l (Cicchella et al., 2016) (Table 1B). In the hair samples, Zn ranges from 163,000 to 520,000 µg/kg. The median of 224,000 µg/kg exceeds both the one calculated by Dongarrà et al. (2011) of 17,200 µg/kg and the one calculated by Cicchella et al. (2016) of 167,107 µg/kg (Table 1C). The Zn concentrations in the corn range from 10.9 to 35.4 mg/kg with median of 24.3 mg/kg (Table 1D).

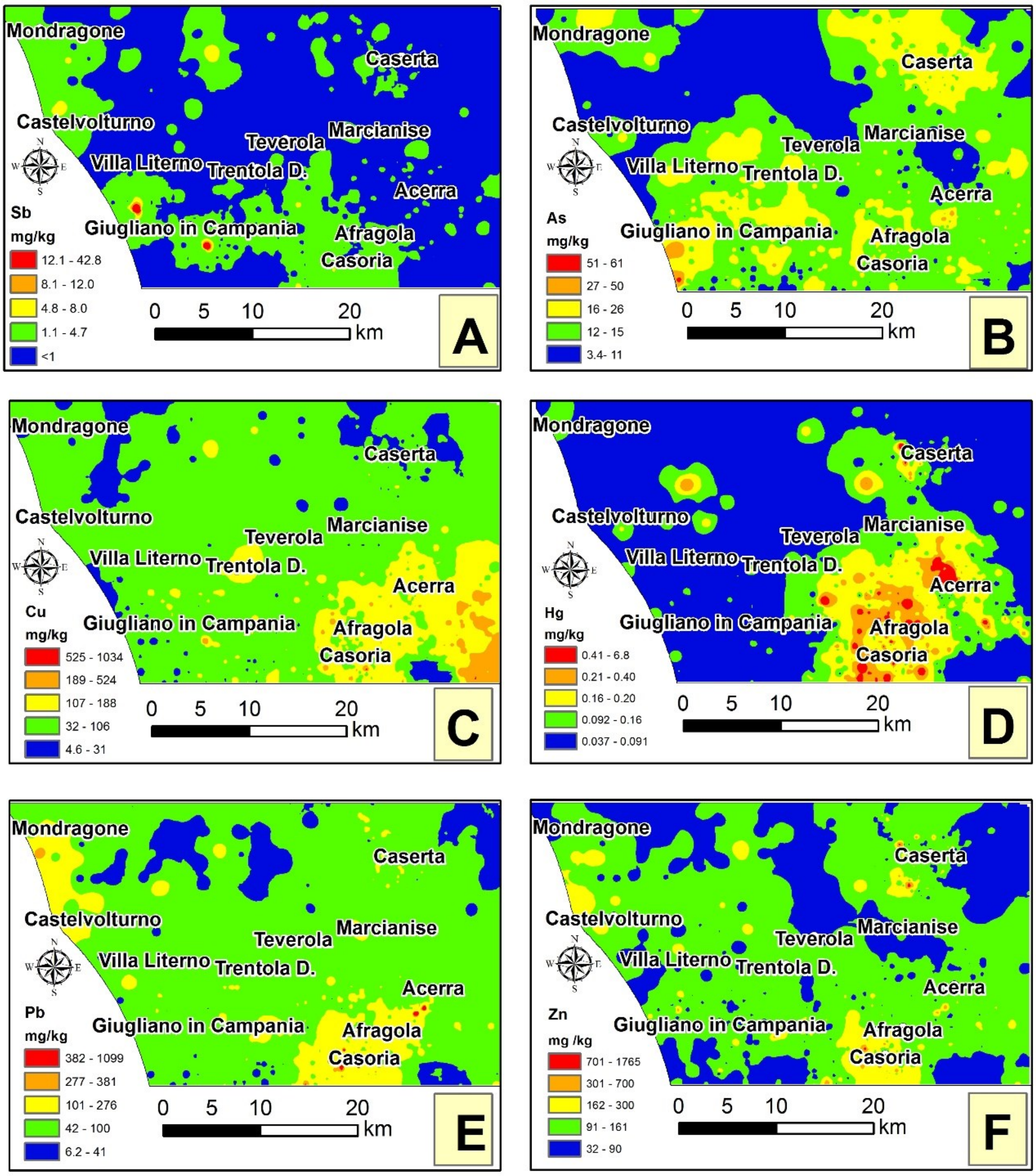

Figure 4 Interpolated map (Sb, As, Cu, Hg, Pb, Zn)

4. Discussion

4.1 Contamination factor (CF) and degree of contamination

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

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

Figure 4 shows selected CF maps for Pb, Hg and Sb. Thallium and vanadium were excluded from the evaluation of degree of contamination because their concentrations are attributed to a geological source (Cicchella et al. 2005, Lima et al. 2012).

The CF map for As shows that 97% of the study area has CF<1, and the rest (3%) has a CF between 1 and 3, confirming the mostly geogenic nature of As in the environmental media and suggesting that it can be related to the volcanic origin of soils in this area.

For Cd, the CF map shows that 75 % of the study area has CF<1 and the rest (25 %) has a CF between 1 and 3 (moderate contamination). The CF map for Cr shows that 59 % of the study area has CF <1 and the 41 % has a CF between 1 and 3; we speculate that this moderate pollution may be related in some cases to anthropogenic activities. The comparable trend of Co and Cu, where the percentage of CF >1 is 99 % and 98 % respectively, demonstrate that the distribution of concentrations is for the most part geogenic, while the remaining samples (only 1% for Co and 2% for Cu), with CF between 1 and 3, are associated with agricultural practices, as perhaps in the use of fertilizers. It is possible that the trends of Pb, Hg, Sb, are different from the others. Hg and Sb (Fig. 4) show similar trends with values of 70 % and 74 % and CF <1 (no contamination); the rest of the samples for Hg and Sb have values of 27 % and 23 %, respectively, and CF between 1-3 (moderate contamination). Perhaps 2-3 % of the total area has CF values between 3-6 (high contamination) and some samples exceed values of CF ≥6 (very high contamination). The occurrence of several anomalous values might represent the presence of illegal landfill close these cities.

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

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

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

$$CD = \sum CF$$

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

- $CD<11$ Low degree of contamination
- $11 \leq CD \geq 22$ Moderate degree of contamination
- $22 \leq CD \geq 33$ High degree of contamination
- $CD \geq 33$ Very high degree of contamination

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

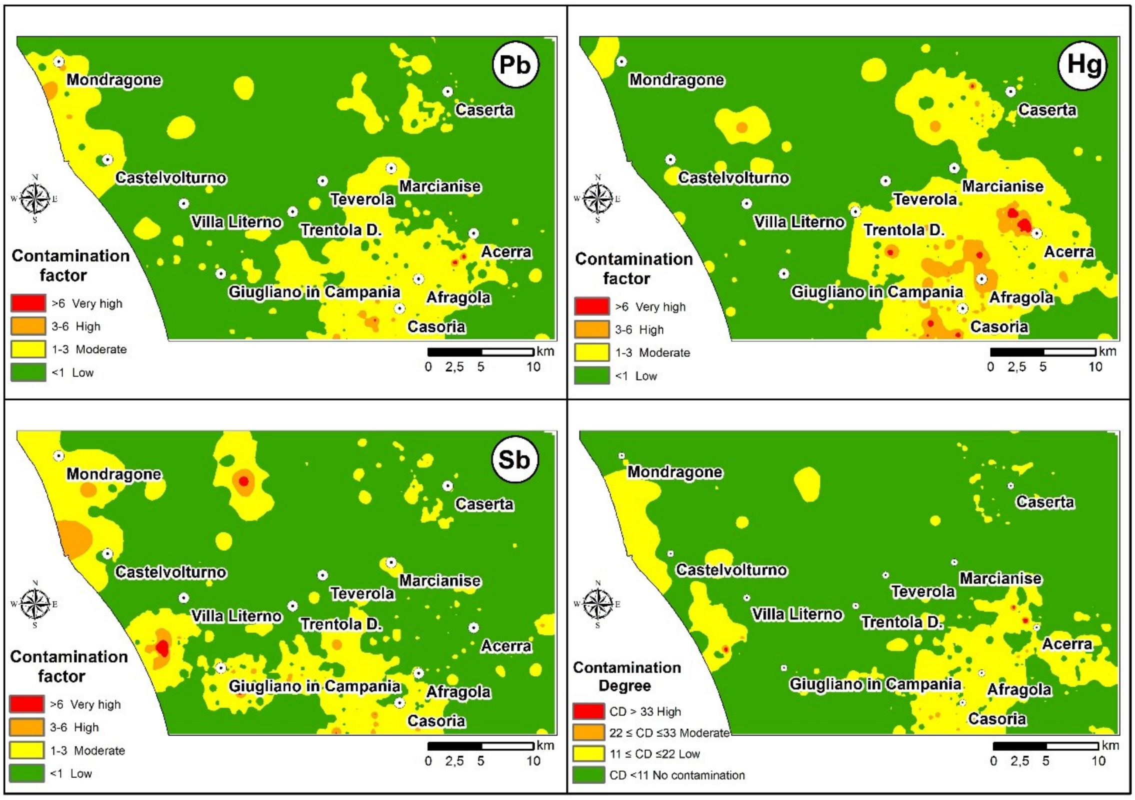

Figure 5 Contamination factor maps for Pb. Hg, Sb and contamination degree map in topsoil

4.2 Pb isotopic compositions

Anthropogenic contamination by lead in soils is an acute problem particularly in urban and industrial areas (Komarek et al., 2007). Pb isotopic studies provide a way to determine how enrichment of Pb in soil may reflect an interplay of natural and anthropogenic sources.

Environmental studies commonly report the isotopic composition of Pb ratios ^{206}Pb/^{207}Pb and^{208}Pb/^{207}Pb. Table 3 shows Pb isotopic results. The two box plots of ^{206}Pb/^{207}Pb and ^{208}Pb /^{207}Pb (Figure 5 e, f) show the range of all environmental media analysed. The samples plot intermediate to the fields for geogenic (volcanic rocks) and anthropogenic (gasoline, fly ash, aerosols) sources.

The dot map (Fig. 5) shows ^{208}Pb /^{207}Pb and ^{206}Pb/^{207}Pb distributions for leached soil (a, b) and soil residues (c, d) for the study area. The dot map also shows Pb isotopic data obtained by Bove et al., 2011, Grezzi et al., 2011, and Civitillo et al., in prep, for leached soil. The ^{206}Pb/^{207}Pb isotopic distributions for leached soil (Fig.5 b) demonstrate that values between 1,13 to 1,18 are common in the area. Near the towns of Acerra, Casoria, Teverola, Mondragone and Castelvolturno, such ^{206}Pb/^{207}Pb values are linked mostly to anthropogenic sources. The soil residues (Fig 5 d) have values of ^{206}Pb/^{207}Pb (1,21 – 1,23) that are more likely controlled by the natural/geogenic component, in contrast to the compositions of the leached soils which are more closely related to anthropogenic factors. Plots involving Pb isotopic compositions and heavy metals such as Pb, Sb, Zn (Table 2 and Fig. 6b), show the correlation with soil leaches and residues and suggest mixing. The estimates of anthropogenic contributions are preliminary and represent a first pass at determining the impact of human activities. This mixing trend can be examined using the value of 1/Pb versus isotopic composition ($^{206}Pb/^{207}Pb$) involving different anthropogenic sources (gasoline and combustion processes). Figure 6 shows the isotopic ratio $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$ for topsoil, groundwater, human hair and corn. The linear correlation (R^2= 0.98) may represent a mixing scheme, whereby two

different end members (geogenic and anthropogenic) are involved, as deduced from statistical analysis. In detail, figure 6 shows the regular trend of leached and residue surface samples of this study. Some topsoil samples (LD 41 and LIFE 05) in Castelvolturno and Villa Literno have isotopic values close to the CRITTAM pesticide value, in agreement with results by Grezzi et al. (2011*)*.

Leached samples have an isotopic composition close to that of the Pb signature in aerosols (Tommasini et al., 2000), fly ash (Carignan et al., 2005), and urban incinerator products (Geagea et al., 2008). The soil residues, in contrast, plot closer to the compositions of regional volcanic rocks (Ayuso et al., 2008; D'Antonio et al., 1995). Leached samples (LD 42, LD 50 and LD 62) from the city of Castelvolturno and the town of Villa Literno have values closer to the fly ash (Carignan et al., 2005). These results may indicate that the elemental and isotopic variations are related to refuse burning activities in this area. Leached samples CAS 45, CAS 72, CAS 142 and ACE 29 are closer to the urban incinerator concentration reported by Geagea et al. 2008, particularly samples near the towns of Casoria and Acerra.

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

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

Pb isotopic compositions of hair show that three samples from Acerra (ACE-HF-01, ACE-HF-02, ACE-HF-04) plot in the field of aerosol products (Tommasini et al., 2000). One hair sample in the town of Castelvolturno has a value as high as 86 %, suggesting an anthropogenic source (CAS-HF-04). However, we caution that the effects of hair dyes have not been fully examined and that they could have strongly affected the isotopic compositions of the samples. Moreover, Pb in hair analysed in this study cannot be shown to be directly related to a single individual and, although Pb may be anthropogenic in origin, it may not represent the internal Pb isotopic composition (blood composition). Thus, because we used composite hair samples (from hair salons involving hair from several individuals), the results are at best an approximation of the total amount of Pb and point to an average isotopic composition.

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

	SOIL RESIDUES ^{206}Pb/^{207}Pb	**SOIL RESIDUES ^{207}Pb/^{208}Pb**	**% Pb Anthropogenic***	**SOIL LEACHED ^{206}Pb/^{207}Pb**	**SOIL LEACHED ^{207}Pb/^{208}Pb**	**% Pb Anthropogenic**	**Pb (mg/kg)**	**Zn (mg/kg)**
ACE 24	*1.1839*	*2.4624*	*49*	*1.1680*	*2.4629*	*58*	*102.7*	*103.4*
ACE 29	*1.1795*	*2.4567*	*56*	*1.1536*	*2.4199*	*91*	*111.6*	*158.6*
ACE 10a	*1.1790*	*2.4542*	*41*	*1.1743*	*2.4437*	*29*	*69.6*	*114.5*
ACE 13	*1.1906*	*2.4727*	*36*	*1.1797*	*2.4538*	*58*	*69.1*	*109.6*
ACE 4	*1.1960*	*2.4740*	*31*	*1.1766*	*2.4509*	*63*	*101.2*	*85.8*
ACE 56d	*1.1642*	*2.4498*	*73*	*1.1769*	*2.4495*	*64*	*1,099.1*	*627.9*
ACE 66a	*1.1663*	*2.4505*	*71*	*1.1622*	*2.4437*	*79*	*1,095.4*	*496.7*
NOL-B 35	*1.1864*	*2.4595*	*49*	*1.1691*	*2.4515*	*68*	*162.7*	*173.0*
ACE 61	*1.2046*	*2.4749*	*23*	*1.1828*	*2.4599*	*52*	*88.4*	*117.1*
NOL-B 16	*1.1866*	*2.4578*	*50*	*1.1692*	*2.4548*	*65*	*107.8*	*175.8*
AV119T1	*1.1972*	*2.4668*	*35*	*1.1758*	*2.4578*	*58*	*108.5*	*175.0*
LIFE 01	*1.1928*	*2.4629*	*41*	*1.1568*	*2.4371*	*88*	*97.2*	*176.0*
LIFE 02	*1.2041*	*2.4765*	*23*	*1.1804*	*2.4562*	*56*	*68.1*	*121.0*
LIFE 04	*1.1998*	*2.4797*	*23*	*1.1831*	*2.4562*	*54*	*26.0*	*59.3*
LIFE 05	*1.1707*	*2.4405*	*75*	*1.1616*	*2.4421*	*81*	*186.9*	*45.2*
LIFE 06	*1.1999*	*2.4705*	*30*	*1.1692*	*2.4548*	*65*	*57.7*	*87.0*
LD 4	*1.2120*	*2.4823*	*12*	*1.1982*	*2.4728*	*30*	*53.2*	*58.0*
LD 15	*1.1963*	*2.4695*	*34*	*1.1786*	*2.4634*	*52*	*159.7*	*114.3*
LD 42	*1.1627*	*2.4284*	*87*	*1.1474*	*2.4244*	*94*	*157.1*	*207.3*
LD 62	*1.1603*	*2.4308*	*89*	*1.1470*	*2.4225*	*93*	*166.9*	*243.9*
LD 41	*1.1707*	*2.4456*	*72*	*1.1616*	*2.4417*	*81*	*225.6*	*222.1*
LD 49	*1.1588*	*2.4287*	*91*	*1.1470*	*2.4231*	*93*	*250.6*	*153.5*
LD 50	*1.1613*	*2.4325*	*88*	*1.1503*	*2.4257*	*97*	*327.9*	*153.0*
LD 52	*1.1645*	*2.4385*	*82*	*1.1323*	*2.4098*	*72*	*265.4*	*108.1*
	GW ^{206}Pb/^{207}Pb	**GW ^{207}Pb/^{208}Pb**					**Pb (µg/l)**	**Zn (ug/l)**
GW 02	*1.1977*	*2.4569*	*41*				*4*	*20.7*
GW 06	*1.1742*	*2.4444*	*69*				*1.6*	*463.4*
GW 11	*1.1771*	*2.4482*	*65*				*1.1*	*89.2*
GW 12	*1.1702*	*2.4288*	*79*				*0.9*	*17.7*
GW 13	*1.1565*	*2.4305*	*93*				*1.4*	*8.2*
GW 15	*1.1622*	*2.4368*	*85*				*1.4*	*40.9*
GW 25	*1.1571*	*2.4369*	*88*				*2.9*	*265.9*
GW 26	*1.1587*	*2.4360*	*88*				*1.1*	*28.6*
GW 27	*1.1659*	*2.4354*	*82*				*0.8*	*17.2*
	HAIR ^{206}Pb/^{207}Pb	**HAIR ^{207}Pb/^{208}Pb**					**Pb (µg/kg)**	**Zn (µg/kg)**
ACE-HF-01	*1.1597*	*2.4383*	*85*				*1,120*	*214,000*
ACE-HF-02	*1.1589*	*2.4428*	*82*				*849*	*223,000*
ACE-HF-04	*1.1598*	*2.4460*	*78*				*1,190*	*163,000*
ACE-HF-05	*1.1790*	*2.4303*	*70*				*2,840*	*198,000*
MR-HF-01	*1.1698*	*2.4371*	*77*				*1,590*	*208,000*
PM-HF-01	*1.1871*	*2.4295*	*61*				*1,090*	*256,000*
CAS-HF-02	*1.1633*	*2.4353*	*85*				*2,150*	*289,000*
CAS-HF-03	*1.1704*	*2.4394*	*76*				*598*	*244,000*
CAS-HF-04	*1.1620*	*2.4208*	*86*				*322*	*220,000*
	CORN ^{206}Pb/^{207}Pb	**HAIR ^{207}Pb/^{208}Pb**					**Pb (mg/kg)**	**Zn (mg/kg)**
C-01	*1.1909*	*2.4459*	*72*				*0.3*	*29.7*
C-03	*1.1897*	*2.4604*	*45*				*0.7*	*34.6*
C-05	*1.1700*	*2.4605*	*46*				*0.3*	*35.4*
C-09	*1.1844*	*2.5011*	*14*				*0.1*	*19.3*

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

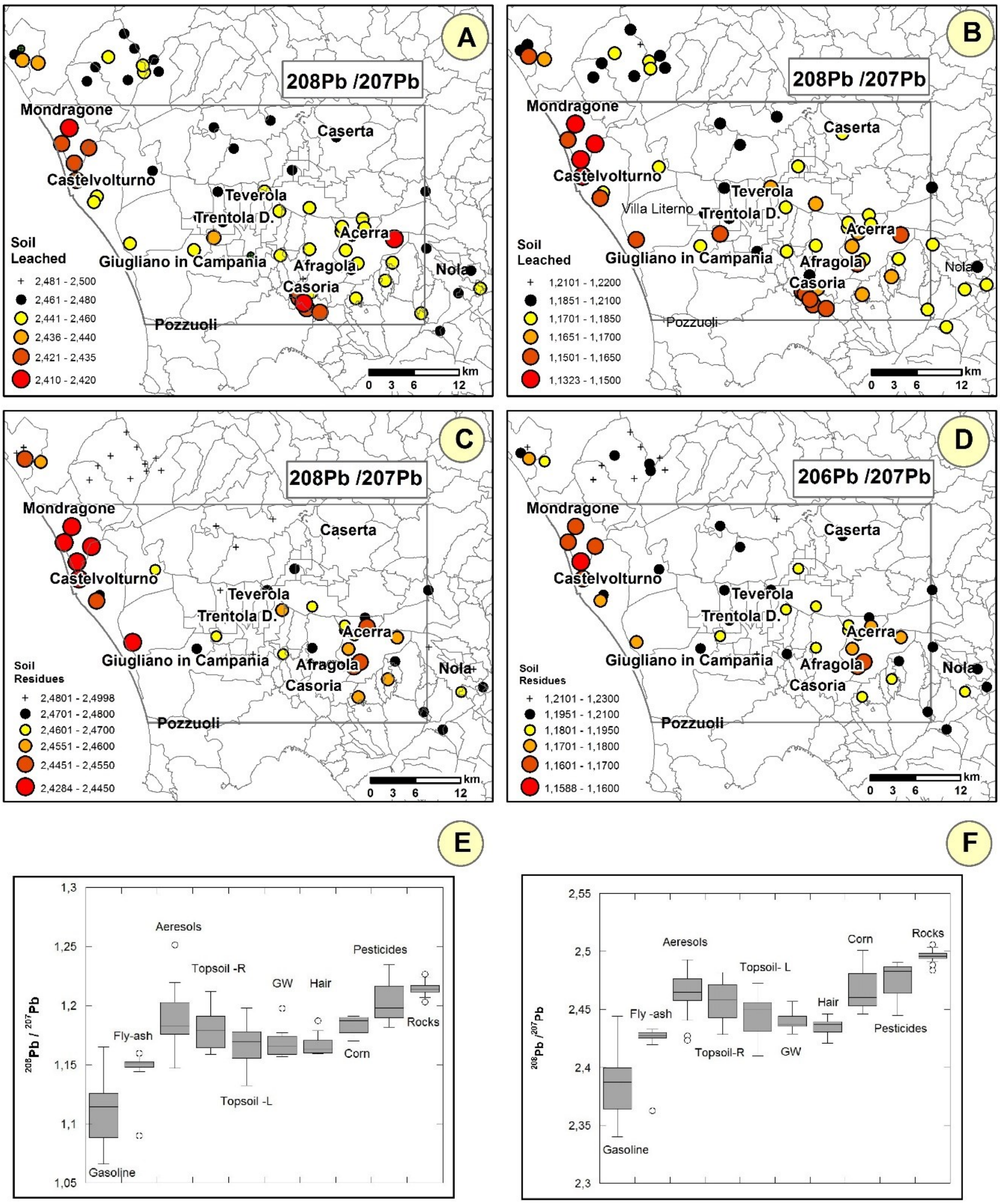

Figure 6 (A, B, C, D) dot maps showing the concentration of each isotopic ratio 206Pb/207Pb and 207Pb/208Pb. Intervals classified by soil residues and soil leached cumulative frequency graphs; (E,F) 206Pb/207Pb and 207Pb/208Pb box plots for analysed environmental media (this paper) and for other reference media.

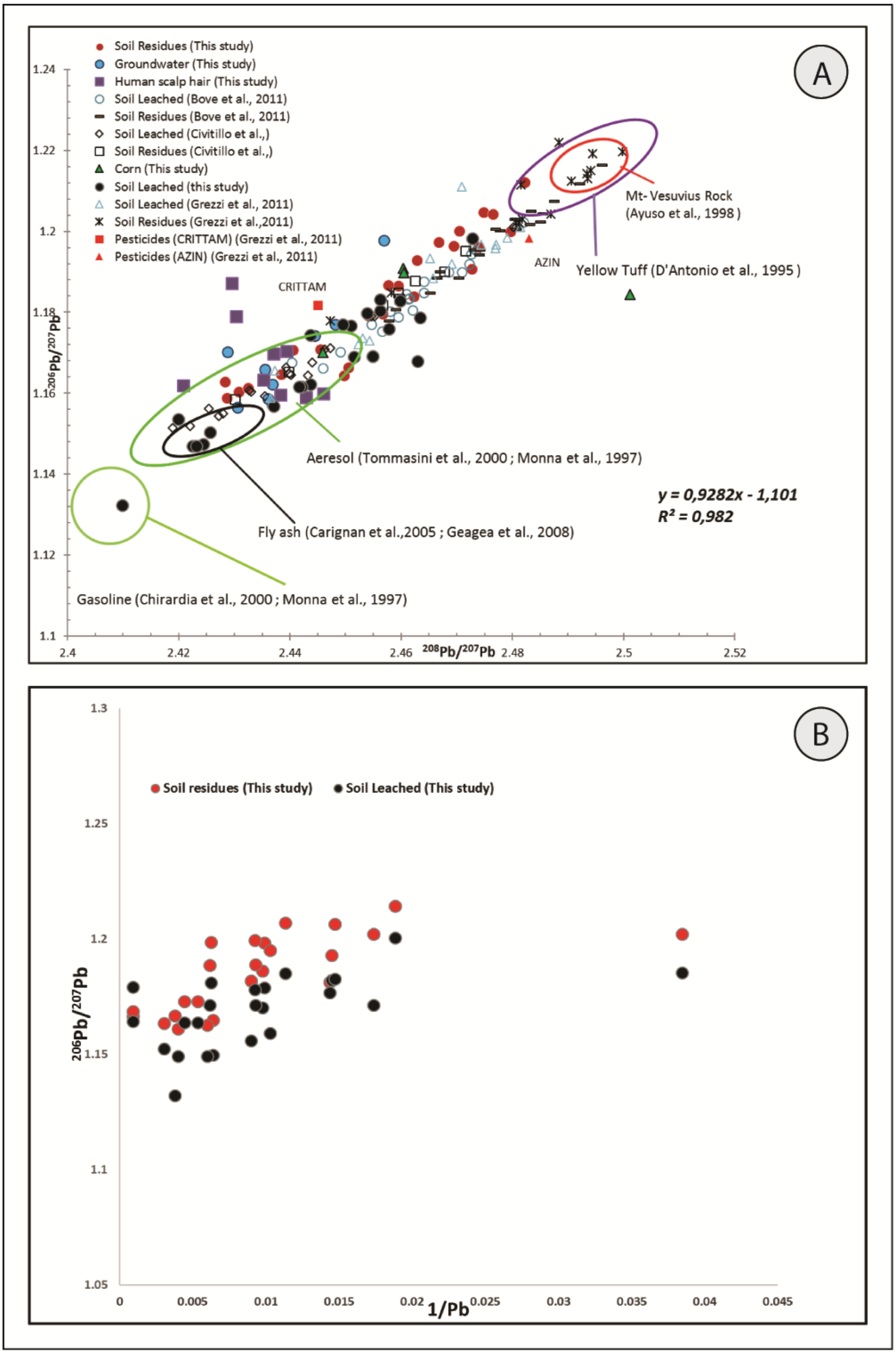

Figure 7 (A) 206Pb/207Pb versus 207Pb/208Pb isotopic composition of all sample collected for this study. Also shown data from previous study and field for natural and anthropogenic reference data. (B) 206Pb/207Pb versus 1/Pb for soil residues and soil leached.

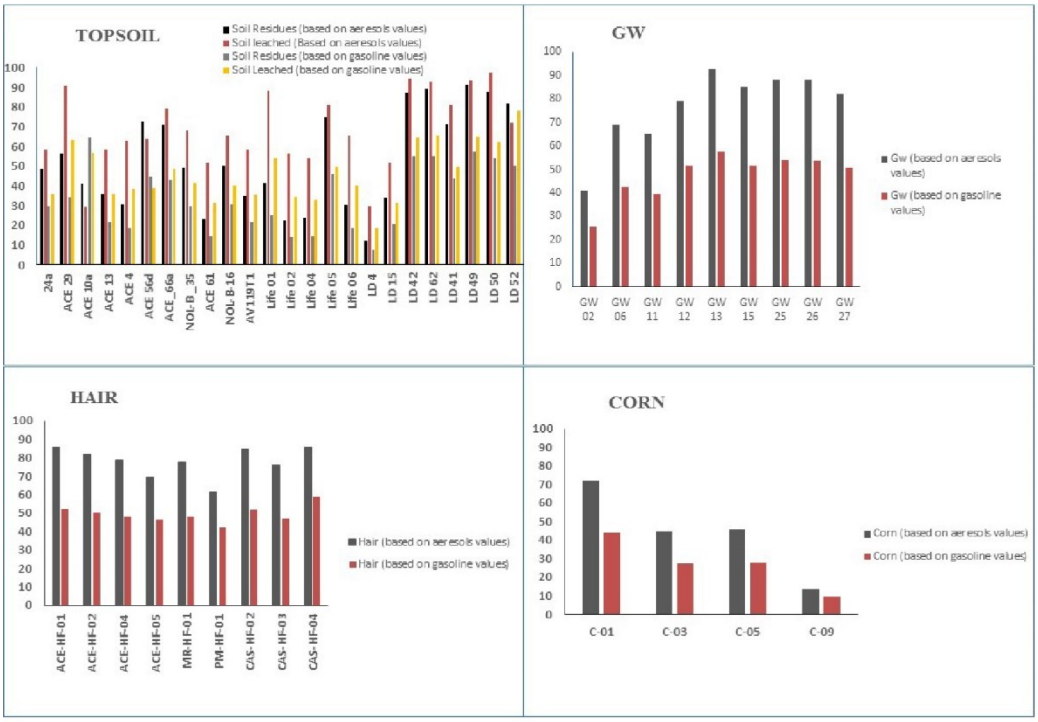

Figure 8 Comparison with 'anthropogenic content' (in %) in all analysed media calculated by taking as reference both aerosols and gasoline Pb isotopic contents. In abscissa sample ID.

5. Conclusions

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

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CHAPTER II

Geochemical Distribution of Inorganic Chemicals in soils of the Domizio Flegreo Littoral and Agro Aversano area

Introduction

The Atlas: Geochemical Distribution of Inorganic Chemicals in soils of the Domizio Flegreo Littoral and Agro Aversano area (Lima A., Rezza C., Giaccio L., Albanese S., Cicchella. De Vivo B.) is intended to be a tool of considerable importance, both for the evaluation of the degree of pollution in the mentioned area and for the determination of background levels indicated as "background/baseline" because in some cases these values are not the natural level (background), but baseline, that is influenced by anthropogenic impact.

This work represents a "snapshot" which dates back to the time of sampling and which may be used in the future as a reference for the environmental impact assessment of human activities in this area. They are also important tools to evaluate the assessment of background levels (background) of the various chemical elements examined.

In an area of around 1555 Km^2, 967 soil samples were collected, analysed with a methodology which combines the ICP-MS (mass spectrometry Inductively Coupled Plasma) and ICP-ES (Emission Spectrometry coupled plasma inductively). It shows the properties of each chemical element, applications, health effects, as well as its distribution in soils geochemistry of Campania. The compiled geochemical maps are:

- Dot and interpolated to illustrate the concentrations distribution of the 47 analysed chemical elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr;
- Background / baseline map of 47 elements;
- Factor associations, from the factor in R-mode;
- the "geochemical" risk only for potentially toxic elements compiled bearing in mind the contamination thresholds concentration (CSC) by Legislative Decree no. 152/06.

1. Study area

The Domizio-Flegreo Littoral is located along the north western coast of the Campania region (Italy) and it stretches for about 855 km$^{2.}$ The area of the Domizio Flegreo Littoral is located along the north-western coast of the Campania region (Italy) and it stretches for about 855 km^2 covering most of the Campanian Plain, including, among others, the municipalities of Pozzuoli, Castelvolturno, Villa Literno, Mondragone; in the northern part, it includes the municipalities of Sessa Aurunca and Carinola. Agro Aversano is an area that stretches for about 700 Km^2 located in northern Campania. It consists of 57 municipalities, belonging to both Neapolitan and Caserta provinces and including Caserta town. The fact that there is such a large number of urban settlements on such a wide area (the Domitio-Flegreo Littoral) includes 26 municipalities covering about 864 Km^2), is the reason for the very high urbanization rate found on it. The main municipalities of the Agro Aversano are: Caserta Acerra, Aversa Marcianise ,Pomigliano d'Arco and Maddaloni. (Fig.1)

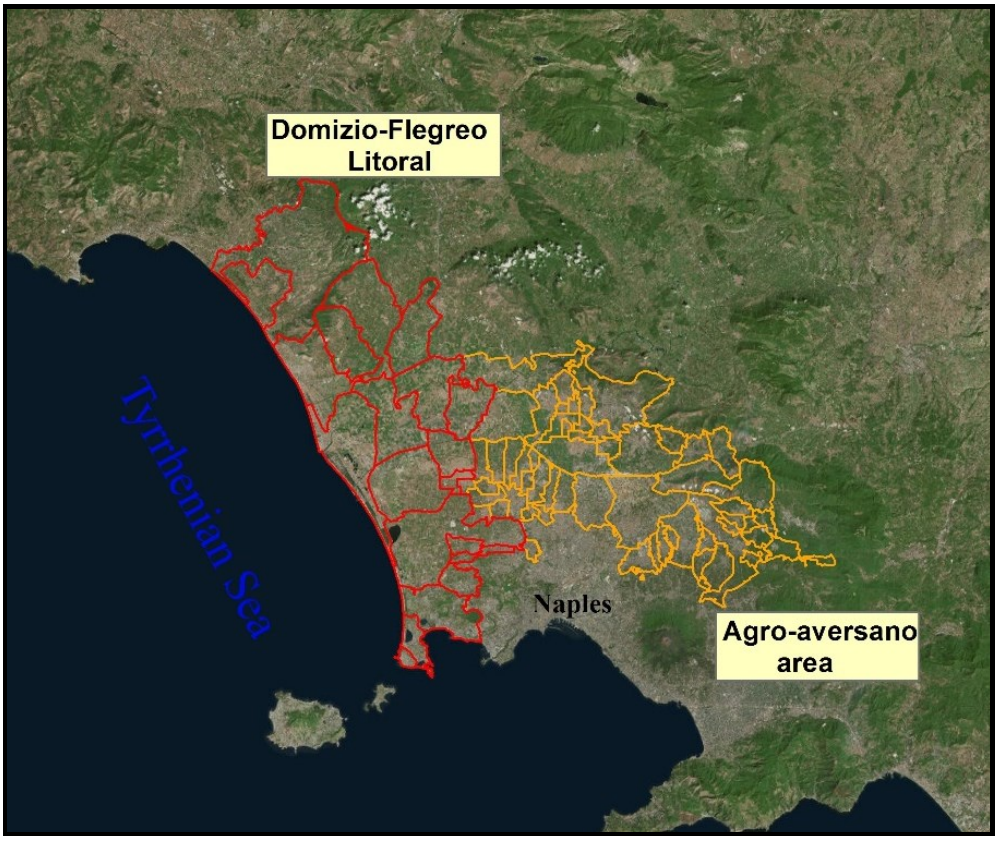


Figure 1 Study area

Morphologically, the Domizio- Flegreo Littoral includes part of the Campania Plain and the volcanic areas located at its edges: the Campi Flegrei district and the Mt. Roccamonfina volcano (Grezzi et al., 2011).

The upper border of the Agro Aversano is represented by the natural hydrographic border of the Volturno river, whose average flow of about 82m^3/s, is the highest of all southern Italy. It increases in Capo Volturno, in the Molise region, and has a length of about 175 Km; within its transit in the Campanian Plain it flows as a meander channel and then, finally, reaches the sea near Castelvolturno town, in the Domitio-Flegreo Littoral. The main hydrological feature characterizing the Agro Aversano is the Regi Lagni artificial channel. It is the result of a drainage and canalization work of the ancient Clanius river, provided by the Bourbons in the 1610. Nowadays the Regi Lagni channel is in a completely careless condition, in total contrast not only with its historical importance, but especially, with its environmental role in terms of the improvement of territory conservation (Bove et al., 2011).

2. Material and Methods

For the achievement of ‘Geochemical Distribution of Inorganic Chemicals in soils of Domizio Flegreo Littoral and Agro Aversano area 967 samples of topsoil (10-15 cm) were collected, where the whole territory has a surface of 1555 km^2, and the density is approximately 2 sample for 3 km^2 (Fig.2).

For the sampling methods, the protocol given in FOREGS Manual (*Salminen et al., 1998*) was followed in order to limit the sample contaminations in the sampling operation, listed below:

- use of tools, well-cleaned, plastic or stainless steel 18/10, unglazed, in order to avoid contamination from metal;
- use of disposable plastic gloves, to change to the withdrawal of each single sample;
- pre-decontamination of tools to reduce the presence of a ‘contamination’ from the other elements taken before;
- before sieving, on the field, in order to reduce the bigger component characterized mostly by pebbles, roots, foliage, etc. and keep the thinnest fraction useful for the analysis;
- accurate samples labelling;
- field records containing information on the depth of each sample, the depth of the entire section (and therefore of the source rock), proximity to possible sources of anthropogenic contamination (road, gas stations, garages / nautical, industries, pesticides, insecticides, herbicides, etc.), morphological description of the site, vegetation, moisture content of the sample and its organic content;
- Pictures of sections of the site with the meter used as reference.

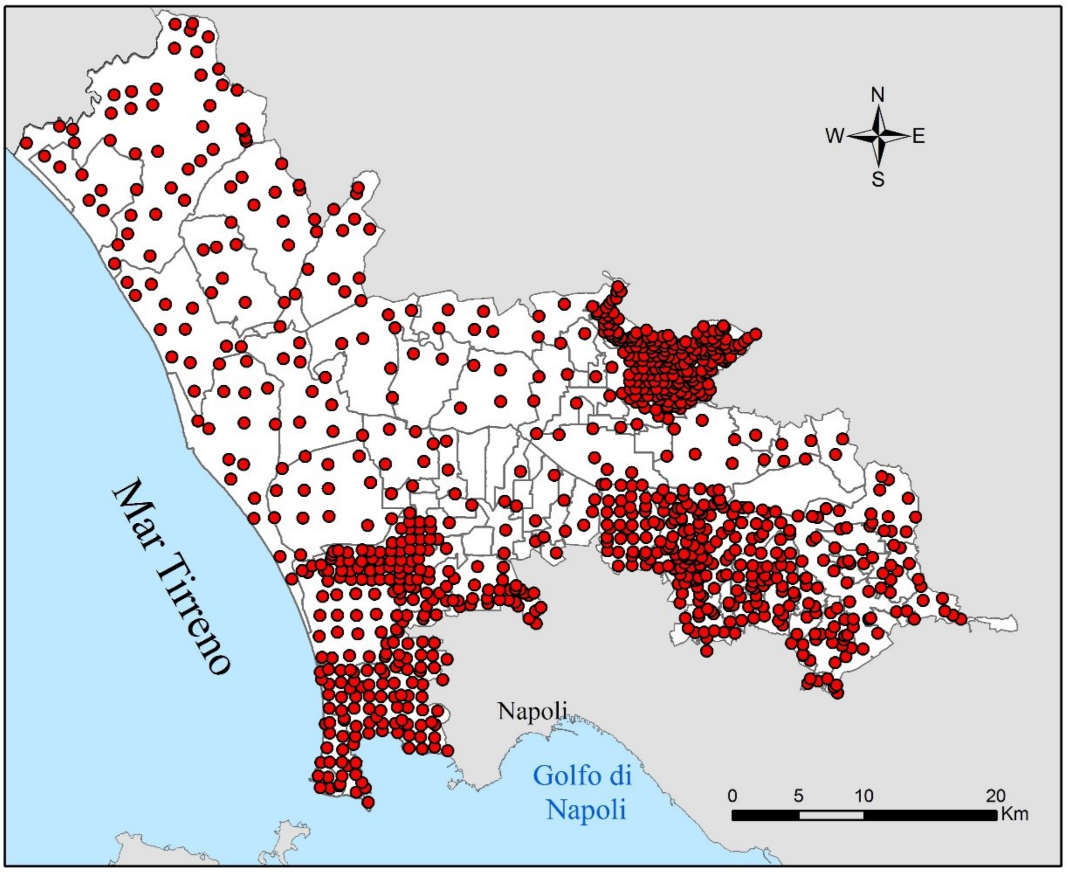


Figure 2 Map of sampling sites

In particular, for each sampling site a total quantity of soil equal to about 2.5 kg has been collected; aliquots were taken in 0.5 kg five different points at a distance of about 10 m from each other. Soil samples were then homogenized in a single sample and stored in plastic bags, then closed with string, in order to remove metal contamination. The samples were collected during the collection of more samples in the year 2010, the last of which was collected in 2016. The big database used for this atlas has been achieved in the space of ten years. Once collected, the samples were taken to the laboratory for their preparation, before being shipped to the laboratory for chemical analysis. The soils were dried with the use of infrared lamps, in such a way that the temperature did not exceed 35 ° C. The sieve used a fraction of <2 mm, which best meets the objectives of this geochemical survey for environmental purposes (*De Vivo et al., 2004*).

The chemical analyses, performed at Bureau Veritas (Vancouver, Canada) have affected 47 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr. They were determined through an analytical methodology that combines the ICP-MS (mass spectrometry inductively coupled plasma) and plasma ICP-ES (Inductively Coupled Emission Spectrometry).

In order to process only those data that have a good analytical value, quality controls on the laboratories data have been applied. *Table 1* shows the accuracy and precision values sample's geochemical data of the Campania Region considered in this work, after the application of the selected analytical technique.

Accuracy is defined as the closeness degree of the measurement of a quantity to its true value. The laboratory accuracy error has been determined using the following formula:

$$[(|X - TV|) / TV] * 100 \qquad (1)$$

X= laboratory's analysis result for the standard sample, TV= true value of the standard sample.

For the measurement of the analysis accuracy error, Acme's in-house reference materials have been used: for soil samples, the standard was DS7. Acceptable accuracy error values shall not exceed 15%.

Precision is defined as the degree of reproducibility of a measurement; in other words, it is the degree of how repeated measurements offer the same results under the same conditions. The precision has been calculated as relative percentage difference (% RPD) using the formula:

$$\% \text{ RPD} = [\,|S-D| / (\,|S+D| /2)] *100 \qquad (2)$$

S = Standard sample concentration, D= Duplicate

Precision of the performed analysis has been calculated on 6 in-house replicates and one blind duplicate for soils. Values can be considered good if the RPD is < 35% for soils.

Element	Unit	LRS	Accuracy %	Precision %
Al	%	0,01	4,5	3,8
Ca	%	0,01	4,1	3,3
Fe	%	0,01	2,6	4,5
K	%	0,01	3,1	1,5
Mg	%	0,01	2,7	3,6
Na	%	0,001	7,2	4,2
P	%	0,001	3,7	6,8
S	%	0,02	2,8	6,2
Ti	%	0,0	6,8	7,9
Ag	µg/kg	2,0	4,3	7,0
As	mg/kg	0,1	2,6	2,7
Au	µg/kg	0,2	5,0	8,7
B	mg/kg	1,0	0,4	8,2
Ba	mg/kg	0,5	4,3	5,6
Be	mg/kg	0,1	6,9	11,1
Bi	mg/kg	0,0	8,5	16,2
Cd	mg/kg	0,0	5,2	6,9
Ce	mg/kg	0,1	9,2	7,1
Co	mg/kg	0,1	5,5	8,9
Cr	mg/kg	0,5	5,2	4,6
Cs	mg/kg	0,02	3,4	4,3
Cu	mg/kg	0,01	4,8	8,4
Ga	mg/kg	0,1	5,0	5,2
Hf	mg/kg	0,02	18,8	7,5
Hg	µg/kg	5	9,0	17,7
La	mg/kg	0,5	10,1	6,2
Li	mg/kg	0,1	4,3	5,2
Mn	mg/kg	1,0	2,7	3,8
Mo	mg/kg	0,0	6,0	4,4
Nb	mg/kg	0,0	15,4	14,0
Ni	mg/kg	0,1	3,5	3,7
Pb	mg/kg	0,0	4,8	3,3
Rb	mg/kg	0,1	3,8	2,5
Sb	mg/kg	0.02	14,7	3,5
Sc	mg/kg	0,1	7,2	4,2
Se	mg/kg	0,1	4,3	10,4
Sn	mg/kg	0,1	5,7	4,7
Sr	mg/kg	0,5	6,9	5,1
Te	mg/kg	0,02	5,1	9,1
Th	mg/kg	0,1	6,2	5,6
Tl	mg/kg	0,02	3,6	3,5
U	mg/kg	0,1	6,9	2,2
V	mg/kg	2	4,6	10,0
W	mg/kg	0,2	5,6	4,8
Y	mg/kg	0,0	8,4	5,4
Zn	mg/kg	0,1	3,6	4,7
Zr	mg/kg	0,1	11,5	18,0

Table.1 Accuracy and precision

2.1 Univariate statistics

A traditional statistical analysis of the analytical data of the soils (*Sinclair, 1976*) has been performed by KaleidaGraph 4.0 program. The distribution of the elemental concentrations for all the 3535 soil samples has been plotted using histograms and cumulative frequency curves. (*Tab.2)*

2.2 Geochemical map production

In this part of the work, the various types of geochemical maps are presented and described, compiled for the chemical elements in soil analysed by Domizio Flegreo and Angro Aversano area.

2.2.1 Dot map

Dot map is the distribution of concentrations dot map, useful for information on the exact concentration distributions when the sample was collected.

2.2.2 Interpolated map

Interpolated data maps help to get information of a spatial range. In fact, it is not possible to know the exact concentration at any point of the study area. This type of map is the best possible approach to the exact concentration values at not sampled points. Based on the cell size used during the sampling it is possible, using a detected radius interpolation regarding the element concentration, to reclassify the dot value on a spatial value through a Multifractal Inverse Distance Weighted (MIDW) method (*Cheng, 1999*) available in the software GeoDAS (*Cheng, 2003*); to perform interpolated maps, the multifractal analysis filter method used is Concentration-Area model (C-A). (Fig.4).

2.2.3 Baseline/background map:

Baseline maps have also been executed in this work. This kind of maps are the principal way to get information about the statistically higher concentration levels found in a detected area. On literature, the term “background content” (natural background) designates the concentration of natural elements, including the presence of abnormal concentrations due to mineralization. The term baseline should mean measured concentrations of elements present in a given site, including, therefore, the presence of elements of anthropogenic origin.

Element	Unit	N° sample	Max	Min	Mean	Geometric Mean	Median	Mode	St.Deviation
Al	%	967	8,27	0,61	4,26	4,01	4,38	5,29	1,32
Ca	%	967	25,4	0,2	3,80	2,37	2,12	0,54	4,26
Fe	%	967	3,8	0,6	2,41	2,33	2,41	2,14	0,60
K	%	967	4,53	0,14	1,27	1,00	0,95	0,56	0,95
Mg	%	967	8,81	0,07	0,58	0,50	0,49	0,35	0,45
Na	%	967	1,83	0,01	0,34	0,23	0,24	0,07	0,29
P	%	967	1,18	0,01	0,16	0,13	0,12	0,07	0,12
S	%	967	0,61	0,005	0,04	0,03	0,04	0,03	0,04
Ti	%	967	0,27	0,005	0,14	0,12	0,14	0,14	0,05
Ag	μg/kg	967	6390	1,5	130,5	93,3	90	68	247,7
As	mg/kg	967	103	2,6	14,1	13,1	13,6	12,5	6,4
Au	μg/kg	967	373,4	0,1	10,1	5,80	5,5	2,4	19,8
B	mg/kg	967	54	4	14,1	12,4	11	10	7,7
Ba	mg/kg	967	1562,9	22,6	394,6	354,8	392,3	439,9	167,6
Be	mg/kg	605	12	0,7	4,7	4,4	4,8	4,3	1,63
Bi	mg/kg	967	3,08	0,03	0,47	0,44	0,46	0,47	0,18
Cd	mg/kg	967	13	0,01	0,45	0,37	0,38	0,18	0,44
Ce	mg/kg	967	170	22	79,8	77,3	80,1	80,1	19,7
Co	mg/kg	967	34	2,3	8,99	8,30	8,6	6,6	3,50
Cr	mg/kg	967	178	1	13,59	11,23	11,6	7	10,98
Cs	mg/kg	451	34	2	13,3	12,7	13,6	11,5	3,6
Cu	mg/kg	967	1206	4,6	90,7	61,9	58,1	23,6	94,3
Ga	mg/kg	967	17	1,5	8,9	8,4	9,1	9,9	2,6
Hf	mg/kg	451	3,75	0,05	0,38	0,32	0,31	0,28	0,28
Hg	μg/kg	967	6775	3	104,54	68,10	62	45	272,1
La	mg/kg	967	141	8,2	46,7	43,4	45,6	40,4	15,95
Li	mg/kg	967	52	6	19,13	18,27	18,6	21,6	5,77
Mn	mg/kg	967	6695	203	839	794	786	730	356
Mo	mg/kg	967	20,4	0,3	1,3	1,2	1,1	1	1,1
Nb	mg/kg	451	17,8	1,4	7,98	7,39	7,8	7,33	2,94
Ni	mg/kg	967	86,6	1,3	11,81	10,13	11,4	14,2	6,68
Pb	mg/kg	967	1099	6	71	61,3	58,3	55,8	64,6
Rb	mg/kg	967	429	25	150,8	140	141	106	55,9
Sb	mg/kg	967	43	0,22	0,97	0,75	0,67	0,58	2,01
Sc	mg/kg	951	5,8	0,3	2,21	2,04	2,1	1,8	0,88
Se	mg/kg	967	2	0,05	0,42	0,34	0,4	0,3	0,24
Sn	mg/kg	605	63	0,7	4,35	3,86	3,8	2,6	3,47
Sr	mg/kg	967	533	10	177	157	156	134	86
Te	mg/kg	967	0,3	0,01	0,04	0,03	0,04	0,03	0,03
Th	mg/kg	967	59,1	1	13,8	12,4	13,5	15,2	5,96
Tl	mg/kg	967	3,6	0,1	1,6	1,5	1,6	1,2	0,62
U	mg/kg	967	13	0,6	3,63	3,26	3,4	3,8	1,66
V	mg/kg	967	144	20	65,3	61	60	44	24,4
W	mg/kg	967	3,9	0,075	1,11	1,04	1,1	1	0,38
Y	mg/kg	967	27,9	4,68	14,39	13,9	14,3	14,5	3,3
Zn	mg/kg	967	1488	28	108,6	97,6	92,7	81,1	80,6
Zr	mg/kg	967	269	4,2	34	29	28	25	22

Table.2 Statistical parameters

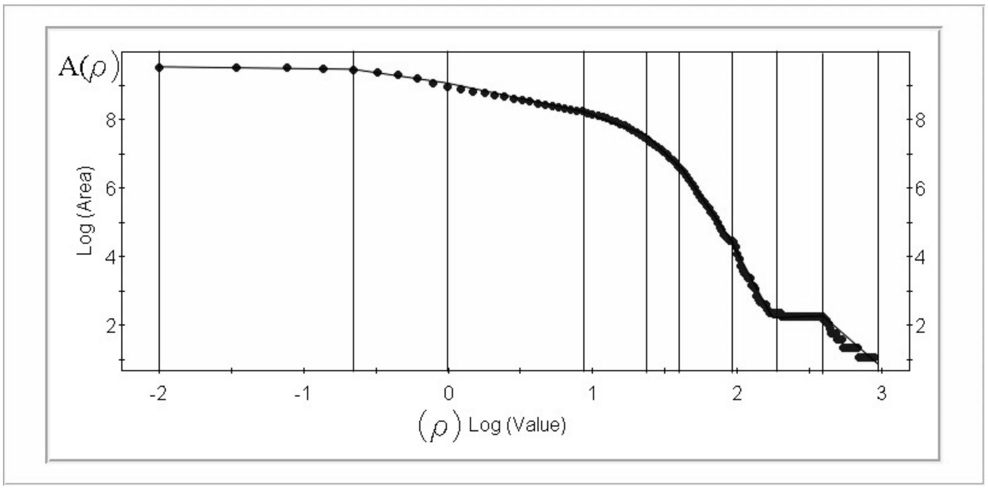


Figure 3 C-A Plot

2.2.4 Factor scores association map

Interpretation and evaluation of geochemical concentrations of different elements have been performed, both for geo-mining and environmental purposes. For this information it is very useful the use of multivariate statistical techniques such as factor analysis in R-mode.

It allows a quantitative assessment of different variables and their mutual influence, thus allowing to group elements by factorial associations depending on their coefficient of correlation. This allows to identify possible correlations between the distribution of the individual elements, lithological characteristics, potential mineralizing processes, enrichment phenomena associated surface environment, pollution and other anthropogenic elements (*De Vivo et al. 1981, 2004*).

Through the distribution of factorial associations, it is possible to assess the impact of each association of elements in each site. In the case of Domizio Flegreo- Agro Aversano 's soils, it has been chosen the five factor model and the interpolated maps of the distribution of the factor scores. The four associations of elements were compiled using the same methodology (IDW Multifractal) used for the compilation of interpolated maps.

The file is considered to be formed by the concentrations of 27 inorganic chemicals measured in the soils of 967 sites together with the information on the coordinates, geology and surface phenomena. This study has allowed identifying five macro arising from the associations of geo-lithological conditions and distribution of the elements:

1. Association F1: La - Th - Ti - Al - Be - Fe - Tl - U - Ba - V - As - (- Ca) regarding soils originated from volcanic activity. (Fig.);
2. Association F2: K - Sr - B- Cu - V - P - Tl - Ba - Co, regarding volcanic activity and the associated volcanic rock. F2 (Fig.)

3. Association F3: Ni- Co - Cr - Fe -Mn -V, reflect surface enrichment phenomena in alluvial environment, with low drainage and presence of organic matter and clay minerals. F3 (Fig.)
4. Association F4: Sn - Zn - Pb - Sb - Cd, related to anthropogenic activity from vehicular traffic and industrial or commercial activities. (Fig.)
5. Association F5: S -As. The higher values of this association on Campi Flegrei are related to volcanic activity, while higher values near Villa Literno, Giugliano in Campania , Acerra and Caivano municipalities depend on the presence of fertilizers generated by agricultural activities. (Fig)

2.3 Map of CSC intervention limit

Maps of 15 exceedances elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) have been obtained by substituting the values of concentration contamination threshold established by Legislative Decree 152/06, for each of the destination-specific use, our ranges of dot maps previously determined in a statistical analysis (*Table 2*). Like this, it was possible to determine, for each sampled site, which are the points that exceed or are lower than these thresholds (residential / public parks, commercial / industrial) for each of the elements considered.

3. Results and discussions

In this paragraph, the most important results of atlas are mentioned: Geochemical Distribution of Inorganic Chemicals within the soils of the Domizio Flegreo Littoral and Agro Aversano area, in press, I executed most of the sampling and execution of the geochemical-maps during my PhD programme.

In detail, the distribution of concentration (dot, interpolated, background-baseline and CSC map) about the most critical PTE elements of this area: Sb, As, Cu, Hg, Pb, Zn, are described below.

3.1 Potentially toxic metals (PTEs)

3.1.1 Antimony (Sb)

Antimony (Sb, atomic number 51) is a rare metalloid; it is the 58th most abundant element in the Earth'a upper continental crust (UCC) with an estimated abundance of 0.75 mg/kg (Hu & Gao 2008). Compared to the UCC total Sb average, the value for aqua regia extractable Sb is low in the European agricultural soil samples (ratio median Ap/UCC = 0.312); the low Sb median in Ap soil compared to the total UCC value most likely indicates a low availability of Sb in an aqua regia extraction. Antimony occurs in oxidation states -3, 0, +3 and +5, with the two latter ones being dominant. It has two naturally occurring stable isotopes (^{121}Sb and ^{123}Sb with an abundance at 57.21 % and 42.79 % of its total mass, respectively). Typical, but rare Sb minerals are euther sulphides (e.g., stibnite, Sb_2S_3) or oxides (e.g., valentinite, Sb_2O_3) or mixtures thereof (e.g., kermesite, $_2Sb2S_3\cdot Sb_2O_3$); sporadically Sb can also occur in its native form. Of greater importance, for its overall occurrence in nature, is that trace amounts can be incorporated in common sulphides, such as galena, sphalerite and pyrite or in minerals like ilmenite and olivine. In exploration geochemistry, Sb is used as 'pathfinder' (together with As and Bi) for epithermal and mesothermal ore (especially gold) deposits. It is generally enriched in hydrothermal alteration zones. Most common rock types contain low concentrations of Sb, i.e., from 0.05 mg/kg (sandstone) to 1 mg/kg (shale, shist) with little variation observed between the different igneous rocks (0.1 - 0.3 mg/kg). Coal can show relatively high concentrations of Sb (average 2 mg/kg). The mobility of Sb in soil and sediments is limited due to its tendency to sorb strongly to secondary iron oxyhydroxides, as well as to clay and organic matter.

Antimony can be co-mitted by metal smelters and coal combustion. Most antimony is used to produce Sb2O3, which is in turn used as flame retardant in textile, plastic and rubber products. Some Sb is used as a catalyst in the production of PET or in the production of pigments, paints, glass and ceramics. Antimony is also used for the production of brake pads and friction linings. Car traffic is thus a possible source of Sb in the urban environment. Antimony is considered non-essential. Usually Sb is not harmful to the environment or humans. Only exposure to excessive Sb (III) dust concentrations via inhalation might be hazardous to human health: irritation to eyes, skin and lungs. If the exposure is long, can cause more serious effects such as: diarrhoea, severe vomiting and stomach ulcers, lung diseases and heart problems.

Sb content in the Domizio Flegreo Littoral and Agro Aversano area ranges from 0.22 mg/kg to 43 mg / kg, with a median value of 0.67 mg / kg. In surface soils, values higher than those of the European soils are found (they range from 0.02 to 31.1 mg / kg, with a median value of 0.60 mg / kg) (De Vos et al., 2006). Comparing these regional values with the values of the Italian soils (including an interval from 0.13 mg / kg to 4.26 mg / kg and median of 0.71 mg / kg), it is clear that the maximum concentration for those is lower than the Campania region values, while the median values are comparable to them (De Vivo et al., 2008a). These data are shown in Fig.18, where values > 98% of the sampled sites (3,7 mg/kg) are collected close to Giugliano, Qualiano, Villaricca municipalities where the highest values of Sb are found (42,8 mg/kg). Interpolated map clearly shows (Fig.11), as the dot map that in general, most of this area is characterized by low concentrations of Sb <3 mg / kg, with the areas with relatively higher concentrations (Sb> 10 mg / kg) which are not very extended. Map of baseline/background (Fig.12) shows that generally the Domizio Flegreo presents values higher than the bottom of the Agro Aversano probably due to urbanization involved in this area. In the Agro Aversano the higher background values (0.9 -1.6 mg / kg) are close to urbanized centres (Marigliano, Acerra, Nola, Pomigliano d'Arco).

In the map of CSC (Fig.13) it can be observed that no samples exceed the (CSC) of residential use (RAL) equal to 10 mg / kg, as established by Legislative Decree 152/06, while the samples exceeding CSC commercial / industrial (IAL) (30 mg / kg) are only two. These values are limited to the Quarto and Giugliano municipalities.

3.1.2 Arsenic (As)

Arsenic (As, atomic number 33) is a trace element, and the 40th most abundant element in the Earth's upper continental crust with an abundance of 5.7 mg/kg (Hu and Gao, 2008). Compared to the estimated upper continental crust As average (aqua regia extractable As) is higher in the European agricultural soil samples (ratio median Ap/UCC = 1.23), most likely an indication that this element will be enriched in soil during weathering (Reimann et al., 2014). It is often named among the so-called 'heavy metals' in the environmental literature, although it has predominantly a non-metallic character. It appears in oxidation states -3, +3 and +5, and has only one naturally occurring isotope (75As). Arsenic has a strongly chalcophile character (having an affinity to sulphur), and its occurrence in the natural environment is most often associated with its own sulphur mineral arsenopyrite (FeAsS), and with other sulphides and sulphoarsenides. In silicates, As3+ can, to a certain extent, substitute for Fe^{3+} and Al^{3+}, and thus trace amounts of As can occur in common silicates, like feldspar. More interesting, in relation to agricultural soil, is probably the ability of

As5+ to replace P5+ in phosphate minerals, such as apatite, which are often, used as mineral fertilisers. In exploration geochemistry, As is used as a ’pathfinder’ for epithermal and mesothermal ore (especially gold) deposits. It is generally enriched in hydrothermal alteration zones.

Most common rock types contain low concentrations of As – between 0.5 mg/kg (sandstone -though phosphatic sandstone can contain much more As) and 3 mg/kg (granite, granodiorite). A notable exception are shale and schist with an order of magnitude higher average As concentration (13 mg/kg) and coal (10 mg/kg). Coal that is strongly enriched in As (several hundred mg/kg) is known, and burning of such coal has caused severe environmental and health problems. While the solubility of many As minerals is high, the mobility of As in soil and sediments is limited, due to its tendency to sorb strongly to secondary iron oxy-hydroxides, as well as to clay and organic matter. Oxidation/reduction reactions strongly govern the mobility of As in soil.

Arsenic has been used in the manufacture of alloys since the Bronze Age. More importantly, when studying agricultural soil, is the widespread use of As in many herbicides, insecticides and fungicides. Because it promotes growth in some animals it has also been used as food supplement in pig and poultry farm-ing, and sewage coming from such farms can be expected to show high As con-centrations. If such material is spread on agricultural land as fertiliser or organic soil improver, then high levels of As can be transferred to soil. In terms of emis-sions to the atmosphere, the most important sources today are probably Cu, Pb and Zn smelting, coal combustion, and herbicide use (Matschullat and Des-champs, 2011). Humans take-up As via water and food. Luckily, with the excep-tion of some kinds of seafood, plants usually avoid the uptake of As from soil, and there are only a few plants that accumulate As (e.g., radish, rice).

Thus, As does not enter the food chain easily. High As concentrations in ground water, usually related to specific geological settings, pose the greatest risk to humans. Such settings are known in several parts of Europe.

Arsenic in the form of Arsenic trioxide (As_2O_3) is one of the best known and most used poisons in human history (’the king of poisons’). Probably even more important than the toxicity are its carcinogenic properties. Arsenic is the first chemical for which carcinogenic properties were understood, as early as 1879, when high rates of lung cancer in miners were attributed in part to inhaled As dust (Neubauer, 1947; Smith et al., 2002).

As the content in soils ranges from a minimum value of 2,6 mg / kg to a maximum value of 103 mg/kg, the median value is 13,6 mg / kg. Dot map shows that only 75% of the sites have concentrations of As < 16 mg / kg; Other higher values (> 16 mg/kg) are found as well between Sessa Aurunca and Carinola, where the concentrations are higher (33-103 mg/kg) (Fig.14).

Interpolated map shows that the areas with low-concentrations of As (<17 mg / kg) are located within the whole territory. Concentrations of > 25 mg / kg are found close to volcanic systems of the Phlegraen Fields (Pozzuoli and Bacoli) and in correspondence to the northern part of the Domizio Littoral.

Background/baseline map confirms that the region shows values > 14 mg /kg.

CSC map (Fig.17) shows that 5 % of the values exceed the threshold (CSC) residential use (20 mg / kg) as established by the Legislative Decree 152/06, while 0.7% are higher than IAL (Industrial and commercial use) thresholds (50 mg / kg).

3.1.3 Copper (Cu)

Copper (Cu, atomic number 29) is a transition metal; it is the 30th most abundant element in the Earth's upper continental crust (UCC), with an estimated abundance of 2 mg/kg (Hu and Gao, 2008). Compared to the UCC total Cu average, total Cu, measured by XRF is low in the European agricultural soil samples is low in the European agricultural soil samples (ration median Ap/UCC = 0.48). This may indicate that the UCC concentration is seriously overestimated, because it appears unlikely that about 50 % of Cu is lost during weathering and soil formation. Copper occurs in oxidation states + 2 (dominant), +1 and 0, and has two naturally occurring isotopes, 63Cu and 65Cu, the former being the most abundant at 69.17% of its mass. It can occur as metallic Cu in nature and forms a variety of its own Cu minerals (e.g., chalcopyrite, bornite, chalcocite, malachite, covellite, digenite and tetrahedrite); more important for its overall occurrence in nature s its incorporation into common minerals, such as olivine, magnetite, pyroxene, amphibole and mica (biotite). In geochemical exploration, it is used to indicate all types of Cu mineralization, and is an important pathfinder for many types of Au deposits. Copper is en-riched in mafic rocks (80-90 mgkg), while intermediate rocks (20 mg/kg) and granite (12 mg/kg) contain less Cu. In unmineralised sediments, Cu concentrations are often low (5-20 mg/kg) and depend on the content of mafic detritus, clay minerals and organic matter. Black shale, for example, is typically enriched in Cu (50 mg/kg). The mobility of Cu, once released by weathering, depends on pH and redox conditions. Under acidic and oxidizing conditions, its mobility is highest. Copper can be co-precipitated with Fe-hydroxides and has a strong affinity for organic matter. Typical anthropogenic sources of Cu transfer to the environment include emissions from metal smelters (especially Cu, Ni) and mining; copper has been mined for more than 5000 years. Furthermore, Cu is used in roofing, pipework, plumbing, countless electrical applications and in car brake pads and, consequently, it is often enriched in the urban environment (Johnson et al., 2011). In the context of agricultural soil, it is important to note that Cu compounds are widely used in agriculture (e.g., fungicides, herbicides). Manure spread on agricultural land often contains high levels of Cu. Copper is essential for human, animal and plant health. Excess Mo in soil can lead to Cu deficiencies. Copper deficiencies for plant occur at concentrations of less than 5 mg/kg in soil (note that about 10% of the European agricultural soil samples show lower concentrations – deficiency may thus be a substantially more important problem than toxicity for this element). While humans and pigs tolerate rather high levels of Cu, cows and sheep are very vulnerable to Cu poisoning. At high doses, Cu is toxic to most living organisms.

Cu concentrations in soils range from 4,6 to 1206 mg / kg, the median value is 58 mg/kg. Dot map shows that the highest concentrations > 120 mg/kg, are assembled in the Agro-Aversano area, while the values on the Domizio Flegreo Littoral are <120 mg/kg. Interpolated map shows that some areas with high concentrations of Cu are located in correspondence of the Nola, Saviano Cicciano and Cimitile municipalities with values > 261 mg/kg. The remaining part of this area shows values < 85mg/kg. Background/baseline (Fig.20) confirms that concentration values are < 85 mg / kg. Higher concentrations (86-193 mg/kg) are found in the Phlegrean and Vesuvian municipalities.

It is quite clear that the soils that have been originated on volcanic lithologies naturally present levels, while there is an anthropogenic contribution (especially in agricultural areas of Nola) associated to agricultural practices.

The 25 % of the analysed samples exceed concentration contamination thresholds (CSC) established by the Legislative Decree 152/06 for residential use soils and industrial use (0,3 % of the analysed samples).

3.1.4 Mercury (Hg)

Mercury (Hg, atomic number 80) is a rare transition metal. It is the 69th most abundant element in the Earth's upper continental crust (UCC). Compared to the latter estimated UCC mercury average, aqua regia extractable Hg is lower in the European agricultural soil samples (ratio median Ap/UCC = 0.6); this may suggest an overestimation of the most recent UCC average. Mercury occurs in oxidation states 0, +1, +2 (dominant) and +3, and has seven naturally occurring isotopes (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{204}Hg of which the most abundant are ^{202}Hg, ^{200}Hg, ^{199}Hg and ^{201}Hg at 29.86%, 23.1%, 16.87% and 13.18% of its total mass, respectively). The principal Hg mineral is cinnabar (HgS); Hg can also occur in the form of little droplets of na-tive Hg, and as a trace constituent in some sulphides, such as tetrahedrite ($Cu_{12}Sb4S_{13}$) and sphalerite (ZnS). It is usually not taken up into most of the rock-forming minerals, but amphibole, aegirine and sphene can contain traces of Hg.

Most common rock types contain very low concentrations of Hg – between 0.004 (ultramafic rocks) and 0.2 mg/kg (shale, schist). Black shale can show especially high Hg levels (up to several mg/kg), and highly variable Hg concentrations are reported in coal (again up to the mg/kg range). The mobility of Hg in soil is highly dependent on its form and, in general, it has a strong tendency to bind to organic material. Mercury is a good pathfinder element for many ore deposits, and high Hg levels often indicate fault zones. It occurs frequently in connection with volcanic activity.

Humanity has used Hg for more than 3000 years. The main sources of Hg transfer to the environment are considered to be coal burning, waste incineration, crematoria, chlor-alkali factories, paper factories and metal smelters. Elevated Hg concentrations have also been reported in sewage sludge. Mercury was widely used in many applications (e.g., thermometers, barometers, diffusion pumps, mercury-vapour lamps, detonators, and in pesticides, fungicides, dentistry, antifouling agents, gold mining and processing, the chemical industry and in batteries). In agriculture, it has been used for fungicidal seed treatment. Due to its high toxicity it has been banned in many countries and replacements have been developed for most of its applications. At present, however, it has been re-introduced into the common household via energy saving light bulbs (EU regulations). It is one of the elements that is typically enriched in urban soil (Albanese et al., 2011; Johnson et al., 2011; Ottesen et al., 2011). Mercury is non-essential and highly toxic to most forms of life and, due to its ability to methylate, it has a strong tendency to build-up in the food chain.

Hg concentrations in soils range from 3 to 6775 µg/kg, the median value is 62 µg / kg. Dot map shows that the highest concentrations are <102 mg / kg. Interpolated map (Fig.23) shows that some areas with high concentrations of Hg (Hg > 396 /kg) are located in correspondence of Acerra and Caivano municipalities. The Domizio Flegreo Littoral shows lower concentrations (Hg< 63 µg/kg). The remaining part of this area shows values < 85 mg/kg. Background/baseline (Fig.24) confirms that concentration values are < 161 µg/kg. Higher concentrations (Hg > 394 µg/kg) are found between the Acerra and Ssversa municipalities, regarding anthropogenic activities

CSC map (Fig.25) shows that two samples exceed the threshold (CSC) residential use (1000 µg/kg) as established by the Legislative Decree 152/06, while one value is higher than IAL (Industrial and commercial use) threshold (5000 µg/kg).

3.1.5 Lead (Pb)

Lead (Pb, atomic number 82) is a trace element with a metallic character and one of the seven metals known to humanity since antiquity, because of its ease of extraction and workability as a metal. It is the 34th most abundant element in the Earth's upper continental crust (UCC) with an estimated abundance of 17 mg/kg (Rudnick and Gao, 2003), but note that estimates vary from 14 to 20 mg/kg depending on source). Compared to the estimated UCC lead average, to-tal Pb, measured by XRF, is slightly higher in the European agricultural soil samples (ratio median Ap/UCC = 1.20). This indicates that the old '20 mg/kg' estimate for the UCC is probably more realistic than the newer 17 mg/kg. Lead occurs in oxidation states +2 and +4, and has four naturally occurring stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, of which ^{208}Pb at 52.4% of its total mass is the most dominant). The main Pb mineral is galena (PbS); anglesite (PbSO4), ceussite (PbCO3)) and minium (Pb3O4) are further examples of lead minerals, demonstrating its ability to occur as sulphide, sulphate, carbonate and oxide. Lead is present as an accessory element in many common minerals, especially

K-feldspar (which can contain up to the % level Pb), but also feldspar in general, mica, zircon and magnetite.

Lead typically exhibits elevated concentrations in felsic rocks (e.g., granite – 20 mg/kg), and fine-grained sedimentary rocks (shale – 22 mg/kg) and coal (20 mg/kg). Limestone contains on average about 5 mg/kg Pb, but note that some of the largest Pb deposits of the world are hosted by limestone. Ultramafic and mafic rocks (0.05-1 mg/kg) are characterised by especially low Pb concentrations. The mobility of Pb in the secondary environment is generally low, be-cause it is restricted by sorption to clay, organic matter, secondary Fe and Mn oxyhydroxides and the formation of secondary minerals with low solubility, e.g., Pb-phosphate, carbonate or -sulphate. Lead is one of the elements where Goldschmidt (1937) had already recognised a tendency to be naturally enriched in organic-rich surface soil without any human interference.

Lead has been mined by humanity for over 5500 years and the cumulative historical Pb production is estimated to have reached 300,000,000 tonnes (Reimann et al., 2012). Lead has been widely used for the manufacture of water pipes, as a pigment, in glass production and pottery glazes. Presently, the majority of the lead produced ends up in batteries. Lead mining and smelting, coal combustion and traffic, prior to the ban on leaded petrol, are major sources of Pb emissions to the atmosphere. Lead has also been used as a pigment in white paint and anthropogenic accumulations of Pb are quite commonly observed in urban soil (Johnson et al., 2011).Lead is considered non-essential for all living organisms and it is highly toxic to humans and aquatic life.

Analysed Pb concentrations in soils (dot map) vary between 6 and 1099 mg / kg, while the median value is 58 mg / kg,

Dot map (Fig 26) shows a very high concentration in urban areas and close to roads with traffic. 25% of the sites sampled along the urban fabric, starting from the Domizio Phlegraen Littoral, have > 76 mg/kg values; Across the Agro Aversano values are found between 76 and 149 mg/kg and higher concentrations are found in correspondence of the Caserta, Acerra, Pomigliano and Marigliano municipalities. The distribution of interpolated data (Fig.27) confirms that the largest area where we can find diffuse pollution of Pb within the soils, with concentration values between 62 and 142 mg/kg, lower concentrations (Pb<62 mg/kg) are found in non-urbanized territory. Background / baseline map (Fig.24) confirmed higher values (<83 mg/kg) in most of this area, affected by human impact, lower values are found in correspondence of the inland part of the Domizio Flegreo Littoral.

As a result of the study of the CSC map (Fig.29) regarding lead, it can be observed that 11% of the analysed samples exceed the threshold (> 100 mg / kg) of residential / recreational use, while 0.2% is higher than the one of soils for industrial / commercial use (> 1000 mg / kg). The critical areas, where this value exceeds the threshold, are found in Acerra, Caivano, Pomigliano agro-aversano area and in Giugliano, Villaricca, Melito and Castelvolturno (Domizio Flegreo littoral).

Lead is a persistent element and high concentrations within the soils of urban areas, as confirmed Cicchella et al., 2005 are essentially due to the Pb used until the '90s as an additive in gasoline.

3.1.6 Zinc (Zn)

Zinc (Zn, atomic number 30) is a transition metal and the 22nd most abundant element in the Earth's upper continental crust (UCC), with an estimated abundance of 75 mg/kg (Hu and Gao, 2008). Compared to the estimated UCC zinc average, total Zn, measured by XRF, is low in the European agricultural soil samples (ratio median Ap/UCC = 0.807), which may either indicate that the estimated UCC value is somewhat too high or that Zn is somewhat depleted in the agricultural soil, which is possible because Zn is an important minor nutrient for plants. Zinc occurs in oxidation state +2, and has five naturally occur-ring stable isotopes (^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, ^{70}Zn of which the most dominant are ^{64}Zn, ^{66}Zn and ^{68}Zn with an abundance at 48.6%, 27.9% and 18.8% of its total mass, respectively). There exist many naturally occurring Zn minerals; sphalerite (ZnS), smithsonite (ZnCO3) and zincite (ZnO) are but a few examples. Zinc is present as an accessory element in many common minerals, such as pyroxene, amphibole, mica garnet, sulphides and magnetite.

Zinc typically exhibits elevated concentrations in mafic rocks (e.g., basalt – ca. 100 mg/kg) and lower values in felsic rocks (granite – ca. 50 mg/kg). Most sediment rocks contain between 20 and 100 mg/kg Zn (shale and schist with the highest values). High concentrations of Zn have been observed in oil shale, in olitic ironstone and in recently formed ferro-manganese nodules. In the secondary environment, mobile Zn ions can be sorbed to secondary Fe and Mn ox-ides and oxyhydroxides, clay minerals and organic matter.

Zinc mining, smelting and steel processing are the primary sources of Zn emissions to the atmosphere. Zinc is much used as an anti-corrosion coating (galvanisation) of steel, in alloys (brass is an alloy of Cu and Zn), in solders, pipe-work, plumbing and water components, as a pigment in paint, in rubber products, in deodorants and in the manufacture of batteries. In the context of agricultural soil, Zn is used as a fertilizer and high concentrations of Zn can be observed in some phosphate fertilisers. Furthermore, Zn compounds are also used in pig and chicken farming, and thus sewage sludge can contain high levels of the element.

Zinc is an essential element for all organisms and has a low toxicity; in general, Zn deficiency is much more widespread than Zn toxicity. However, at levels above 300 mg/kg in soil, it may lead to growth suppression in plants. Uptake of Zn by plants differs substantially from species to species; the existence of Zn accumulators and hyperaccumulators is documented.

Zn concentrations in soils vary between 28 and 1488 mg / kg, the median value is 93 mg / kg.

Dot map (Fig. 30) shows very high concentration in urban areas and close to roads with traffic. 75% sites sampled show concentrations < 119 mg/kg. Higher values are found along the urban fabric, such as lead, in correspondence of Pozzuoli, Bacoli, Quarto and Giugliano, Villa Literno and Castelvolturno. Across the Agro Aversano values can be found between 119 and 196 mg/kg and higher concentrations are found in correspondence of the municipalities of Caserta, Acerra, Pomigliano and Marigliano. The distribution of interpolated map shows concentration values < 122 mg/kg, higher concentrations (Zn> 339 mg/kg) are found in the northern part of Caserta. Background / baseline map (Fig.32) confirmed higher values (140-184mg/kg) in most of this area, affected by human impact; lower values are found in correspondence of the inland part of Domizio Flegreo Littoral.

CSC map (Fig 33) shows that 25 % of the samples exceed the threshold of CSC (150 mg/kg) of residential / recreational use, while any excess of the thresholds of industrial/ commercial use (1500 mg/kg) is not found.

Figure 4 Sampling soils in the Acerra's area.

4. APPENDIX

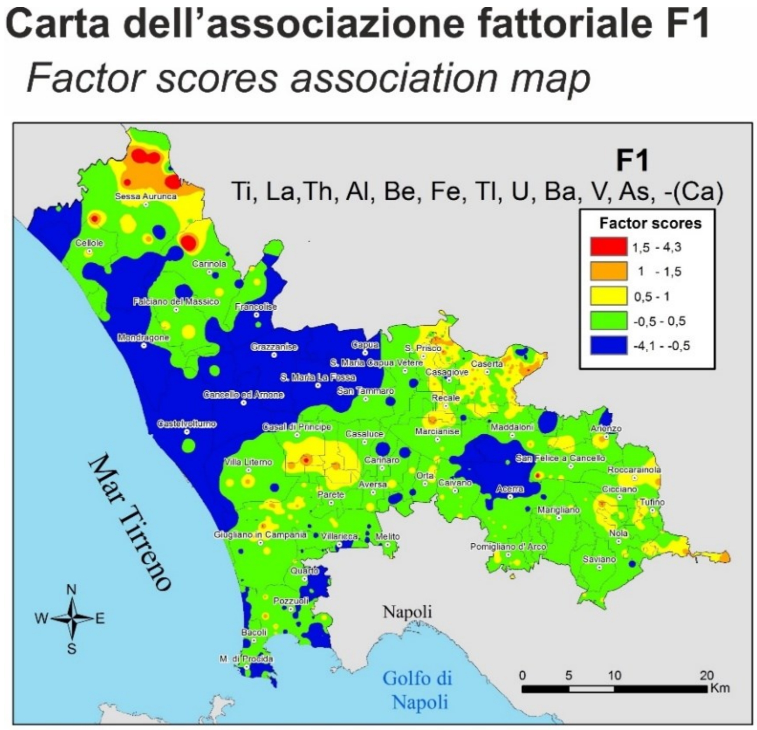


Figure 5 Factor scores association map (F1)

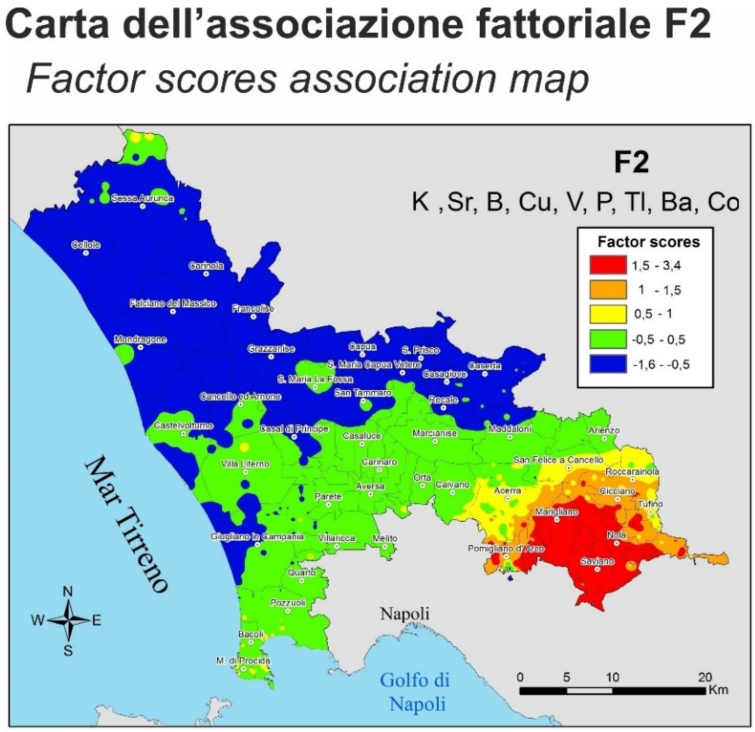


Figure 6 Factor scores association map (F2)

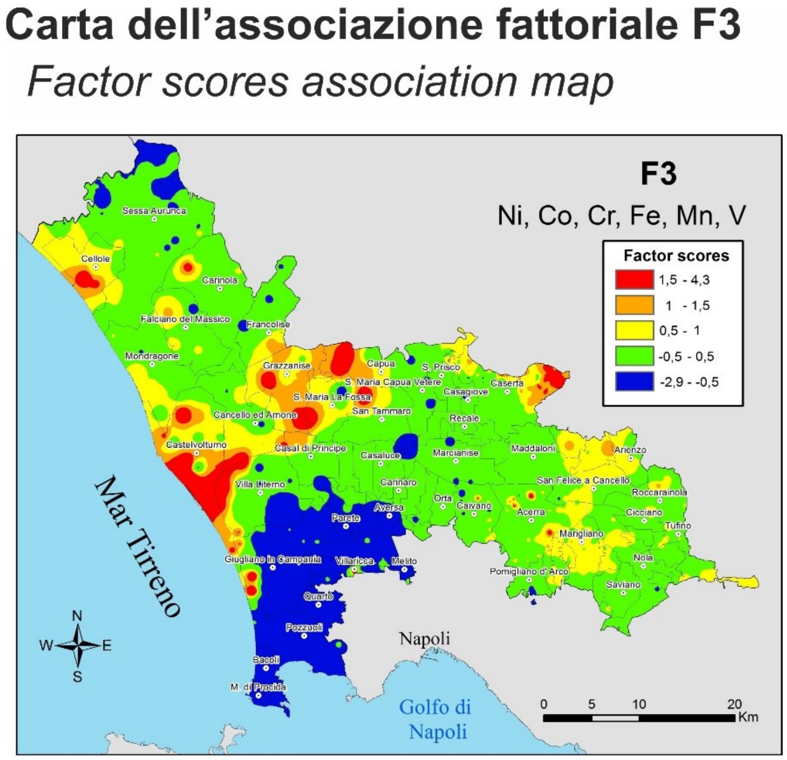


Figure 7 Factor scores association map (F3)

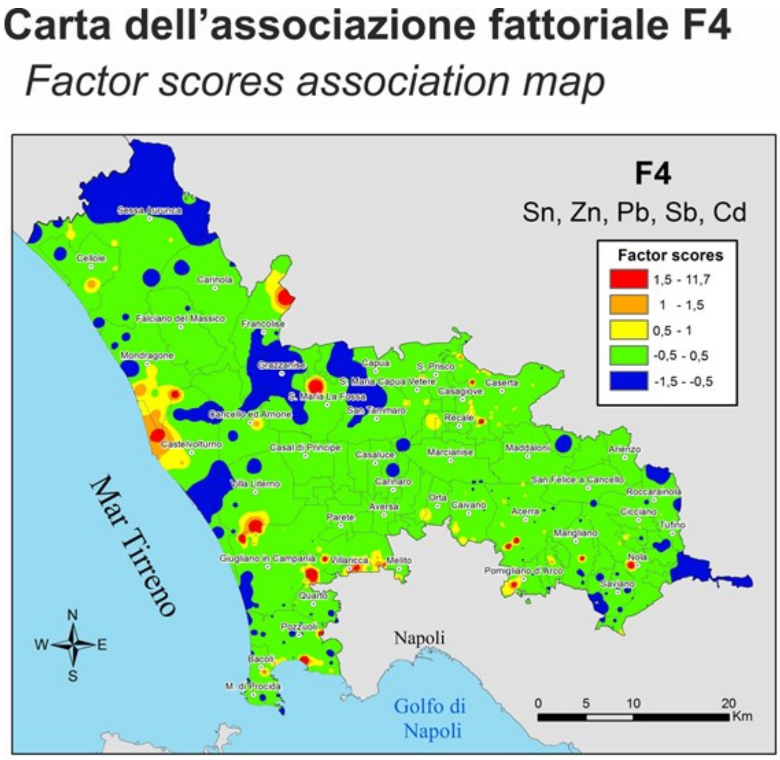


Figure 8 Factor scores association map (F4)

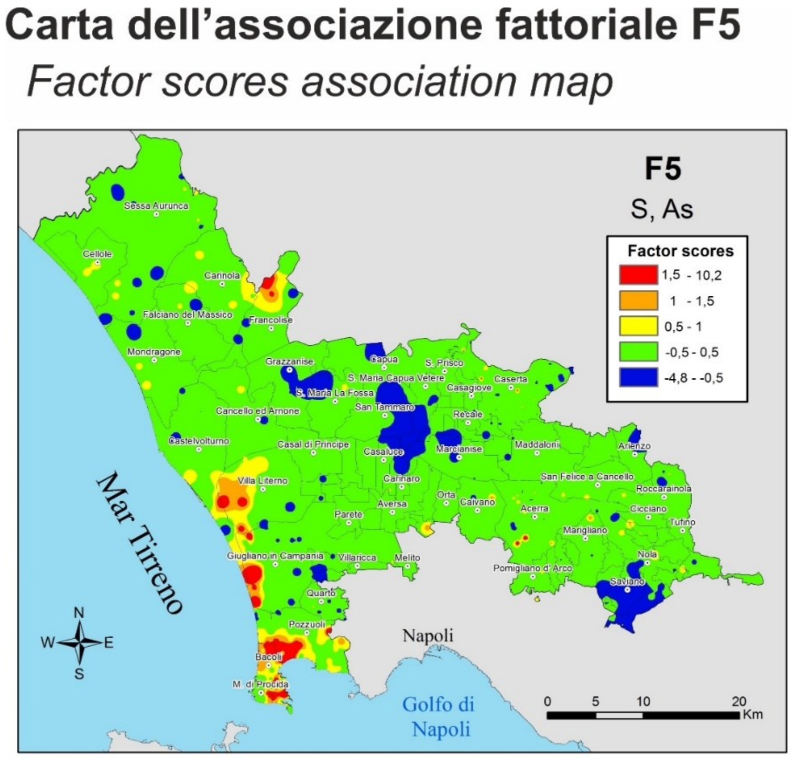
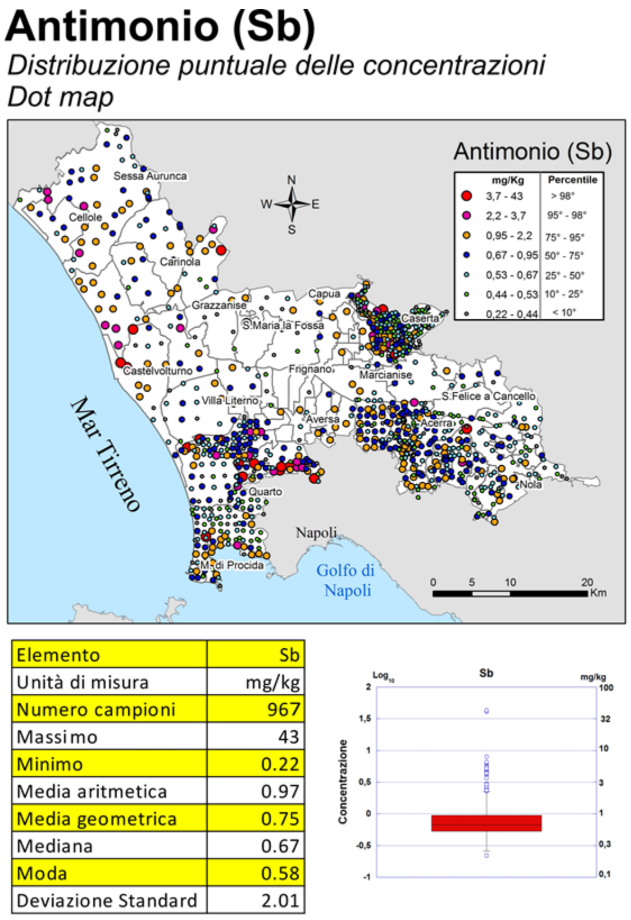


Figure 9 Factor scores association map (F5)

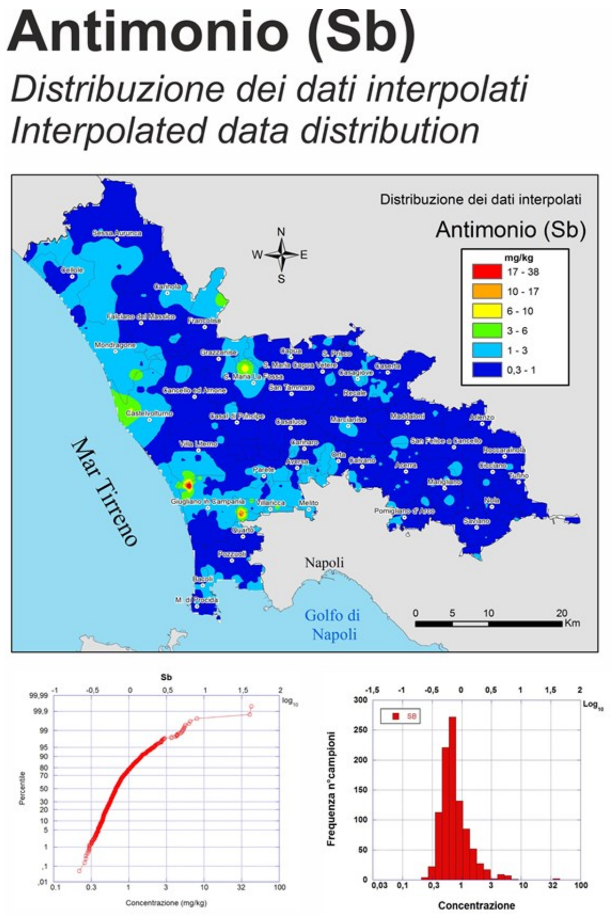


Antimonio (Sb)

Distribuzione puntuale delle concentrazioni
Dot map

Elemento	Sb
Unità di misura	mg/kg
Numero campioni	967
Massimo	43
Minimo	0.22
Media aritmetica	0.97
Media geometrica	0.75
Mediana	0.67
Moda	0.58
Deviazione Standard	2.01

Figure 10 Dot map (Antimony)



Antimonio (Sb)

Distribuzione dei dati interpolati
Interpolated data distribution

Figure 11 Interpolated map (Antimony)

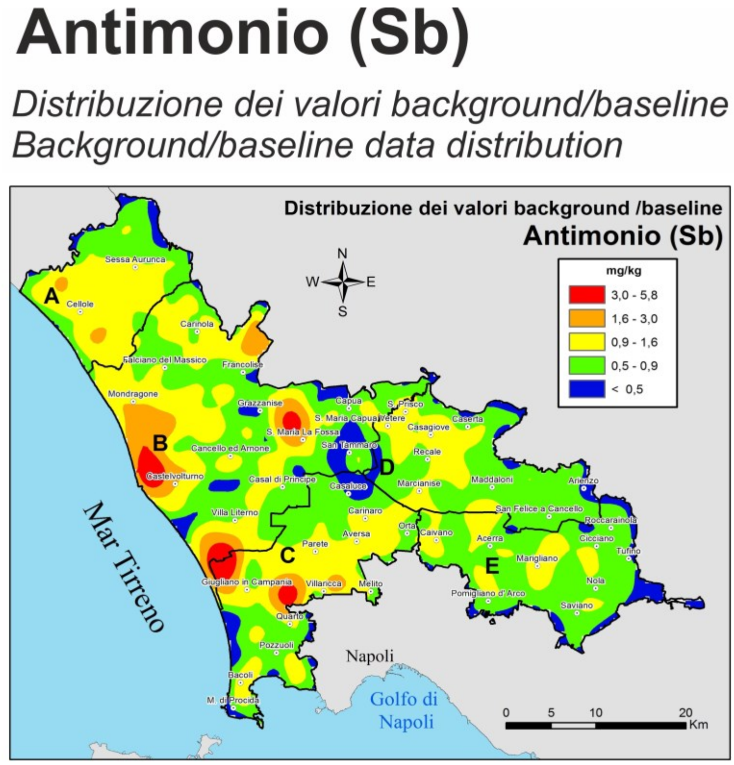


Figure 12 Background-Baseline map (Antimony

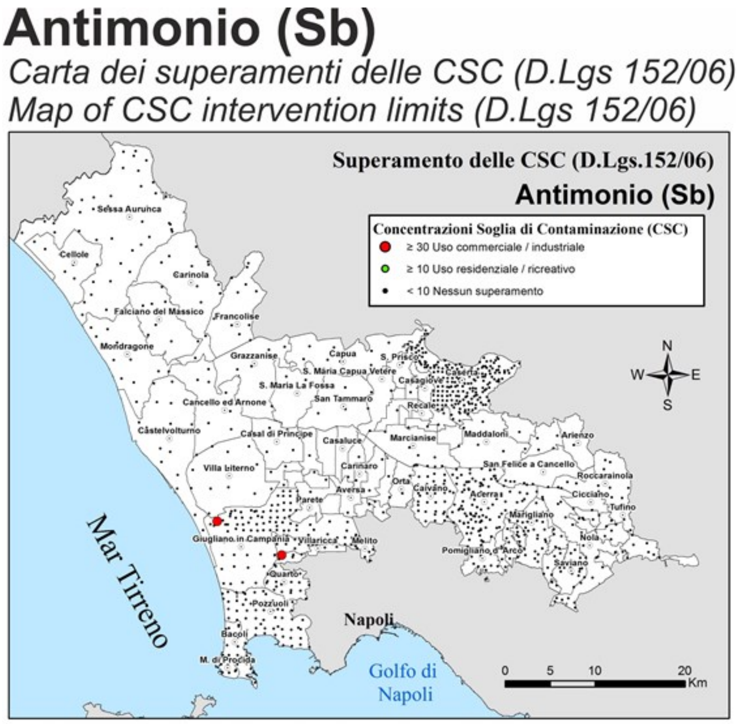
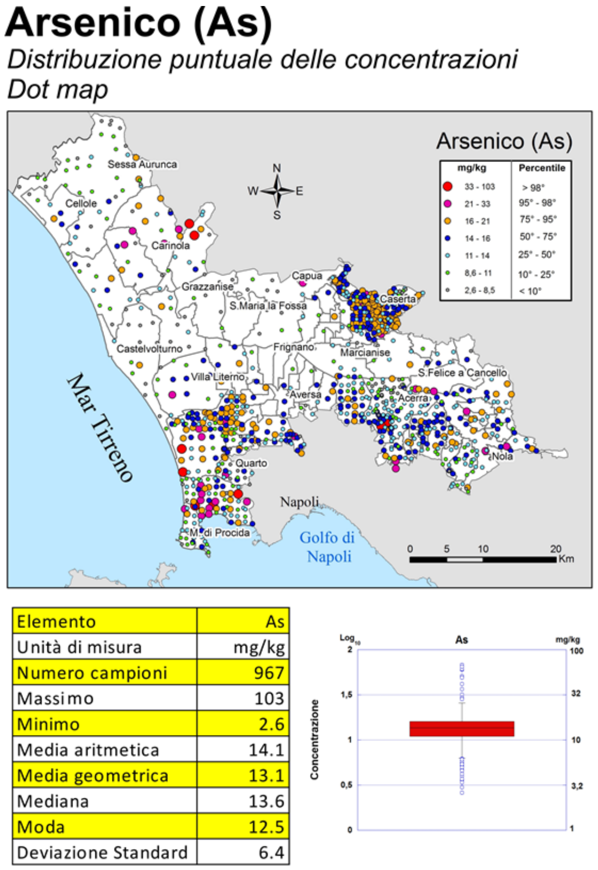


Figure 13 Background-Baseline map (Antimony)



Elemento	As
Unità di misura	mg/kg
Numero campioni	967
Massimo	103
Minimo	2.6
Media aritmetica	14.1
Media geometrica	13.1
Mediana	13.6
Moda	12.5
Deviazione Standard	6.4

Figure 14 Dot map (Arsenic)

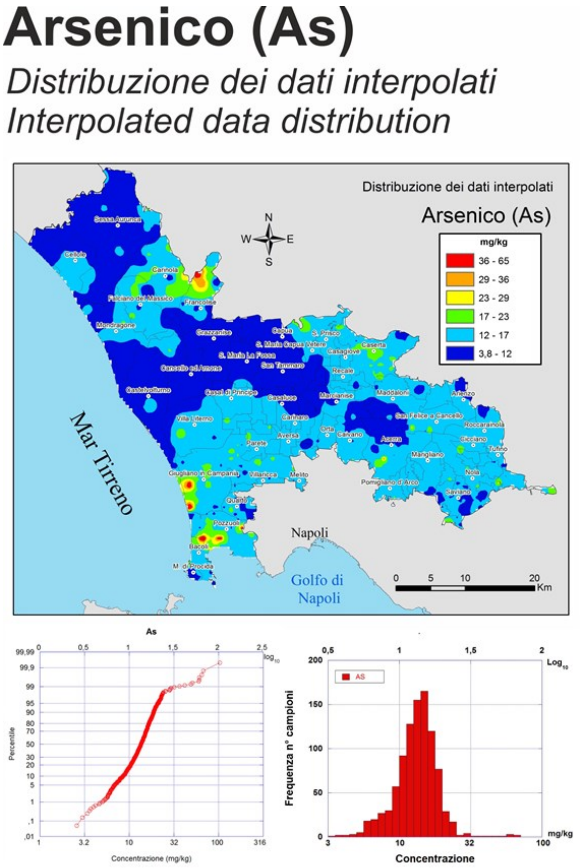


Figure 15 Interpolated map (Arsenic)

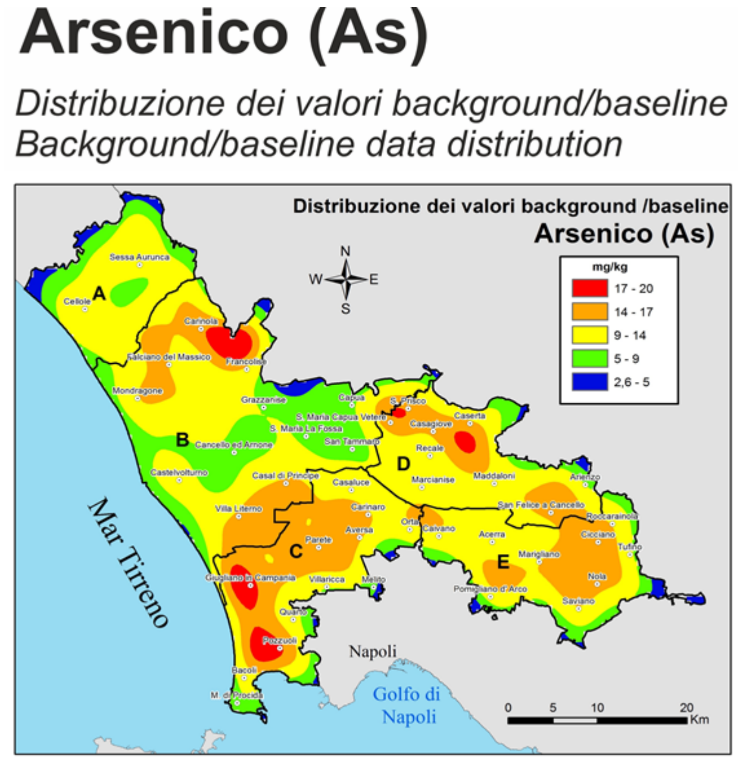


Figure 16 Background-Baseline map (Arsenic)

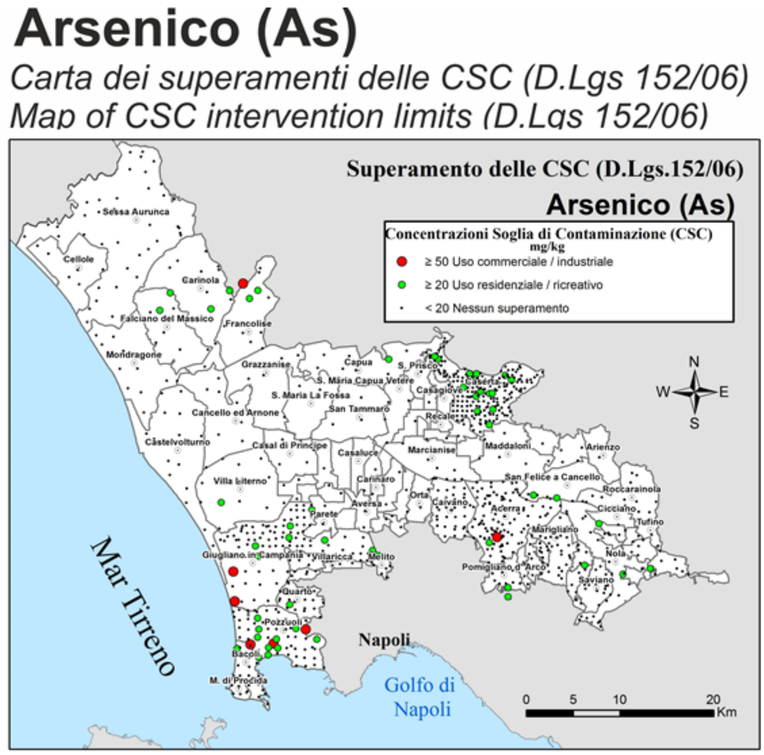
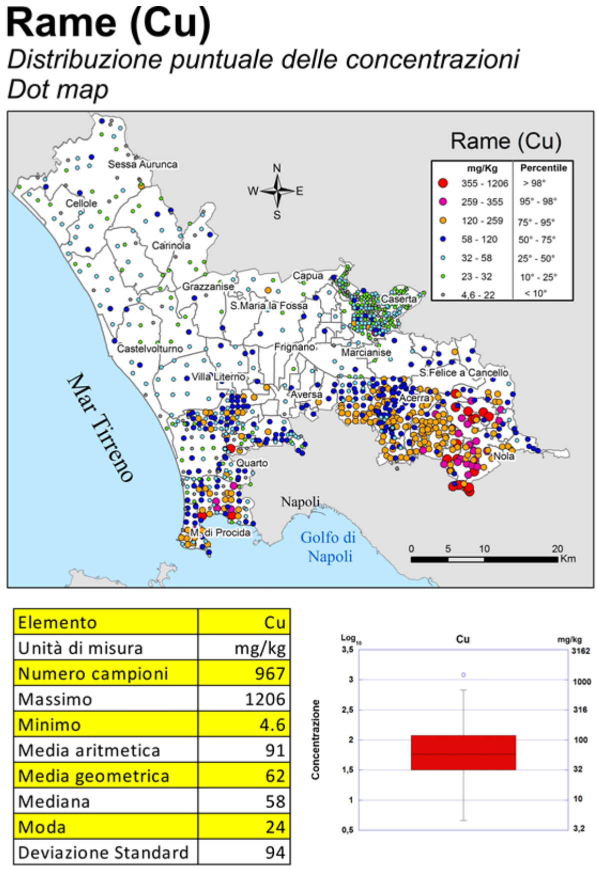


Figure 17 CSC map (Arsenic)



Elemento	Cu
Unità di misura	mg/kg
Numero campioni	967
Massimo	1206
Minimo	4.6
Media aritmetica	91
Media geometrica	62
Mediana	58
Moda	24
Deviazione Standard	94

Figure 18 Dot map (Copper)

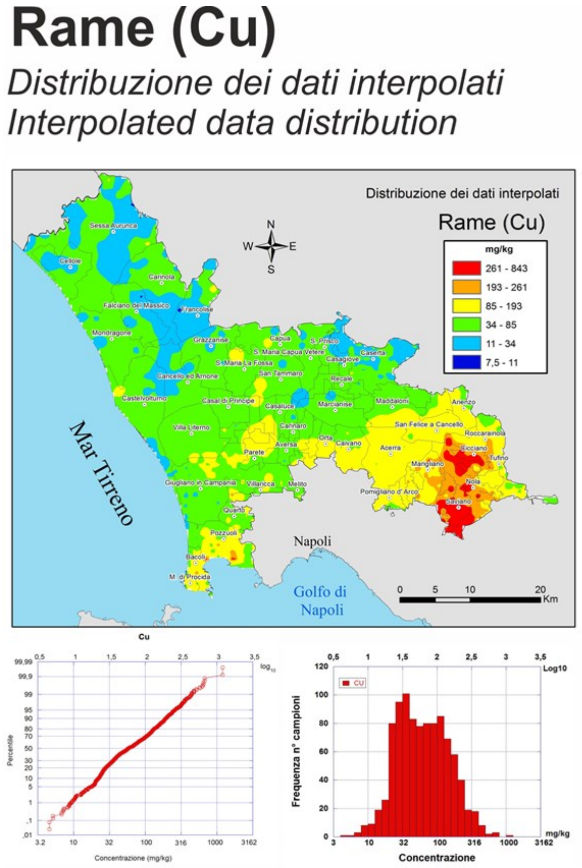


Figure 19 Interpolated map (Copper)

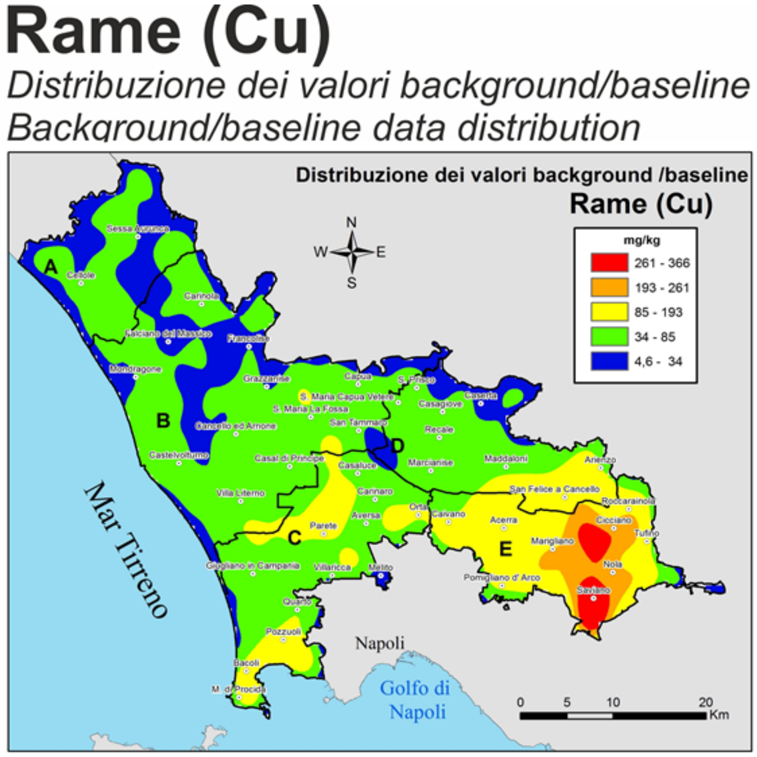


Figure 20 Background-baseline map (Cu)

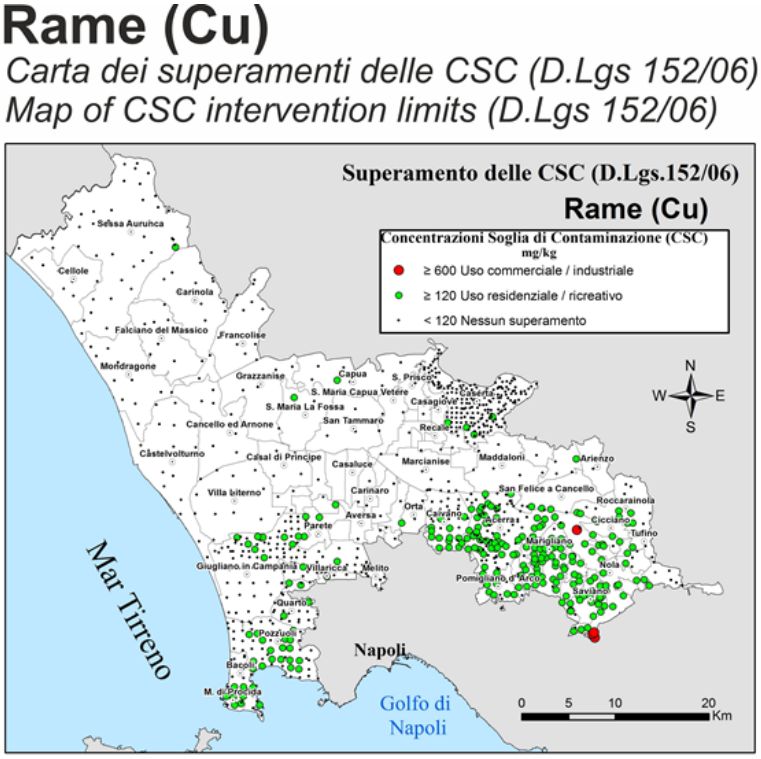
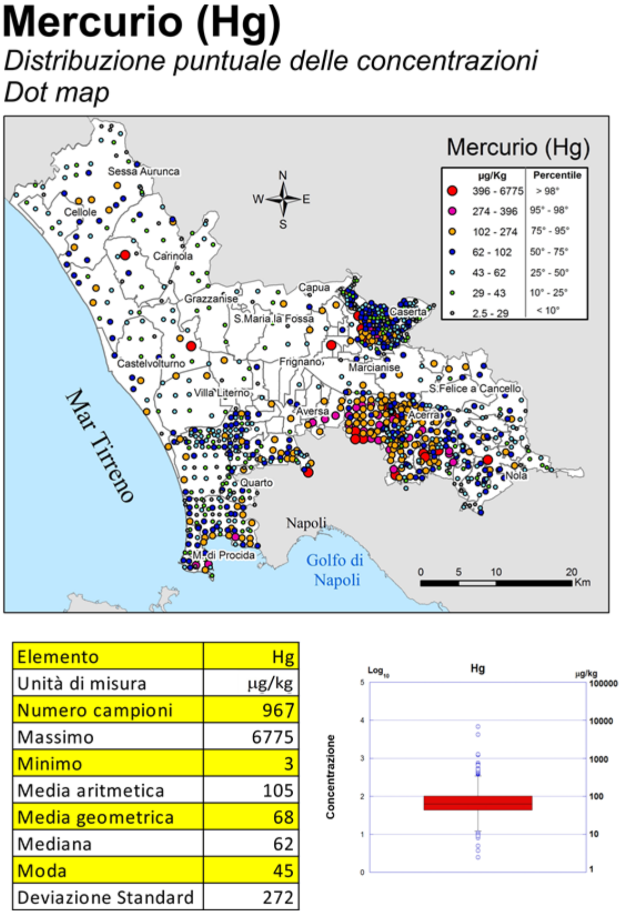


Figure 21 CSC map (Copper)



Elemento	Hg
Unità di misura	µg/kg
Numero campioni	967
Massimo	6775
Minimo	3
Media aritmetica	105
Media geometrica	68
Mediana	62
Moda	45
Deviazione Standard	272

Figure 22 Dot map (Mercury)

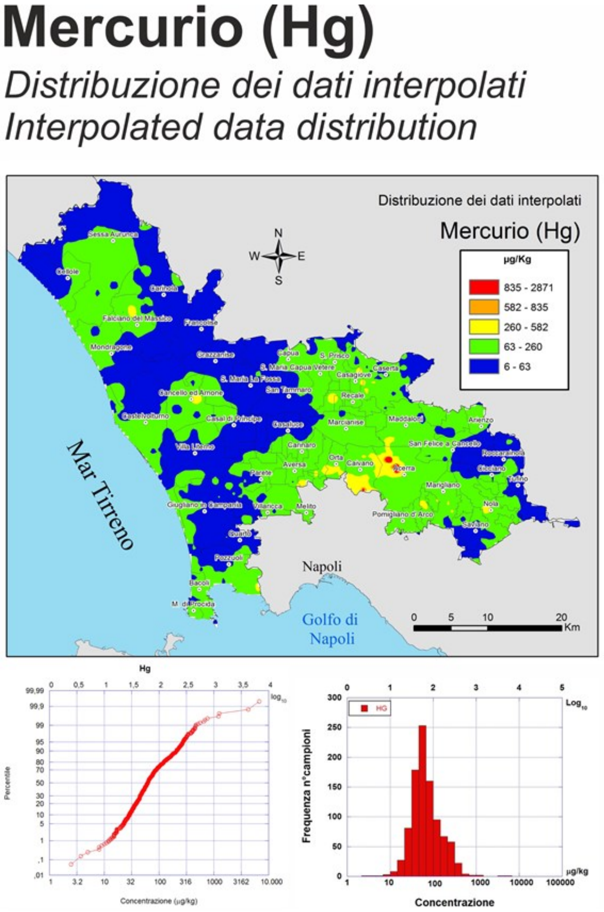


Figure 23 Interpolated map (Mercury)

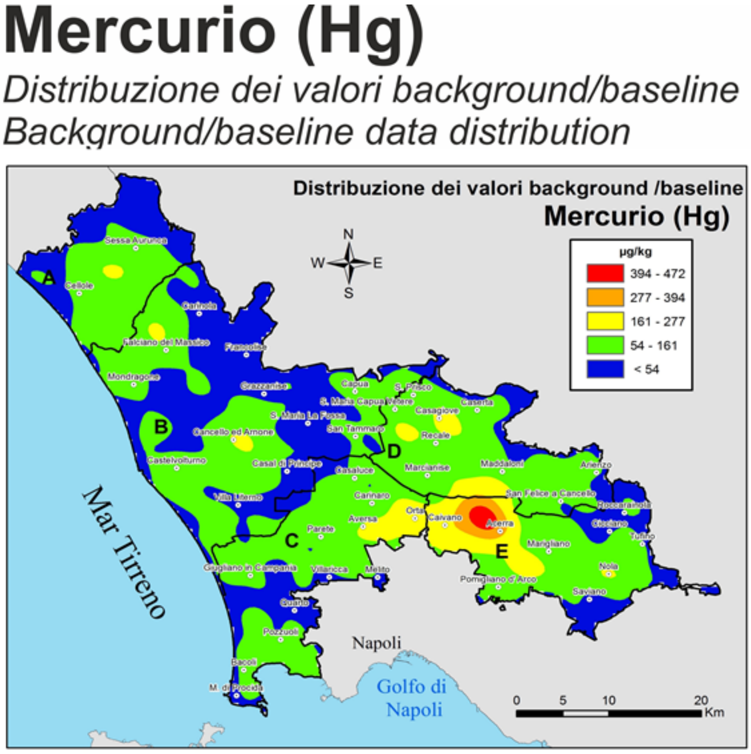


Figure 24 Background – baseline map (Mercury)

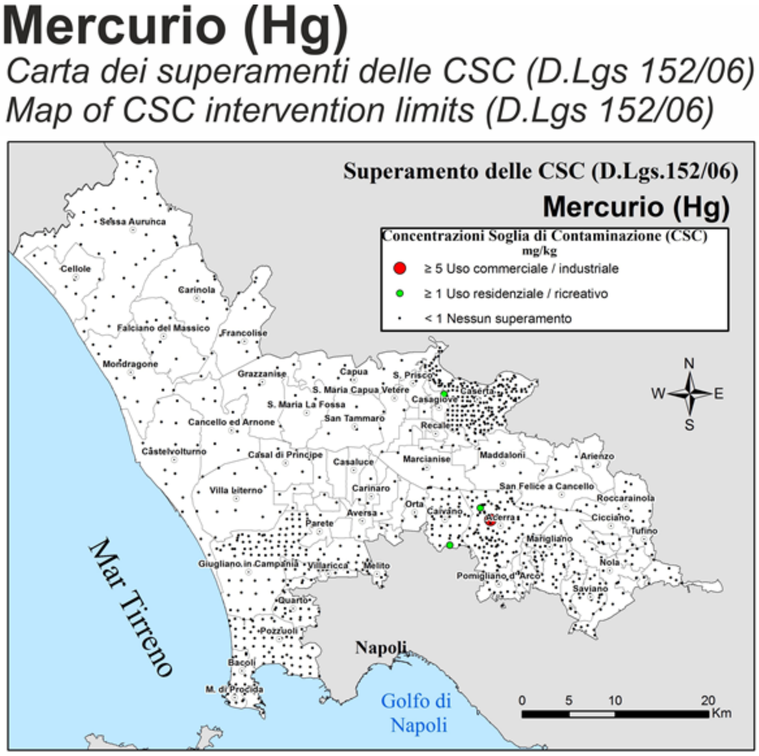
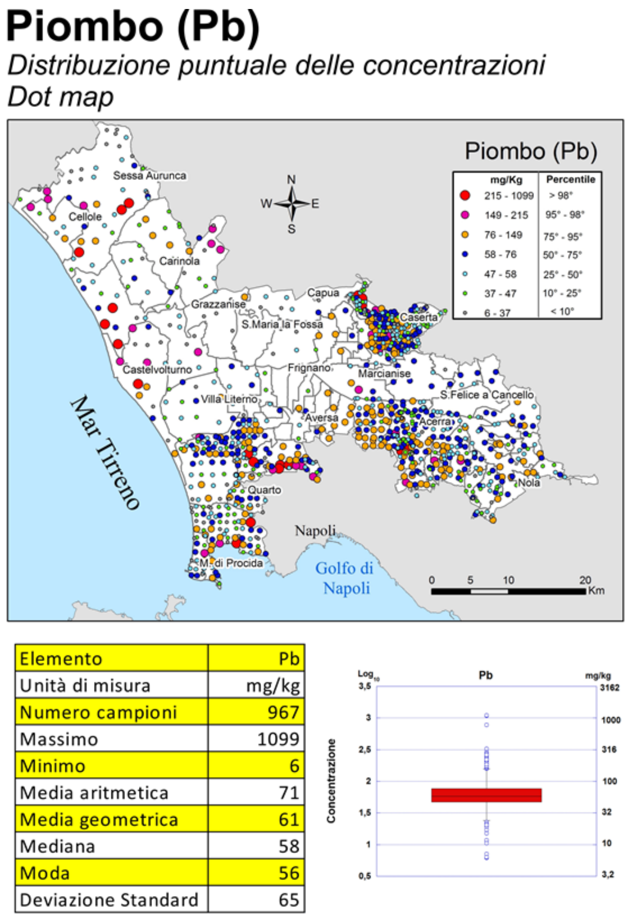


Figure 25 CSC map (Mercury)



Elemento	Pb
Unità di misura	mg/kg
Numero campioni	967
Massimo	1099
Minimo	6
Media aritmetica	71
Media geometrica	61
Mediana	58
Moda	56
Deviazione Standard	65

Figure 26 Dot map (Lead)

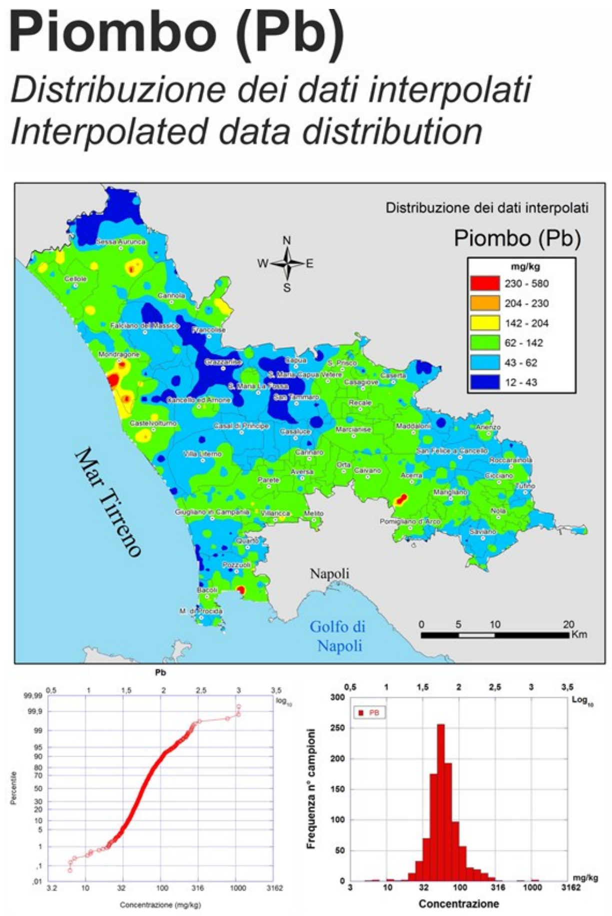


Figure 27 Interpolated map (Lead)

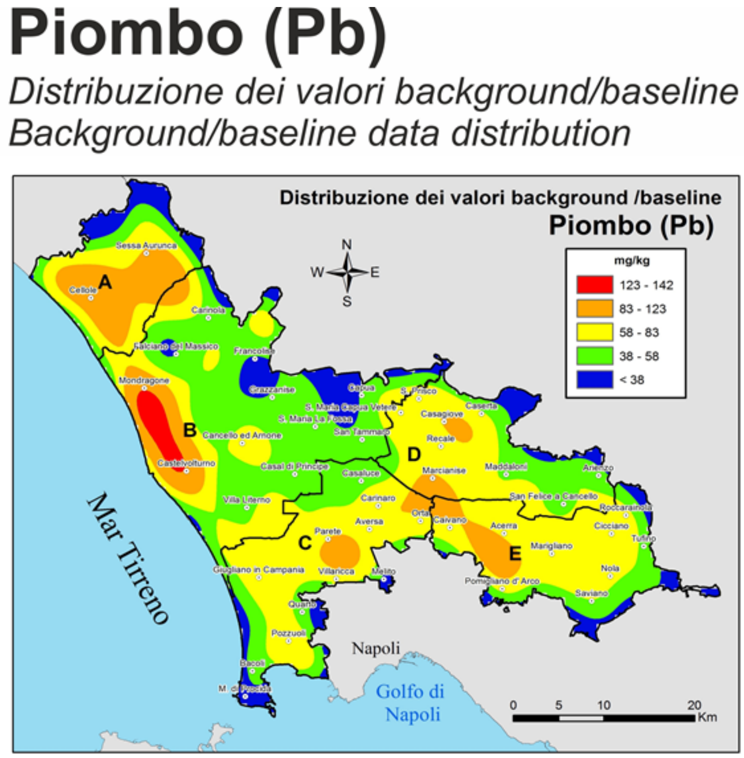


Figure 28 Background-baseline map (Lead)

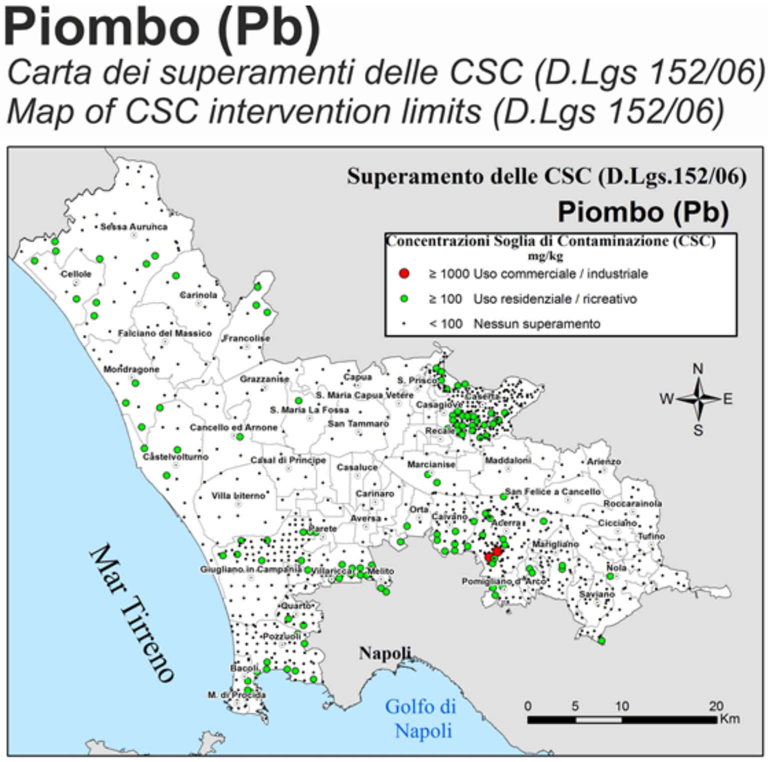
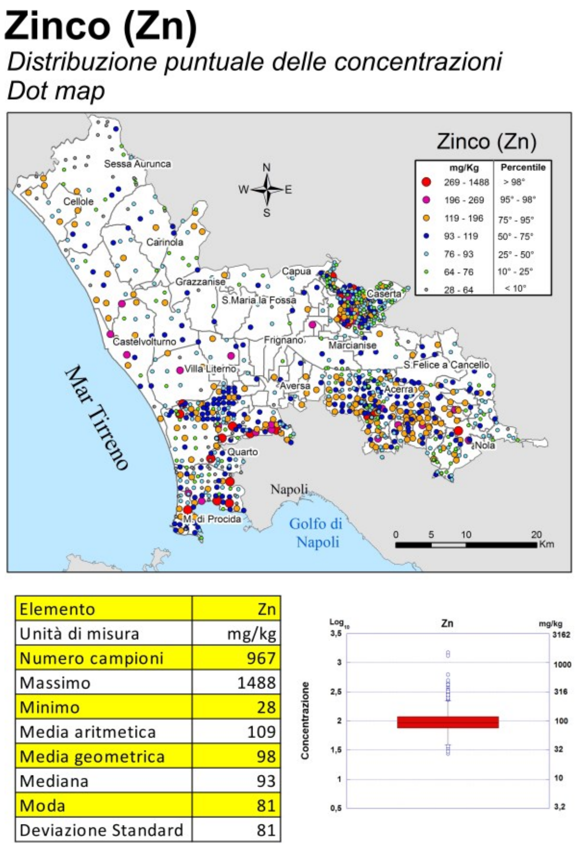


Figure 29 CSC map (Lead)



Elemento	Zn
Unità di misura	mg/kg
Numero campioni	967
Massimo	1488
Minimo	28
Media aritmetica	109
Media geometrica	98
Mediana	93
Moda	81
Deviazione Standard	81

Figure 30 Dot map (Zn)

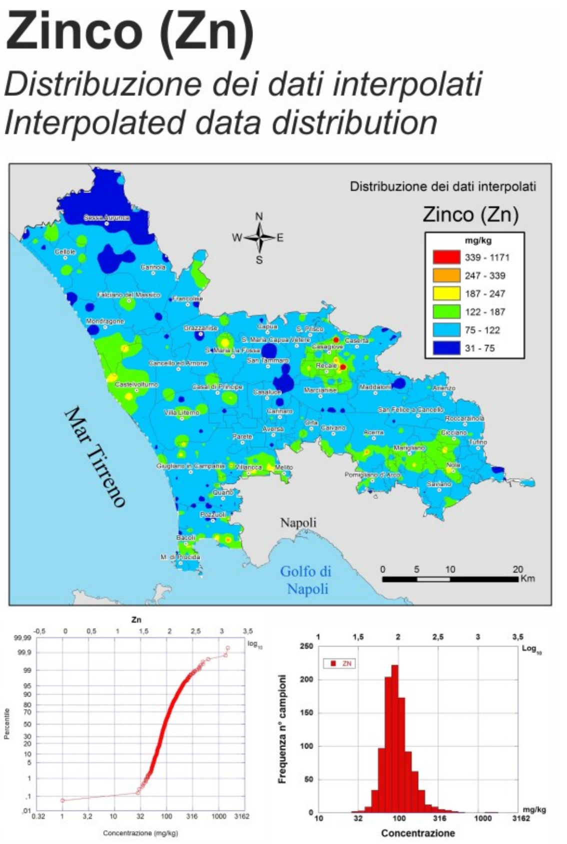


Figure 31 Interpolated map (Zn)

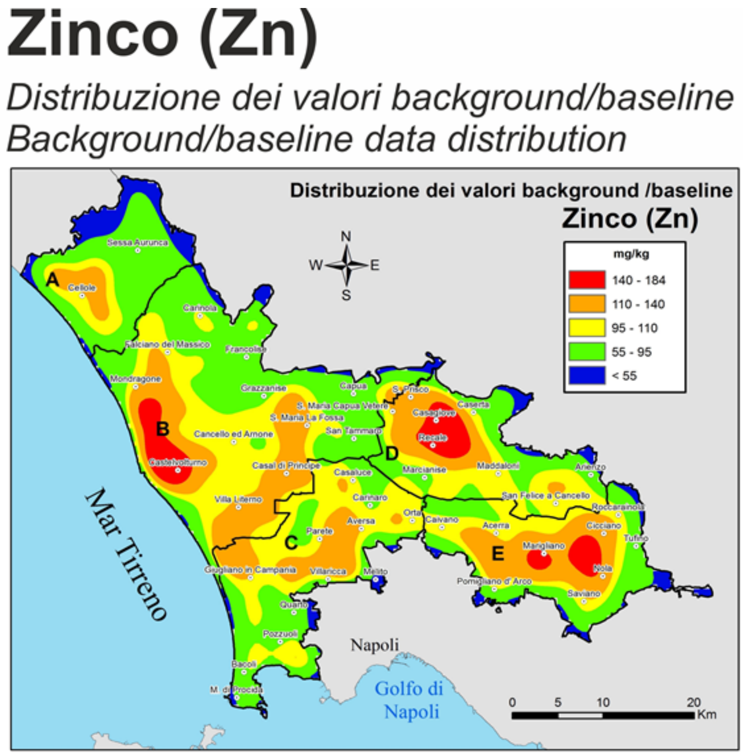


Figure 32 Background-baseline map (Zinc)

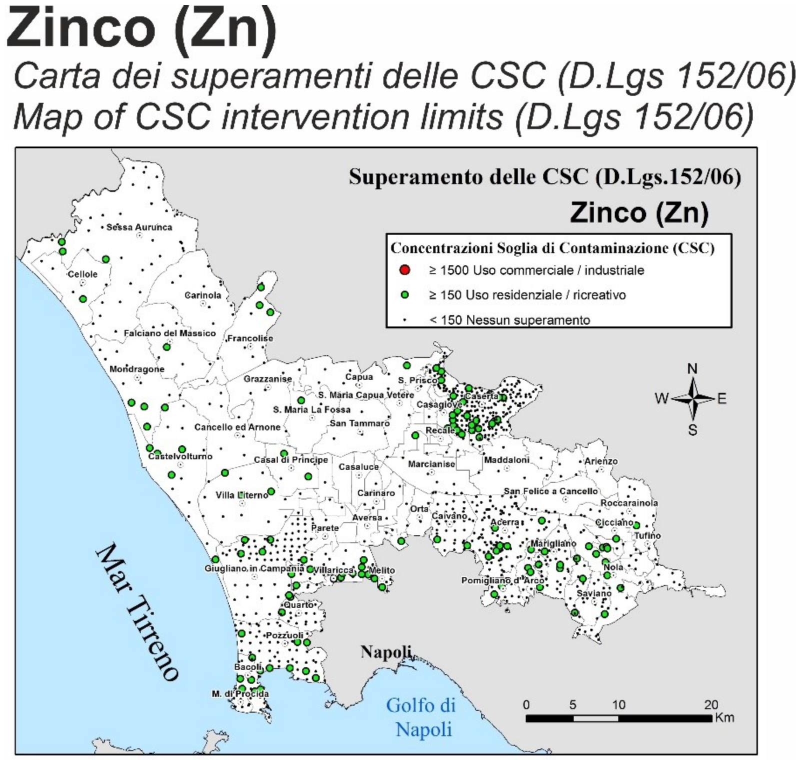


Figure 33 CSC map (Zinc)

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CHAPTER III
The Acerra - Marigliano - Pomigliano conurbation

Introduction

Urban soils, are mainly characterized by a strong lateral spatial variability with a composition and structure due to mixing with dusts and rubble during building activities, compaction and contamination phenomena related to the presence of industrial settlements, human mobility, waste disposal and malfunction of public facilities. Urban soils contaminations are mainly given by potentially harmful metals (PHEs), hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), fertilizers (or pesticides), solvents and mineral oils. It is important to understand how complex is the urban system since contamination processes are often affected not only by source features but also by random variables such as the type of road coverage, the presence of water flow lines that deviate their natural course, the geographic location, the weather and climatic conditions, and other time- and spatial-limited events.

Regarding soils, it is very difficult to determine the <u>background</u> (geogenic**)** value of an element in an urban environment since the diffuse nature of the pollution, mostly dependent on both the fallout processes and the 'mobility' of the sources, makes it virtually impossible to find places that may be considered completely uncontaminated. In general terms, the only available option to define background reference values for the soils of an urban area is to characterize soil samples collected at presumed uncontaminated locations at a distance from the urban area that are of the same pedological and geological nature as the urban soils.

In the urban environment, the concept of baseline, which indicates the "wide distributed" actual content of an element in the superficial environment, can be more suitable than the one of background. Basically baseline is the result of a sum among background and the increase in concentration due to a diffuse pollution.

Finally, if we consider an urban area as part of a regional context, we can define two baselines and, as consequence, two anomaly thresholds:

- the <u>regional anomaly threshold</u>, which is, basically, coincident with the upper limit of the natural background concentration interval;
- The <u>local anomaly threshold</u>, which refers to the baseline of the area influenced by diffuse urban pollution.

The main objective of the study was to determine the local geochemical baselines both for 53 elements (among which the toxic ones) and for some organic compounds, including PAHs and OCPs. Furthermore, the study aimed at supporting epidemiological researches and establishing a record of the actual environmental conditions to evaluate the future impact of the incinerator on both the territory and the public health.

1. Study area

The Acerra-Marigliano conurbation covers a total area of about 100 sqkm, including 6 municipalities (Acerra, Pomigliano D'Arco, Castello di Cisterna, Brusciano, Mariglianella and Marigliano). The total population is about 160,000 and the average population density is about 1600 inhabitants/sqkm. Bearing in mind the entire extension of the urbanized areas (18-20 sqkm) the average population density could be corrected to 6-7000 inhabitants /sqkm. (*Fig.1*).

Figure 1 Study area

In the area (between Acerra and Pomigliano D'Arco) a branch of the Italian automotive industries FIAT is present. In the factory, car models of the Alfa Romeo brand have been mostly assembled since the beginning. The factory came into activity in the early 70's and nowadays it has about 6000 employees.

In the northern sector of the Acerra municipal territory another industrial settlement can be found (The ASI consortium). The settlement covers a total area of 2.601.000 sqm mostly occupied by the Montefibre factory. Since the beginning of the 80's, the Montefibre factory produces polyester fibers and it is accused of being one of the main culprits of pollution of soil and groundwater in the area. Close to the ASI-Montefibre area and in the middle of the crops, in 2009, an incinerator for urban waste treatment was inaugurated and started to burn non-differentiated waste coming from every part of the Napoli metropolitan area. The waste was accumulated during the waste crises of the Campania region notorious worldwide (2004, 2008-2009).

Epidemiological studies demonstrated that the rate of cancer mortality in the Acerra area (better known as “Triangle of death”) is higher than the regional average value, although the higher rate has been mostly due to the presence of many illegal waste disposals which have been contaminating soils and waters for decades.

Land use map shows that 60 % of the total study area is under agricultural use, while urban and peri-urban areas cover 20%; the remaining area comprises vineyard, orchards and woods. (Fig.2)

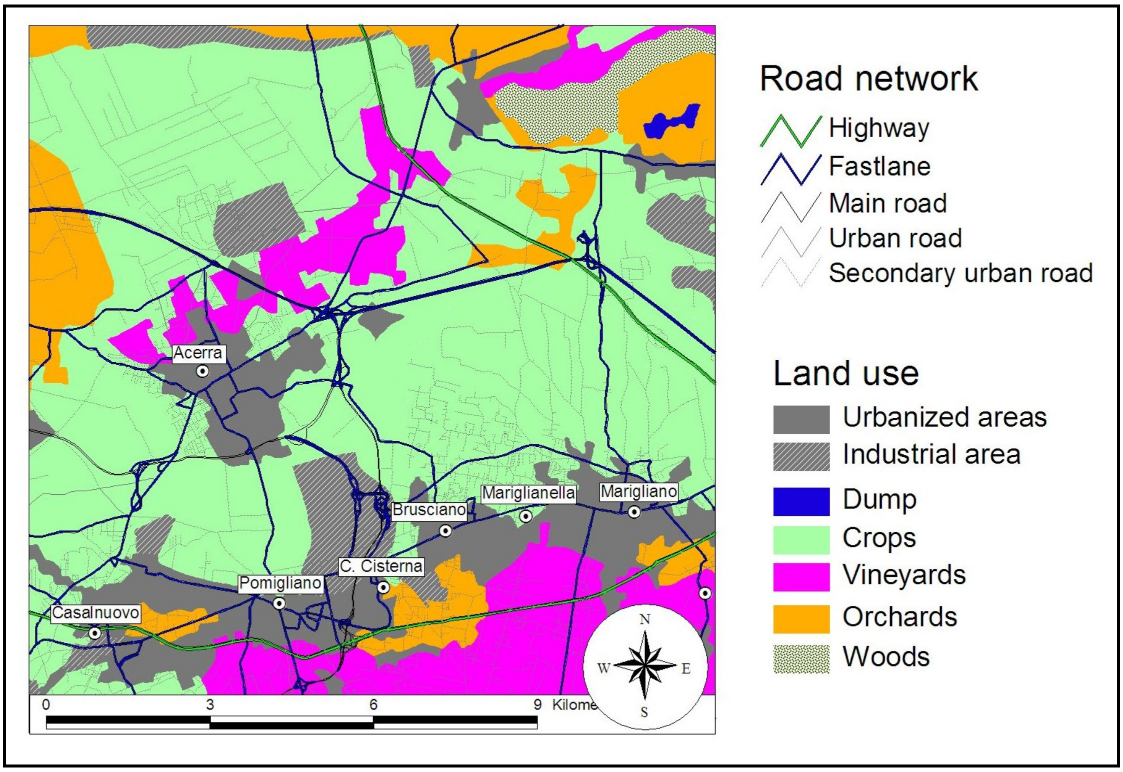


Figure 9 Land use map (Corine 2012)

2. *Material and methods*

2.1 Soil sampling and analytical analysis

A total of 121 samples were collected to analyse potentially harmful elements PHEs (13): As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, Zn, performed to ACME Analytical Laboratories Lab. Ltd. (Vancouver, Canada), now Bureau Veritas by ICP-MS by Jarrel Ash Atomcomp 975 ICP-Emission Spectrometer and a Perkin Elmer Elan 6000 ICP-Mass Spectrometer.

A total of 33 samples were collected for analysis of PAHs. These samples were stored in plastic bags and kept at a temperature of 4°C by means of a portable cooler during the transport at each site, a composite sample of 0.5 kg was collected, by joining together five aliquots taken at the center and at the corners of an ideal square with a 5 m side. For every 20 sampling sites, a duplicate sample was collected in the same cell of the 20th sample in order to allow the blind control of the analytical quality. Each sampling site was regularly described for spatial coordinates, soil and air temperature, local geology, type and main properties of soils, land use, and any additional details related to anthropic activities in the surroundings. (*Albanese et al., 2015*),

33 soil samples collected for PAHs analyses, packed in polystyrene boxes together with dry ice pellets (to keep temperature of samples conveniently low), were sent to the Key Laboratory of Bio geology and Environmental Geology of Ministry of Education at China University of Geosciences in Wuhan for PAHs analyses : Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[oa]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,I]perylene. An HP6890N gas chromatograph equipped with mass selective detector (5975MSD) was used to detect the levels of polycyclic aromatic hydrocarbons (PAHs) in soil samples.

2.2 Univariate Statistics

A univariate statistical analysis was performed on the chemical data (Table 1 and 2) which were, subsequently, georeferenced and mapped by means of a geochemistry-dedicated GIS software named GEODAS (Cheng 2003).

2.3 Environmental Risk assessment

Environmental risk assessment for PHEs has been performed by means of three different methods (Potential Hazard, Contamination Degree and Pollution Load Index).

The map of the Potential Hazard (PH) has been generated by reclassifying the pixels of the interpolated map of each PHE and PAH compound by using as a criterion the overcoming of the corresponding ILVR (residential action limit established by Italian law) Table 1. For each map, an integer value of 1 has been associated to the pixels characterized by concentrations overcoming the ILRV and an integer of 0 has been assigned to the remaining pixels. After reclassification, by adding the 13 grids obtained for PHE, the maps of PH will have been generated; in the PH maps, each pixel is characterized by an integer value corresponding to the total number of elements/compounds, which are not in line with Italian environmental guidelines within its own spatial domain. Beryllium, Sn and Tl are generally characterized by concentration values above the corresponding ILRV across the whole study area; thus the minimum value of PH associated to any pixel in the map for PHEs is not lower than 3.

The map of the Contamination Degree (CD) for both PHEs and PAHs has been performed by first, generating the grid of the contamination factors (CF) for each element and PAH compound, then by using the relation described by *Hakanson (1980*) successfully applied on soil data by *Albanese et al., (2013)* and *Cicchella et al. (2013):*

$$CF_i = \frac{C_i}{C_b} \qquad \textbf{(1)}$$

Where,

C_i refers to the concentration value of the element/compound in the i- pixel of the interpolated grid

C_b refers to the reference values of the element/compound for the background (geogenic).

In this study, the Vesuvian Soil Background Reference Interval (VSBI) (Table 1) set by *Cicchella et al. (2008)* for the Neapolitan volcanic soils is used as a reference value (C_b) for PHEs.

For PAHs, which are generally mainly anthropogenic, reference values (C_b) (mostly dependent on volcanic emissions, wood burning…) for the background of Neapolitan soils were retrieved from Maisto et al., 2006.

Subsequently, the grids of CD for both PHEs were produced by summing all the generated CFs grids by means of the following equation:

$$CD = \sum_1^{13} CF \qquad \textbf{(2)}$$

The CD grids of PHEs (Fig. 3B) were classified according to *Håkanson (1980)* and three value intervals were established in the map to depict the overall contamination status of the study area.

The map of the Pollution Load Index (PLI) *(Gong et al., 2008)*, is also based on the CF grid of each contemplated metal in the soil of the Acerra-Pomigliano-Marigliano conurbation. The PLI grid has been generated by calculating the i-esim root (according to the number of the considered elements/compound) of the product of the CFs grids using the following relation:

$$PLI = \sqrt[13]{\prod_{1}^{13} CF_i} \tag{3}$$

Values of PLI equal to or below 1 indicate PHEs loads close to the background levels, and values above 1 indicate a condition of pollution.

Element	**Unit**	***N°***	***Min***	***Max***	***Mean***	***Geometric Mean***	***Median***	***RMS***	***Std Dev.***	***ILVR (Dlgs.152/06)***	*VSBI* ***Cicchella et al. 2008***
Sb	***mg/kg***	121	0,38	5,41	0,88	0,78	0,73	1,05	0,58	10	0,3-0,9
As	***mg/kg***	121	6,40	60,90	13,82	13,13	13,20	15,11	6,15	20	6-18
Be	***mg/kg***	121	1,90	12,20	4,70	4,53	4,60	4,87	1,29	2	-
Cd	***mg/kg***	121	0,18	1,38	0,51	0,48	0,51	0,53	0,16	2	0.1-0.5
Co	***mg/kg***	121	5,30	17,40	11,95	11,54	12,50	12,31	2,95	20	3-1
Cr	***mg/kg***	121	4,00	177,80	19,47	16,69	15,80	27,45	19,44	150	1-16
Hg	***ug/kg***	121	28,00	563,00	136,17	107,22	109,00	168,94	100,40	1	15-100
Ni	***mg/kg***	121	5,60	25,40	15,46	15,16	15,80	15,73	2,90	120	4-14
Pb	***mg/kg***	121	35,94	1099,09	85,95	68,69	64,22	158,59	133,83	100	13-80
Cu	***mg/kg***	121	17,90	329,58	144,87	134,30	140,21	154,02	52,53	10	5-200
Se	***mg/kg***	121	0,20	1,60	0,65	0,63	0,60	0,68	0,20	3	0,1-0,4
Sn	***mg/kg***	121	2,40	18,90	4,90	4,48	4,10	5,52	2,55	1	-
Tl	***mg/kg***	121	0,87	2,91	2,12	2,05	2,21	2,18	0,50	1	0,3-1,6
V	***mg/kg***	121	36,00	117,00	85,22	82,17	89,00	87,85	21,39	90	29-72
Zn	***mg/kg***	121	42,80	627,90	119,22	110,86	109,60	136,16	66,06	150	56-100

Table 1. Statistical parameters for PHEs in the soil of Acerra - Marigliano - Pomigliano conurbation.

	Count	**Min**	**Max**	**Mean**	**Geometric mean**	**Median**	**Std Deviation**	**ILVR (D.lgs 152/06)**
Naphthalene	33	2,5	25,3	9,5	8,0	8,5	5,8	5000
Acenaphthylene	33	0,1	33,1	8,4	4,5	5,5	8,3	5000(1)
Acenaphthene	33	0,0	4,9	0,9	0,3	0,6	1,2	5000
Fluorene	33	0,0	7,5	2,2	1,4	1,8	1,6	5000(1)
Phenanthrene	33	3,4	111,4	33,5	23,7	22,5	27,9	5000
Anthracene	33	0,5	27,3	6,8	4,5	4,7	6,1	5000(1)
Fluoranthene	33	4,2	410,3	86,4	55,0	58,0	83,8	5000(1)
Pyrene	33	4,0	396,7	79,9	51,6	55,2	79,0	5000
Benzo[a]anthracene	33	3,3	424,9	70,6	44,0	51,3	80,9	500
Chrysene	33	19,7	780,6	234,1	167,0	174,2	184,2	5000
Benzo[b]fluoranthene	33	15,8	878,8	224,1	153,0	172,0	208,7	500
Benzo[k]fluoranthene	33	6,5	381,8	108,1	71,5	73,7	94,8	500
Benzo[a]pyrene	33	19,0	1131,7	302,5	204,0	234,6	267,8	100
Indeno[1,2,3-d]pyrene	33	13,9	1078,7	254,6	165,0	171,0	248,1	100
Dibenzo[a,h]anthracene	33	0,0	181,1	40,7	19,0	28,0	41,6	100
Benzo[g,h,i]perylene	33	8,4	615,4	162,2	106,0	108,5	148,7	100

Table 2. Statistical parameters for PHAs in the soil of Acerra - Marigliano - Pomigliano conurbation.

(1) ISS 2010

3. Results and discussion

Map of Potential hazard (Fig.3A), referred to PHEs distribution, shows that the value of PH is higher (7-8) in correspondence to the south –western part of Acerra, south of Pomigliano and in the urban center of Marigliano municipalities.

Fig 3B shows that in the Acerra municipality, the contamination degree is < 15 in most of the territory, meanwhile in the center of the city the value is between 15 and 30 (low pollution) with a hot spot (> 30) that indicates moderately pollution; Values between 15 and 30 were distributed in Acerra, Pomigliano and Marigliano municipalities.

The Pollution Load Index (Fig 3C) indicates a Low pollution (>1) regarding urban center of Acerra's city, in Pomigliano and Marigliano's municipalities.

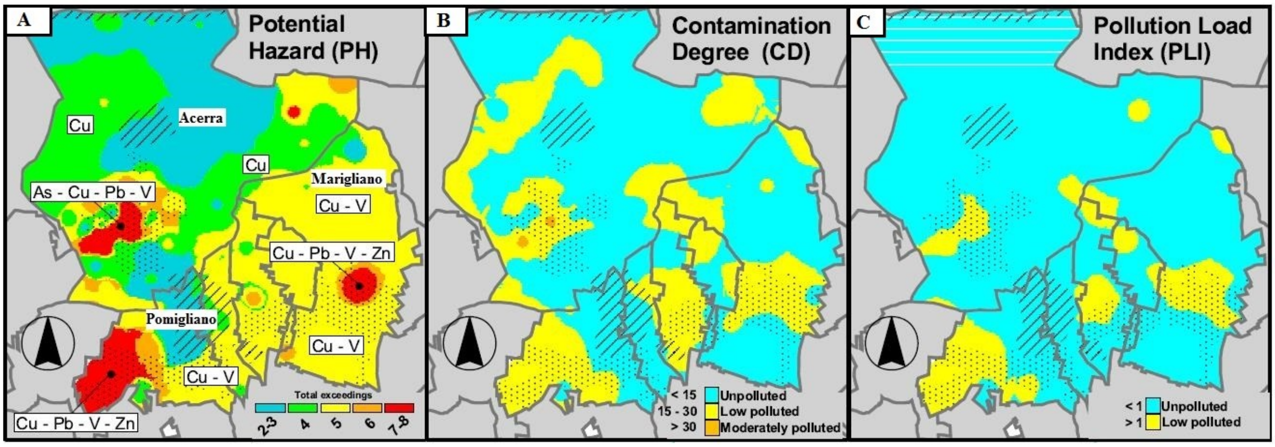


Fig 3. PHE s distribution A) Potential Hazard (PH) B) Contamination Degree C) Pollution Index (PLI)

Fig.4 shows that the map of Potential hazard (Fig.4A), referred to PHAs distribution, has values > 5 in the area between the Acerra and Brusciano municipalities, while values between 3 and 4 are found in most of the study area, only the northern part presents lower values.

The map of Contamination Degree (Cd) (Fig.4B) shows that values > 15 are found in the central part of study area, in detail in the Acerra municipality and in Castello di Cisterna and Brusciano municipality, the remaining part has values < 15.

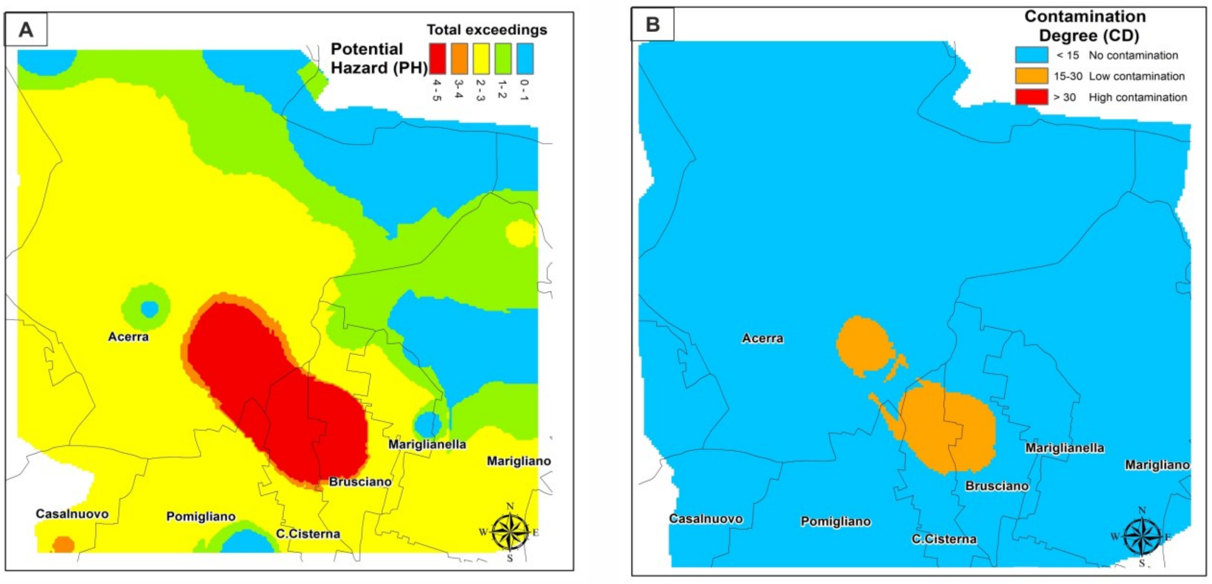


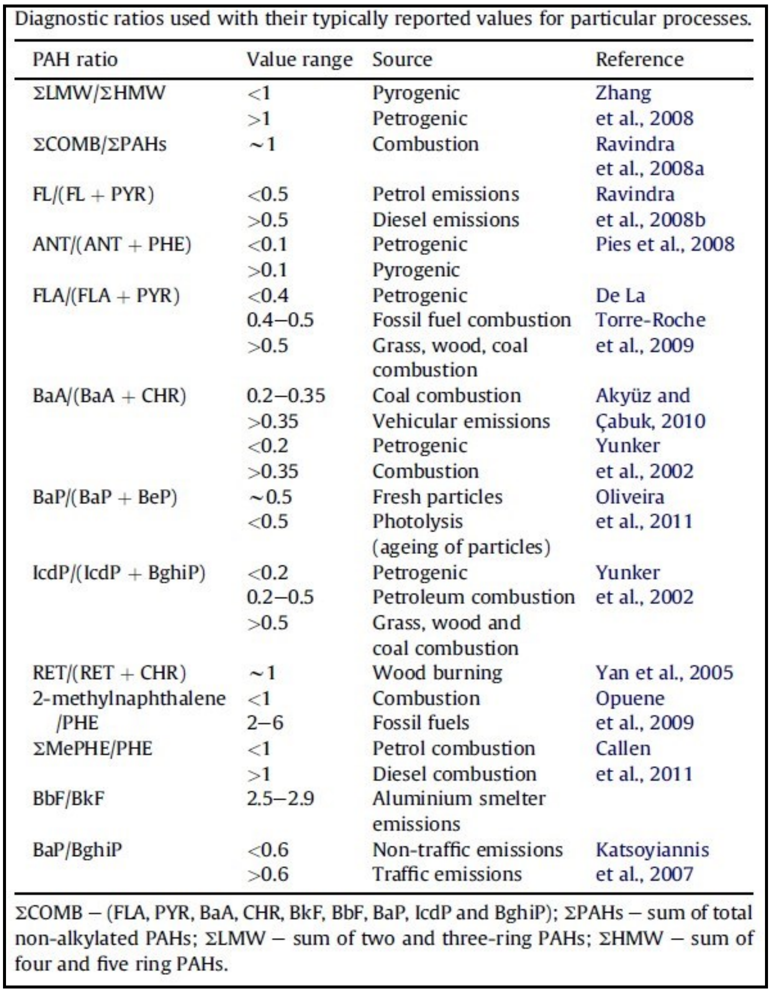
Fig 4. PAH s distribution A) Potential Hazard (PH) B) Contamination Degree

PHAs are divided in three categories: Low molecular weight (LMW), Middle molecular weight and High molecular weight (HMW) (Table 3).

Low molecular weight (LMW)	• **Naphthalene (Biomass combustion)** • **Acenapthylene** • **Acenaphthene** • **Fluorene** • **Anthracene**
Middle molecular weight	• **Phenanthrene (Biomass combustion)** • **Fluoranthene** • **Pyrene** • **Benzo(a)anthracene** • **Chrysene**
High molecular weight	• **Benzo(b)fluoranthene** • **Benzo(k)fluoranthene** • **Benzo(a)pyrene** • **Dibenzo(a,h)anthracene** • **Benzo(g,h,i)perylene** • **indeno (1,2,3-c,d) pyrene**

Table 3 PAHs classification (LMW, MMW, HMW)

This classification is useful to discern the source of PAHs between pyrogenic, petrogenic or derived from biomass combustion (Table 4).



Diagnostic ratios used with their typically reported values for particular processes.

PAH ratio	Value range	Source	Reference
ΣLMW/ΣHMW	<1	Pyrogenic	Zhang et al., 2008
	>1	Petrogenic	
ΣCOMB/ΣPAHs	~1	Combustion	Ravindra et al., 2008a
FL/(FL + PYR)	<0.5	Petrol emissions	Ravindra et al., 2008b
	>0.5	Diesel emissions	
ANT/(ANT + PHE)	<0.1	Petrogenic	Pies et al., 2008
	>0.1	Pyrogenic	
FLA/(FLA + PYR)	<0.4	Petrogenic	De La Torre-Roche et al., 2009
	0.4–0.5	Fossil fuel combustion	
	>0.5	Grass, wood, coal combustion	
BaA/(BaA + CHR)	0.2–0.35	Coal combustion	Akyüz and Çabuk, 2010
	>0.35	Vehicular emissions	
	<0.2	Petrogenic	Yunker et al., 2002
	>0.35	Combustion	
BaP/(BaP + BeP)	~0.5	Fresh particles	Oliveira et al., 2011
	<0.5	Photolysis (ageing of particles)	
IcdP/(IcdP + BghiP)	<0.2	Petrogenic	Yunker et al., 2002
	0.2–0.5	Petroleum combustion	
	>0.5	Grass, wood and coal combustion	
RET/(RET + CHR)	~1	Wood burning	Yan et al., 2005
2-methylnaphthalene /PHE	<1	Combustion	Opuene et al., 2009
	2–6	Fossil fuels	
ΣMePHE/PHE	<1	Petrol combustion	Callen et al., 2011
	>1	Diesel combustion	
BbF/BkF	2.5–2.9	Aluminium smelter emissions	
BaP/BghiP	<0.6	Non-traffic emissions	Katsoyiannis et al., 2007
	>0.6	Traffic emissions	

ΣCOMB – (FLA, PYR, BaA, CHR, BkF, BbF, BaP, IcdP and BghiP); ΣPAHs – sum of total non-alkylated PAHs; ΣLMW – sum of two and three-ring PAHs; ΣHMW – sum of four and five ring PAHs.

Table 4. Diagnostic ratios about PHAs source identification

In this study the ratio BaA/BaA + Chr, Flt/Pyr and Inp / (Inp + BP) is used. As Fig 5 (a, b, c) shows, all the analyzed ratios, indicate that, the source of PAHs in this study area, in particular BaA/BaA + Chr, Flt/Pyr and Inp / (Inp + BP), depend on the process of biomass combustion. In detail, only some sample analyzed for ratio Ant/Ant +Phe shows fuel combustion's source, other ratios show that the PAhs source depend mainly on biomass combustion.

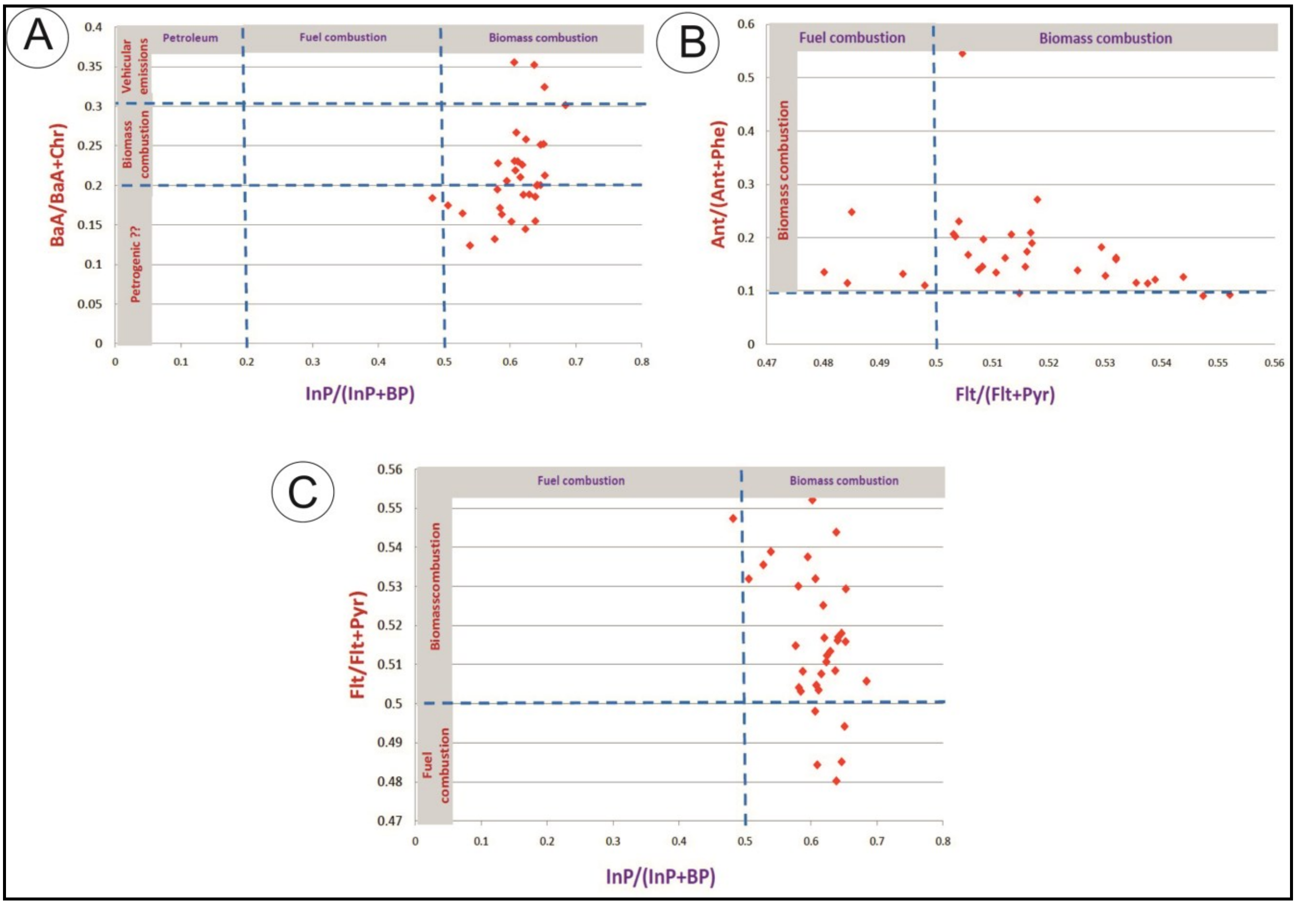
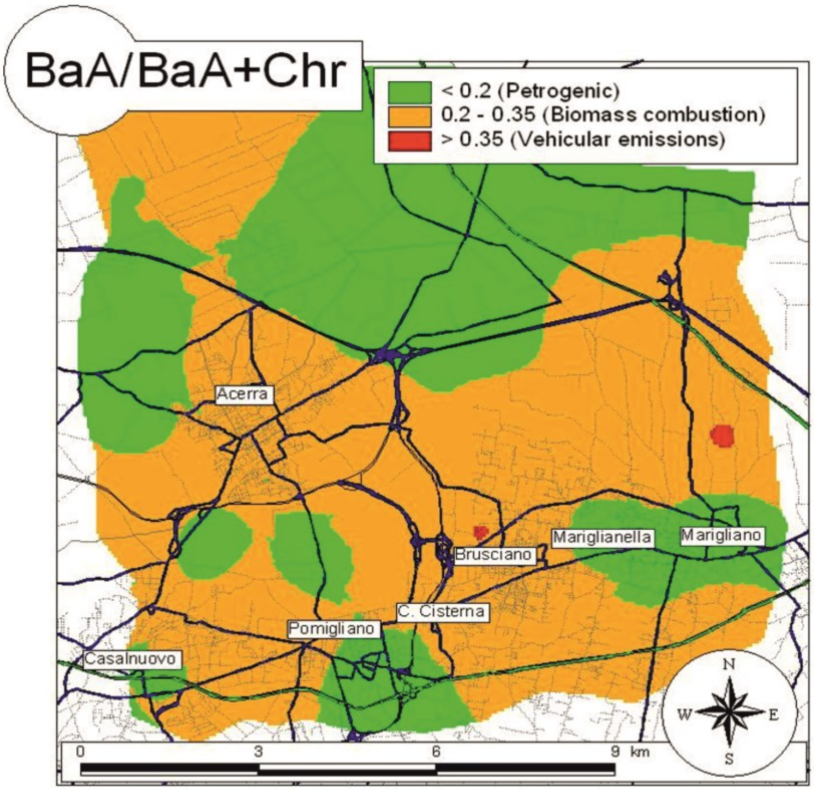
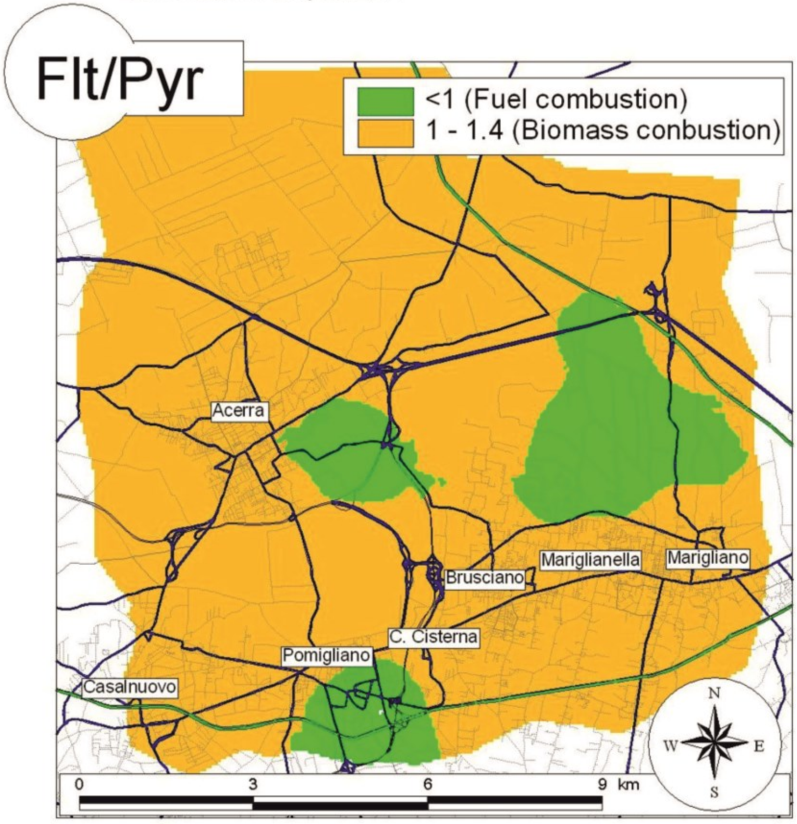


Fig.5 A) BaA/BaA + Chr and Inp / (Inp + BP) ratio;, B) Ant/Ant +Phe and Flt/Pyr ratios; C) Flt/Pyr and Inp / (Inp + BP) ratios

Fig.5 shows the BaA/BaA + Chr and Flt/Pyr ratios´ distribution. It is possible to observe regarding BaA/BaA+Chr ratio that values <0.2 are distributed in the north of the study area and in some site of the area in the south; they depend on petrogenic source (*Yunker et al., 2002*).



Alkyuz and Kabuk., 2010; Yunker et al., 2002; Oliveira et al., 2011.



Lee et al., 1982

Fig. 6 BaA/BaA+Chr and Flt/Pyr ratio's distribution.

Values > 0.2 are found in most of the area, and they can be associated with biomass combustion's processes (*Akyuz et al., 2010*). There are some 'hot spots' with values > 0.35 regarding the Brusciano and Marigliano municipalities and they may depend on vehicular emissions (*Olivera et al, 2011*).

Related to Fig., Flt/Pyr ratio shows that most of the study area has values between 1 and 1,4 that depend on biomass combustion *(Lee et al., 1982*). Values < 1 are found in few sites of this area.

4. Conclusions

In this study, the results showed that 1) the most urbanized areas of the conurbation are characterized by concentrations of Pb, Zn and V exceeding the trigger limits established by the Italian Environmental law (D.Lgs. 152/2006); 2) agricultural soils, in the surroundings of the urbanized areas, are enriched in Cu, Co, Cd, Be and Ni, 3) in the incinerator area Se, Hg.

Cu, Cd and Sb baselines are generally higher than in the rest of the territory. Furthermore, the PAHs distribution pattern and their diagnostic ratios suggested that the agricultural waste burning in the rural sector of the study area could be a relevant source of pollution.

In detail, PAHs distribution pattern showed anomalous values across the whole study area. Especially, Benzo[a]pyrene values exceeds the trigger limits established by the Italian Environmental law (D.Lgs. 152/2006) in most of the analyzed soils and the diagnostic ratios calculated among several PAHs compounds suggested that the biomass burning in the rural sector of the study area could be a relevant source of pollution (Akyuz et al., 2010 ;Lee et al., 1982).

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CHAPTER IV

Human health risk assessment for potentially toxic metals (PTEs) in Acerra' s area (Campanian Region, Italy)

Introduction

Soil is the primary reservoir of potentially toxic metals in the atmosphere, hydrosphere and biota, and it is very important in the cycle of nature (Cao et al., 2010). Many authors in the recent years have dedicated themselves to study the importance of potentially toxic metals (PTEs) in the environment (Albanese et al., 2011; Saeedi et al., 2012; Liu et al., 2013; Wu et al., 2015).

Anthropogenic activities, such as industrialization and urbanization, are important sources of PTEs and organic compound in soil. Many researchers have demonstrated (Lu et al., 2010; Wu et al., 2010, Xu et al., 2013) that toxic metals can be transported long distances across the atmosphere and expand the pollution in a specific area. Polluted soil can enter in the human body, for example from food, e.g. from vegetables. In fact, several studies show that this is the main route of human exposure to toxic metals in soil (Cui et al., 2004; Zhao et al., 2012; Adamo et al., 2014 Avila et al., 2016). Other exposure routes include soil ingestion, dermal absorption and inhalation (of particle-bound or volatile contaminants). The formation of risks depends on many site-specific factors, e.g. contaminants involved, soil properties, environmental conditions, land use and characteristics of human receptors. Site-specific risk assessment is a procedure that takes into account these specific conditions and combines the information on the source, transport pathway, exposure routes and dose-response relationships in the final receptor.

In the last 30 years, Campania region has been affected by considerable industrialization and urbanization. From the 1990's the economy of Campania region exhibits a distinct change by transforming from the traditional industrial/productive activities, such as mechanical and textile industry, into small scale businesses focusing on services and tourism. Industry related contamination of stream water, ground-water and sediment can be ascribed to a lack of proper maintenance of the waste-water treatment systems (Minolfi et al., 2017; Albanese et al.,2013). In Campania region, the municipality of Acerra is situated in the Agro Aversano area that suffers from considerable anthropogenic pollution caused by illegal dumping and burning of waste since the 1990's (Rezza et al., 2016, Bove et al., 2011, Albanese et al., 2011),. This area is also characterized by a high degree of urbanization and by continuously changing land-use patterns.

This study is focused on the environmental contamination in Acerra. The goal was to determine the enrichment factors and pollution indexes of potentially toxic elements (PTE) in soil and vegetables and bio concentration factors for critical PTEs and finally, to evaluate the consequent human health risks.

1. Material and methods

1.1 Study area

Acerra's municipality lies 14 Km from Naples city (Italy) (latitude: 40°56′41″N - longitude: 14°22′17″ E). The area covers 178 Km^2 (ISTAT, 2010) and about 60,000 inhabitants. It is located in the middle part of Campania Plain. *Corniello and Ducci*, 2005 reported upper pyroclastic deposits followed by welded tuffaceous deposits (Campanian Ignimbrite – I.C.), incoherent tuffaceous deposits (Campanian Ignimbrite –I.C.), lower pyroclastic deposits, clay and sand deposits and carbonate deposits (Fig. 1a).

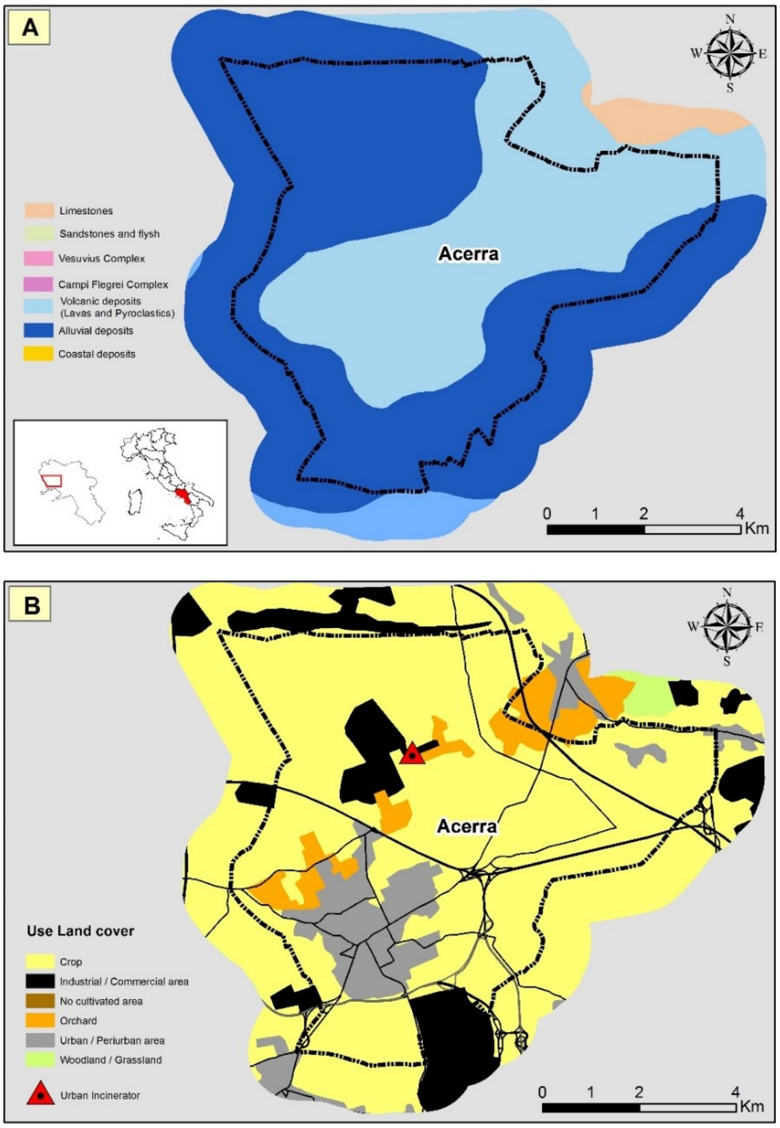

Figure 1 Geological features (a) and land use (b) of the study area

Some 60 % of the total area is dedicated to agricultural use, cereals, potato, tobacco and vegetables being the main crops, while 20 % is urban and peri-urban area (Fig. 1b). The remaining part is in industrial use. Acerra is an industrialized area mostly occupied by the factories of Fidion (ex Montefibre), which produces polyester fibres, and Sideralba, which processes steel. The waste treatment plant that incinerates municipal solid waste since 2009 from most municipalities situated around the city of Naples is an additional potential source of pollution (Rezza et al., 2017). Moreover, the car factory of FIAT, with about 6000 employees in Pomigliano d'Arco municipality, is very close to Acerra.

1.2 Samples and their analysis

Definition of the contamination level was based on analyses of samples taken from topsoil, corn and endives grown in the area.

Altogether 178 topsoil samples were retrieved from former studies focused on the area (Lima et al., 2012, Grezzi et al., 2011, Bove et al., 2011), corresponding a sampling density of one sample per approximately 5 km2. Each sample consisted of 1 kg of soil taken from the depth of 0-20 cm. Total concentrations of metals were analysed by inductively coupled plasma mass spectroscopy (ICP-MS) from dried samples digested with aqua regia (Cicchella et al., 2008., Bove et al., 2011, Grezzi et al., 2011). In addition, EDTA extractions were used to find out the potentially available concentrations.

Five (5) corn (Zea mays) samples and five (5) endive (Cichorium endivia) samples were collected at different farms within the study area. Only the edible part of these vegetables were analysed. For corn, after collection, 100 g of each sample was dried in a temperature of 60 °C and ground to a powder. Then 20 g of the sample was taken and digested with nitric acid in a hot water bath and Nb, Ni, P, Pb, Pd, Pt, Rb, Re,S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, U, V, W, Y, Zn, Zr were analysed from the eluates by ICP-MS.

The samples of endive were dissolved with cold nitric acid following digestion in a hot water bath. After cooling, a modified aq. reg. solution consisting of equal parts of concentrated HCl, HNO_3 and de-ionized H_2O was added to each sample, to be further treatedin a hot water bath. Then the sample was diluted with dilute HCl and filtered ng a 1 g split digested in HNO3 then aqua regia. Finally, a total of 53 elements (Ag, Al, As, Au, B, Ba, Be, Bi, ca, Vd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na) were analysed by ICP-MS.

1.3 Determination of Enrichment Factor (EF)

Enrichment factors (EFs) that reflect soil contamination in a long time scale (Barbieri 2016; Wu et al., 2015; Avila et al., 2015; Saeedi et al., 2012) were determined for each heavy metal identified as a PTE. EFs were calculated on the basis of concentrations of PTEs analysed from soil samples and reference concentrations (Eq.1).

$$EF = \frac{\left(\frac{Cx}{Cref}\right)sample}{\left(\frac{Cx}{Cref}\right)background} \qquad (1)$$

Where C_x is the concentration of the PTE *x* and C_{ref} is the concentration of a reference element. Herereference element is an element that is particularly stable in the soil. The stability is demonstrated by vertical immobility and/or and chemical stability (Barbieri et al. 2016 ; Reimann et al., 2008). On the basis of the EF index, the status of soil can be classified to different classes (Table 4).

In this study, aluminium was selected as a reference element to calculate the EFs. Al was selected because generally the reference element is chosen among elements of definitely natural origin; such elements include at least Al, Sc, Ti (Barbieri et al., 2016). Aluminium is a conservative element and a major constituent of clay minerals.

EF value	**Enrichment category**
EF <2	Deficiency to minimal enrichment
2 ≤ EF< 5	Moderate enrichment
5≤ EF < 20	Significant enrichment
20 ≤ EF < 40	Very high enrichment
EF≥40	Extremely high enrichment

Table 4 Enrichment category based on the Enrichment Factor (EF)

1.4 Determination of Pollution Indexes

Pollution index (PI) imply the level of pollution (e.g. Wu et al., 2015; Avila et al., 2016).. PIs of PTEs were calculated using Italian (Legislative Decree 152/06) (Eq. 2).

$$PI = \frac{C_i}{S_i} \qquad (2)$$

Where C_i is the measured concentration of element *i* in soil (mg kg^{-1}), S_i is the soil quality standard or reference value of that element *i* (mg kg^{-1}), by D.lgs152/06. The level of pollution can then be determined on the basis of classification presented in Table 5.

PI value	**Pollution category**
PI ≤ 1	No contamination
1 < PI ≤ 3	Slight contamination
3 < PI ≤ 5	Moderate contamination
PI > 5	Severe contamination

Table 5 Pollution categories as per the Pollution Index (PI).

1.5 Determination of Translocation Factor (TF)

The mobility of the heavy metals from soil to plants can be expressed by a Translocation Factor (TF) (Avila et al., 2016; Adamo et al., 2014; Pandey et al., 2014, Antoniejevic et al., 2012), which is equivalent to Uptake Factor (UF), used in some literature sources (Lopes et al., 2012). The calculation of TFs is based on dry weights of PTEs (Eg. 3)..

$$TF = \frac{C_i plant}{C_i soil} \tag{3}$$

Where C_{plant} and C_{soil} denote the concentration of element *i* in plant (fresh weight) and in soils, respectively. (Jolly et al., 2013).

1.6 Identification of COPCs and determination of their statistics

The Contaminants of Potential Concern (COPC) that should be considered in the health risk assessment were identified by comparing the concentration of each PTE analysed against the Italian RAL (Residential Action Limit from D.lgs 152/06) and IAL (Industrial Action Limit from D.lgs 152/06) values.

KaleidaGraph 4.5 software was employed for producing a graph plotting of the concentration data of each COPC. The statistical variables and parameters considered included the land use –specific minimum, maximum, mean, and median value, standard deviation, RAL, IAL (Industrial/Commercial action limit) and background value (from De Vivo et al.2006) (Tab.1 a, b, c,). The statistics of major crops grown in the area (corn, vegetables) were also considered (Table 2 a and b).

The Tier 1 health risk assessment was based on using the 95% Upper Confidence Limits (UCLs) (see also chapter 2.6) of measured PTE concentrations. The 95% UCL is "a number that one can be 95% confident that the true mean (average) concentration of the population is below that value." A slightly simpler definition is that it is a level considered protective. ProUCL 5.1 software was used to calculate the UCLs.

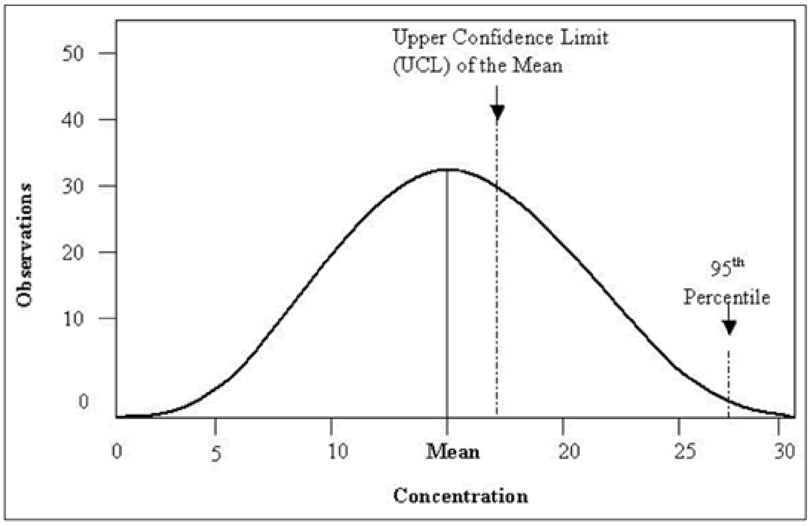

Figure 2 Graphic of UCl definition

1.7 Risk assessment

The assessment of risks to human health followed a tiered approach as generally recommended (Sorvari et al, 2006; Sorvari et al., 2010; Sorvari, J. & Jakkonen, 2000,) . In Tier 0 the concentration of PTEs found in soil were compared against the generic soil guideline values. This comparison was also used for the identification of COPCs that should be considered at the next assessment level (see chapter 2.6). Tier 1 risk assessment was based on deterministic calculations (chapter 2.7.2). For those PTEs, for which Tier 1 produced risk estimates exceeding the acceptable level, a Tier 2 risk assessment was conducted (chapter 2.7.3).

1.7.1 Conceptual site model

Based on the information on the land use and environmental conditions at the study area the following exposure routes were identified as relevant in the formation of human health risks:

- ingestion of soil
- dermal intake from soil particles
- food consumption (corn and vegetables)
- inhalation of soil particles.

Figure 3. shows the conceptual site model that summarizes the formation of risks.

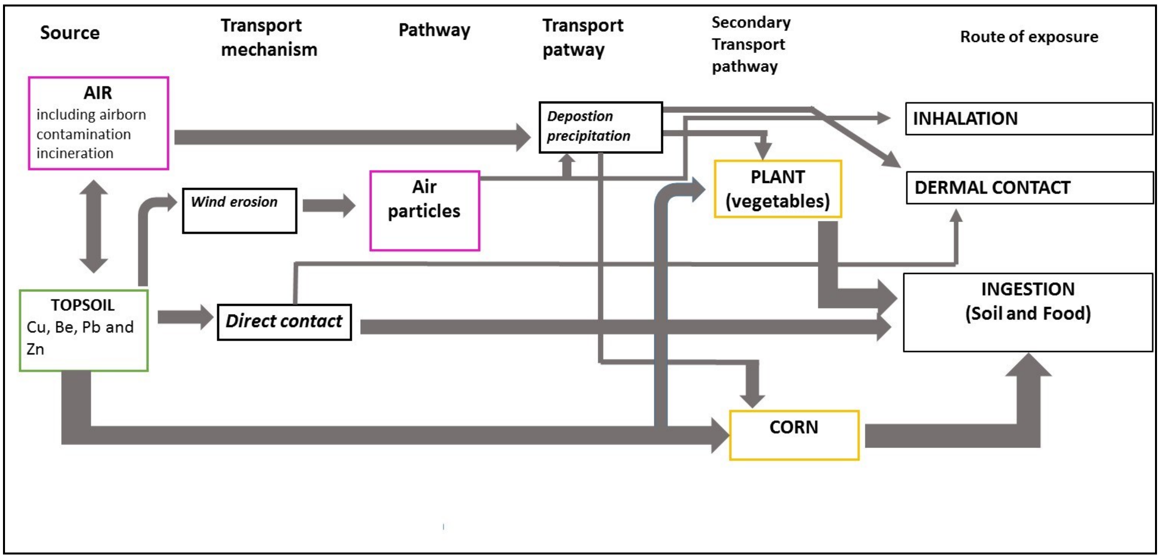

Figure 3Conceptual site model describing the formation of human health risks in the study area.

1.7.2 Tier 1 risk assessment

The generic exposure models (Table 3, Eqs. 3-9) presented by United States Environmental Protection Agency (US EPA, 1989) were used to determine the human health risks posed by each identified COPC, using their 95% UCL values.

Equations used in the calculation of deterministic estimates for the human exposure (US EPA; 2000, 2002, 2004). The parameters are described in Table 3.

$$CDI\ ing = \frac{CS*IR*CF*FI*EF*ED}{BW*AT} \tag{3}$$

$$CDI\ dermal = \frac{CS*CF*SA*AF*ABS*EF*ED}{BW*AT} \tag{4}$$

$$CDI\ ing\ vegetables = \frac{CF*IR*FI*EF*ED}{BW*AT} \tag{5}$$

$$DI\ ing = \frac{CSc*IRc*CF*FIc*EFc*EDc}{BWc*AT} \tag{6}$$

$$CDI\ dermal = \frac{CSc*CF*SAc*AFc*ABSc*EFc*EDc}{BWc*AT} \tag{7}$$

$$CDI\ ing\ vegetables = \frac{CF*IRc*FIc*EFc*EDc}{BWc*AT} \tag{8}$$

$$HQ = \frac{HQing+HQ\ dermal+HQinh}{Rfd} \tag{9}$$

2. Results and discussions

2.1 Identified COPCs and their statistics

The results of the metal analyses are presented in Table 1.

	unit	*N°sample*	*Minimum*	*Maximum*	*Range*	*Mean*	*Median*	*Std. Dev*	*UCL*	*RAL**	*IAL***	*BCRIN****
As	*mg/kg*	56	5.9	60.9	5.9 - 6.9	15.2	13.8	8.3		20	50	6 - 18
Be	***mg/kg***	**56**	**2**	**7**	**2 - 7**	**4.6**	**5.1**	**1.7**	**6.2**	**2**	**10**	**-**
Cd	*mg/kg*	56	0.11	1.4	0.1 - 1.4	0.47	0.5	0.2		2	15	0.1 - 0.5
Co	*mg/kg*	56	5	17.4	5 - 17.4	12	12	2.8		20	250	3 - 17
Cr	*mg/kg*	56	1.5	29.9	1.5 - 29.9	14	13	5		150	800	1 - 16
Cu	***mg/kg***	**56**	**11**	**268**	**11- 268**	**134.5**	**130.6**	**58.3**	**139.4**	**120**	**600**	**4 - 200**
Hg	*µg/kg*	56	34	471	34 - 471	153.1	114.5	111.5		1	5	0.01 – 0.1
Ni	*mg/kg*	56	3.2	18.7	3.2 – 18.7	14.7	15.4	3.1		120	500	1 - 19
Pb	***mg/kg***	**56**	**36.9**	**1099.1**	**36.9 -1099.1**	**116**	**74.2**	**193.6**	**390.2**	**100**	**1000**	**20 - 80**
Sb	*mg/kg*	56	0.4	1.9	0.4 – 1.9	0.9	0.8	0.4		10	30	0.2 - 1.1
Zn	***mg/kg***	**56**	**66.6**	**627.9**	**56 – 66.6**	**133.3**	**118.9**	**91.6**	**249.9**	**150**	**1500**	**35 - 100**
Al(1)	*mg/kg*	56	24,000	57,100	24,000 - 57,100	47381	48,400	8119				77440 (1)

Table1 a. Statistical parameters in "urbanized "area soils of Acerra

	unit	*N°sample*	*Minimum*	*Maximum*	*Range*	*Mean*	*Median*	*Std. Dev*	*UCL*	*RAL**	*IAL***	*BCRIN****
As	*mg/kg*	107	4.2	17.0	4.2 - 17	12.0	12.4	2.7		20	50	6 - 18
Be	***mg/kg***	**107**	**2**	**7.2**	**0 - 7.2**	**3.8**	**4.2**	**1.8**	**4.5**	**2**	**10**	**-**
Cd	*mg/kg*	107	0.2	0.9	0.2 - 0.9	0.5	0.5	0.1		2	15	0.1 - 0.5
Co	*mg/kg*	107	4.0	17.5	4 - 17.5	10.9	11.3	3.3		20	250	3 - 17
Cr	*mg/kg*	107	6.9	177.8	6.9 - 1177.8	20.5	16.5	21.7		150	800	1 - 16
Cu	***mg/kg***	**107**	**44.4**	**329.6**	**44 -329.6**	**137.2**	**126.4**	**51.8**	**132.7**	**120**	**600**	**4 - 200**
Hg	*µg/kg*	107	24.0	4224.0	24 - 4224	184.7	120.0	407.9		1	5	0.01 – 0.1
Ni	*mg/kg*	107	6.0	26.4	6 - 26.4	14.7	15.0	15.0		120	500	1 - 19
Pb	***mg/kg***	**107**	**30.4**	**192.7**	**30.4 - 192.7**	**67.9**	**63.7**	**25.6**	**70.5**	**100**	**1000**	**20 - 80**
Sb	*mg/kg*	107	0.4	2.8	0.4 - 2.8	0.8	0.7	0.4		10	30	0.2 - 1.1
Zn	***mg/kg***	**107**	**64.3**	**246.7**	**64.3 – 246.7**	**112.3**	**108.9**	**33.6**	**112.7**	**150**	**1500**	**35 - 100**
Al(1)	*mg/kg*	107	13,400	58,800	13,400 - 58,800	40313	43,450	14,235				77440 (1)

Table 1 b. Statistical parameters in "agricultural" area soils of Acerra

	unit	*N° sample*	*Minimum*	*Maximum*	*Range*	*Mean*	*Median*	*Std. Dev*	*UCL*	*RAL**	*IAL***	*BCRIN****
As	*mg/kg*	15	5.1	15.8	5.1 - 17.8	11.5	12.5	3		20	50	6 - 18
Be	***mg/kg***	**15**	**2**	**6.1**	**2 – 6.1**	**3.6**	**4.1**	**2**	**4.5**	**2**	**10**	**-**
Cd	*mg/kg*	15	0.2	0.7	0.2 – 0.7	0.5	0.4	0.1		2	15	0.1 - 0.5
Co	*mg/kg*	15	3.3	14.8	3.3 – 14.8	9.6	10.2	3.5		20	250	3 - 17
Cr	*mg/kg*	15	5.4	23.3	5.4 – 23.3	14.9	16.6	5.6		150	800	1 - 16
Cu	***mg/kg***	**15**	**33.5**	**180.4**	**33.5 – 180.4**	**103.7**	**101.5**	**45**	**122.9**	**120**	**600**	**4 - 200**
Hg	*µg/kg*	15	44	6775	44 - 6775	564.7	88.0	1719.8		1	5	0.01 – 0.1
Ni	*mg/kg*	15	6	21.1	6 – 21.1	13.4	15.0	5		120	500	1 - 19
Pb	***mg/kg***	**15**	**39.8**	**96.7**	**39.8 – 96.7**	**62.7**	**60.3**	**17.1**	**67.21**	**100**	**1000**	**20 - 80**
Sb	*mg/kg*	15	0.4	5.4	0.4 – 5.4	1.2	0.8	1.3		10	30	0.2 - 1.1
Zn	***mg/kg***	**15**	**53.8**	**176.3**	**53.8 -176.3**	**95.6**	**89.6**	**29**	**110.2**	**150**	**1500**	**35 - 100**
Al	***mg/kg***		13,600	57,000		38607	40,300	14,235				77440 (1)

Table 1-C Statistical parameters in "industrialized" area soils of Acerra
RAL = Residential use limit (D.lgs 152/06) **IAL = Industrial use limit (D.lgs 152/06) * BCRIN= Background value (De Vivo et al.2006).*

The results show that from all the metals analysed, the concentrations of Cu, Sb, Zn and Pb are the highest. From these, Cu, Be, Pb and Zn in topsoil exceed the Italian RAL (Residential Action Limit from D.lgs 152/06) and in some cases the concentrations of Pb and Zn are higher than IAL (Industrial Action Limit from D.lgs 152/06). Therefore, we identified these four metals as the contaminants of potential concern (COPC) that need to be included in the risk assessment.

	unit	*N° sample*	*Min*	*Max*	*Range*	*Mean*	*Median*	*Std. Dev*	*UCL**	*F***
As	*mg/kg*	5	0.01	0.08	0.01-0.08	0.05	0.06	0.03	-	-
Be	***mg/kg***	**5**	0.004	0.02	**0.004-0.02**	0.01	0.02	0.01	**-**	**-**
Cd	*mg/kg*	5	0.01	0.03	0.01-0.03	0.02	0.02	0.01	-	0,20
Co	*mg/kg*	5	0.02	0.07	0.02-0.07	0.05	0.06	0.02	-	-
Cr	*mg/kg*	5	0.12	0.31	0.12-0.31	0.22	0.22	0.09	-	-
Cu	***mg/kg***	**5**	1.48	3.77	**1.48-3.7**	2.67	2.72	1.11	**-**	**-**
Hg	*µg/kg*	5	0.94	2.91	0.94-2.91	1.80	1.68	0.85	-	-
Ni	*mg/kg*	5	0.08	0.11	0.08-0.11	0.10	0.10	0.01	-	-
Pb	***mg/kg***	**5**	0.10	0.41	**0.1-0.4**	0.24	0.24	0.14	**0.4**	**0.20**
Sb	*mg/kg*	5	0.03	0.13	0.03-0.13	0.08	0.08	0.05	-	-
Zn	***mg/kg***	**5**	2.33	4.85	**2.3-4.85**	3.46	3.32	1.07	**-**	**-**

Table 2 a. Statistical parameters in the vegetables (Chicorium endive) fresh weight
UCL (upper confidential limit) F reference value of metals in vegetables (FAO 2011)*

	unit	***N° sample***	***Minimum***	***Maximum***	***Range***	***Mean***	***Median***	***Std. Dev***	***UCL****	***F*****
As	*mg/kg*	5	0.05	0.2	0.05-0.2	0.12	0.10	0.08	-	-
Be	***mg/kg***	**5**	0.05	0.05	**-**	-	-	-	-	-
Cd	*mg/kg*	5	0.02	0.06	0.02-0.06	0.03	0.03	0.02	-	-
Co	*mg/kg*	5	0.03	0.07	0.03-0.07	0.05	0.06	0.02	-	-
Cr	*mg/kg*	5	2.1	3.5	2.1 – 3.5	2.96	3.10	0.57	-	-
Cu	***mg/kg***	**5**	3.88	7.6	**3.88-7.6**	5.58	5.13	1.45	-	-
Hg	*µg/kg*	5	0.5	11	0.5-11	4.10	3.00	4.07	-	-
Ni	*mg/kg*	5	0.2	0.4	0.2 – 0.4	0.30	0.30	0.10	-	
Pb	***mg/kg***	**5**	0.22	0.71	**0.22 – 0.71**	0.41	0.28	0.22	**0,6**	**0.2**
Sb	*mg/kg*	5	0.001	0.02	0.001 – 0.02	0.01	0.01	0.01	-	-
Zn	***mg/kg***	**5**	15.2	35.4	**15.2 – 35.4**	29.60	33.10	8.34	-	-

Table 2 b. Statistical parameters in the corn samples
UCL (upper confidential limit) F reference value of metals in vegetables (FAO 2011, EFSA 2011*

2.2 Enrichment factor

The EFs show elevated concentrations of Cd, Cr, Cu, Hg, Pb and Zn. for all the three land uses for Acerra's area (Fig. 4-5-6), with EFs being above 2 (from moderate to significant enrichment) but below 10 (significant enrichment). In addition, the EF of Ni is in some cases exceeded in the agricultural area.

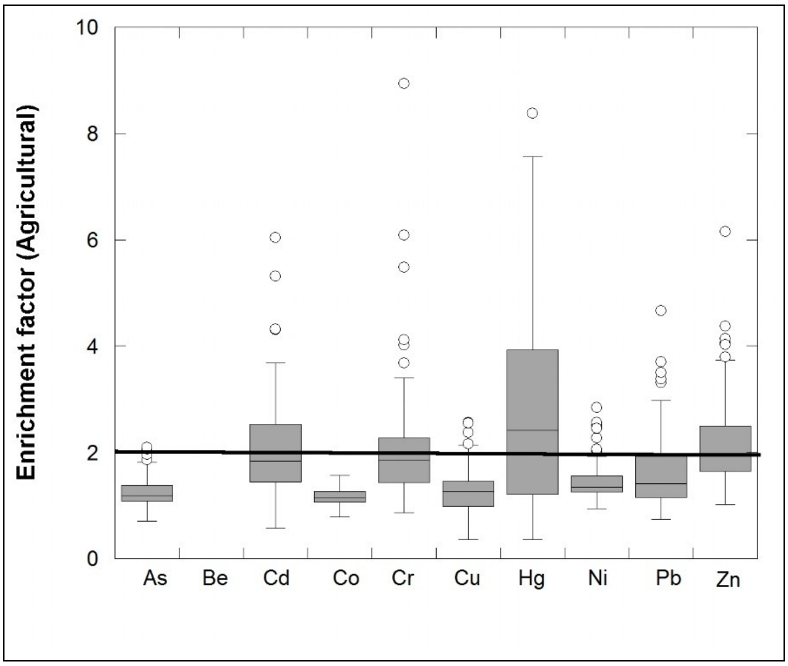

Figure 4 Enrichment factor of the major metals in agricultural area soils of Acerra

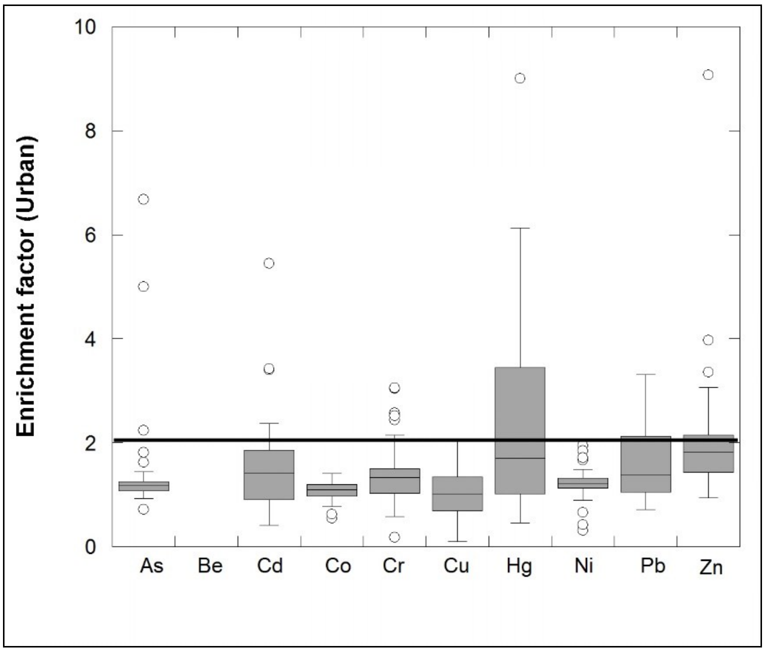

Figure 5 Enrichment factor of the major metals in urbanized area soils of Acerra

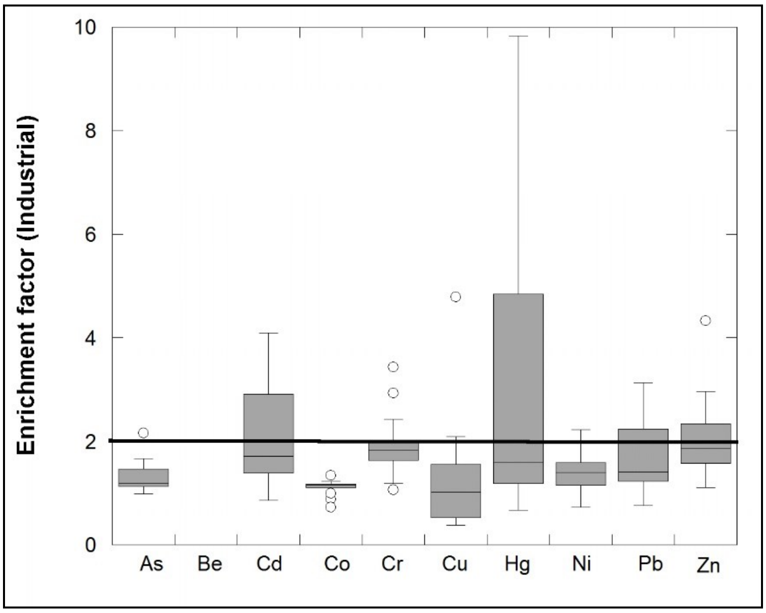

Figure 6 Enrichment factor of the major metals in industrialized area soils of Acerra

2.3 Pollution indexes of PTEs

Pollution indexes were calculated for Sb, As, Be, Cd, Co, Cu, Cr, Hg, Ni, Pb and Zn, by comparing each PTE's concentrations against the corresponding Italian soil quality standard (D.Lgs 152/06). The results show that the soils in the Acerra area are contaminated especially by four metals: Cu, Be, Pb and Zn (Fig.7- 8-9) for these metals, PI is > 1 (slight contamination). In the agricultural and industrial areas PI exceeds the limit value 1 for Cu, Be, Pb and Zn (Fig. 3-4). In the industrial area, PI is <1 for all studied PTEs (Fig 5).

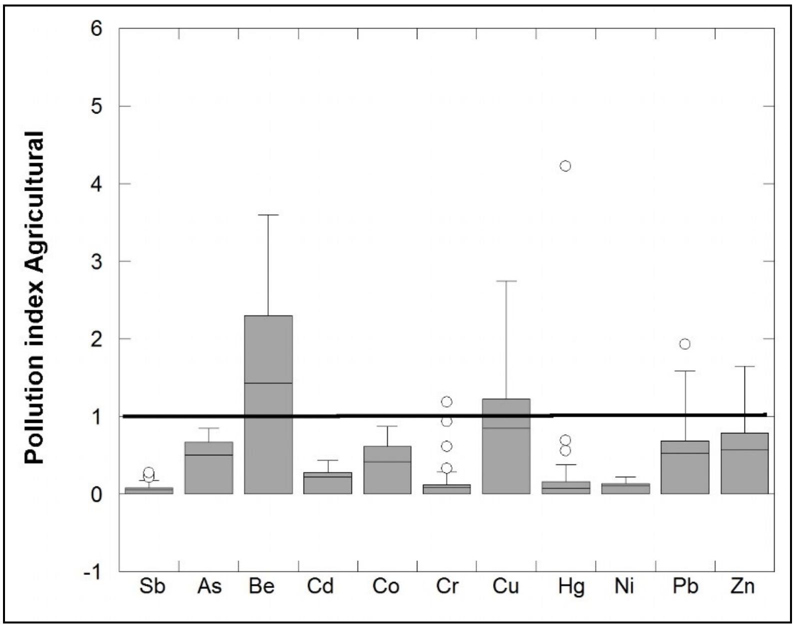

Figure 7 Pollution index of the major metals in agricultural area soils of Acerra

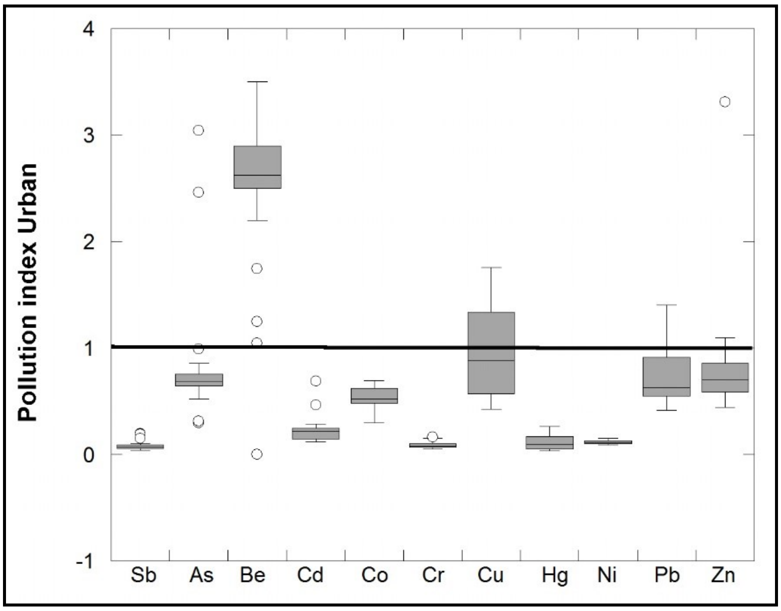

Figure 8 Pollution index of the major metals in urbanized area soils of Acerra

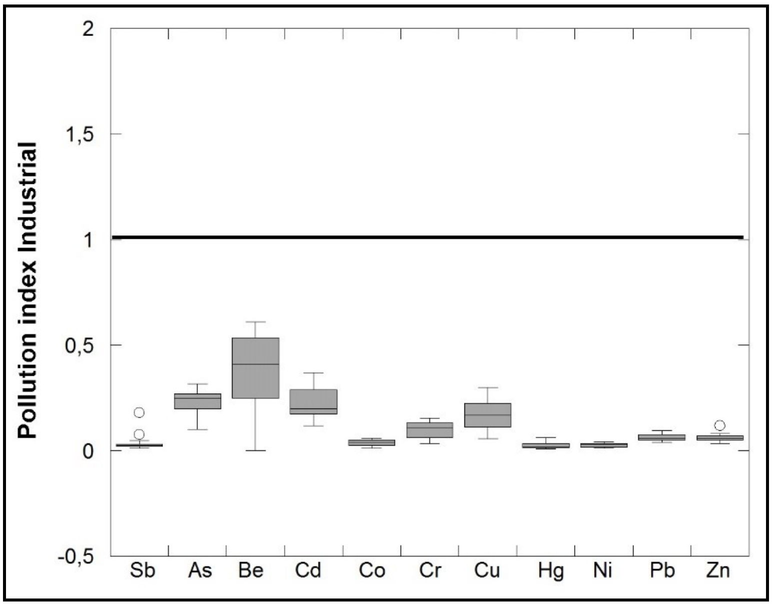

Figure 9 Pollution index of the major metals in industrialized area soils of Acerra

2.4 Translocation factor

Fig.10 shows the TF value for Cu, Pb, Zn. Ni, Co, As, Cd, Sb, Cr, Hg, Be for the edible part of vegetables samples (Chicorium endive). TF $_{total}$ value was below 1 for Zn, Cu ,Hg showing thus accumulation in plants. In case plant uptake is only from soil, such a value indicates the plants being a a hyper accumulator of that metal. The order of was accumulation as indicated by the TF was Zn > Cu > Hg (Fig. 10).

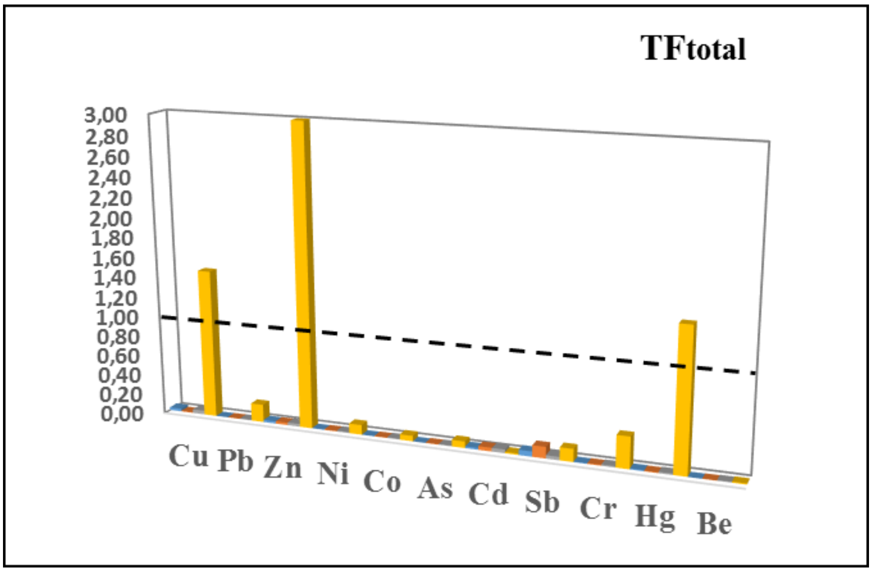

Figure 10 Translocation Factor indicating the transfer from soil to vegetables (Chicorium endive)

Fig.11 shows the TF total value of Cu, Pb, Zn. Ni, Co, As, CD, Sb, Cr, Hg, Be for soil to edible part of corn (Zea mais). TF total values from soil to vegetable was < 1, in this case they are considered as metal tolerant plants.

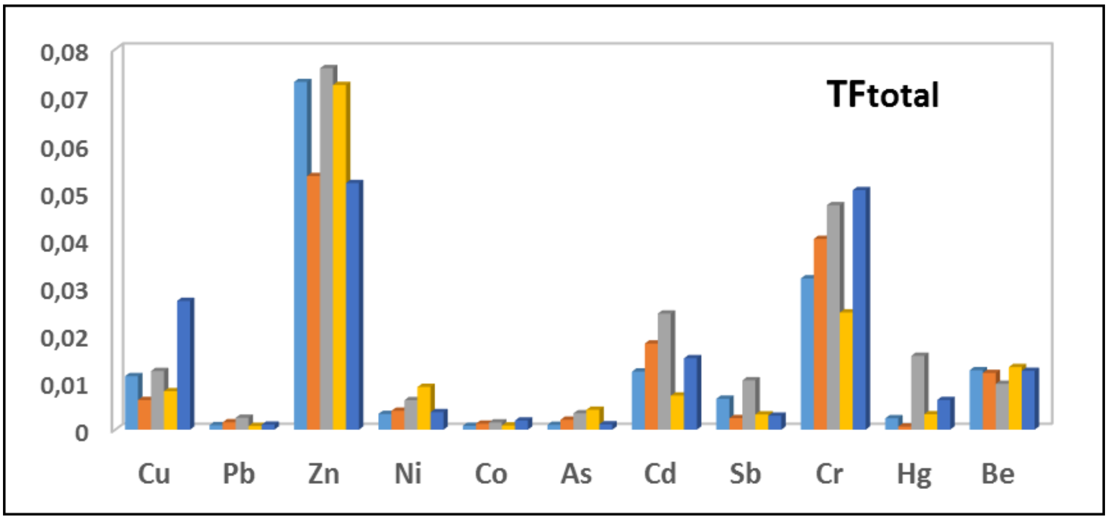

Figure 11 Translocation Factor on soil to corn (Zea mays)

2.5 Risks to human health

2.5.1 Tier 1 assessment

Fig.12. presents the results from the deterministic risk assessment. In the urban area, the estimated chronic daily intake (CDI) of children is higher than that of adults ($2,5*10^{-2}$). The CDI in the agricultural area is highest for Cu ($9*10^{-4}$), followed by Zn, Pb and Be. In the industrial area the corresponding order of the magnitude of CDI is Cu>Zn>Pb>Be. Children were considered as receptors only in the land use "urban" and not in the case of agricultural and industrial land use because they were assumed not to reside in the latter two areas.

Table 3. Parameters used in the determination of human exposure in Tier 1 risk assessment

Symbol (units)	Definition	Value	References
Cs	Concentration of COPC in soil	UCL (Table 1 a,b,c)	EPA
Cf	Concentration of COPC in food (vegetables and corn)	UCL (Table 2 a,b)	EPA
CA (Pm$_{10}$)	Concentration used for inhalation	Cs*Cpa*Fres*10^{-6}	Hawley et al.
ABS$_o$, ABS$_d$	Absorption efficiency factor of COPC by human body trough oral ingestion and dermal contact of soil particles, respectively	Abso = 100 Absd =0,1	EPA
AF	Soil to skin adherence factor		
AT$_{nc}$ (d)	Average time for non-carcinogenic effects		
BWa, BWc (kg)	Average body weight of adults and children, respectively	BWa: 70 ; BWc:15	EFSA
CD$_{ing}$,CDI$_{derm}$, CDI $_{inh}$	Chronic daily intake or exposure dose through oral ingestion, dermal contact and inhalation of soil particles, respectively		
DAIR$_a$, DAIR$_C$	Daily air inhalation rate of adult and child, respectively	DAIR$_a$ DAIR$_c$	
ED$_a$, ED$_c$	Exposure duration of adult and child, respectively	ED=25 Edc=6	EPA (2014)
EF	Exposure frequency of adult and child, respectively	EF= 350	EPA (2014)
Af	Frequency of daily event for skin contact with soil	Af = 0,18	
HI	Hazard index of heavy metal		
HQ$_{ing}$, HQ$_{derm}$, HQ$_{inh}$	Hazard quotient of heavy metal through oral ingestion, dermal contact and inhalation of soil particles, respectively		
IR*a*, IR*c*	Inhalation rate	IR$_a$ = 0,85; IR$_c$=0,48	
IRvegetables	Ingestion rate	IRa=0,14 (kg/meal) IRc = 0,059	EFSA (2005-2006)
IRcorn	Ingestion rate	IRa=0,066 IRc=0,0673	EFSA (2005-2006)
OSIR$_a$, OSIR$_c$ (mg*d)	Oral ingestion rate of soil for adult and child, respectively	OSIRa=200 OSIRc = 100	
RFd$_o$, RFd$_d$, Rfd$_i$	Reference dose of heavy metal through oral ingestion, dermal contact and inhalation of soil particles, respectively		EPA
SAE$_a$, SAE$_c$ (cm^2)	Surface area of exposed skin for adults and children, respectively	SAEa= 6032 SAEc= 2373	RAIS (EPA)
FI	fraction ingested from contaminated sites	FI=1	EPA

Table 3 Definition and reference value of some parameters for health risk assessment COPC in soil and food

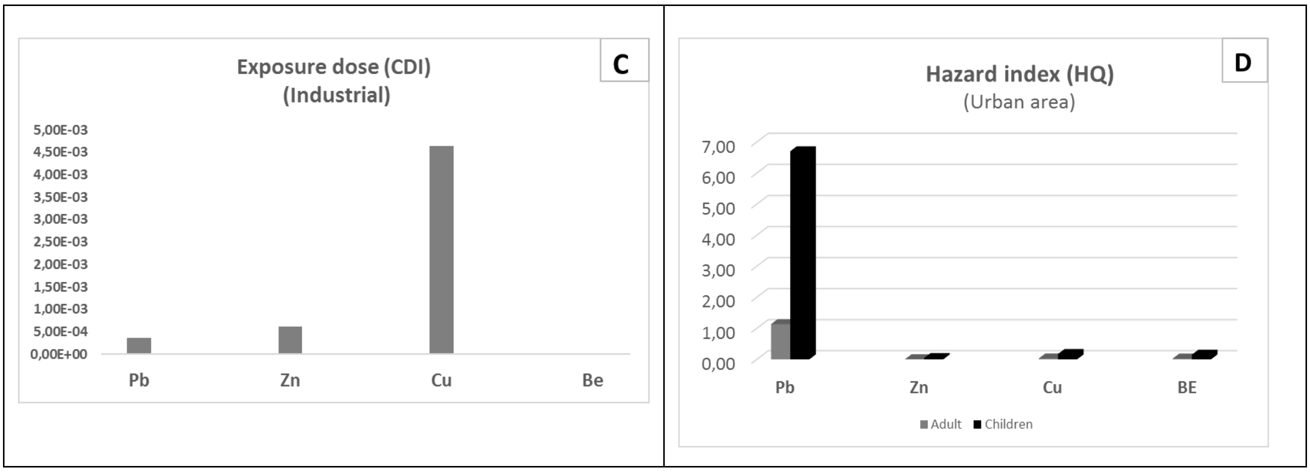

Figure 12 A, B, C Exposure dose related to Pb, Zn,Cu and Be. CDI = CDI ing + CD dermal + Cd inhalation HQ is the hazard index of Pb, Zn, Cu and Be related to adult and children.

Fig. 12 (d) shows that HI (hazard index) in the urban area is >1 only in the case of lead exposure of both children and adults.

3. *Conclusions*

In this study, we analysed the concentration of critical potentially toxic metals (COPCs): Be, Cu, Pb and Zn in topsoils from Acerra area and examined pollution index and enrichments factor, as compared with background values (De Vivo et al.2006). We observed that there is a slight contamination for these metals according to the Italian soil quality standards (D.lgs 152/06), and the element Pb is the most important contaminant in this area. Pb present in our samples comes from anthropogenic activities. Most of the samples imply the contribution of aerosols and fly ash as a source of lead as demonstrated from Pb isotopic approach in this area (Rezza et al., 2017).

We also determined the uncertainties where the concentration in the air are unknown and we estimated the value considered. The vegetables species (Chicorium endive) are a hyperaccumulator of that metal and maybe the pollution can be associated to different transport from the air to soil and later in the plants

The deterministic risk assessment indicate that exposure dose (CDI) of Pb, is higher for children in the urban soil and the hazard index (HQ) exceeds the permissible value, referred to reference dose from EPA. In case the deterministic calculations showed unacceptable risks (HQ > 1), analysis Tier 2, i.e. a probabilistic, risk assessment will be conducted using the CrystalBall software by Oracle (Dinis et al. 2010; Schumacher et al., 2001) .In probabilistic risk assessment, both the uncertainty (e.g. in concentration data) and the natural variability (related to exposure) are considered. This approach could be considered as future advancement of all this study. The analysis it is based on Monte Carlo simulation, the sampling technique most frequently used in risk site-specific risk assessment.

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CHAPTER V

Soil Geochemical Environmental Atlas of Campania Region

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ATLANTE
GEOCHIMICO-AMBIENTALE
DEI SUOLI DELLA CAMPANIA

Soil Geochemical Environmental Atlas of Campania

Introduction

The environmental contamination with toxic substances is due, among other reasons, to human activities, carried out for decades of negligence, decided by politicians with the aim of transforming those sites in more industrialised countries. It has finally become a crucial issue both in the relations between industrialized countries and within individual States. In this framework, we need a detailed understanding of these circumstances which depend on the variations of the environment due to the contamination of the territory. In studies whose objective is environmental investigations on a territory to assess the "health" of an area, environmental geochemistry helps. The outcome of result of this research is useful to identify hazards, the presence of substances harmful to human health and ecosystems. The origin of contamination can be attributed to different factors both natural and anthropogenic; the chemical reactivity, the ability to accumulate and transform plants and / or animals; these are some features that affect the dynamics of contaminants. This shows that the polluting substances are more dangerous if they are able to better accumulate; potentially toxic metals have the mentioned characteristics, and pose a risk to the health of animal and plant organisms as well as human being. Toxic metals such as Pb, Hg, Cd, Zn and Cu are very dangerous, and they have increased significantly within the environment as a result of human activities. The natural environment involved due to potentially toxic metals, are mostly at the surface of the water, groundwater and marine, river sediments, sea and lake, soils, vegetation and atmosphere. Therefore, it is important to activate an assessment and control of the environmental deterioration due to pollution; for this purpose, it is important to determine the natural background levels for every area (background) of certain elements in environmental matrices. The determination of the background concentration values allows us to characterize the levels of environmental contamination, discriminating the two human activities (anthropogenic) component compared to that of geological nature (geogenic). In the very urbanized area, the basic contents are referred to as background / baseline (see this atlas), because the concentration of an element, measured in a specific site, not always reflects precisely the natural content (background) but it might also reflect a not quantifiable anthropic contribution. In this case, the bottom levels should be defined as values of "current concentrations", indicated in scientific literature as a baseline value (*Salminen and Gregorauskiene, 2000*); they are still useful because they represent the reference values for the assessment of the anthropogenic impact on the territory. Therefore, the knowledge of the chemical composition of the national territory, assessment of possible changes due to the pollution and dissemination of these data, using modern techniques of graphic representation, are essential components for the preparation of plans monitoring and control of land resources, for the development of industrial activities, and human in general, bearing in mind the serious consequences that these may cause to the environment and to humans.

This geochemical and environmental atlas reports the results obtained from the surveys about the surface soils of Campania. In an area of around 13,595 km^2, 3535 soil samples were collected, analysed with a methodology which combines the ICP-MS (mass spectrometry Inductively Coupled Plasma) and ICP-ES (Emission Spectrometry coupled plasma inductively). It shows the properties of each chemical element, applications, health effects, as well as its distribution in soils geochemistry of Campania. The compiled geochemical maps are:

- Dot and interpolated to illustrate the concentrations distribution of the 47 analysed chemical elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr;
- Background / baseline map of 47 elements;
- Factor associations, from the factor in R-mode;
- the "geochemical" risk only for potentially toxic elements compiled bearing in mind the contamination thresholds concentration (CSC) by Legislative Decree no. 152/06.

The geochemical and environmental papers which comprise this Atlas represent a "snapshot" dating back to the time of sampling and may be used in the future as a reference for the environmental impact assessment of human activities in the area. They are also important tools, to evaluate the assessment of background levels (background) of the various chemical elements examined.

1. Study area

Campania (Southern Italy) is bordered to the North West by Lazio, to the north by Molise and to the east by the Puglia and Basilicata. The west-southwest is occupied of the Tyrrhenian Sea. Campania Region offers different morphologies. The Eastern hilly and mountainous areas were formed by the Apennine orogeny and are characterised by a series of peaks, plateau and highlands where the two main rivers (Volturno and Sele) flow. The western coastal area, developed in the NW–SE direction, is about 15% of the study area and represents a large structural depression now occupied by the Campanian and Sele plains and three volcanic complexes: Roccamonfina, Campi Flegrei, and Somma–Vesuvius. The plains, developed in subsiding grabens, have been filled by sediments originated from the erosion of the Apennine ridge and also from products of intensive volcanic activity. (Buccianti et al., 2015).

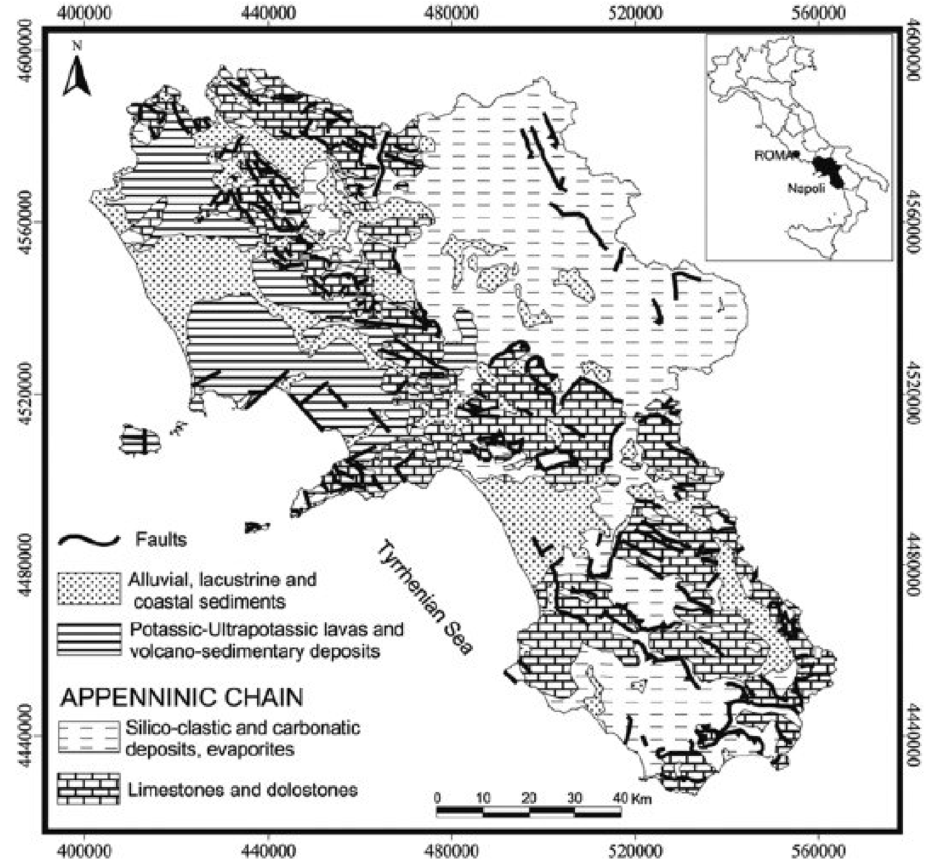


Figure 1 Simplified geological map of Campania region, Italy. From Lima et al. (2003).

Campania, with a 13,595 square kilometres area, has a 5,861,529 inhabitants' population (2015 ISTAT data on the resident population) and a density of around 429 inhabitants per km^2. It appears to be the first region by housing density and the third by population. The municipalities of Campanian Region are 550, divided in 5 provinces. The province of Naples is the one with the highest population (3,118,149 inhabitants in 92 municipalities) and the majority population density (2,645 inhabitants per km^2). The second province by population is Salerno (1,108,509 residents divided in 158 municipalities with a population density of 224 inhabitants per km^2), followed by Caserta (924,614 divided in 104 municipalities with a density of 349 inhabitants per km^2), Avellino (427,936 inhabitants divided into 118 municipalities with a population density of 153 inhabitants for km^2) and Benevento (282,321 inhabitants divided into 78 municipalities with a population density of 136 inhabitants per km^2).

Figure 2 Provinces of Campania Region

2. *Material and Methods*

For the achievement of 'Soil Geochemical Environmental Atlas of Campania', 3535 samples of topsoil (10-15 cm) were collected, where the whole territory has a surface of 13,595 km^2, and the density is approximately 1 sample for km^2 (Fig.3)

For the sampling methods, the protocol given in FOREGS Manual (*Salminen et al., 1998*) was followed in order to limit the sample contaminations in the sampling operation, listed below:

- use of tools, well-cleaned, plastic or stainless steel 18/10, unglazed, in order to avoid contamination from metal;
- use of disposable plastic gloves, to change to the withdrawal of each single sample;
- pre-decontamination of tools to reduce the presence of a 'contamination' from the other elements taken before;
- before sieving, on the field, in order to reduce the bigger component characterized mostly by pebbles, roots, foliage, etc. and keep the thinnest fraction useful for the analysis;
- accurate samples labelling;

- field records containing information on the depth of each sample, the depth of the entire section (and therefore of the source rock), proximity to possible sources of anthropogenic contamination (road, gas stations, garages / nautical, industries, pesticides, insecticides, herbicides, etc.), morphological description of the site, vegetation, moisture content of the sample and its organic content;
- Pictures of sections of the site with the meter used as reference

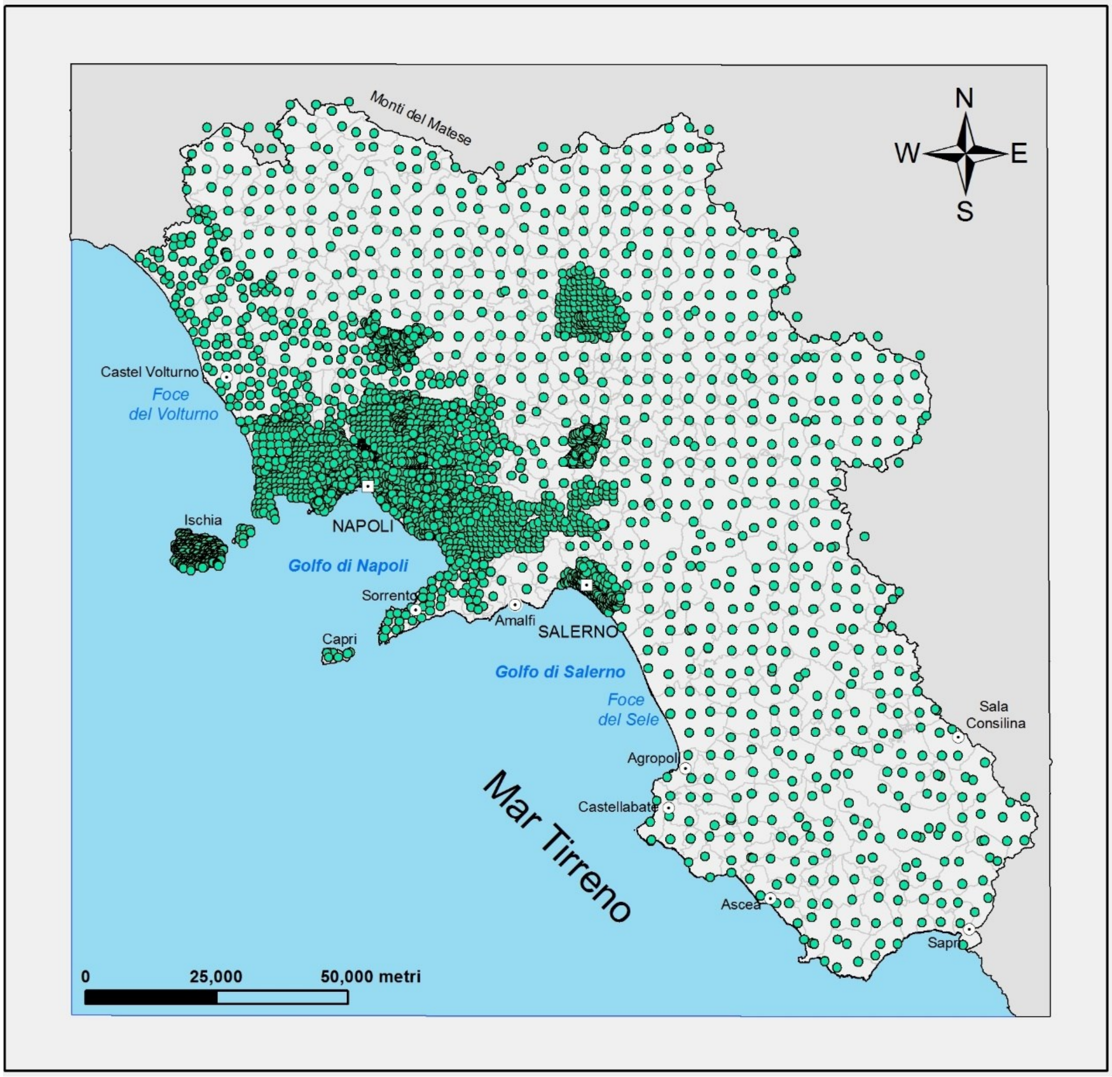


Figure 3 Map of sampling sites

In particular, for each sampling site a total quantity of soil equal to about 2.5 kg has been collected; aliquots were taken in 0.5 kg five different points at a distance of about 10 m from each other. Soil samples were then homogenized in a single sample and stored in plastic bags, then closed with string, in order to remove metal contamination. For the precise location of sampling sites it has been used topographic boards I.G.M. scale 1: 25.000, using informatics support. The samples were collected during the collection of more samples in the year 2011, the last of which was collected in 2015. The big database used for this atlas has been achieved in the space of ten years. Once collected, the samples were taken to the laboratory for their preparation, before being shipped to the laboratory for chemical analysis. The soils were dried with the use of infrared lamps, in such a way that the temperature did not exceed 35 ° C. The sieve used a fraction of <2 mm which best meets the objectives of this geochemical survey for environmental purposes (*De Vivo et al., 2004*).

The chemical analyses, performed at ACME Analytical Laboratories Lab. Ltd. (now Bureau Veritas) (Vancouver, Canada) have affected 47 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr. They were determined through an analytical methodology that combines the ICP-MS (mass spectrometry inductively coupled plasma) and plasma ICP-ES (Inductively Coupled Emission Spectrometry).

In order to process only those data that have a good analytical value, quality controls on the laboratories data have been applied. *Table 1* shows the accuracy and precision values sample's geochemical data of the Campania Region considered in this work, after the application of the selected analytical technique.

Accuracy is defined as the closeness degree of the measurement of a quantity to its true value. The laboratory accuracy error has been determined using the following formula:

$$[(|X - TV|) / TV] * 100 \qquad (1)$$

X= laboratory's analysis result for the standard sample, TV= true value of the standard sample.

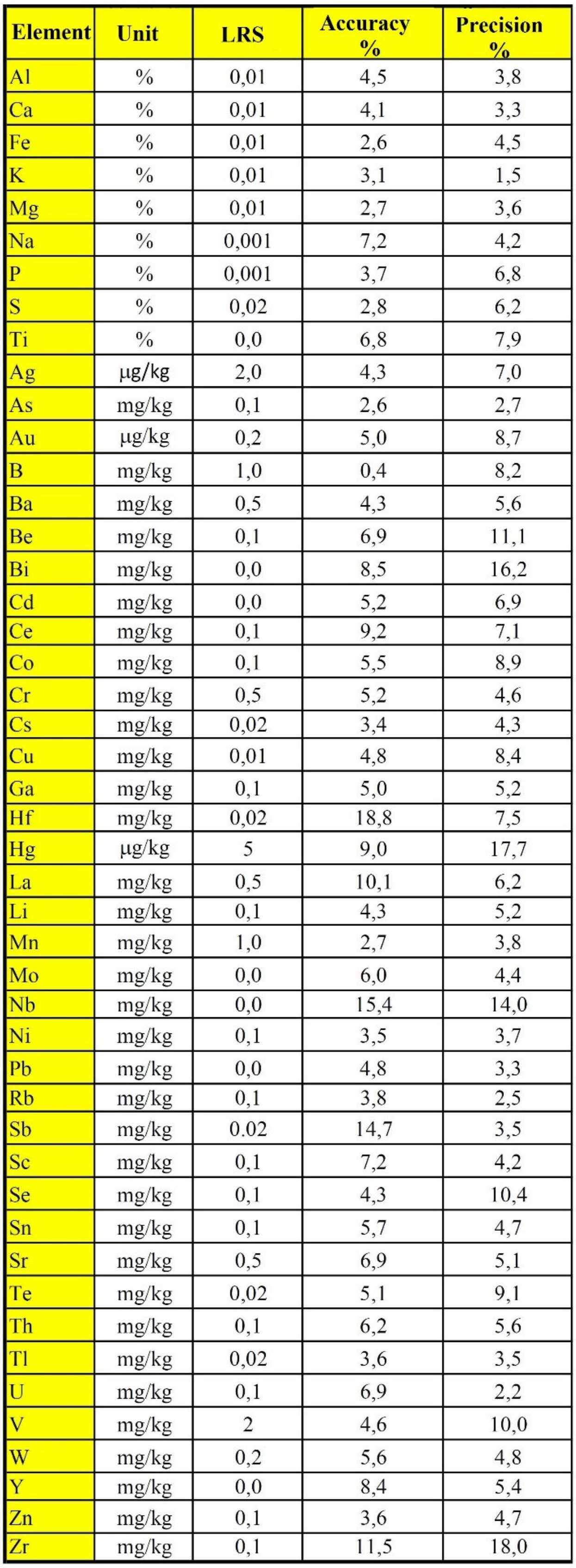
For the measurement of the analysis accuracy error, Acme's in-house reference materials have been used: for soil samples the standard was DS7. Acceptable accuracy error values shall not exceed 15%.

Precision is defined as the degree of reproducibility of a measurement; in other words, it is the degree of how repeated measurements offer the same results under the same conditions. The precision has been calculated as relative percentage difference (%RPD) using the formula:

$$\%\,RPD = [\,|S\text{-}D| / (|S+D|/2)]\ {*}100 \qquad (2)$$

S = Standard sample concentration, D= Duplicate

Precision of the performed analysis has been calculated on 6 in-house replicates and one blind duplicate for soils. Values can be considered good if the RPD is < 35% for soils.

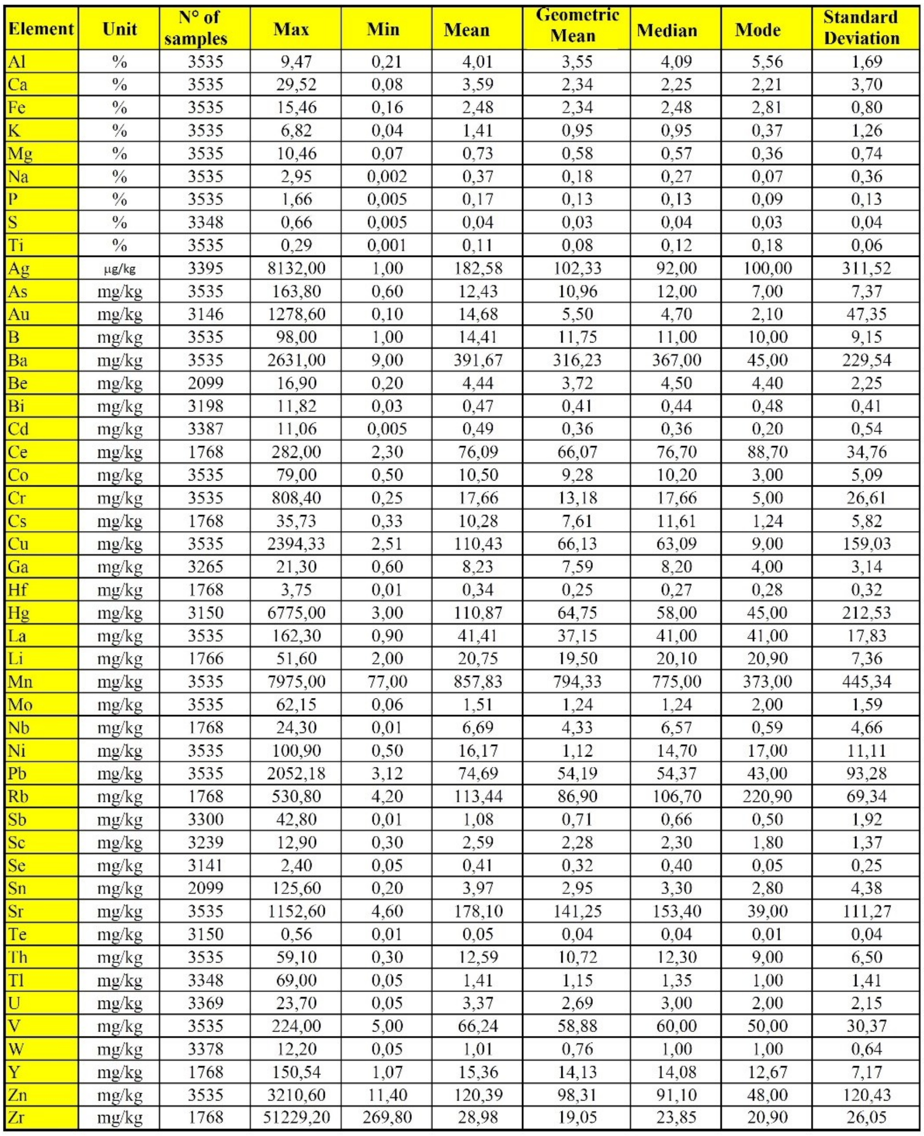


Element	Unit	LRS	Accuracy %	Precision %
Al	%	0,01	4,5	3,8
Ca	%	0,01	4,1	3,3
Fe	%	0,01	2,6	4,5
K	%	0,01	3,1	1,5
Mg	%	0,01	2,7	3,6
Na	%	0,001	7,2	4,2
P	%	0,001	3,7	6,8
S	%	0,02	2,8	6,2
Ti	%	0,0	6,8	7,9
Ag	µg/kg	2,0	4,3	7,0
As	mg/kg	0,1	2,6	2,7
Au	µg/kg	0,2	5,0	8,7
B	mg/kg	1,0	0,4	8,2
Ba	mg/kg	0,5	4,3	5,6
Be	mg/kg	0,1	6,9	11,1
Bi	mg/kg	0,0	8,5	16,2
Cd	mg/kg	0,0	5,2	6,9
Ce	mg/kg	0,1	9,2	7,1
Co	mg/kg	0,1	5,5	8,9
Cr	mg/kg	0,5	5,2	4,6
Cs	mg/kg	0,02	3,4	4,3
Cu	mg/kg	0,01	4,8	8,4
Ga	mg/kg	0,1	5,0	5,2
Hf	mg/kg	0,02	18,8	7,5
Hg	µg/kg	5	9,0	17,7
La	mg/kg	0,5	10,1	6,2
Li	mg/kg	0,1	4,3	5,2
Mn	mg/kg	1,0	2,7	3,8
Mo	mg/kg	0,0	6,0	4,4
Nb	mg/kg	0,0	15,4	14,0
Ni	mg/kg	0,1	3,5	3,7
Pb	mg/kg	0,0	4,8	3,3
Rb	mg/kg	0,1	3,8	2,5
Sb	mg/kg	0.02	14,7	3,5
Sc	mg/kg	0,1	7,2	4,2
Se	mg/kg	0,1	4,3	10,4
Sn	mg/kg	0,1	5,7	4,7
Sr	mg/kg	0,5	6,9	5,1
Te	mg/kg	0,02	5,1	9,1
Th	mg/kg	0,1	6,2	5,6
Tl	mg/kg	0,02	3,6	3,5
U	mg/kg	0,1	6,9	2,2
V	mg/kg	2	4,6	10,0
W	mg/kg	0,2	5,6	4,8
Y	mg/kg	0,0	8,4	5,4
Zn	mg/kg	0,1	3,6	4,7
Zr	mg/kg	0,1	11,5	18,0

Table.1 Accuracy and precision

2.1 Univariate statistics

A traditional statistical analysis of the analytical data of the soils (*Sinclair, 1976*) has been performed by KaleidaGraph 4.0 program. The distribution of the elemental concentrations for all the 3535 soil samples has been plotted using histograms and cumulative frequency curves. (*Tab.2*)



Element	Unit	N° of samples	Max	Min	Mean	Geometric Mean	Median	Mode	Standard Deviation
Al	%	3535	9,47	0,21	4,01	3,55	4,09	5,56	1,69
Ca	%	3535	29,52	0,08	3,59	2,34	2,25	2,21	3,70
Fe	%	3535	15,46	0,16	2,48	2,34	2,48	2,81	0,80
K	%	3535	6,82	0,04	1,41	0,95	0,95	0,37	1,26
Mg	%	3535	10,46	0,07	0,73	0,58	0,57	0,36	0,74
Na	%	3535	2,95	0,002	0,37	0,18	0,27	0,07	0,36
P	%	3535	1,66	0,005	0,17	0,13	0,13	0,09	0,13
S	%	3348	0,66	0,005	0,04	0,03	0,04	0,03	0,04
Ti	%	3535	0,29	0,001	0,11	0,08	0,12	0,18	0,06
Ag	μg/kg	3395	8132,00	1,00	182,58	102,33	92,00	100,00	311,52
As	mg/kg	3535	163,80	0,60	12,43	10,96	12,00	7,00	7,37
Au	mg/kg	3146	1278,60	0,10	14,68	5,50	4,70	2,10	47,35
B	mg/kg	3535	98,00	1,00	14,41	11,75	11,00	10,00	9,15
Ba	mg/kg	3535	2631,00	9,00	391,67	316,23	367,00	45,00	229,54
Be	mg/kg	2099	16,90	0,20	4,44	3,72	4,50	4,40	2,25
Bi	mg/kg	3198	11,82	0,03	0,47	0,41	0,44	0,48	0,41
Cd	mg/kg	3387	11,06	0,005	0,49	0,36	0,36	0,20	0,54
Ce	mg/kg	1768	282,00	2,30	76,09	66,07	76,70	88,70	34,76
Co	mg/kg	3535	79,00	0,50	10,50	9,28	10,20	3,00	5,09
Cr	mg/kg	3535	808,40	0,25	17,66	13,18	17,66	5,00	26,61
Cs	mg/kg	1768	35,73	0,33	10,28	7,61	11,61	1,24	5,82
Cu	mg/kg	3535	2394,33	2,51	110,43	66,13	63,09	9,00	159,03
Ga	mg/kg	3265	21,30	0,60	8,23	7,59	8,20	4,00	3,14
Hf	mg/kg	1768	3,75	0,01	0,34	0,25	0,27	0,28	0,32
Hg	mg/kg	3150	6775,00	3,00	110,87	64,75	58,00	45,00	212,53
La	mg/kg	3535	162,30	0,90	41,41	37,15	41,00	41,00	17,83
Li	mg/kg	1766	51,60	2,00	20,75	19,50	20,10	20,90	7,36
Mn	mg/kg	3535	7975,00	77,00	857,83	794,33	775,00	373,00	445,34
Mo	mg/kg	3535	62,15	0,06	1,51	1,24	1,24	2,00	1,59
Nb	mg/kg	1768	24,30	0,01	6,69	4,33	6,57	0,59	4,66
Ni	mg/kg	3535	100,90	0,50	16,17	1,12	14,70	17,00	11,11
Pb	mg/kg	3535	2052,18	3,12	74,69	54,19	54,37	43,00	93,28
Rb	mg/kg	1768	530,80	4,20	113,44	86,90	106,70	220,90	69,34
Sb	mg/kg	3300	42,80	0,01	1,08	0,71	0,66	0,50	1,92
Sc	mg/kg	3239	12,90	0,30	2,59	2,28	2,30	1,80	1,37
Se	mg/kg	3141	2,40	0,05	0,41	0,32	0,40	0,05	0,25
Sn	mg/kg	2099	125,60	0,20	3,97	2,95	3,30	2,80	4,38
Sr	mg/kg	3535	1152,60	4,60	178,10	141,25	153,40	39,00	111,27
Te	mg/kg	3150	0,56	0,01	0,05	0,04	0,04	0,01	0,04
Th	mg/kg	3535	59,10	0,30	12,59	10,72	12,30	9,00	6,50
Tl	mg/kg	3348	69,00	0,05	1,41	1,15	1,35	1,00	1,41
U	mg/kg	3369	23,70	0,05	3,37	2,69	3,00	2,00	2,15
V	mg/kg	3535	224,00	5,00	66,24	58,88	60,00	50,00	30,37
W	mg/kg	3378	12,20	0,05	1,01	0,76	1,00	1,00	0,64
Y	mg/kg	1768	150,54	1,07	15,36	14,13	14,08	12,67	7,17
Zn	mg/kg	3535	3210,60	11,40	120,39	98,31	91,10	48,00	120,43
Zr	mg/kg	1768	51229,20	269,80	28,98	19,05	23,85	20,90	26,05

Table.2 Statistical parameters

2.2 Geochemical map production

In this part of the work the various types of geochemical maps are presented and described, compiled for the chemical elements in soil analysed by the Campania Region.

2.2.1 Dot map

Dot map is the distribution of concentrations dot map, useful for information on the exact concentration distributions when the sample was collected.

2.2.2 *Interpolated map*

Interpolated data maps help to get information of a spatial range. In fact, it is not possible to know the exact concentration at any point of the study area. This type of map is the best possible approach to the exact concentration values at not sampled points. Based on the cell size used during the sampling it is possible, using a detected radius interpolation regarding the element concentration, to reclassify the dot value on a spatial value through a Multifractal Inverse Distance Weighted (MIDW) method (*Cheng, 1999*) available in the software GeoDAS (*Cheng, 2003*); To perform interpolated maps, the multifractal analysis filter method used is Concentration-Area model (C-A). (Fig.4)

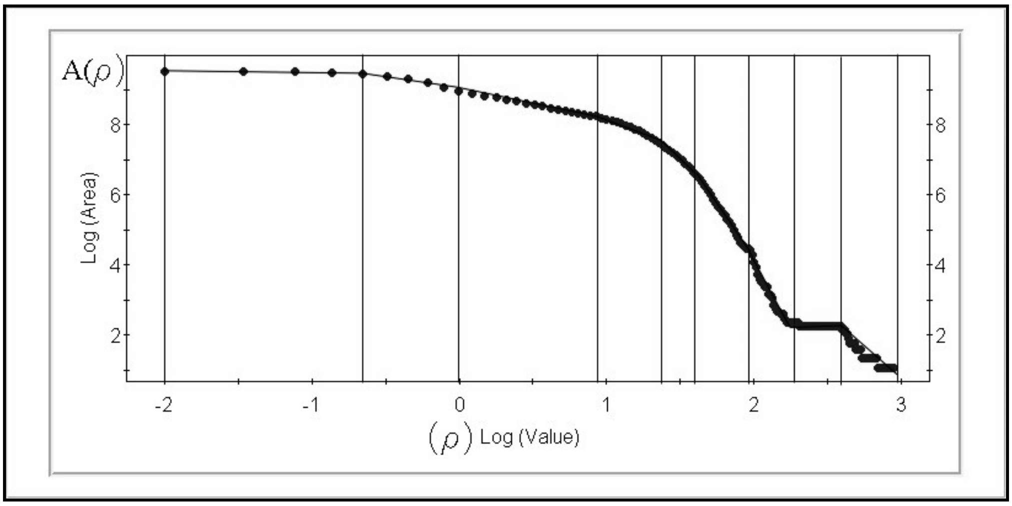


Figure 4 C-A Plot

2.2.3 *Baseline/background map:*

Baseline maps have also been executed in this work. This kind of maps are the principal way to get information about the statistically higher concentration levels found in a detected area. On literature, the term "background content" (natural background) designates the concentration of natural elements, including the presence of abnormal concentrations due to mineralization. The term baseline should mean measured concentrations of elements present in a given site, including, therefore, the presence of elements of anthropogenic origin.

2.2.4 *Factor scores association map*

Interpretation and evaluation of geochemical concentrations of different elements have been performed, both for geo-mining and environmental purposes. For this information it is very useful the use of multivariate statistical techniques such as factor analysis in R-mode.

It allows a quantitative assessment of different variables and their mutual influence, thus allowing to group elements by factorial associations depending on their coefficient of correlation.

This allows to identify possible correlations between the distribution of the individual elements, lithological characteristics, potential mineralizing processes, enrichment phenomena associated surface environment, pollution and other anthropogenic elements (*De Vivo et al. 1981, 2004*).

Through the distribution of factorial associations, it is possible to assess the impact of each association of elements in each site. In the case of Campania's soils, it has been chosen the four factor model and the interpolated maps of the distribution of the factor scores. The four associations of elements were compiled using the same methodology (IDW Multifractal) used for the compilation of interpolated maps.

In addition to factor analysis in R-mode, these data on the surface soils of Campania have been used by Buccianti et al. (2015) for an elaboration of statistical multivariate through compositional analysis data (CoDA) with the objective of exploring an extensive data file, in order to characterize its structure.

The file is considered to be formed by the concentrations of 23 inorganic chemicals measured in the soils of 3535 sites together with the information on the coordinates, geology and surface phenomena. This study has allowed to identify four macro arising from the associations of geo-lithological conditions and distribution of the elements:

6. Association La, Th, Ti, Na, K, regarding soils originated from volcanism activity (Na-K) F1 (Fig.5);
7. Association of Ca, Mg and Sr, regarding limestone and dolomites and related terrigenous compounds F2 (Fig.5);
8. Association of Co, Cr and Ni, regarding 'flysh' formation F3 (Fig.6);
9. Association B, P, Sr and Cu, regarding the presence of fertilizers by agricultural activities F4 (Fig.6).

In addition, the enrichment of certain elements (eg. Pb, Zn, Cr, Cd) together with being linked to specific natural geochemical conditions, are affected, especially in urban areas, by human activity.

2.3 Map of CSC intervention limit

Maps of 15 exceedances elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn) have been obtained by substituting the values of concentration contamination threshold established by Legislative Decree 152/06, for each of the destination-specific use, our ranges of dot maps previously determined in a statistical analysis (Table 2). Like this, it was possible to determine, for each sampled site, which are the points that exceed or are lower than these thresholds (residential / public parks, commercial / industrial) for each of the elements considered.

3. ***Results and discussions***

In this paragraph, part of the results of this research is shown: Soil Geochemical Environmental Atlas of Campania (Lima et al., 2016), that I executed to perform the part of sampling and realization of maps during my PhD programme.

I described the results in detail about some elements of this area, such as: S (major element); Sb, As, Cu and Pb, (toxic metals); U (trace elements).

3.1 Major elements

The description of each element refers to that of the Geochemical Atlas of Europe: FOREGS (Salminen, R.; Batista, M.J.; Bidovec, M.; Demetriades, A.; De Vivo, B.; De Vos, W.; Duris, M.; Gilucis, A.; Gregorauskiene, V.; Halamić, Josip; Heitzmann, P.; Lima, A.; Jordan, G.; Klaver, G.; Klein, P.; Lis, J.; Locutura, J.; Marsina, K.; Mazreku, A.; O'Connor, P.J.; Olsson, S.A.; Ottesen, R.-T.; Petersell, V.; Plant, J.A.; Reeder, S.; Salpeteur, I.; Sandstrom, H.; Siewers, U.; Steenfelt, A.; Tarvainen, T.)

3.1.1 Sulphur (S)

Sulphur belongs to group 16 of the periodic table, along with O, Se and Te. Sulphur primarily occurs in four oxidation states in geological environments: S^{2-} (sulphides and sulfosalts), S^0 (elemental sulphur), S^{4+} (SO2 in volcanic gas) and S^{6+} (SO_3 in volcanic gas). Its oxidation state determines how S is incorporated into mineral phases (Wedepohl 1978). The most important occurrence of S associated with igneous rocks is in metal sulphide mineralisation. Many metals exhibit limestone tendencies, leading to the formation of many sulphide and sulfosalt ore minerals, such as chalcosite, pyrite, sphalerite, galena, cinnabar, stibnite and oldhamite (Wedepohl 1978). Evaporite minerals generally take the form of anhydrous or hydrated sulphates, e.g., barite, gypsum, anhydrite and epsomite. Pyrite present in sediments is another source of sulphate. Common rock-forming silicate minerals, including feldspar, mica and pyroxene, also contain significant amounts of sulphur, typically in the range 20 to 500 mg kg^{-1}. Sodalite commonly contains S up to percentage levels, and non-silicates, such as apatite, can contain up to 1100 mg kg^{-1} (Wedepohl 1978).

Sulphates are discharged into the aquatic environment in wastes from industries that use sulphates and sulphuric acid, such as mining and smelting operations, kraft pulp and paper mills, textile mills and tanneries. Other potential anthropogenic sources include fertiliser and pesticide production and use, coal combustion, petrol refining, and vulcanisation of rubber. Sulphur is essential to life; it is a major element in all plants, and a minor constituent of virtually all parts of the human body, including fats, body fluids and skeletal minerals. It is used in cell protection, liver function and digestive processes, and is an important part of vitamin B1 and insulin. Sulphate is one of the least toxic 311 anions, although relatively high levels (>1000 mg l^{-1}) may cause adverse effects in some aquatic species and catharsis and gastrointestinal irritation in humans (USEPA 1971). The presence of sulphate in drinking water can also result in a noticeable taste. Taste threshold concentrations for various sulphate salts are generally agreed to be about 500 mg $l^{-1.}$

S content in soils ranges from a minimum value of 0.005% to a maximum value of 0.7% with a median value of 0.04%. Concentrations are on average higher than those for European soils (median 0.02%) although the maximum value of European concentration is significantly higher (11.2%). The Italian level concentrations are similar, although slightly lower, compared to surface soils of Campania (concentration range from 0.009 to 0.6% and median 0.02%).

Dot map shows that concentrations at regional scale are low; 70% of the samples have a <0.05% content, while only 5% have higher concentrations with values between 0.09 and 0.7%. The latter are distributed in a way point in the coastal soils, in the high north of Caserta Alife, all along the Sorrento peninsula, in the Vesuvius, in the Agro Sarnese-Nocerino, at the mouth of the Sele in the Vallo di Diano (Fig.7).

Interpolated map (Fig.8) shows that most of the territory shows <0.04% concentrations, and that the areas affected by relatively high values (S> 0.07%), focused on the coast of Domizio-Phlegraen area, near Mt. Matese, from Sorrento to Agro Sarnese-Nocerino, and, in the Salerno area between Monte Pennacchio and Laviano, at the mouth of the Sele in the Vallo di Diano. High concentrations are located, in detail, in soils of the Vesuvian municipality and especially across Phlegraen Fields (Monte di Procida, Bacoli and Pozzuoli). This higher concentration is attributed to volcanic activity, which is very intense in this area and it is characterized by the presence of the Solfatara in Pozzuoli and numerous fumaroles scattered throughout the territory. The high values discovered in other areas are most likely influenced by human activities, especially by agricultural practices.

The intensive use of fertilizers in farming areas, such as those between Laviano and San Gregorio al Magno, Mt. Matese, in the Agro Sarnese Nocerino- and Vallo di Diano, can have relatively high concentrations of S associated with those P.

Background/baseline map shows that concentrations present low values territory (S <0.05%). The concentrations > 0.05% fall in correspondence of soils that were formed on volcanic lithologies and/or located in cultivated areas. In these cases, the natural component could be added to an anthropic contribution, mainly due to the use of fertilizers and pesticides in agricultural practices (Fig.9).

3.2 Toxic metals

The description of each element refers to that of the Geochemical Atlas of Europe: FOREGS (Salminen, R.; Batista, M.J.; Bidovec, M.; Demetriades, A.; De Vivo, B.; De Vos, W.; Duris, M.; Gilucis, A.; Gregorauskiene, V.; Halamić, Josip; Heitzmann, P.; Lima, A.; Jordan, G.; Klaver, G.; Klein, P.; Lis, J.; Locutura, J.; Marsina, K.; Mazreku, A.; O'Connor, P.J.; Olsson, S.A.; Ottesen, R.-T.; Petersell, V.; Plant, J.A.; Reeder, S.; Salpeteur, I.; Sandstrom, H.; Siewers, U.; Steenfelt, A.; Tarvainen, T.)

3.2.1 Antimony (Sb)

Antimony is a member of group 15 of the periodic table, along with N, P, As and Bi. The chemistry and geochemistry of Sb is most similar to that of As. Antimony is a low-abundance limestone element forming several rather rare minerals including stibnite, valentinite and kermesite, but is more usually present at trace levels in minerals such as ilmenite, Mg-olivine, galena, sphalerite and pyrite. During magmatic processes Sb can be substituted for Fe in minerals such as olivine and ilmenite, but it tends not to be preferentially enriched at any stage of magmatic fractionation (Ure and Berrow, 1982). Boyle and Jonasson (1984) state that there appear to be some differences in the Sb content of igneous rocks; intermediate and felsic rocks being slightly enriched compared to other igneous rock types. *Lueth (1999b*) mentions a crustal abundance of 0.5 mg kg-1, and a systematic increase in its concentration in igneous rocks from mafic <1.0 mg kg-1 to felsic 7.8 mg kg-1. Fine-grained argillaceous and organic-rich sediments are typically enriched in Sb (>1 mg kg-1) relative to their parent igneous lithologies, reflecting the strong tendency for the element to become adsorbed to hydrous oxides, organic residues and clay minerals in favourable environments (*Ure and Berrow 1982*).

In stream sediment, Sb is present primarily in detrital sulphide minerals, e.g., stibnite, sphalerite and galena, some of which may weather relatively rapidly under acid, oxidising conditions. Further remobilisation of Sb is rather limited due to the tendency of Sb3+ to hydrolyse to insoluble basic salts and be adsorbed by secondary hydrous oxides of Fe, Al and Mn at pH levels within the range 4.0–8.0. Antimony in the form of Sb_2O_3 is largely immobile. In studies of polluted stream sediment from North Carolina, USA, *Shuman et al. (1978)* found that in clean sediments most Sb was in crystalline minerals, whereas in the polluted sediment, containing higher levels of Sb, the element was largely held in oxide coatings, and with some in the organic fraction.

In soil, Sb is enriched in the surface horizon due chelation with organic matter, but there is also an enrichment in the B-horizon as a result of strong adsorption and absorption of Sb by hydrous Fe-oxides, clay minerals and wad (*Boyle and Jonasson 1984*). Average values for soil are given by *Wedepohl (1978*) as 1 mg kg-1 and by *Kabata Pendias (2001)* as 0.9 mg kg^{-1}. With its low natural abundance, Sb is a useful indicator of industrial contamination. Anthropogenic Sb is associated with metalliferous mining (gold and sulphides) and metal smelting (Edwards et al. 1995). It is also associated with coal combustion, urban waste and car exhaust fumes, and is used in the manufacture of lead solder, batteries, arms and tracer bullets, composite car body panels and dashboards (*Reimann and de Caritat 1998*), as well as flame proofing compounds, paints, ceramic enamels, glass and pottery.

Sb content in the Campania region ranges from 0.01 mg/kg to 43 mg / kg, with a median value of 0.66 mg / kg. In surface soils, values greater than that of European soils appear (range 0.02 to 31.1 mg / kg, with a median value of 0.60 mg / kg) (De Vos et al., 2006). To compare this regional values with values of Italian soils (including an interval from 0.13 mg / kg to 4.26 mg / kg and median of 0.71 mg / kg), it is clear that the maximum concentration for those is lower than Campania region values, while the median values are comparable (De Vivo et al., 2008a). This data is shown in the Fig.10, where 95% of the sampled sites had <3 mg / kg concentrations, equal to Italian soil, 5% of the samples show > 3 mg / kg concentrations, 4.2% have concentrations between 3 and 10 mg / kg, 0.7% concentrations between 10 and 30 mg / kg and only three samples representing 0.1%, have concentrations between 30 and 43 mg / kg. Concentrations of Sb> 3 mg / kg are collected in the Agro Sarnese-Nocerino (in the Solofrana basin), in that Domizio- Aversa and in a small area of Vallo di Diano. The remaining part of the region (80%) has values of <1 mg / kg similar to the background values (Cicchella et al., 2005).

Interpolated map shows clearly, like the dot map that in general, most of Campania Region is characterized by low concentrations of Sb, <0.8 mg / kg, with the areas with relatively higher concentrations (Sb> 1.6 mg / kg) which are not very extended (Fig.11).

Map of baseline/background (Fig.12) shows that there are two large areas: one including the Apennines with <0.5 mg / kg values, and the other more along the coast, with <1.5 mg / kg values, which included higher values (Sb> 1.5 mg / kg) corresponding to Naples and Salerno city, the basin of Solofra, the Vesuvian and Domizio – Phlegraean territories, reflecting a big contribution from intensive human activity.

In the map of CSC (Fig.13) it can be observed that 0.3% samples exceed the (CSC) of residential use (RAL) which is equal to 10 mg / kg, as established by Legislative Decree 152/06, while the samples that exceed CSC commercial / industrial (IAL) (30 mg / kg) are only three. These values are limited to Naples and Salerno cities and the Agro Nocerino area.

3.2.2 Arsenic (As)

Arsenic, along with P, Sb and Bi, is a chemical element belonging to group 15 of the periodic table. The chemistry and geochemistry of As is most similar to that of Sb. Arsenic is strongly limestone, and is partitioned into a variety of sulphide and sulpharsenide minerals, notably arsenopyrite. It is also widely present as an accessory element in other sulphide minerals such as galena pyrite and sphalerite. High As anomalies are a common characteristic of epithermal and mesothermal gold deposits. Arsenic is not preferentially enriched in felsic or mafic igneous rocks; though hydrothermal processes lead to its enrichment.

In sedimentary rocks, As is concentrated in clays, hydrous Fe and Mn oxides, sulphides and phosphates (*Ure and Berrow 1982*).

Arsenic in stream sediment occurs mainly as the oxide, which form soluble arsenates and arsenates in acidic water (*Irgolic et al.1995*), and as sulphides, heavy-metal arsenates and co-precipitated complexes with iron oxides, which are much less soluble (*Wedepohl 1978*). The relatively small amount of As released into stream water during weathering will remain mobile only if pH and Eh are sufficiently low to favour its persistence in trivalent form. Otherwise, dissolved As is rapidly oxidised to relatively insoluble As^{5+} and, as arsenate becomes adsorbed to hydrous oxides of Fe and Mn, clays and organic matter.

Arsenic adsorption onto Fe oxides occurs more readily at acid pH, and consequently As can be preferentially removed from acid effluents (such as acidified mine drainage) by natural precipitates of Fe oxide under conditions that do not favour adsorption of other metals such as Cu, Pb and Zn (Webster 1999). The reactions of As in soil are strongly governed by its oxidation state. However, arsenate ions are known to be readily fixed by clays, phosphatic gels, humus, and calcium; hydrated Fe (goethite) and Al oxides are the most active for As retention (*Kabata-Pendias 2001, Reimann et al. 2003*).

Although adsorbed As in soil is unlikely to be desorbed again, it may be liberated when As is combined with Fe and oxides by hydrolysis caused by the reduction of soil potential. Arsenic enrichment in argillaceous sediments (13 mg kg $^{-1}$), as well as in surface soil, in comparison to concentrations in igneous rocks, possibly reflects some external As sources, such as volcanic exhalations and anthropogenic pollution (*Kabata-Pendias 2001*). Arsenic in soil is present in the heavy mineral fraction, but its contribution to the total As content is very small 60 (commonly about 1%); a much higher proportion of total As is associated with clay fraction (27-90 %). Anthropogenic sources of arsenic include coal combustion, geothermal power plants, sulphidic ore roasting and smelting, and pig and poultry sewage (*Reimann and de Caritat 1998*). Arsenic contamination of the environment as a result of mining and smelting is relatively common. Chronic exposure increases the risk of cancer and skin pigmentation (*WHO 1996, Chappell et al. 1999*). Arsenic has great notoriety as a poison, though there are great differences in the toxicity of different arsenic compounds.

As content in soils ranges from minimum value of 0.6 mg / kg to a maximum value of 164 mg/kg, the median value is 12 mg / kg. The concentrations of Campania soils are higher than those in Italian surface soil with a range of 2.67 to 63 mg / kg and with mean value of 8.20 mg / kg (De Vivo et al., 2008a), while compared to European surface soil the range is larger (0.32 to 282 mg / kg) but the median value (6 mg / kg) (De Vos et al., 2006) is lower. Dot map shows that only 10% of the sites have concentrations of As > 20 mg / kg (90th percentile); these are mostly located in volcanic areas although there are hot spots with locally high values (As > 99th percentile). Other higher values are found as well in the Solofrana basin, in the Vallo di Diano and High Domitius the south-western coast of Roccamonfina (Fig.14).

Interpolated map shows that the areas with low-concentrations of As (<11 mg / kg) are located along the Apennines, in the Avellino and Benevento areas, and in the coastal area of Cilento. Intermediate concentrations (11-25 mg / kg range) are distributed in the surface soils. Close to the Province of Naples, Avellino and Caserta, Domizio area and the southern part of Apennines (from Mt. Picentini to Mt. Cervati). A concentration of > 25 mg / kg is found near volcanic systems of the Somma-Vesuvius, Phlegraen Fields and Roccamonfina, for a limited area where the soil is of volcanic nature and where there is hydrothermal activity, as described in Cicchella et al., 2005. Other areas, instead, are located near soils that have developed on silico-clastic and carbonate sediments as in the Agro Sarnese-Nocerino, especially in the Solofrana basin, and in the Vallo di Diano, in Buonabitacolo and Sapri, where high concentrations of As > 25 mg / kg are generated also by human factors.(Fig.15).

Background/baseline map confirms that the region can be divided into two main areas with geo-lithological background content affected by different conditions. Most of the region, not affected by volcanic sediments, shows values lower than 13 mg / kg (in line with the background values determined for river sediments and soils of Campania, province of Salerno). The areas affected by volcanic activity and/or those with pyroclastic deposits and tuff lithology’s have higher values with a range from 13 to 32 mg / kg (values compatible with the natural background for volcanic soils). High concentrations between 32 to 39 mg / kg, are located in the north of Naples, in the Vallo di Diano and in the Agro Sarnese-Nocerino (Fig.16). They are almost certainly influenced by human activities such as farming practices, due to the use of fertilizers and pesticides.

CSC map (Fig.17) shows that 10 % values exceed the threshold (CSC) residential use (20 mg / kg) as established by Legislative Decree 152/06, while 0.6% are higher than IAL (Industrial and commercial use) thresholds (50 mg / kg). As stated by the analysis of baseline values, the high values of the Phlegraean Vesuvius are comparable with the natural background concentration (32 mg / kg). The values above the CSC / Industrial (50 mg / kg), in a few limited areas, with the exception of those in the potentially related Phlegraen area, hydrothermal activity of the site, are likely to be influenced by human activities (Vallo di Diano, Agro Nocerino- Sarnese, the Solofrana basin).

3.2.3 Copper (Cu)

Copper is a member of the first row transition series of elements, which consists of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 11 of the periodic table, along with Ag and Au. Copper is a limestone element forming several minerals, including chalcopyrite, covellite and malachite but is more widely dispersed at trace levels in mica (biotite), pyroxene and amphibole, thus showing a greater affinity for mafic than for felsic igneous rocks. Copper can occur in its metallic form in nature (i.e. native copper), and is one of the seven metals known in antiquity.

Copper is used in geochemical prospecting as an indicator of all types of copper mineralisation and is an important pathfinder for many types of gold deposit. Elevated Cu values are, however, more likely to indicate the presence of mafic rocks, although Cr and Ni are less ambiguous indicators. In the search for ultramafic-hosted magmatic nickel deposits, elevated Cu values may enable the discrimination of Ni anomalies associated with sulphide from those derived from ultramafic rocks.

Copper usually accumulates in the surface horizons, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic sources (Kabata-Pendias 2001). Copper anthropogenic sources include copper mining and smelting, the electrical industry, agriculture, sewage sludge and steel works. Copper compounds are widely used in agriculture and are a possible source of drainage anomalies.

Cu concentrations in soils range from 2.5 to 2395 mg / kg, the median value is 63 mg / kg. Some concentrations are higher than those found in the Italian surface soils which vary in a range of

3 to 215 mg / kg and have average value equal to 22 mg / kg (De Vivo et al., 2008a) and those values in Europe (interval 0, 81-256 mg / kg and median 12 mg / kg) (De Vos et al., 2006).(Fig.18)

Dot map shows that the highest concentrations > 316 mg / kg, are assembled in the Vesuvian and Neapolitan, including the Phlegraen area and the island of Ischia. Other high values are located in the Agro Sarnese-Nocerino, in the municipalities of the Solofrana basin (Siano, Bra-cigliano, Castel San Giorgio, Mercato San Severino) and near Airiano Irpino. At a regional level the values of Cu are quite high (30% of the sites have concentrations> 120 mg / kg), especially in soils of volcanic origin in the Naples, Vesuvius and Phegrean area, where the values are > 600 mg / kg. In those areas a contribution may also be due to hydrothermal activity, as in the case of Ischia (*Lima et al., 2003; Frattini et al., 2006*). (Fig.18).

Interpolated map shows that some areas with high concentrations of Cu are located in the Vesuvian area, where it is possible to observe the highest concentrations (242-2356 mg / kg), and in Phlegraen municipalities (123-599 mg / kg) as well. Locally also the north-western area of Ariano Irpino shows high values and concentrations of less than 123 mg / kg which are distributed throughout the remaining part of region (Fig.19).

Background/baseline (Fig.20) confirms that concentration values in the Vesuvius are 571-836 mg / kg. These concentrations derived from the soil of volcanic origin and from farming area. The remaining part of the region could be divided into two sectors. The first with concentrations between 42 and 154 mg / kg and the second, which includes the Apennines and the Cilento area, with large areas where soils have values of <42 mg / kg. In particular, for the first zone human contribution and agricultural practices cannot be excluded.

The 30% of the analysed samples on a regional scale, exceed concentration contamination thresholds (CSC) established by Legislative Decree 152/06 for residential use soils and industrial use (2, 5% of the analysed samples). Caserta and Benevento also show values above the threshold, while there are isolated overruns in the rest of the region. A similar distribution pattern can be observed for exceedances of CSC industrial commercial (IAL) (Fig.21).

3.2.4 Lead (Pb)

Lead belongs to group 14 of the periodic table, which also includes C, Si, Ge and Sn. Lead has the most metallic characteristics of this group. Lead is a limestone metallic element constituting several significant minerals including galena, anglesite, cerussite, and minium Pb. It is also widely dispersed at trace levels in a range of other minerals, including K–feldspar, plagioclase, mica, zircon and magnetite. Lead is one of the seven metals known in antiquity, because of its relative ease of extraction as a metal. The Roman civilisation, in particular, used large quantities of lead with plumbing purposes.

Around 35% of Pb in stream sediment occurs in the sand fraction, but the majority is found in the silt and clay fractions, associated with kaolinite and mica.

Natural Pb content in soil is, of course, related to the composition of the parent rock. Although the species of Pb vary considerably depending on the type of soil, it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations (Kabata-Pendias 2001). A baseline Pb value for surface soil at global scale has been estimated to be 25 mg kg-1; levels above this suggest an anthropogenic influence (Kabata- Pendias 2001).

Around 35% of Pb in stream sediment occur in the sand fraction, but the majority is found in the silt and clay fractions, associated with kaolinite and mica.

Lead from vehicle exhausts, in the form of tehtraethyl Pb was, until recently, a significant source of contamination. In urban environments, road dusts can contain very high levels of Pb (Archer and Barret 1976), although the introduction of unleaded petrol has reduced this potentially toxic hazard in developed industrialised countries. In addition, metalliferous mining (especially sulphide ores), metallic detritus, Pb-bearing glass and pottery glazes, batteries, old lead-based paints, the corrosion of lead pipes in areas of soft water and sewage sludge are all potential sources of Pb.

Anthropogenic sources of pollution may cause local enhancement of Pb levels in surface water by an order of magnitude compared to background values (*Patterson 1965*).

Analysed Pb concentrations in soils (dot map) vary between 3.1 and 2053 mg / kg, the median value is 54 mg / kg, higher than the values of European surface soils (concentration range from 5.3 to 970 mg/kg, median 15 mg / kg) (De Vos et al., 2006) and Italian range 2.55 - 204 mg / kg and the median value of 32 mg / kg (De Vivo et al., 2008a).

Dot map (Fig.22) shows very high concentration in urban areas and close to roads with traffic. 15% sites sampled along the urban fabric, starting from the of Domizio Phlegraen Littoral, to the city of Salerno and the remaining provincial cities, have > 100 mg / kg values; 5% have concentrations > 250 mg/kg, 0,2 % > 1000 mg / kg and are distributed in the urban areas of Naples and Salerno (and their metropolitan areas).

The distribution of interpolated data confirms that the largest area where we can find diffuse pollution of Pb in the soils, with concentration values above 100 mg / kg, are the metropolitan areas of Naples and Salerno, the area near Castelvolturno (the Volturno River estuary) and between Nocera and Avellino. Some samples with high values are located in the part of region that includes the Piana Campana to Battipaglia. The inner Apennine areas, including Cilento, generally have low (Pb <42 mg / kg) or very low concentrations (<23 mg / kg) (Fig.23).

Background / baseline map (Fig.24) confirmed higher values (> 65 mg / kg) in most of the sites in the north part of the region, affected by human impact. In particular, in correspondence of the main urban centres (Naples and Salerno) and between Nocera and Avellino municipalities, values exceed 111 mg / kg. The inner areas of the provinces of Caserta, Benevento and Avellino, as well as the Cilento area and more generally the southern sector of the Salerno province have low values, comparable with geo-lithological characteristics.

As a result of the study of the CSC map (Fig.25) for lead, it can be observed that 15% of the analysed samples exceed the threshold (> 100 mg / kg) of residential / recreational use, while 0.2% is higher than the one of soils for industrial / commercial use (> 1000 mg / kg). Lead is a persistent element and high concentrations in soils of urban areas, including on the basis of previous studies (Cicchella et al., 2005), are essentially due to the Pb used until the '90s as an additive in gasoline.

3.3 Trace elements

The description of each element refers to that of the Geochemical Atlas of Europe: FOREGS (Salminen, R.; Batista, M.J.; Bidovec, M.; Demetriades, A.; De Vivo, B.; De Vos, W.; Duris, M.; Gilucis, A.; Gregorauskiene, V.; Halamić, Josip; Heitzmann, P.; Lima, A.; Jordan, G.; Klaver, G.; Klein, P.; Lis, J.; Locutura, J.; Marsina, K.; Mazreku, A.; O'Connor, P.J.; Olsson, S.A.; Ottesen, R.-T.; Petersell, V.; Plant, J.A.; Reeder, S.; Salpeteur, I.; Sandstrom, H.; Siewers, U.; Steenfelt, A.; Tarvainen, T.)

3.3.1 Uranium (U)

Uranium is a member of the actinide series of elements, along with Th and human-made elements such as Pu. Uranium is a lithophile metallic element present in several minerals, including uraninite, brannerite and carnotite. It is also present as an accessory element in zircon, apatite, allanite and monazite, and in complexes with organic matter and phosphatic ironstone. *Kabata-Pendias (2001*) reports that there is very little information regarding U in soil. The global average for soil is given as 0.79 to 11 mg kg-1 U. The mobility of U in soil is the same as Th, it is governed by the formation of the hydrated cation, which is responsible for its solubility over a wide range of pH soil. Organic acids may increase the solubility of U in soil, but its mobility may be limited by the formation of slightly soluble precipitates (e.g., phosphates and oxides) and by adsorption on clay minerals and organic matter. The main anthropogenic sources of U include uranium mining and milling, nuclear effluents, phosphate fertilisers and coal combustion (*Reimann and de Caritat 1998*). Uranium is of great importance as a nuclear fuel. Depleted U is used in inertial guidance devices, gyro compasses, counter weights for aircraft control surfaces, as ballast for missile re-entry vehicles and as a shielding material. Uranium metal is also used for X-ray targets for the production of high-energy X-rays. It is a non-essential element. It is chemotoxic, radiotoxic and a carcinogen. Because U is a radioactive substance, its effects on human health have been widely researched. Long-term exposure to U radionuclides can result in medical conditions such as kidney disease and the development of cancer. The radioactive decay of U releases radon gas, which is itself radiotoxic, highly mobile and of more environmental concern than U itself.

U content in soils ranges between 0.05 and 24 mg / kg, the median value is 3 mg / kg. The Campanian soils have lower concentrations than those of European surface soils (0.21 to 53.2 mg / kg and the median value of 2 mg / kg) (*De Vos et al., 2006*) but higher than Italian (concentration ranges from 0.2 to 9.88 mg / kg and median 2.34 mg / kg) (*De Vivo et al., 2008a*).

Dot map shows that 90% of the samples have concentrations of U of <7 mg / kg. In the provinces of Avellino, Benevento and Salerno and in the coastline areas, values are significantly lower <2 mg / kg. Areas with higher concentrations (> 8 mg / kg) extend from Vesuvius to Avellino, the Lattari Mountains and in the Agro Sarnese-Nocerino and Picentini (Fig.26).

Interpolated data (Fig.27) show that most of the soils of the region have concentrations of U of <4 mg / kg, with big areas where they are significantly reduced (<1 mg / kg). Around volcanic areas there are portions where the values are between 4 and 6 mg / kg; near eruptive centers the U levels are higher, from 6 to 11 mg / kg. The highest concentrations of the region (> 11 mg / kg) are limited to small areas, located near Roccamonfina and in the Agro Nocerino and the Monti Picentini (Giffoni municipality); this area shows high values of Th.

Background / baseline values confirm U values of < 4 mg / kg. Soils with volcanic origin, around Roccamonfina and Vesuvius present higher levels of the deepest part (between 4 and 7 mg / kg) that in some restricted areas are > 7 mg / kg. Some areas, with limited extension, show concentrations of U ranging from 4 to 7 mg / kg near Alife and Monte Maggiore. Since they are areas devoted to agriculture, human contribution due to the use of phosphate fertilizers in agricultural practices cannot be excluded (Fig.28).

APPENDIX

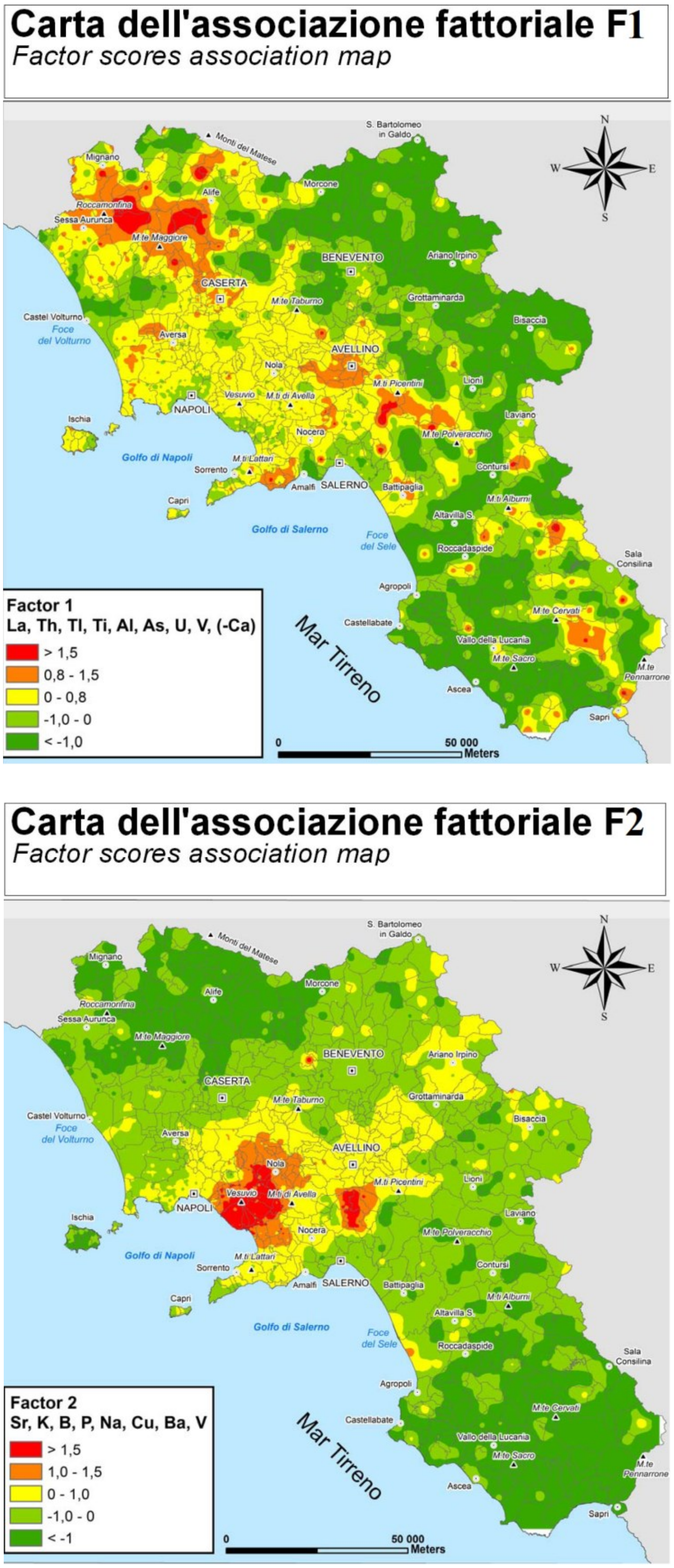
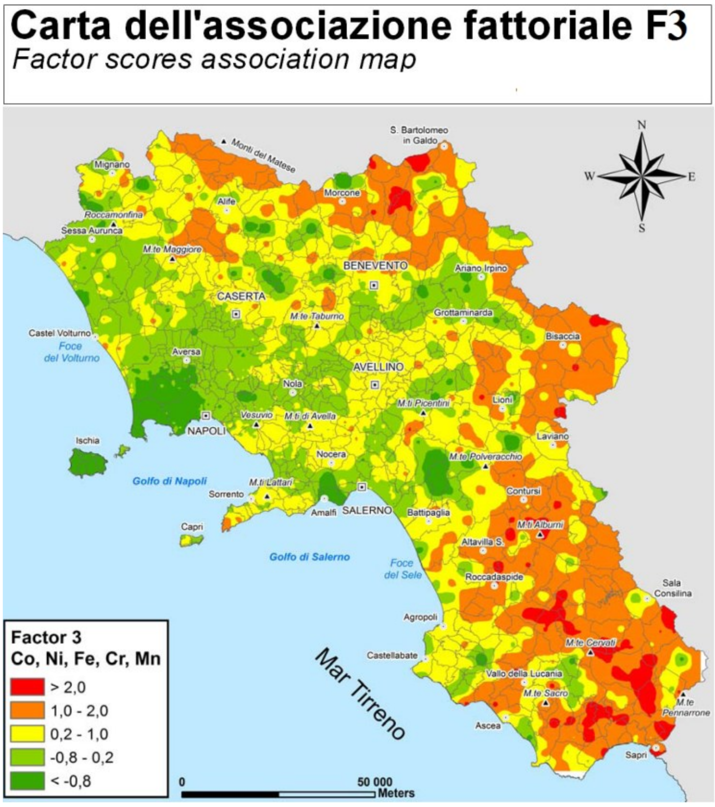


Figure 5 Factor association map (F1 and F2)



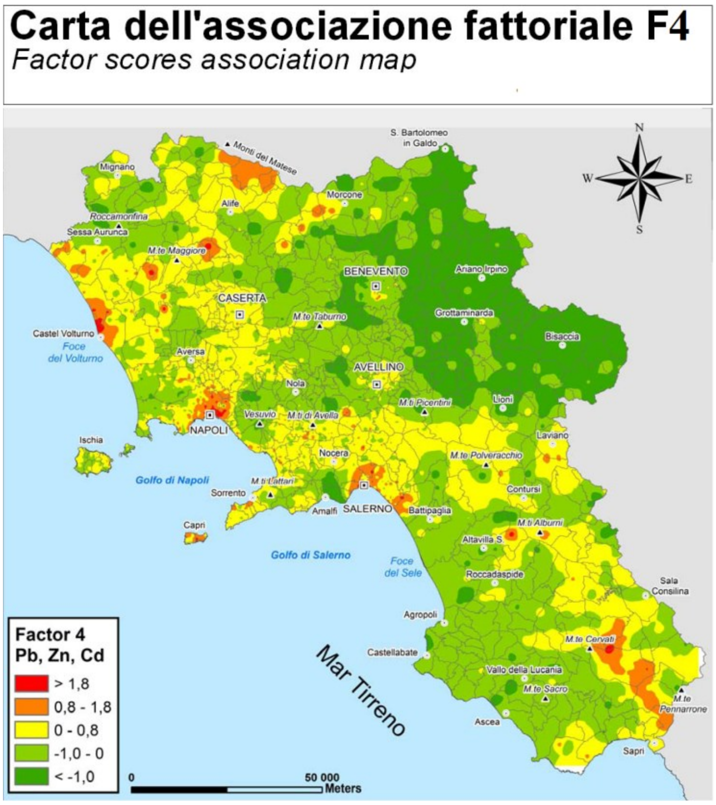
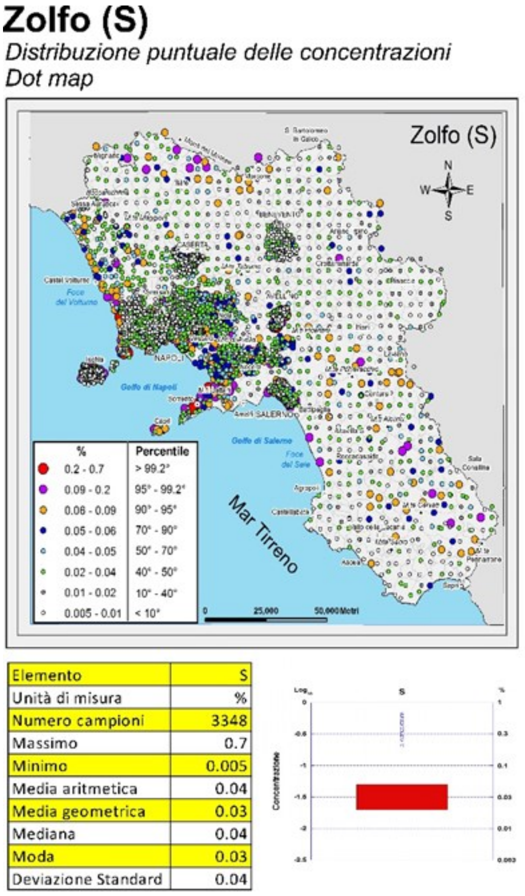


Figure 6 Factor association map (F3 and F4)



Elemento	S
Unità di misura	%
Numero campioni	3348
Massimo	0.7
Minimo	0.005
Media aritmetica	0.04
Media geometrica	0.03
Mediana	0.04
Moda	0.03
Deviazione Standard	0.04

Figure 7 Dot map (Sulfur)

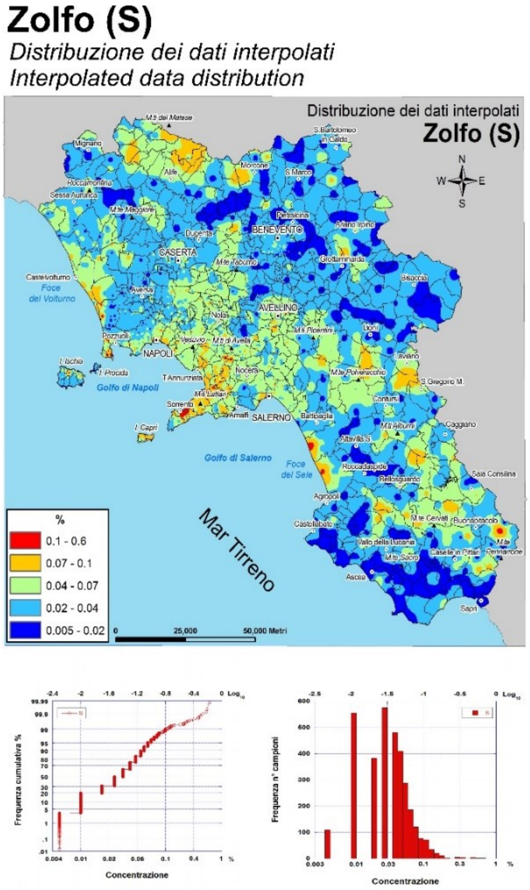


Figure 8 Interpolated map (Sulfur)

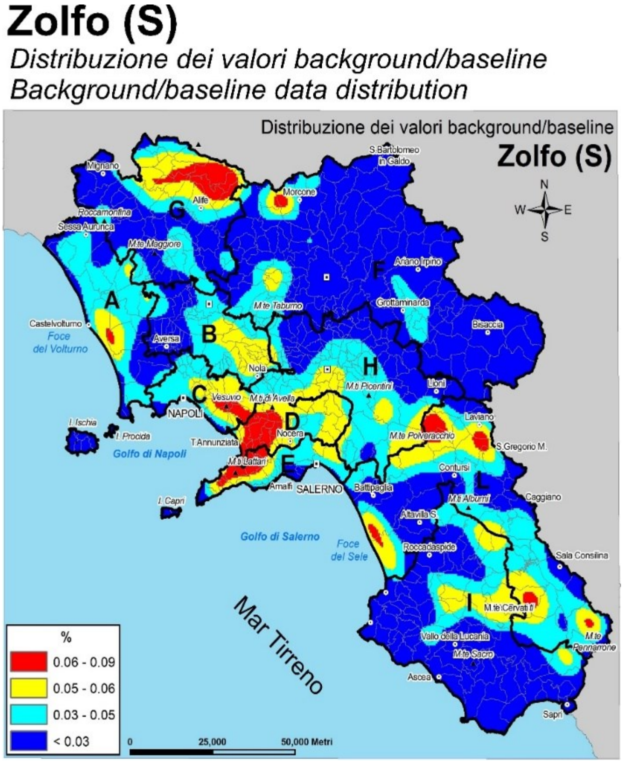
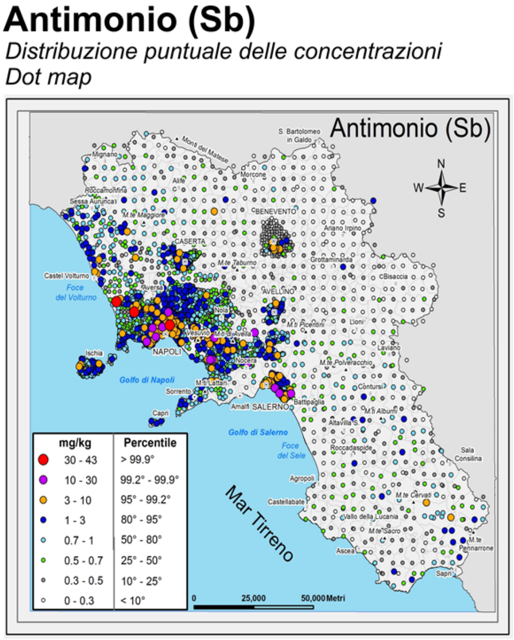


Figure 9 Background map (Sulfur)



Elemento	Sb
Unità di Misura	mg/kg
Numero campioni	3300
Massimo	43
Minimo	0.01
Media aritmetica	1.08
Media geometrica	0.71
Mediana	0.66
Moda	0.5
Deviazione Standard	1.92

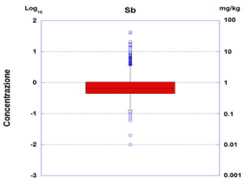


Figure 10 Dot map (Antimony)

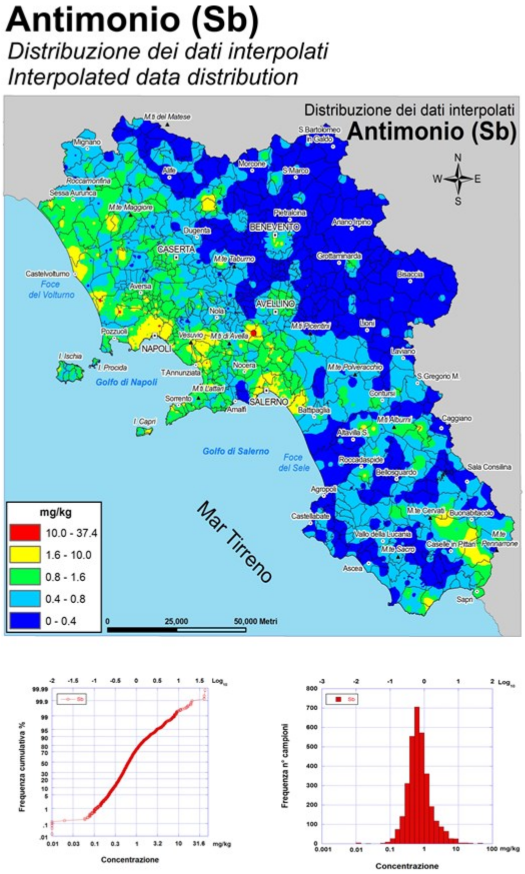


Figure 11 Interpolated map (Antimony)

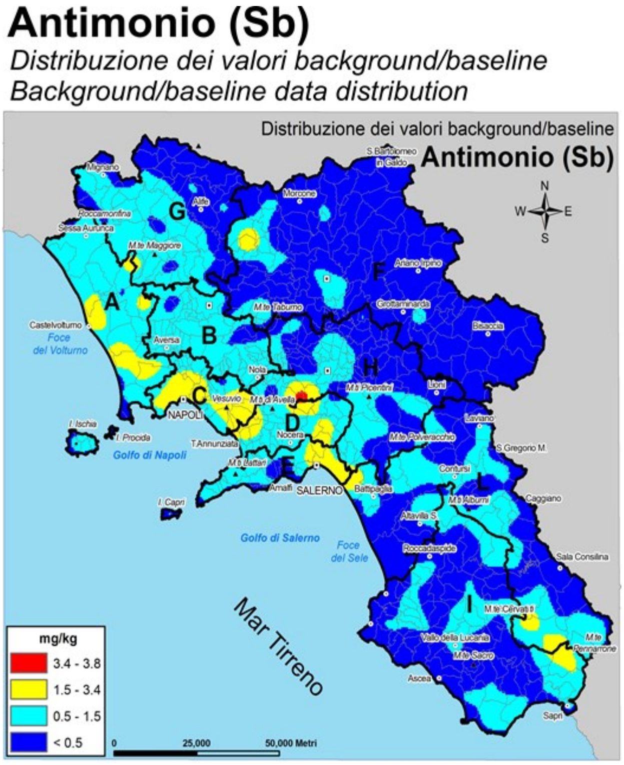


Figure 12 Background map (Antimony)

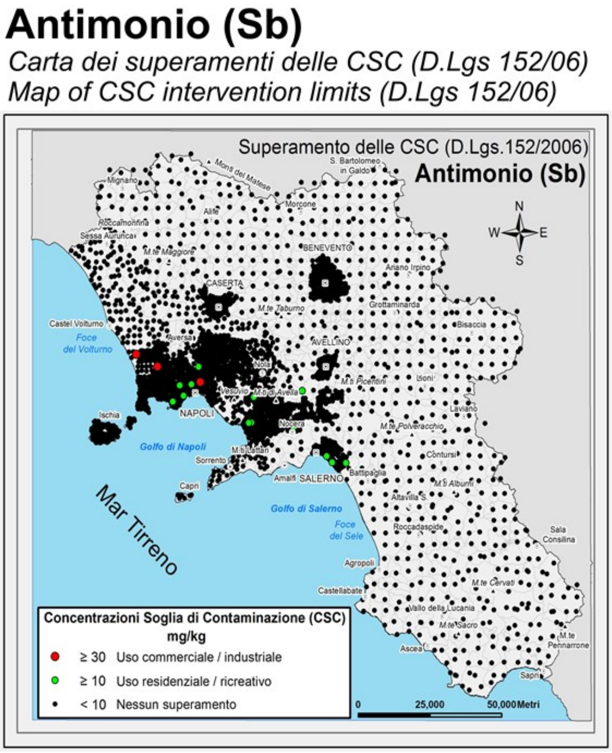
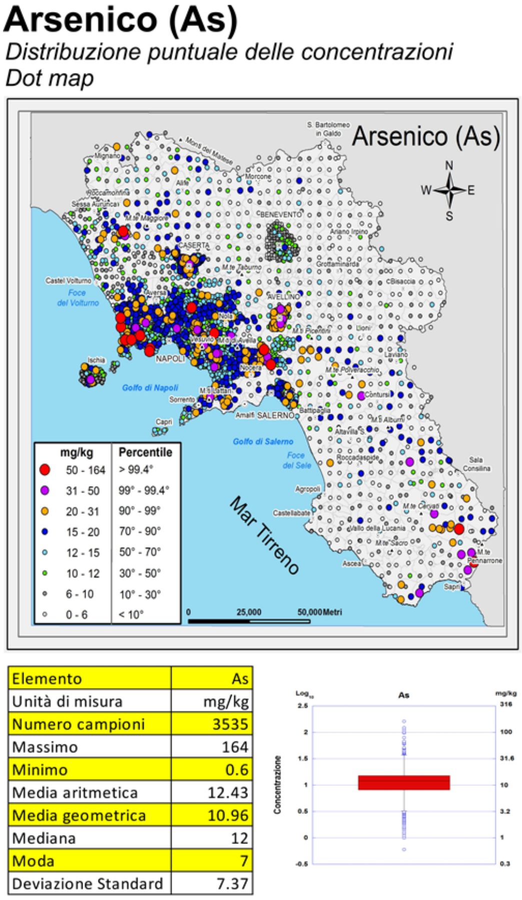


Figure 13 CSC map (Antimony)



Elemento	As
Unità di misura	mg/kg
Numero campioni	3535
Massimo	164
Minimo	0.6
Media aritmetica	12.43
Media geometrica	10.96
Mediana	12
Moda	7
Deviazione Standard	7.37

Figure 14 Dot map (Arsenic)

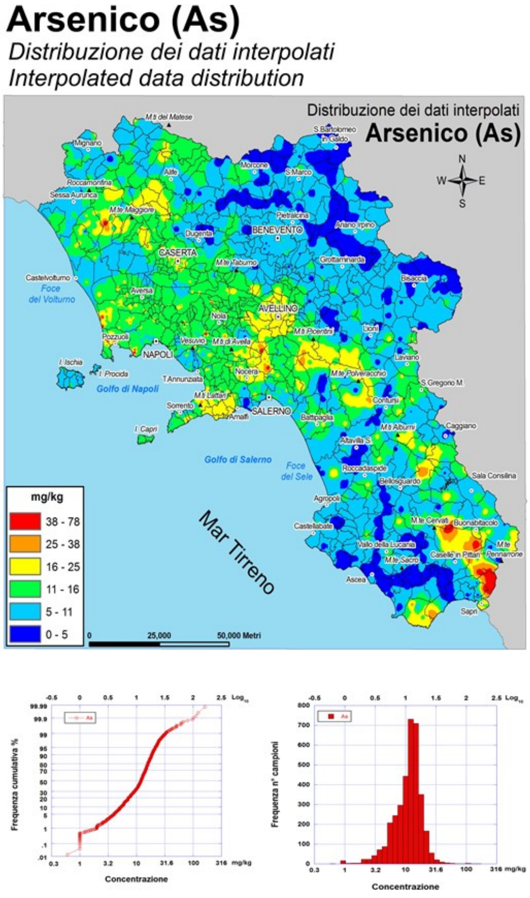


Figure 15 Interpolated map (Arsenic)

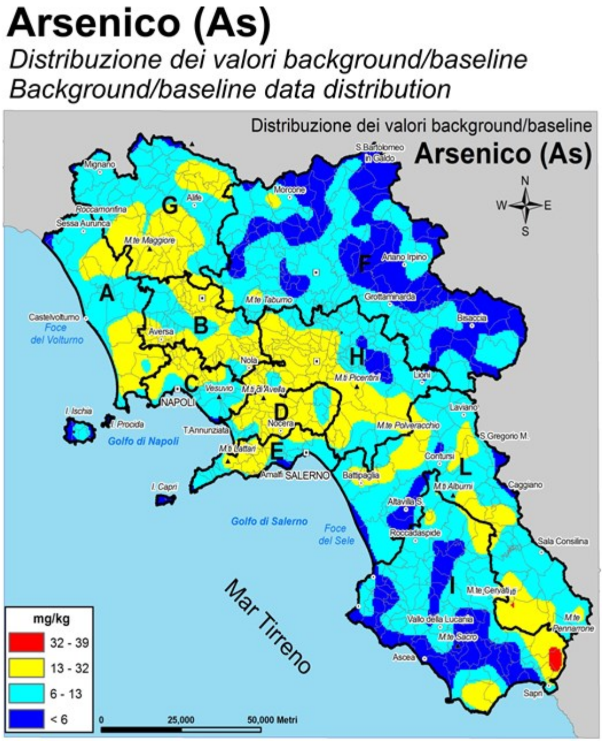


Figure 16 Background map (Arsenic)

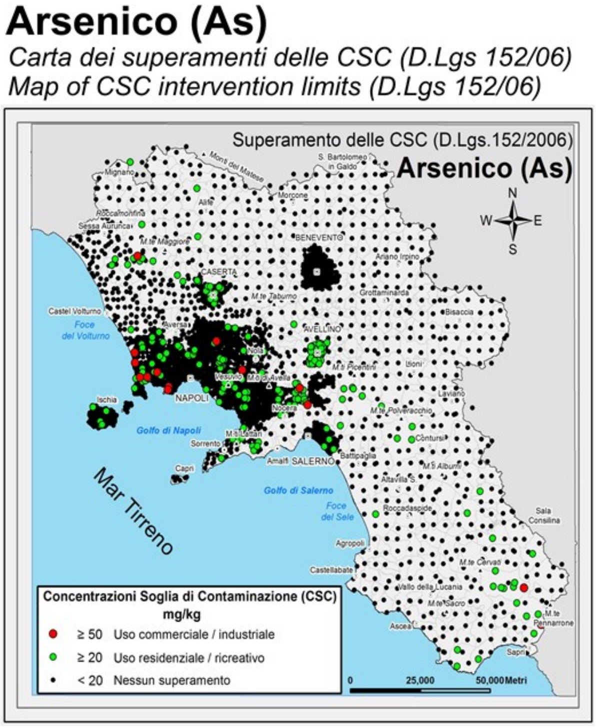
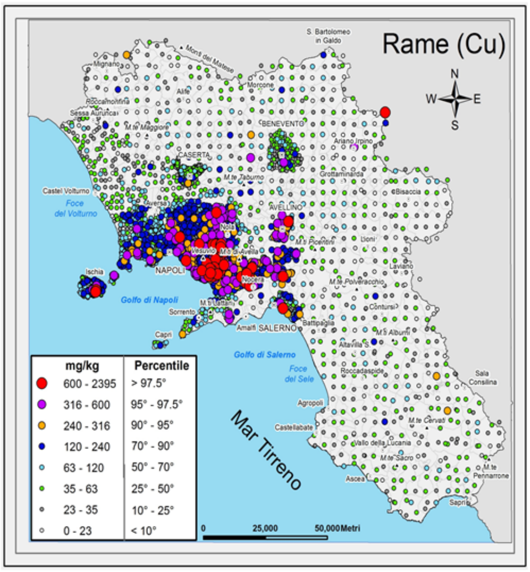


Figure 17 CSC map (Arsenic)

Rame (Cu)

Distribuzione puntuale delle concentrazioni
Dot map



Elemento	Cu
Unità di misura	mg/kg
Numero campioni	3535
Massimo	2395
Minimo	2.5
Media aritmetica	110
Media geometrica	66
Mediana	63
Moda	9
Deviazione Standard	159

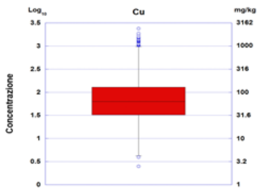


Figure 18 Dot map (Copper)

Rame (Cu)

Distribuzione dei dati interpolati
Interpolated data distribution

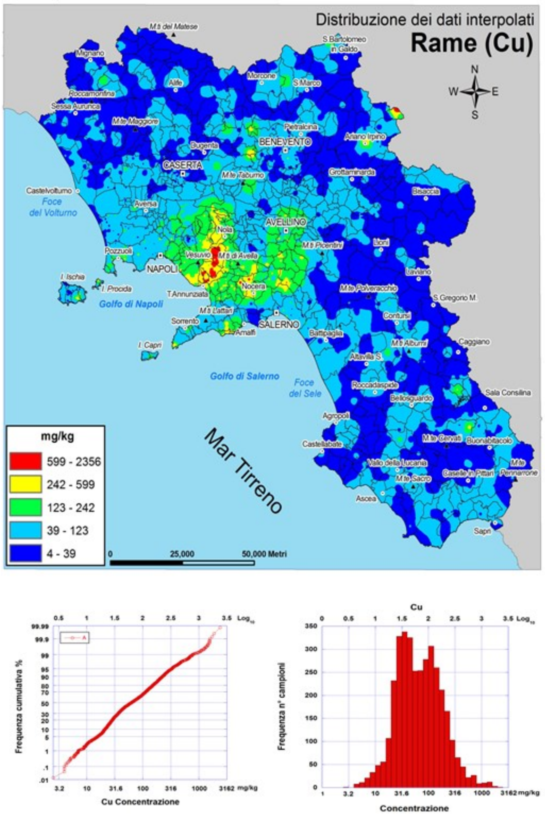


Figure 19 Interpolated map (Copper)

Rame (Cu)

Distribuzione dei valori background/baseline
Background/baseline data distribution

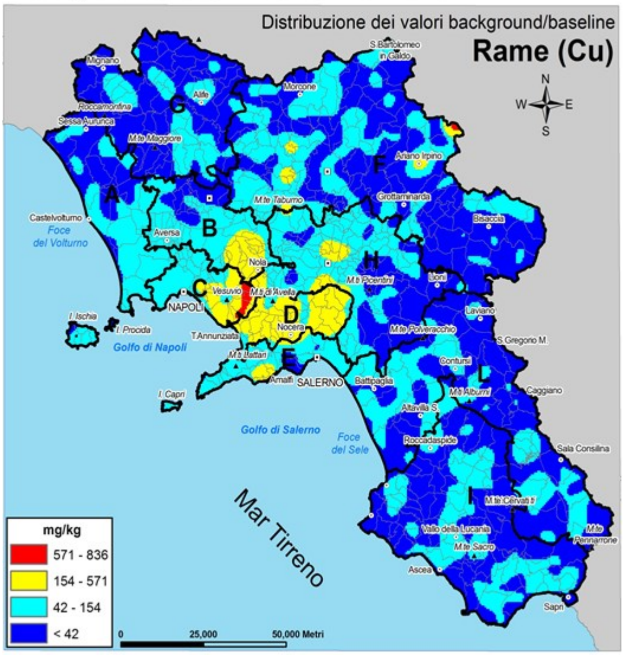


Figure 20 Background map (Copper)

Rame (Cu)

Carta dei superamenti delle CSC (D.Lgs 152/06)
Map of CSC intervention limits (D.Lgs 152/06)

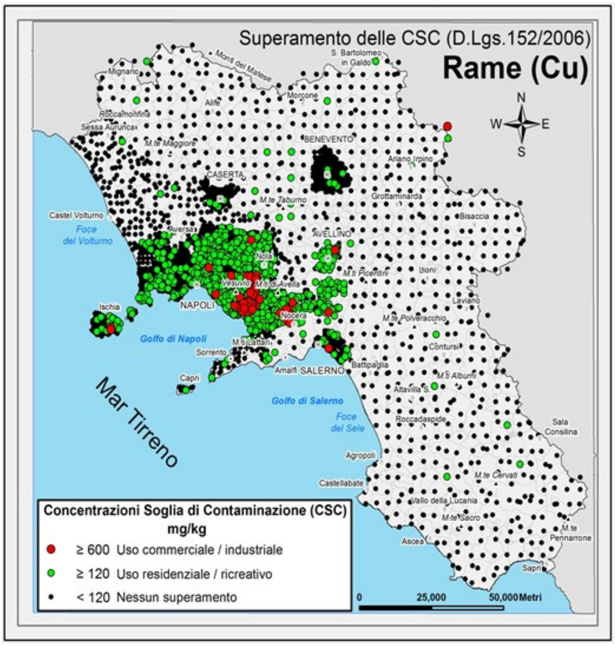
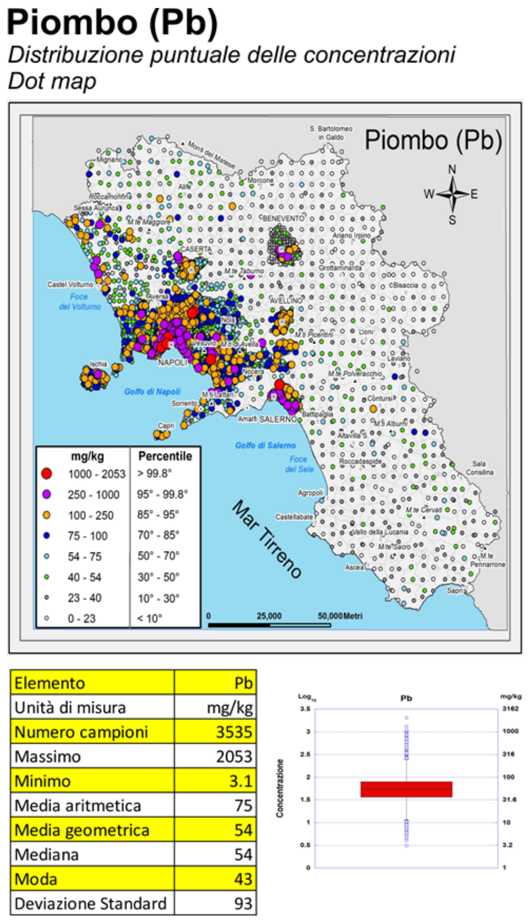


Figure 21 CSC map (Copper)



Elemento	Pb
Unità di misura	mg/kg
Numero campioni	3535
Massimo	2053
Minimo	3.1
Media aritmetica	75
Media geometrica	54
Mediana	54
Moda	43
Deviazione Standard	93

Figure 22 Dot map (Lead)

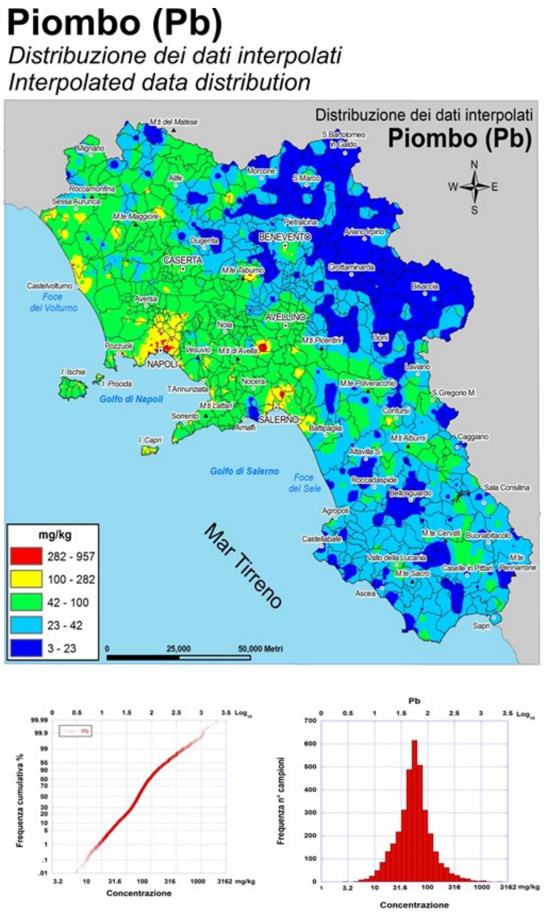


Figure 23 Interpolated map (Lead)

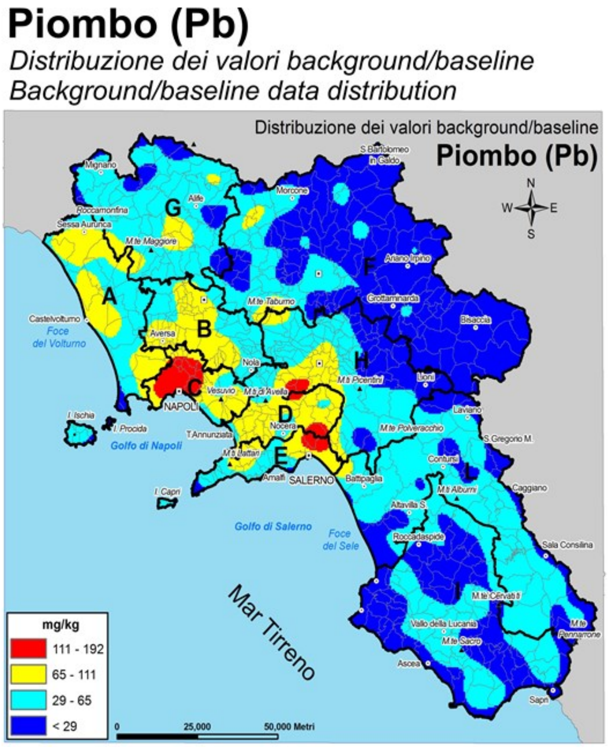


Figure 24 Background map (Lead)

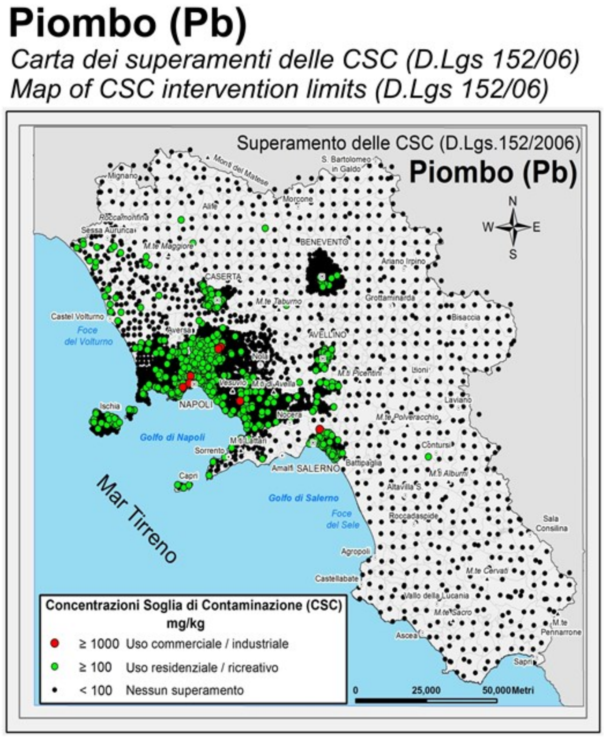
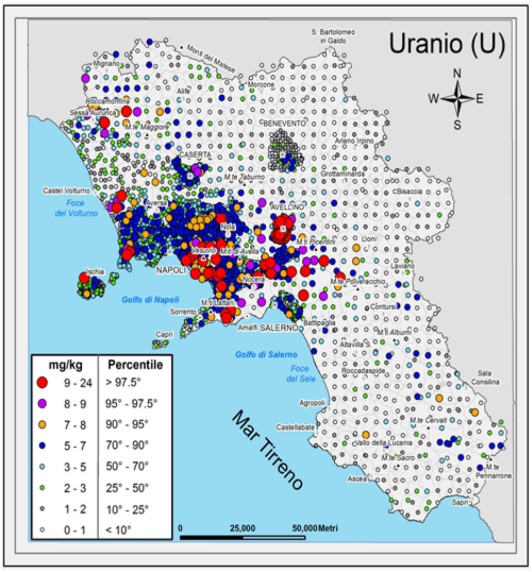


Figure 25 CSC map (Lead)

Uranio (U)
Distribuzione puntuale delle concentrazioni
Dot map



Elemento	U
Unità di misura	mg/kg
Numero campioni	3369
Massimo	24
Minimo	0.05
Media aritmetica	3.37
Media geometrica	2.7
Mediana	3
Moda	2
Deviazione Standard	2.15

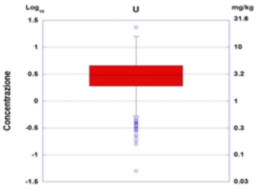
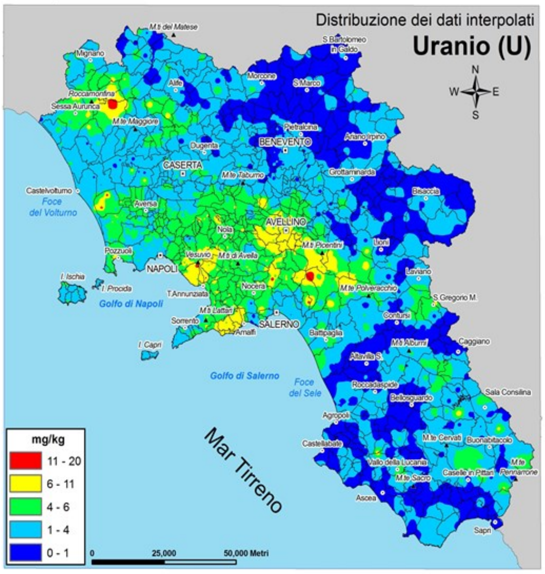


Figure 26 Dot map (Uranium)

Uranio (U)
Distribuzione dei dati interpolati
Interpolated data distribution



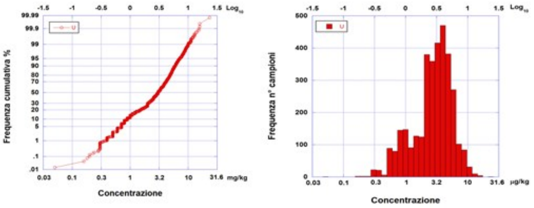


Figure 27 Interpolated map (Uranium)

Uranio (U)
Distribuzione dei valori background/baseline
Background/baseline data distribution

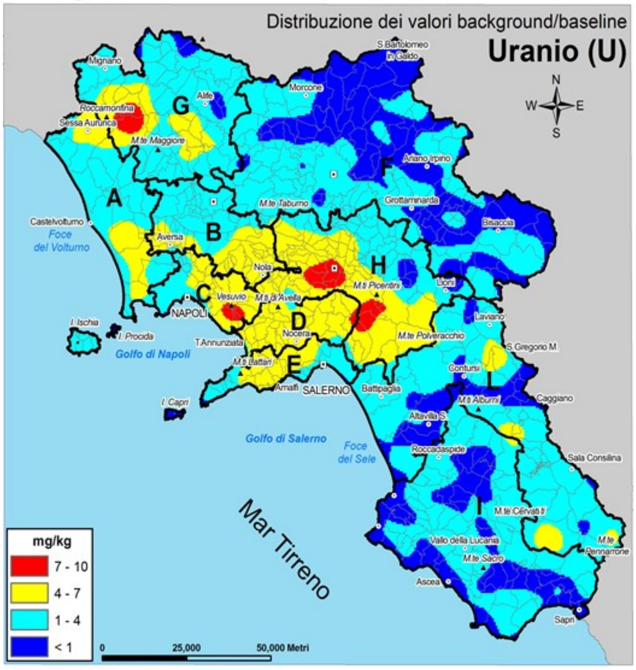


Figure 28 Background map (Uranium)

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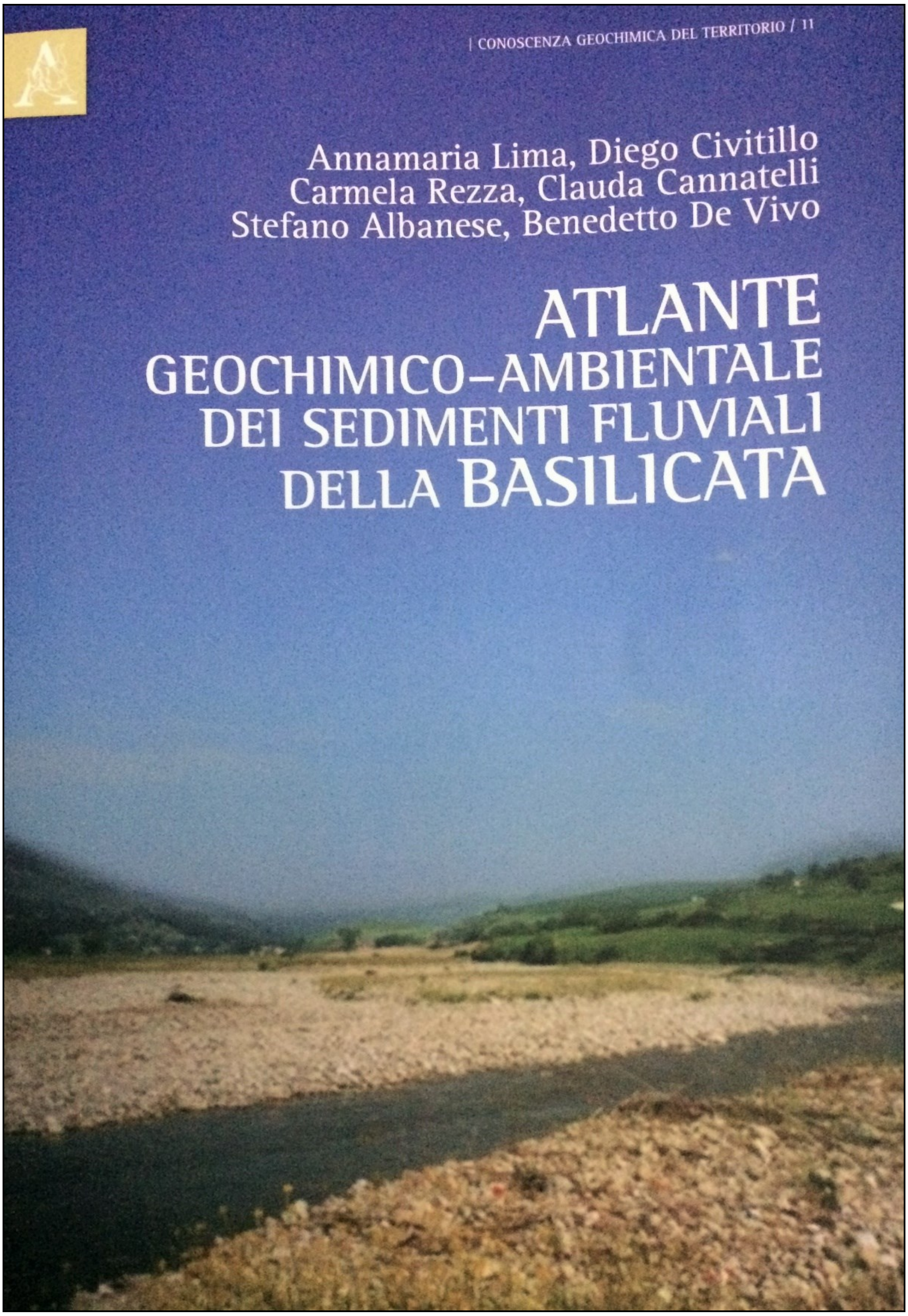
CHAPTER VI
Stream Sediment Geochemical Environmental Atlas of Basilicata Region



| CONOSCENZA GEOCHIMICA DEL TERRITORIO / 11

Annamaria Lima, Diego Civitillo
Carmela Rezza, Clauda Cannatelli
Stefano Albanese, Benedetto De Vivo

ATLANTE
GEOCHIMICO-AMBIENTALE
DEI SEDIMENTI FLUVIALI
DELLA BASILICATA

Stream Sediment Geochemical Environmental Atlas of Basilicata region

Introduction

In the present geochemical and environmental atlas, we show the results obtained from the investigations carried out on the river sediments of the Basilicata region where there has been sampling over the entire territory, with a 9992 km^2 area. With a density of about 12 samples per km^2, 801 samples of stream sediment were collected, analysed with an analytical methodology combining the ICP-MS (plasma mass spectrometry inductively coupled) and ICP-ES (to plasma emission spectrometry inductively coupled) for the determination of concentration of 39 chemical elements. The considerable amount of analytical data has been organized in a database, with the remaining information collected in the field or through a careful literature research. Through elaborations with the use of specific software (ArGIS and Geodas), the production of geochemical-environmental maps is performed. The latter are a "snapshot" of the current distribution of the concentrations of chemical elements in the analysed samples from these rivers and may be used in the future as a reference for the environmental impact assessment as part of the investigated area. It is good to remember that often the natural background values (background), of the various chemical elements analysed in sampled river sediments, defined as baseline, reflecting a more or less significant anthropogenic contribution according to the degree of urbanization in the area (and *Gregorauskiene Salminen, 2000*).

In Basilicata, given the small number of inhabitants, the anthropogenic sources of pollution can be attributed mainly to mining and industrial associated activities. These sources of contamination are to be monitored and evaluated over time and this geochemical-environmental atlas represents one of the essential instruments to achieve this goal.

Specifically, this Atlas collects:

- The geochemical maps (dot and interpolated) of 39 chemical elements analysed in river sediments: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, Zn
- The geochemical maps of the background values of the same 39 items.
- The geochemical maps (dot and interpolated) of the factor scores of 4 associations, arising from the factor in R-mode.

1. *Study area*

Basilicata region is almost 70% mountainous (Apennines Lucano), 22% hilly and only 8% flat. The plains are concentrated mostly in the coastal plain of Metaponto. About a third of the region is located 700 m above sea level. Basilicata includes three major morphological units related to the outcropping lithologies a) the Apennines, in which, from the lithological point of view, two basic complexes can be distinguished: a limestone-dolomite (carbonate series), and one largely silico-clastic, including flysch-formations; b) the Fossa Bradanica; c) the 'Avampaese Apulo' represented by a western offshoot of the karst Murge upland. (Bonardi et al., 2009; Patacca et al., 2007). (Fig.1)

The northern part of the Basilicata Region is characterised by Mount Vulture Volcano, located along the external thrust belt of the chain. It is a complex stratovolcano whose pyroclastic products are the result of both explosive and effusive activity occurring from the Middle Pleistocene to the Upper Pleistocene (Serri et al., 2001). The southern part of the region is characterized by the Pollino Ridge, formed by Meso-Cenozoic rocks, which marks the boundary between Basilicata and Calabria region (Colangelo et al.2008, Schiattarella, 1998).

The river basin of the Basilicata Region is limited and it is quite small. It is constituted by the rivers Ofanto, Sele, Bradano, Basento, La Lama, Cavone, Agri, Noce, Sinni and Lao (Fig.2) river basins chart. Generally, they have a torrential character especially in the upper part where the Apennines have a dense secondary hydrographic network characterized by considerable and short concentration time gradients corresponding to a significant kinetic energy, and thus erosion and sediment transport. The basins of rivers that flow into the Ionian Sea, towards the valley, lose their characteristic shape of Apennine tree and shrink rapidly to average distances between the watersheds of the order of 10 Km.

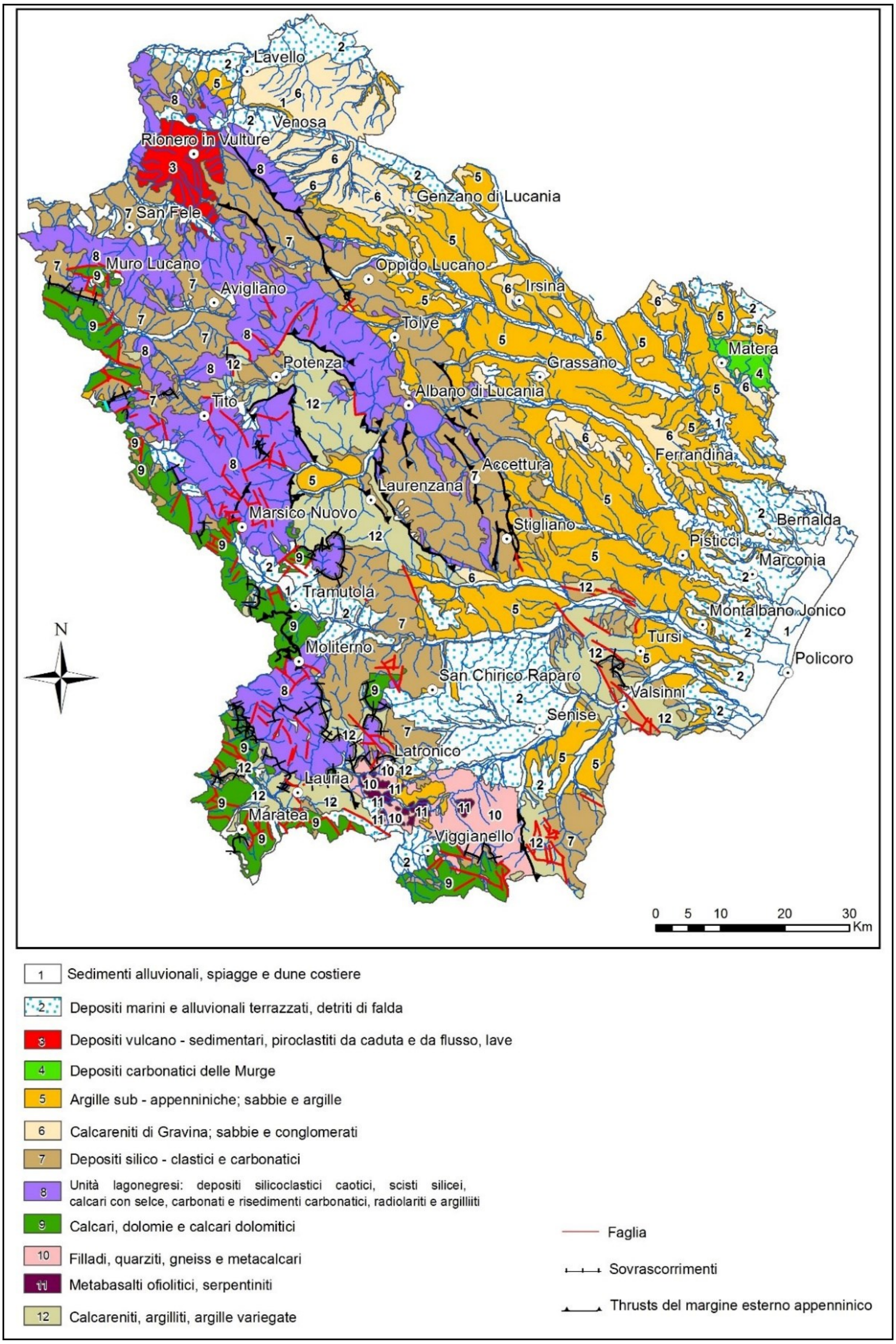


Figure 1 Geo-lithological map of Basilicata region (from Bonardi et al., 2009)

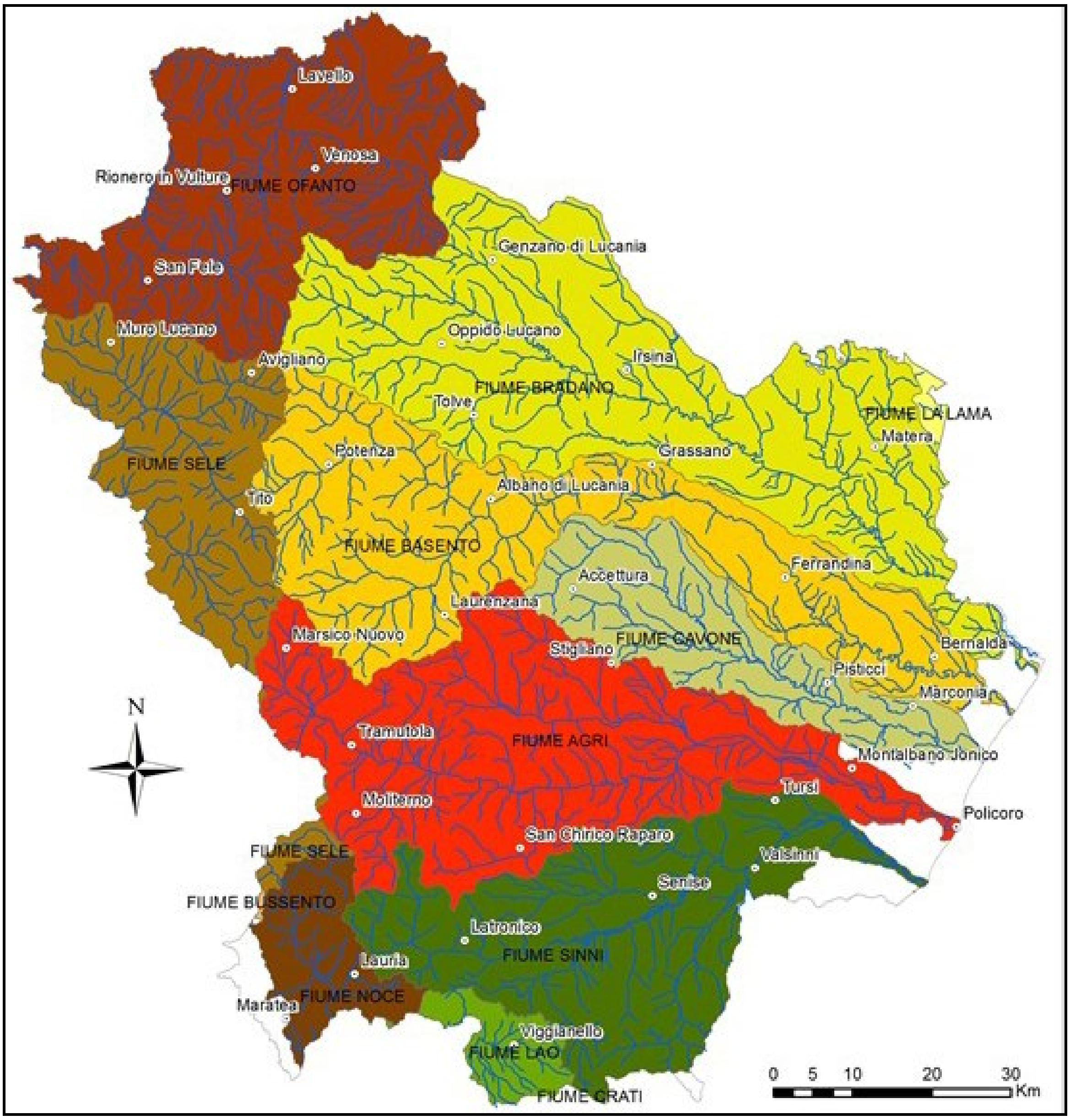


Figure 2. Hydrographic basins of Basilicata region

2. *Material and Methods*

A sampling of active river sediments was carried out for the realization of environmental geochemical Atlas of Basilicata region. An amount of 801 fluvial sediments were picked up, from 2012 to 2014, and considering that the whole territory has a surface of 9992 km^2, the nominal density is about 12 samples for km. (Fig.2)

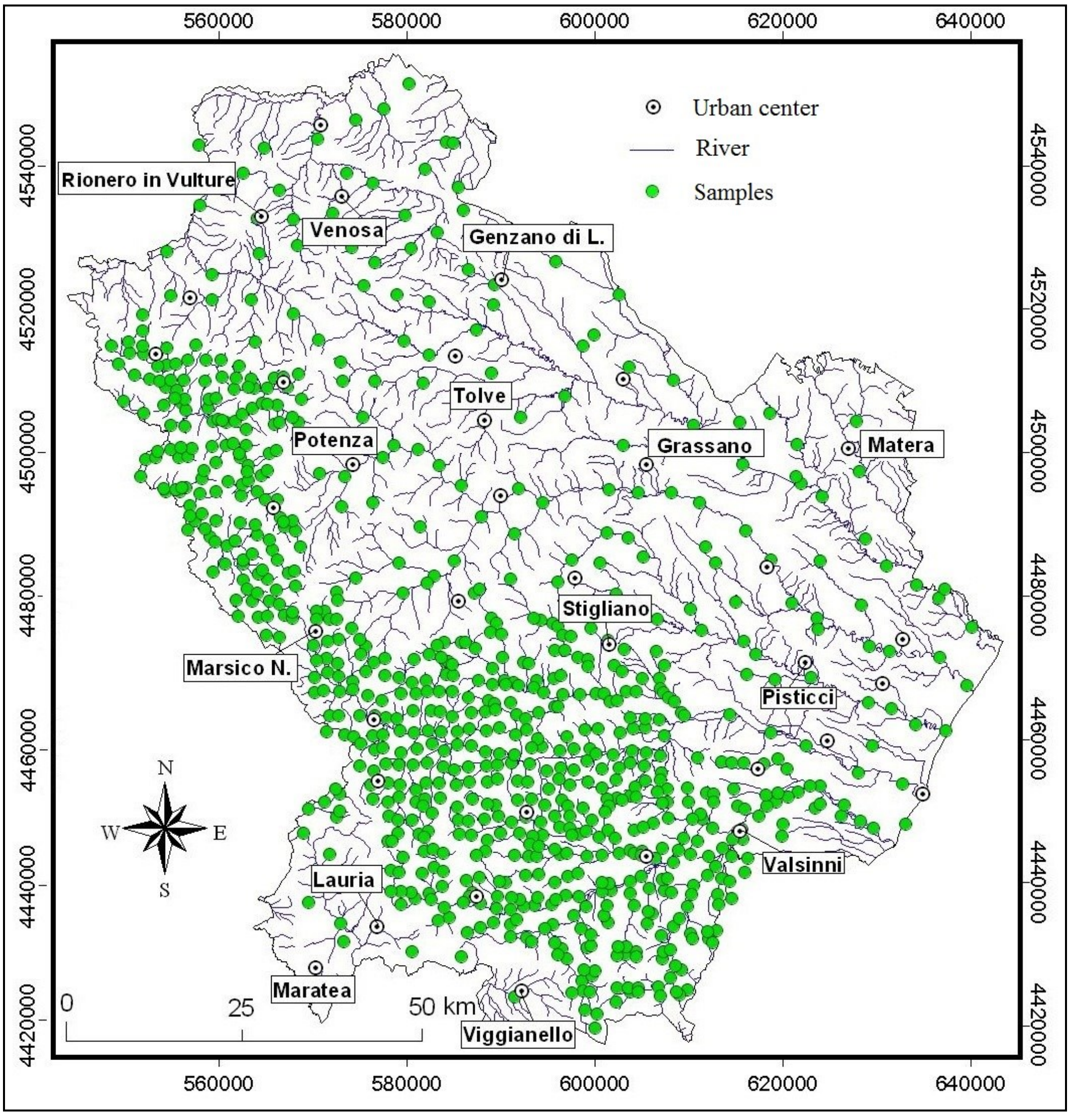


Figure 3 Map of sampling sites

The river sediments, properly taken, are representative of the entire upstream area of the championship site and in comparison to soils can provide identified information on wider areas of the territory. On how the sampling was performed following the protocol given in FOREGS Manual (Salminen et al., 1998). In particular, for each sampling site a total amount of sediment equal to around 2.5 Kg has been levied; aliquots of 0.5 Kg were taken at five different points at a distance of about 50 meters from each other. The samples were generally taken at the center of the beds, at an average depth of 10-15 cm. Once gathered, the samples were taken to the laboratory, dried under infrared lamps, in such a way that the temperature did not exceed 35 ° C. In this transaction followed the screening with the collection of a very fine fraction <150 m (passing 100 mesh) that best meets the objectives of geochemistry exploration for environmental purposes and for the determination of concentrations of selected chemical elements (De Vivo et al., 2004).

The chemical analyzes, performed at ACME Analytical Laboratories Lab. Ltd. (Vancouver, Canada), now Bureau Veritas, have affected 39 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, W, Zn. They were determined through an analytical methodology that combines the ICP-MS (mass spectrometry inductively coupled plasma) and plasma ICP-ES (Inductively Coupled Emission Spectrometry).

In order to process only those data that have a good analytical value, quality controls on the laboratories data have been applied. Table 1 shows the accuracy and precision values of the Basilicata region sample's geochemical data considered in this work, after the application of the selected analytical technique.

Accuracy is defined as the degree of closeness of the measurement of a quantity to its true value. The laboratory accuracy error has been determined using the following formula:

$$[(|X - TV|) / TV] * 100 \qquad (1)$$

With: X= laboratory's analysis result for the standard sample, TV= true value of the standard sample.

For the measurement of the analysis accuracy error, Acme's in-house reference materials have been used: for stream sediment samples, the standard was DS7. Acceptable accuracy error values don't have to be over 15%.

Precision is defined as the degree of reproducibility of a measurement; in other words, it is the degree of how, repeated measurements, show the same results under the same conditions. The precision has been estimated as relative percentage difference (%RPD) using the formula:

$$\% \, RPD = [\,|S-D| / (\,|S+D| /2)] *100 \qquad (2)$$

With S = Standard sample concentration, D= Duplicate

Precision of the performed analysis, has been calculated on 6 in-house replicates and one blind duplicate for stream sediment, values can be considered good if the RPD is < 35% for stream sediment.

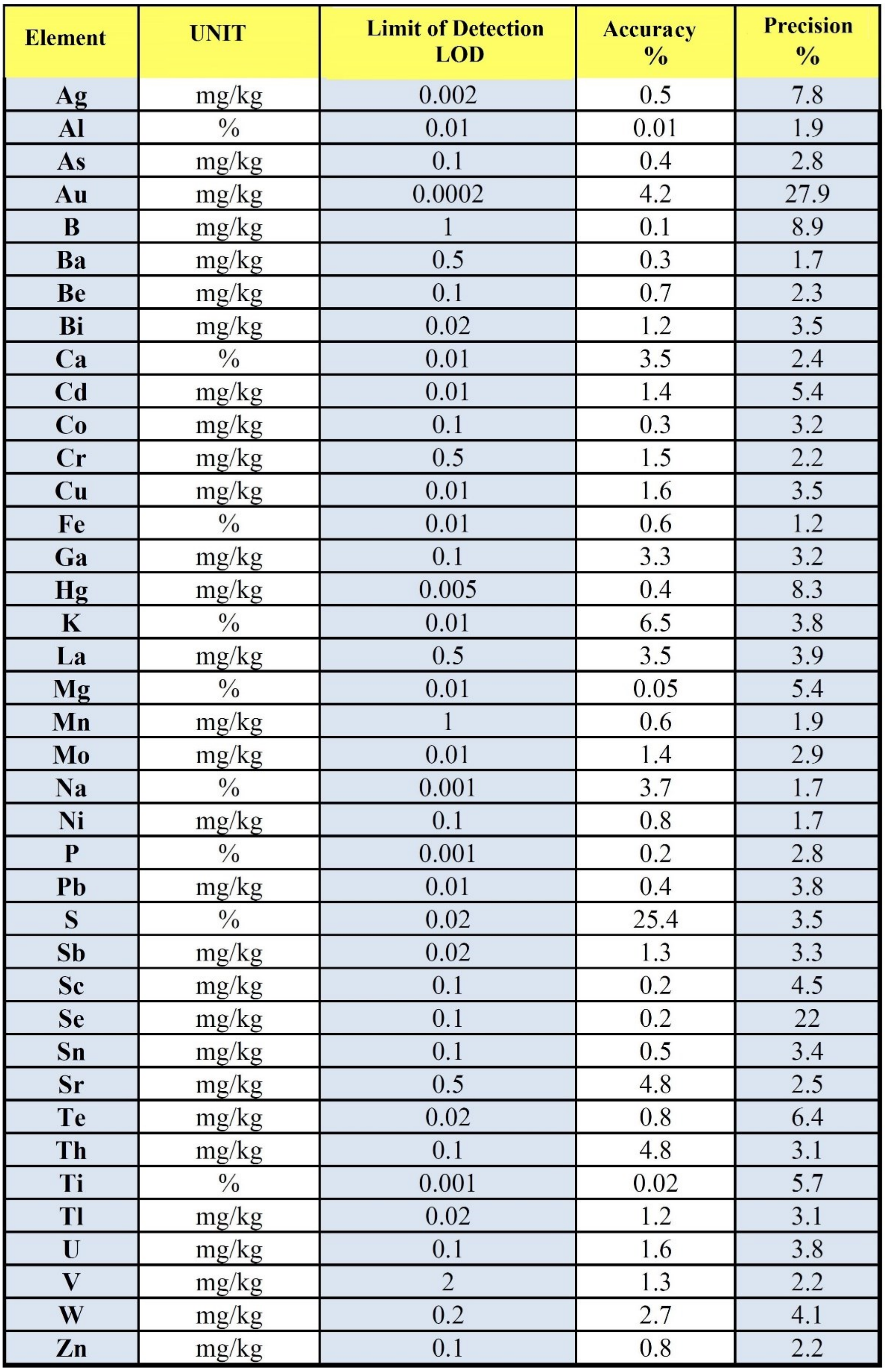
2.1 Univariate statistics

A traditional statistical analysis of the stream sediment analytical data, has been performed by Kaleida Graph 4.0 program. (Tables 1). The distribution of the elemental concentrations for every stream sediment sample (999) has been plotted using histograms and cumulative frequency curves.

2.2 Geochemical map production

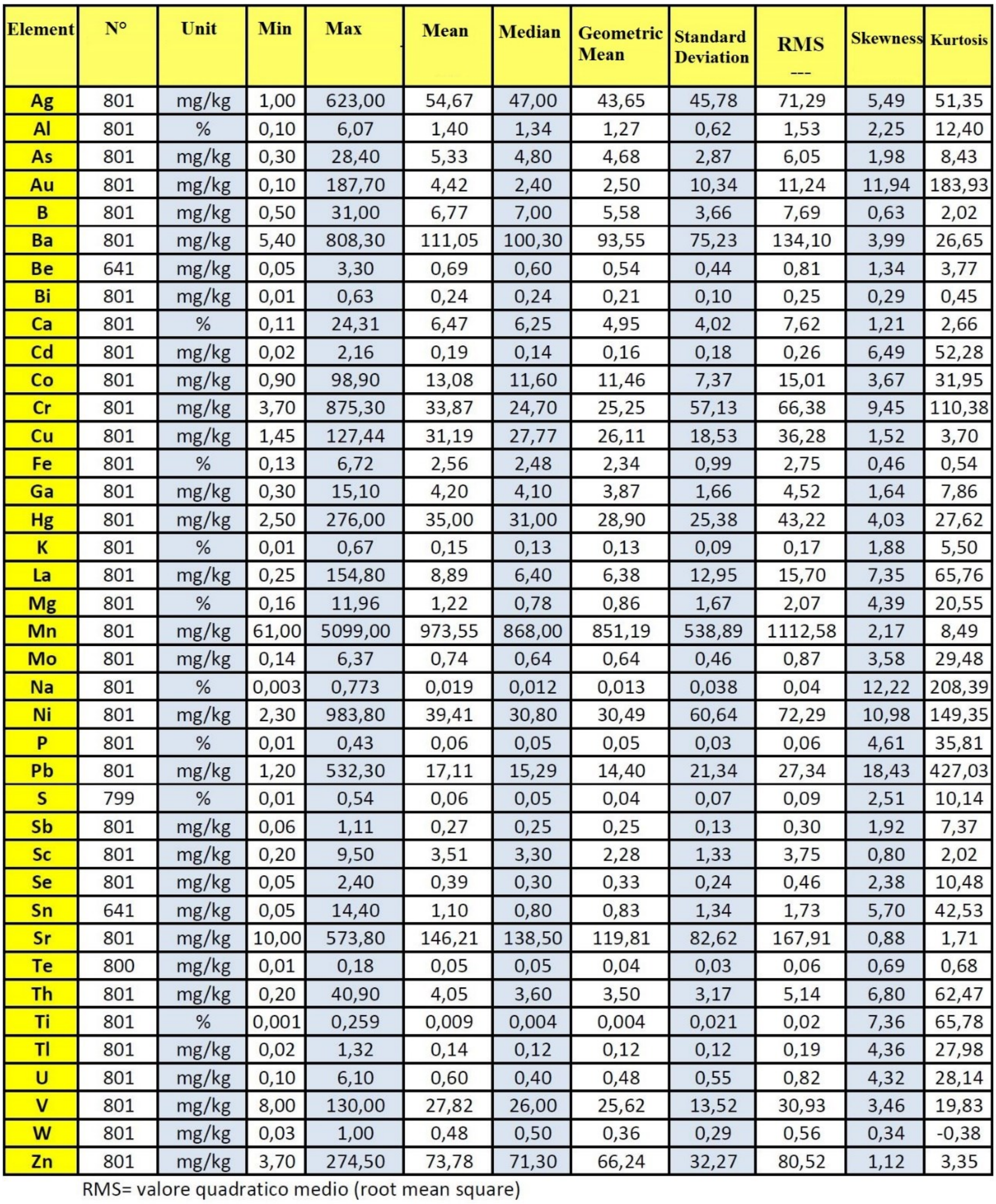
In this part of the work the various types of geochemical maps are presented and described compiled for the chemical elements in stream sediment analysed by the Basilicata region.

As the Soil Geochemical Environmental Atlas of Campania, to perform an interpolated map, the same methodology is used (*Chapter IV, 2.2.1*). Here, it is reported a summary of different typologies of created maps.



Element	UNIT	Limit of Detection LOD	Accuracy %	Precision %
Ag	mg/kg	0.002	0.5	7.8
Al	%	0.01	0.01	1.9
As	mg/kg	0.1	0.4	2.8
Au	mg/kg	0.0002	4.2	27.9
B	mg/kg	1	0.1	8.9
Ba	mg/kg	0.5	0.3	1.7
Be	mg/kg	0.1	0.7	2.3
Bi	mg/kg	0.02	1.2	3.5
Ca	%	0.01	3.5	2.4
Cd	mg/kg	0.01	1.4	5.4
Co	mg/kg	0.1	0.3	3.2
Cr	mg/kg	0.5	1.5	2.2
Cu	mg/kg	0.01	1.6	3.5
Fe	%	0.01	0.6	1.2
Ga	mg/kg	0.1	3.3	3.2
Hg	mg/kg	0.005	0.4	8.3
K	%	0.01	6.5	3.8
La	mg/kg	0.5	3.5	3.9
Mg	%	0.01	0.05	5.4
Mn	mg/kg	1	0.6	1.9
Mo	mg/kg	0.01	1.4	2.9
Na	%	0.001	3.7	1.7
Ni	mg/kg	0.1	0.8	1.7
P	%	0.001	0.2	2.8
Pb	mg/kg	0.01	0.4	3.8
S	%	0.02	25.4	3.5
Sb	mg/kg	0.02	1.3	3.3
Sc	mg/kg	0.1	0.2	4.5
Se	mg/kg	0.1	0.2	22
Sn	mg/kg	0.1	0.5	3.4
Sr	mg/kg	0.5	4.8	2.5
Te	mg/kg	0.02	0.8	6.4
Th	mg/kg	0.1	4.8	3.1
Ti	%	0.001	0.02	5.7
Tl	mg/kg	0.02	1.2	3.1
U	mg/kg	0.1	1.6	3.8
V	mg/kg	2	1.3	2.2
W	mg/kg	0.2	2.7	4.1
Zn	mg/kg	0.1	0.8	2.2

Table 1- Limit of detection, accuracy and precision



Element	N°	Unit	Min	Max	Mean	Median	Geometric Mean	Standard Deviation	RMS ---	Skewness	Kurtosis
Ag	801	mg/kg	1,00	623,00	54,67	47,00	43,65	45,78	71,29	5,49	51,35
Al	801	%	0,10	6,07	1,40	1,34	1,27	0,62	1,53	2,25	12,40
As	801	mg/kg	0,30	28,40	5,33	4,80	4,68	2,87	6,05	1,98	8,43
Au	801	mg/kg	0,10	187,70	4,42	2,40	2,50	10,34	11,24	11,94	183,93
B	801	mg/kg	0,50	31,00	6,77	7,00	5,58	3,66	7,69	0,63	2,02
Ba	801	mg/kg	5,40	808,30	111,05	100,30	93,55	75,23	134,10	3,99	26,65
Be	641	mg/kg	0,05	3,30	0,69	0,60	0,54	0,44	0,81	1,34	3,77
Bi	801	mg/kg	0,01	0,63	0,24	0,24	0,21	0,10	0,25	0,29	0,45
Ca	801	%	0,11	24,31	6,47	6,25	4,95	4,02	7,62	1,21	2,66
Cd	801	mg/kg	0,02	2,16	0,19	0,14	0,16	0,18	0,26	6,49	52,28
Co	801	mg/kg	0,90	98,90	13,08	11,60	11,46	7,37	15,01	3,67	31,95
Cr	801	mg/kg	3,70	875,30	33,87	24,70	25,25	57,13	66,38	9,45	110,38
Cu	801	mg/kg	1,45	127,44	31,19	27,77	26,11	18,53	36,28	1,52	3,70
Fe	801	%	0,13	6,72	2,56	2,48	2,34	0,99	2,75	0,46	0,54
Ga	801	mg/kg	0,30	15,10	4,20	4,10	3,87	1,66	4,52	1,64	7,86
Hg	801	mg/kg	2,50	276,00	35,00	31,00	28,90	25,38	43,22	4,03	27,62
K	801	%	0,01	0,67	0,15	0,13	0,13	0,09	0,17	1,88	5,50
La	801	mg/kg	0,25	154,80	8,89	6,40	6,38	12,95	15,70	7,35	65,76
Mg	801	%	0,16	11,96	1,22	0,78	0,86	1,67	2,07	4,39	20,55
Mn	801	mg/kg	61,00	5099,00	973,55	868,00	851,19	538,89	1112,58	2,17	8,49
Mo	801	mg/kg	0,14	6,37	0,74	0,64	0,64	0,46	0,87	3,58	29,48
Na	801	%	0,003	0,773	0,019	0,012	0,013	0,038	0,04	12,22	208,39
Ni	801	mg/kg	2,30	983,80	39,41	30,80	30,49	60,64	72,29	10,98	149,35
P	801	%	0,01	0,43	0,06	0,05	0,05	0,03	0,06	4,61	35,81
Pb	801	mg/kg	1,20	532,30	17,11	15,29	14,40	21,34	27,34	18,43	427,03
S	799	%	0,01	0,54	0,06	0,05	0,04	0,07	0,09	2,51	10,14
Sb	801	mg/kg	0,06	1,11	0,27	0,25	0,25	0,13	0,30	1,92	7,37
Sc	801	mg/kg	0,20	9,50	3,51	3,30	2,28	1,33	3,75	0,80	2,02
Se	801	mg/kg	0,05	2,40	0,39	0,30	0,33	0,24	0,46	2,38	10,48
Sn	641	mg/kg	0,05	14,40	1,10	0,80	0,83	1,34	1,73	5,70	42,53
Sr	801	mg/kg	10,00	573,80	146,21	138,50	119,81	82,62	167,91	0,88	1,71
Te	800	mg/kg	0,01	0,18	0,05	0,05	0,04	0,03	0,06	0,69	0,68
Th	801	mg/kg	0,20	40,90	4,05	3,60	3,50	3,17	5,14	6,80	62,47
Ti	801	%	0,001	0,259	0,009	0,004	0,004	0,021	0,02	7,36	65,78
Tl	801	mg/kg	0,02	1,32	0,14	0,12	0,12	0,12	0,19	4,36	27,98
U	801	mg/kg	0,10	6,10	0,60	0,40	0,48	0,55	0,82	4,32	28,14
V	801	mg/kg	8,00	130,00	27,82	26,00	25,62	13,52	30,93	3,46	19,83
W	801	mg/kg	0,03	1,00	0,48	0,50	0,36	0,29	0,56	0,34	-0,38
Zn	801	mg/kg	3,70	274,50	73,78	71,30	66,24	32,27	80,52	1,12	3,35

RMS= valore quadratico medio (root mean square)

Table 2- Statistical parameters related to 39 elements of the Basilicata region.

2.2.1 Dot map

Dot map is the map of dot distribution of concentrations, useful for information on the actual concentration distributions when the sample was collected. In detail, the concentrations of different elements have been classified regarding the corresponding percentiles of such concentrations: 10, 25, 50, 70, 90, 95, and 98. These intervals are represented in the map using circular symbols and different colors that depend on an increasing size with an increase on the values of concentrations.

2.2.2 Interpolated map

Based on the cell size used during the sampling it is possible, using a detected radius interpolation related to the element concentration, to reclassify the dot value on a spatial value through a Multifractal Inverse Distance Weighted (MIDW) method (Cheng, 1999) available in the software GeoDAS (Cheng, 2003); To generate interpolated maps the multifractal analysis filter method used is Concentration-Area model (C-A).

2.2.3 Background map

These maps are the principal way to get information about the statistically higher concentration levels found in a detected area. On literature the term background content (natural background) designates the concentration of natural elements, including the presence of abnormal concentrations due to mineralization.

2.2.4 Factor association map

In the interpretation and evaluation of geochemical concentrations of different elements, both for geo-mining and environmental, it is very useful the use of multivariate statistical techniques such as factor analysis in R-mode.

It allows a quantitative assessment of different variables and their mutual influence, thus allowing to group elements in factorial associations depending on their coefficient of correlation. This enables to identify possible correlations between the distribution of the individual elements, lithological characteristics, potential mineralizing processes, enrichment phenomena associated to surface environment, pollution and other anthropogenic (*De Vivo et al. 1981, 2004*).

3. *Results and discussions*

This paragraph shows part of the results of this research: Stream Sediment Geochemical Environmental Atlas of Basilicata region (*Lima et al., 2015*). I collaborated in the part of sampling and in the production of maps, during my PhD programme. In detail; I described the results about some elements from this area such as: Fe, Mg (major element); Ni, Cr (toxic metals); La (trace elements).

The description of each element refers to that of the Geochemical Atlas of Europe: FOREGS (Salminen, R.; Batista, M.J.; Bidovec, M.; Demetriades, A.; De Vivo, B.; De Vos, W.; Duris, M.; Gilucis, A.; Gregorauskiene, V.; Halamić, Josip; Heitzmann, P.; Lima, A.; Jordan, G.; Klaver, G.; Klein, P.; Lis, J.; Locutura, J.; Marsina, K.; Mazreku, A.; O'Connor, P.J.; Olsson, S.A.; Ottesen, R.-T.; Petersell, V.; Plant, J.A.; Reeder, S.; Salpeteur, I.; Sandstrom, H.; Siewers, U.; Steenfelt, A.; Tarvainen, T.)

3.1 Major elements

3.1.1 Iron (Fe)

Iron is a member of the first row transition series of elements, consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group. Iron is the fourth most abundant element and second most abundant metal in the Earth's crust (after aluminium). It is one of the seven metals known in antiquity (along with gold, silver, copper, mercury, tin and lead). It has both lithophile and limestone properties. It is also present in many rock-forming minerals, including mica, garnet, amphibole, pyroxene and olivine. Iron becomes concentrated in mid-stage fractionates during magmatic processes and is generally enriched in mafic rocks relative to felsic, intermediate or ultramafic types. The abundance of Fe in sedimentary rocks is determined by various factors, including provenance, pH-Eh conditions, the extent of diagenetic alteration and grain size. In most instances, secondary hydrous oxides are the dominant Fe phases, although primary oxides may account for some of the iron. The tendency for hydrous Fe phases to form surface oxide coatings can be reflected in a direct relationship between total Fe content and the specific surface areas of sedimentary particles (*Ure and Berrow 1982*).

Iron is a major element in soil with a median value of 2.1% (*Rose et al. 1979*). It is present mostly as Fe^{2+} in Fe-Mg silicates, such as olivine, pyroxene, amphibole and biotite, and as Fe^{3+} in iron oxides and hydroxides, as the result of weathering. The reactions of Fe in weathering processes depend largely on pH-Eh, and on the oxidation state of the Fe compounds involved. It is noted that the mobility of Fe in soil is largely controlled by the solubility of Fe^{3+} and Fe^{2+} amorphous hydrous oxides, although the formation of other Fe compounds, such as phosphates, sulphides and carbonates, may greatly modify Fe solubility (*Kabata-Pendias 2001*).

Controls on dissolved Fe concentrations in stream water are complex. Iron is relatively immobile under most environmental conditions, mainly due to the very low solubility of iron (III). hydroxide in its various forms. Its solubility is strongly influenced by redox conditions. The Fe^{2+} ion is much more soluble in strong acid or reducing conditions, so higher concentrations are found in reducing groundwater (Hylander et al.2000). However, dissolved Fe is generally precipitated rapidly with increasing pH or Eh, and this causes the presence of hydrous oxide coatings, e.g., goethite, limonite and lepidocrocite, on stream clasts in aerobic environments. Anthropogenic sources of iron include the iron and steel industry, sewage and dust from iron mining (*Reimann and de Caritat 1998*). Iron sulphate is also used as a fertiliser and herbicide (*Reimann et al. 2003*).

Iron is an essential nutrient for plants and animals. An amount of 10 to 18 mg per day is needed for adults (Mertz 1987) and iron deficiency is a common medical condition. Its main role in humans is the production of haemoglobin in red blood cells (WHO 1996). High intakes of cobalt, zinc, cadmium, copper and manganese interfere with iron absorption in the human body, which may lead to anaemia (Mertz 1987).

Fe content in stream sediments ranges from a minimum of 0.13% to a maximum of 6.72%, with a median value of 2.48%. This value is comparable with values of Campania Region (maximum value 7, 66%, median 2.11%), and Italian values (maximum 9.10%, median 2.21%). Dot map shows that higher concentrations are observed between 4.76 and 6.72%, statistically determined by the 98th percentile, concentrated in the basin of Sinni near Viggianello, Latronico and Lauria, while lower values (4, 39 - 4.76%) are present in the Agri basin near of Marsico Nuovo. Average values of stream sediments at regional scale are <4.3%, as confirmed by the distribution of interpolated data, offering values in the Lucan area between 0.13 and 4.3 %.(Fig.5) Rather small areas with concentrations > 4.3% are concentrated in the vicinity of Val d'Agri and Sinni. The distribution of background values shows that the geogenic control over regional stream sediments in the lower values are similar to limestone formations, and terrigenous, with higher values influenced by outcrops of ophiolite and metamorphic formations in the area between Viggianello and Latronico. Only the high values in the Val d'Agri might also have recorded an anthropic contribution due to mining activities. (Fig.6).

3.1.2 Magnesium (Mg)

Magnesium belongs to group 2 of the periodic table, along with Be, Ca, Sr and Ba. Magnesium is a lithophile metallic element and a major constituent of many mineral groups, including silicates, carbonates, sulphates, phosphates and borates. In magmatic systems, Mg is concentrated in high temperature minerals like olivine and pyroxene, which precipitate relatively early. However, if water and oxygen fugacity reach critical limits, the precipitating phases are more likely to be amphibole or mica. Magnesium is a significant component of phyllosilicate minerals, such as chlorite, montmorillonite and glauconite. It is low in illite so shale (1.5% Mg) has higher concentrations than sandstone (0.7% Mg). The average concentration of Mg in loess is 0.68%. High Mg values indicate mafic or ultramafic rocks (in association with Cr, Ni, V, etc.) or calcareous rocks (with Ba, Ca and Sr). As many Mg compounds are quite soluble, Mg is highly mobile after its release by weathering, under all environmental conditions. Under the pH, redox and conductivity regimes typically found in streams, Mg is likely to be present almost exclusively as Mg^{2+}. Most limestone contains significant amounts of Mg, so streams draining limestone, and other carbonate-rich rocks, are likely to have high Mg^{2+}concentrations. The average value of Mg in river particulates is 1.2 % .

Anthropogenic sources of magnesium include fertilizers and liming (*Reimann and de Caritat 1998*). Because of its low weight and its ability to form mechanically resistant alloys, it is widely used as structural metal in the building industry and it is essential in airplane and missile construction. It is also used in flashlight photography, flares and pyrotechnics, including incendiary bombs, as well as a reducing agent in the production of pure uranium and other metals from their salts. Magnesium is essential for every organism and is not toxic under normal circumstances. Deficiencies of magnesium are much more common than problems associated to toxicity. Adult daily requirement of magnesium is about 300 mg day-^{1}. Magnesium is a key plant nutrient and is essential for photosynthesis in plants, where it forms the active site in the chlorophyll enzyme molecule.

The Mg concentrations in the examined stream sediments have a range from a minimum of 0.16% to a maximum of 11.92% with a median value of 0.78%. These values are comparable with stream sediment values of the Campania Region (maximum value 8, 81%, median 0.60%), but lower than those observed in Italian river sediments (maximum 25%, median 1.9%). Dot map shows that higher concentrations, determined statistically by the 98th percentile (9-12%) are concentrated in the sediments of the Agri basin near Moliterno and isolated in the basin of the summit in Sinni near Viggianello. (Fig.7). Interpolated data show that in most of 'Lucania', the concentration values are between 0.16 % and 2.1% with values > 2.1 % in restricted areas, close to formations of limestone and dolomite of Apennines 'Lucani' near Moliterno and ophiolite formations.(Fig.8). The distribution of background values shows in fact the geogenic control over regional fluvial sediments. In the lower values they are comparable with varying formations called 'lucanian', while for higher values (6.6 to 10%) it is evident from the dolomitic limestone and ophiolites.(Fig.9).

3.2 Toxic metals

3.2.1 Chromium (Cr)

Chromium is a member of the first row transition series of elements, which consists of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 6 of the periodic table, along with Mo and W. Chromium is a lithophile metallic element forming several minerals, including chromite $FeCr_2O_4$ and the rare crocoite PbCrO4, and is present as an accessory element in several others, such as spinel, amphibole, mica, pyroxene and garnet. Cr is enriched in ultramafic rocks (1000–3000 mg kg^{-1}), along with elements such as Ni. While the principal Cr ore mineral, chromite, is generally mined from ultramafic rocks, it is also a major carrier of Cr in basaltic magmas, along with Cr-enriched magnetite and ilmenite (*Wedepohl 1978*). Elevated Cr values are indicative of mafic or ultramafic rocks, even in strongly-weathered environments, such as laterite; this apparently holds true even when aqua regia digestion is applied, which is unable of breaking down chromite. Very low Cr contents in association with elevated values of K, Th, U and REEs may indicate the presence of felsic rocks, e.g., kaolinised intrusives.

In sedimentary rocks, Cr may be present in primary detrital phases such as chromite, magnetite and ilmenite. During weathering, the behavior of Cr^{3+} resembles that of Fe^{3+} and Al^{3+}, leading to widespread accumulation in secondary oxides and clays. Chromium is a low mobility element, especially under moderately oxidising and reducing conditions and near-neutral pH values.

In soil, Cr behavior is governed by pH, Eh and organic matter. Its adsorption by clay is also highly dependent on pH; Concentrations of chromium in uncontaminated natural water are typically less than 10 µg l^{-1} (*Hem 1992*). The European Commission and US EPA threshold for drinking water is 50 µg l^{-1} Cr (*European Commission 1998*). Chromium, once thought to be non-essential, is now known to have at least one important biological function (*Frausto da Silva and Williams 1991*). It is needed by the human body in small amounts for insulin action and the metabolism of proteins and carbohydrates. Chromium has a varying toxicity depending on its valency and on the speciation in the environment. Soluble Cr^{3+} is considered relatively harmless at normally encountered levels, but Cr^{6+} is highly toxic, causing liver and kidney damage and acting as a carcinogen.

Cr content in stream sediment ranges from a minimum of 3.7 mg / kg to a maximum of 875 mg / kg, the median value is 24.7 mg / kg, all values are comparable with those determined in the river sediments of Campania region (maximum 1117 mg / kg, median 20 mg / kg) and the Italian ones (maximum value 1748 mg / kg, median 23 mg / kg). Dot map shows that these higher concentrations (157-875 mg / kg) are focused in the area near Sinni basin and in the north of Viggianello.(Fig.10). The remaining part of Lucania shows relatively low concentrations, as can also be seen in the map of the distribution of interpolated data. As it has been observed in Co, there are also elevated concentrations of Cr in the river north of Viggianello, they are attributed to the presence of ophiolites in the surface area. Background map (Fig.12) shows in fact rather low regional values (3.7 to 36 mg / kg); higher values (198-317 mg / kg) can be found only in association with ophiolite outcrops. Regarding Co, it is controlled by the lithology.

3.2.2 Nickel (Ni)

Nickel belongs to group 10 of the periodic table, along with Pd and Pt. Nickel is a siderophile metallic element with limestone and lithology. Ni appears in igneous rocks such as: ultramafic 2000 mg kg^{-1}; basaltic 130 mg kg^{-1}; granitic 4.5-15 mg kg^{-1}, and a crustal abundance of 99 mg kg^{-1}. Nickel, like Co, is a siderophile element, but in the Earth's crust it also exhibits limestone and lithophile characteristics. The abundance of Ni in igneous rocks, therefore, is generally correlated with those of Mg, Cr and Co. In sedimentary rocks, Ni is mostly held in detrital ferromagnesian silicate minerals, detrital primary Fe oxides, hydrous Fe and Mn oxides, and clay minerals. A large proportion of the Ni in stream sediment is held in detrital silicate and oxide minerals resistant to weathering. Limited dissolution of Ni^{2+} may occur at low pH, but its mobility is generally limited by its tendency to be absorbed by clay minerals (Short 1961) or hydrous oxides of Fe and Mn (*Ure and Berrow 1982*). In soil, Ni is strongly related to Mn and Fe oxides but, especially in surface soil horizons, occurs mainly in organically bound forms (*Kabata-Pendias 2001*). The range of Ni values in soil vary from 0.2 to 450 mg kg-1 according to rock type.

Nickel is highly mobile under acidic, oxidising conditions. In natural water, Ni may exist in one of the three oxidation states ($^{+2}$, $^{+3}$ and $^{+4}$), although the free ion Ni predominates. River particulates have an average value of 90 mg kg^{-1} (*McLennan and Murray 1999*).

Anthropogenic sources of nickel include fertilisers, steel works, metal plating and coinage, fuel combustion and detergents (*Reimann and de Caritat 1998*). In the presence of some organic complexing agents, Ni is capable of forming neutral or negatively charged complexes, giving the metal a high mobility compared to other trace elements. Consequently, Ni concentrations may be high in stream water contaminated by sewage and leachate from waste tips.

It has been proved that nickel is essential for microorganisms and it has an essential role in human metabolism (*McGrath 1995*). The World Health Organisation recommends a daily intake of 10 µg day^{-1} for humans (WHO 1996). Nickel deficiency retards growth and impairs iron uptake. Most Ni^{2+}compounds are relatively non-toxic, but some compounds are highly toxic, and extreme excesses of Ni are both toxic, causing dermatitis and gastric irritation, and carcinogenic illnesses (*WHO 1996*).

Ni content in the analyzed river sediments vary from a minimum value of 2.3 mg / kg to a maximum value of 984 mg / kg, while the median value is equal to 30.8 mg/kg. Basilicata' s stream sediments show higher values than those of the Campania Region (maximum 352 mg / kg, median 21 mg / kg) but equal to the values found in Italian stream sediments (maximum 1033 mg/kg, median 29 mg/kg). Dot map shows generally low values along the territory of Lucania and one area with high values in the range 62-984 mg / kg, which spreads into the basin of the river Sinni in the north-north-east of Viggianello. (Fig.13). The distribution map of interpolated data shows that the region has concentrations that do not exceed 32 mg / kg and a very limited area with concentrations of 188-984 mg / kg at the outcrops ophiolite north of Viggianello. Background map (Fig.15) confirmed that there is a geolithological control predominant in the area with highest concentrations (53-404 mg / kg). This means that there are outcrops of ophiolite in the summit area of the Agri basin as shown by the Co and Cr concentrations.

3.3 Trace elements

3.3.1 Lanthanum (La)

Lanthanum is one of the rare earth elements (REEs), which is a collective term for the elements from lanthanum to lutetium, atomic numbers 57–71, in the periodic table. Lanthanum is a lithophile element. It is also widely spread in trace quantities in several rock-forming minerals such as biotite, apatite, pyroxene and feldspar. Lanthanum has a strong affinity for felsic igneous and a lower affinity for ultramafic rocks (<10 mg kg-1).

In sedimentary rocks, a large proportion of the total La content is held in resistate accessory minerals, such as monazite. Feldspar may also contain La and provides an important supply of the element for the incorporation into secondary clay minerals during weathering (*Ronov et al. 1974*).

Lanthanum is poorly mobile under most environmental conditions. Its release from resistate phases, such as monazite is generally slow, although a small fraction of the total La burden may be held in apatite and biotite, both of which are weathered relatively rapidly at low pH. Their average concentration in soil corresponds most closely to their contents in sedimentary rocks, with the exception of calcareous rocks, where there is an enrichment with respect to the parent rocks. All REEs are reported to be concentrated in alkaline rather than in acid soil, probably due to the easy removal of their hydroxide complexes (*Kabata-Pendias 2001*). Anthropogenic sources of lanthanum include mining and processing of alkaline rock, petrol production and the disposal of household electrical equipment. La improves alkali resistance of glass and it is used to make special optical glasses. Small amounts of lanthanum are used in the production of nodular cast iron. However, natural sources of La are considered to be more important than anthropogenic ones in the environment (*Reimann and de Caritat 1998*).

Lanthanum is considered biologically inactive and non-essential. Toxicological data for La, and the REE in general, are relatively scarce, but the toxicity of La is generally considered to be from moderate to low. Inhaled REE as dust probably cause pneumoconiosis, and ingested REEs can accumulate in the skeleton, teeth, liver and lungs.

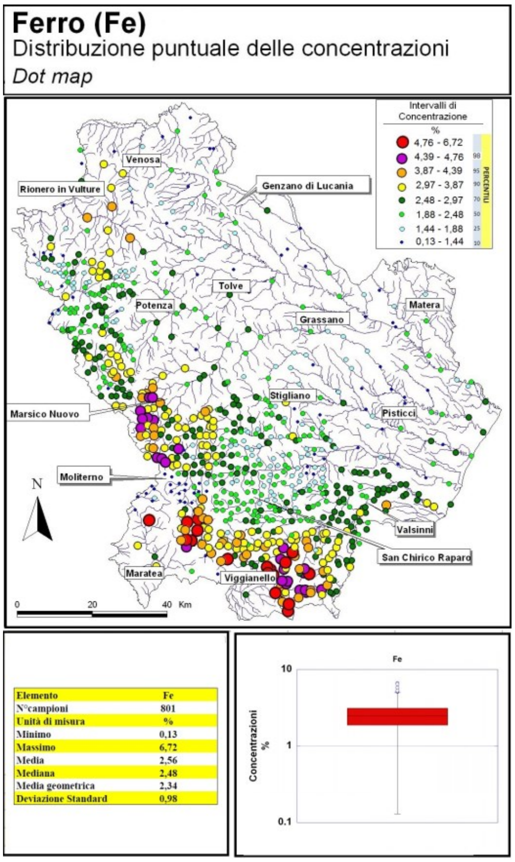
Lanthanum content ranges from a minimum of 0.3 mg /kg to a maximum of 155 mg /kg with a median value of 6.4 mg /kg. These values are compared to the ones found in river sediments from the Campania Region (maximum 124 mg /kg, median 16 mg/kg) and compared with values of the Italian river sediments (maximum 97 mg/kg, median 27 mg/kg). Dot map shows that higher concentrations, statistically determined by the 98th percentile (41-155 mg/kg), are concentrated in the stream sediments of the Ofanto basin in the Vulture. (Fig.16). Average values of river sediments at regional scale are very low (<19 mg/kg), as confirmed by the distribution of interpolated data where the included values in Lucania are generally between 0.3 mg / kg and 13 mg / kg. Higher values (44-155 mg/kg) are concentrated in the northern part of the Vulture. The distribution of the background values shows that there is a lithological control over regional river sediments, with concentrations comparable with the different formations (values generally lower than 10 mg /kg) and, for the highest values (90-140 mg/kg) it is evident the influence of the volcanic formations of the Mt. Vulture.(Fig.18).

3.4 Factor association analysis

Through factor analysis in R-mode, this study area can be divided into 4 groups of associations, 4-factor model, for 76.93% of the total variability of the data. This model was chosen because it was considered the most representative lithological-environmental peculiarity of Basilicata. For the determination of the four associations of elements, the items were considered with a weight (loading) > |0.6. Through the distribution of factor scores you can assess the impact of each of the four factor associations in each league site. To this end, geochemical maps of the following factorial associations were built:

- ***F1: La - Th - Tl - Ba - V - K - U - Al - P - Ga*** reflecting lithology of this area, in correspondence of Genzano di Lucania, Venosa, Rionero in Vulture, San Fele e Muro Lucano, composed by lavas, ignimbrites and pyroclastic soils.(Fig.19).
- ***F2: Zn - Cu - Fe - Sb - Ag - Bi – Mo*** may reflect the enrichment of all natural phenomena, due to the significant role of oxides and hydroxides Fe, leading to a strong effect of geochemical barrier and co-precipitation of the other metallic elements of this association, which a contribution due to human activities such as ‘mining’ present in the Val d'Agri. (Fig.20)
- ***F3: Ni - Cr – Co*** depend on the of ophiolite rocks enriched in these elements. The remaining part of the region is affected by very low values <0.5. This distribution is controlled by region lithology.(Fig.21)
- ***F4: Mg - Ca – U.*** This association suggests a lithological control with the highest values > 3 in correspondence of limestone-dolomite formations.(Fig.22)

APPENDIX



Elemento	Fe
N°campioni	801
Unità di misura	%
Minimo	0,13
Massimo	6,72
Media	2,56
Mediana	2,48
Media geometrica	2,34
Deviazione Standard	0,98

Figure 4 Dot map (Iron)

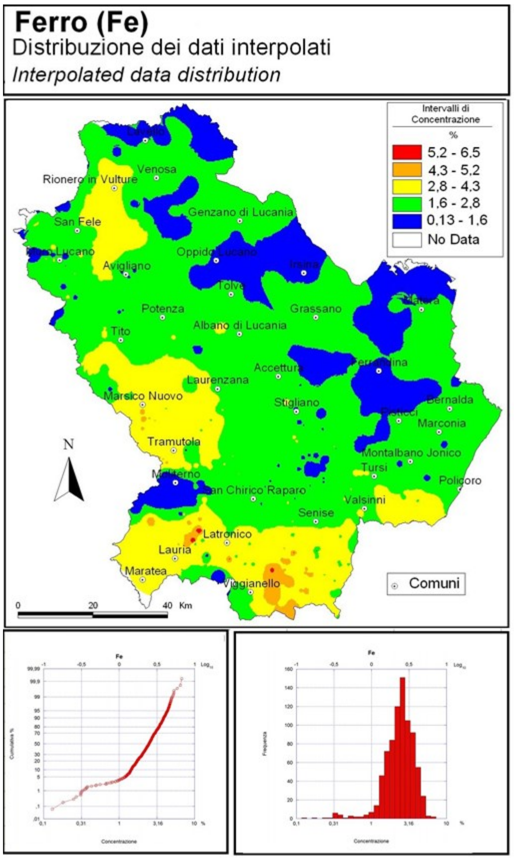


Figure 5 Interpolated map (Fe)

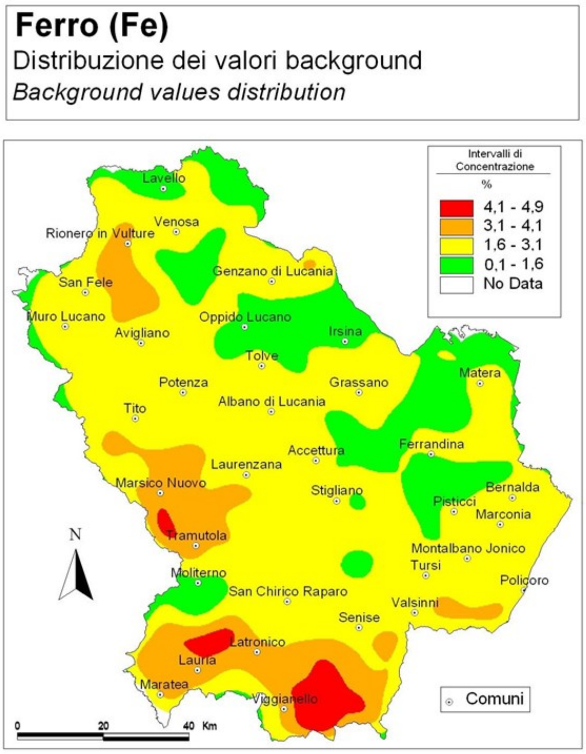
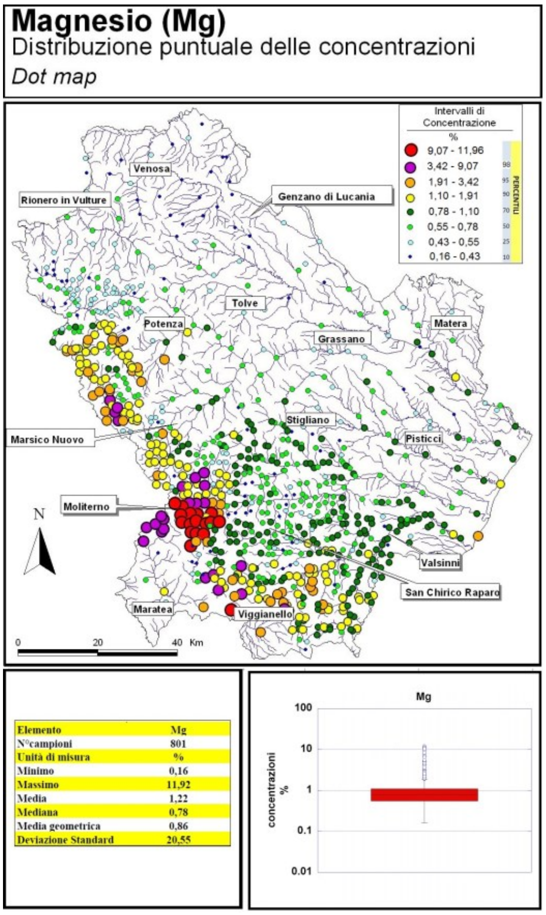


Figure 6 Background map (Iron)



Elemento	Mg
N°campioni	801
Unità di misura	%
Minimo	0,16
Massimo	11,92
Media	1,22
Mediana	0,78
Media geometrica	0,86
Deviazione Standard	20,55

Figure 7 Dot map (Magnesium)

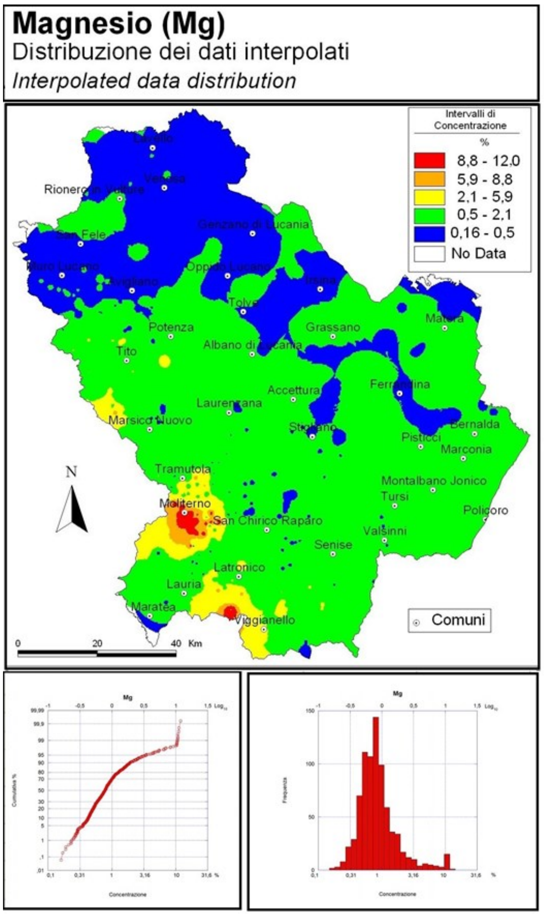


Figure 8 Interpolated map (Magnesium)

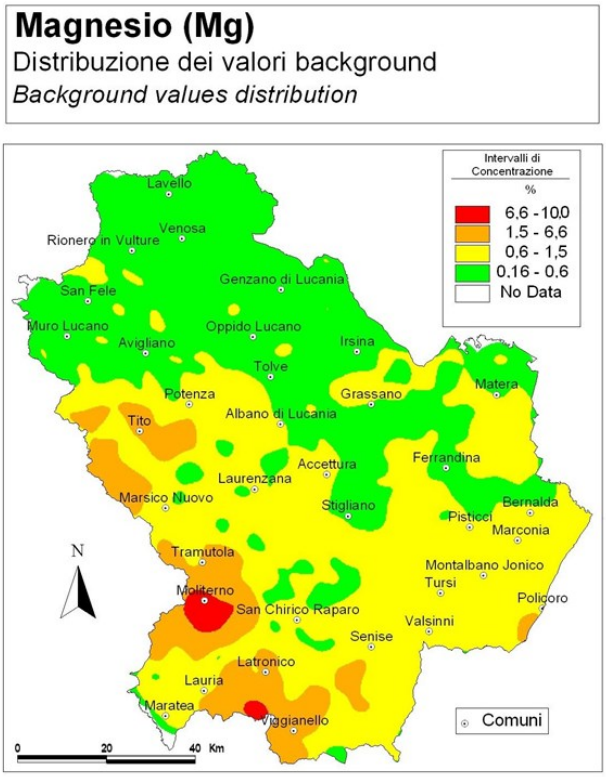
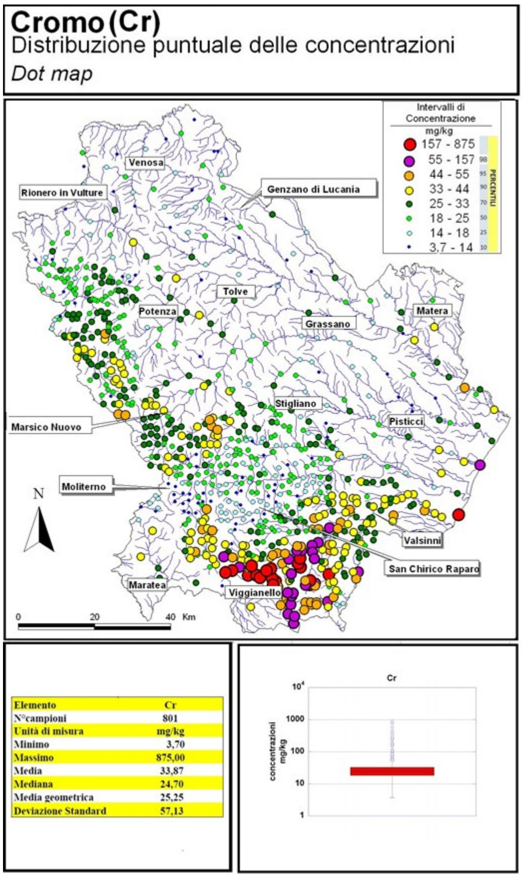


Figure 9 Background map (Magnesium)



Elemento	Cr
N°campioni	801
Unità di misura	mg/kg
Minimo	3,70
Massimo	875,00
Media	33,87
Mediana	24,70
Media geometrica	25,25
Deviazione Standard	57,13

Figure 10 Dot map (Chromium)

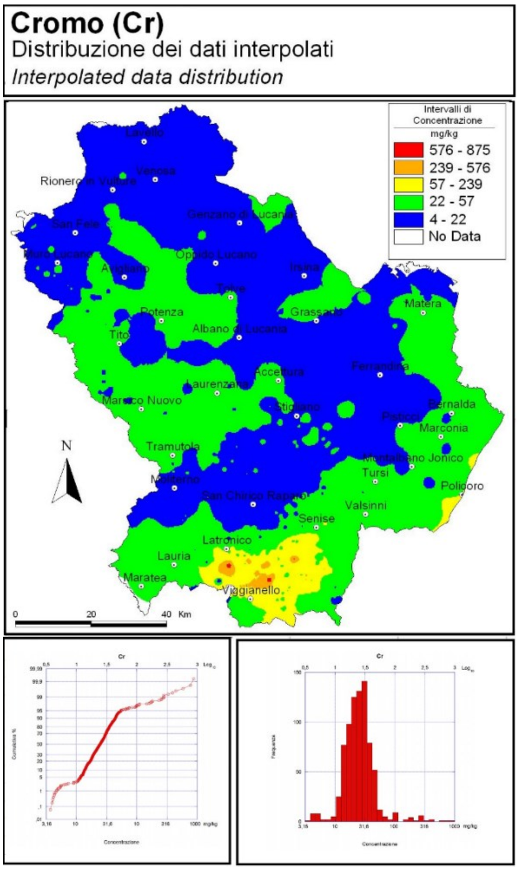


Figure 11 Interpolated map (Chromium)

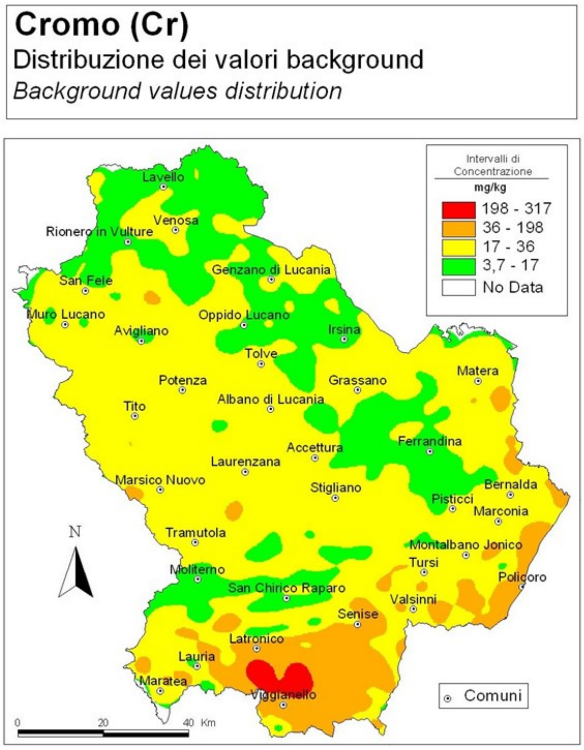
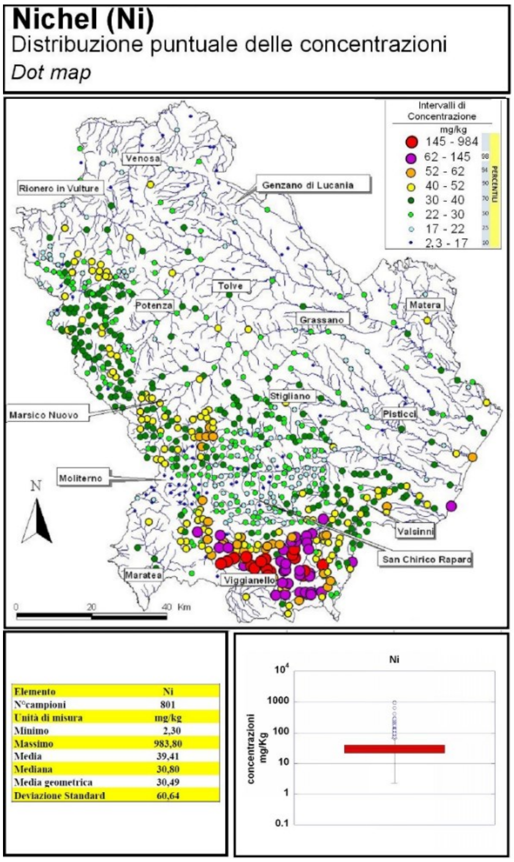


Figure 12 Background map (Chromium)



Elemento	Ni
N°campioni	801
Unità di misura	mg/kg
Minimo	2,30
Massimo	983,80
Media	39,41
Mediana	30,80
Media geometrica	30,49
Deviazione Standard	60,64

Figure 13 Dot map (Nichel)

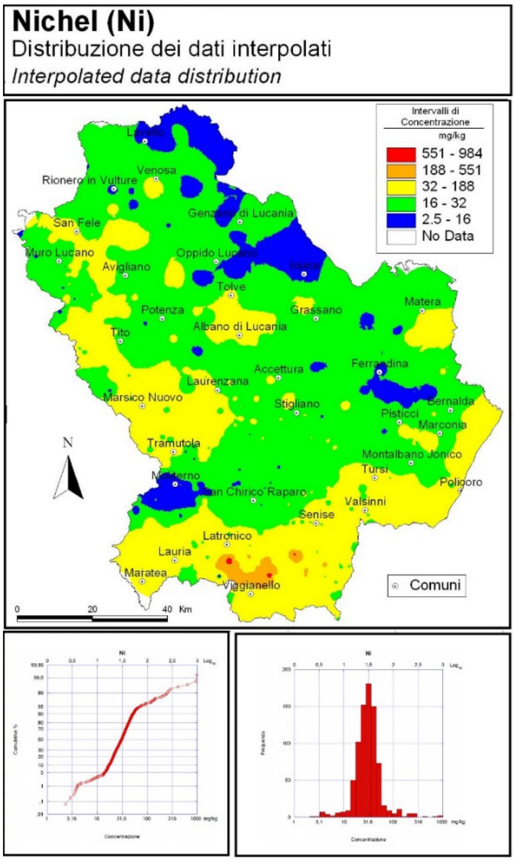


Figure 14 Interpolated map (Nichel)

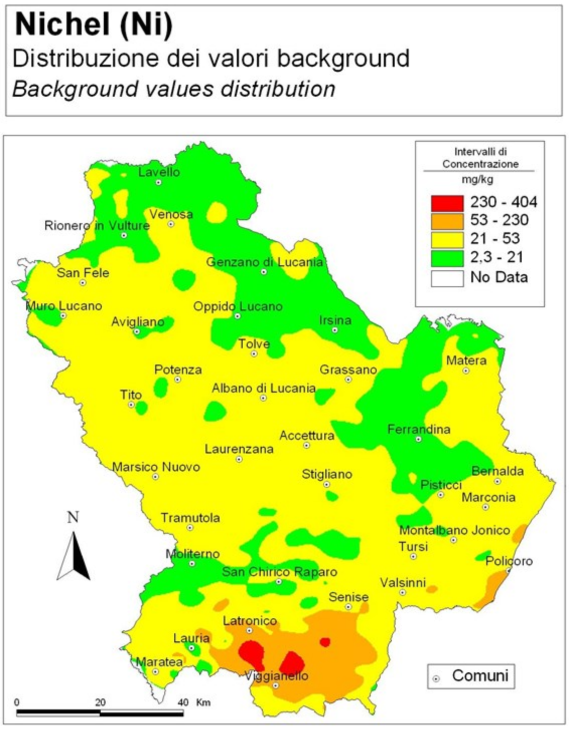
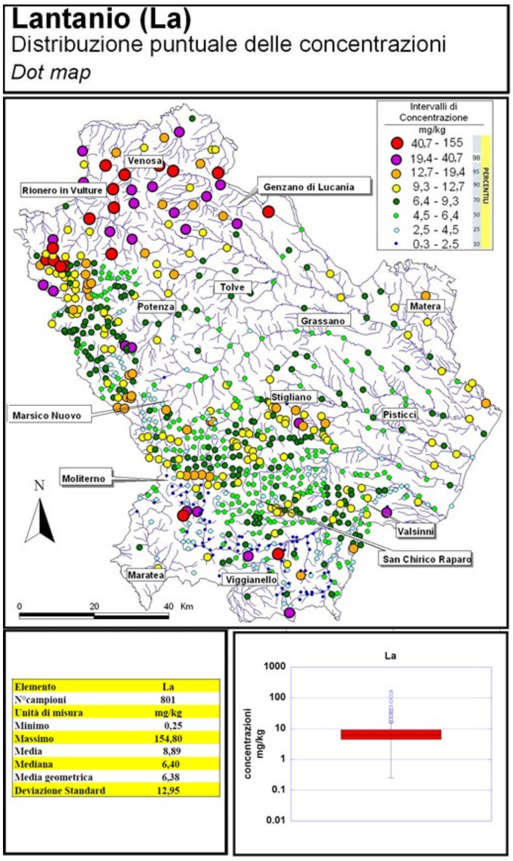


Figure 15 Background map (Nichel)



Elemento	La
N°campioni	801
Unità di misura	mg/kg
Minimo	0,25
Massimo	154,80
Media	8,89
Mediana	6,40
Media geometrica	6,38
Deviazione Standard	12,95

Figure 16 Dot map (Lanthanum)

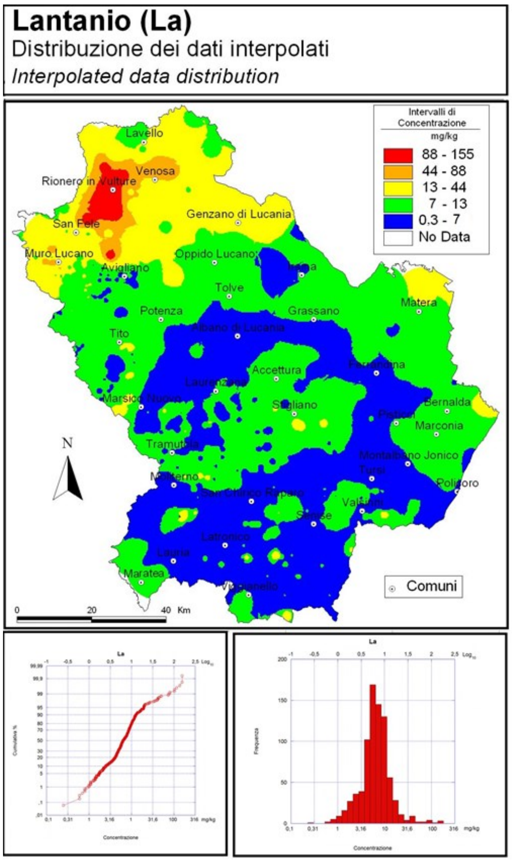


Figure 17 Interpolated map (Lanthanum)

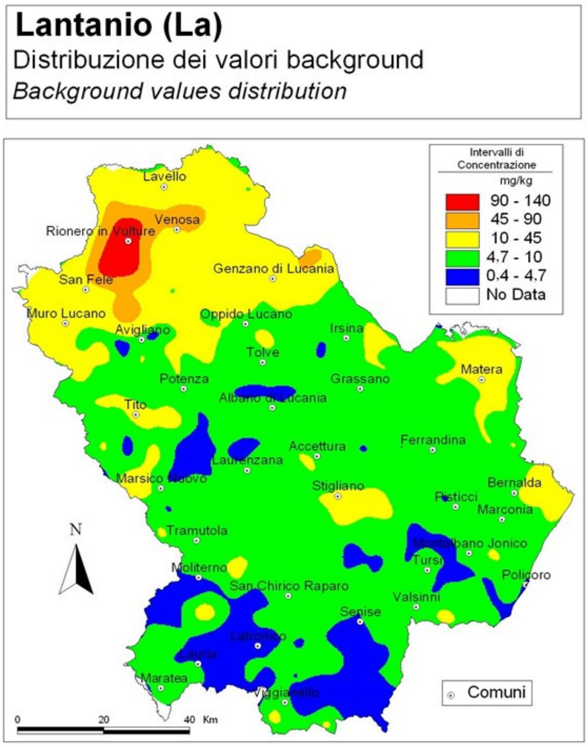


Figure 18 Background map (Lanthanum)

Carta dell'associazione fattoriale F1
Factor scores association map
(Th, La, Ti, Tl, Ba, V, K, U, Al, P, Ga)

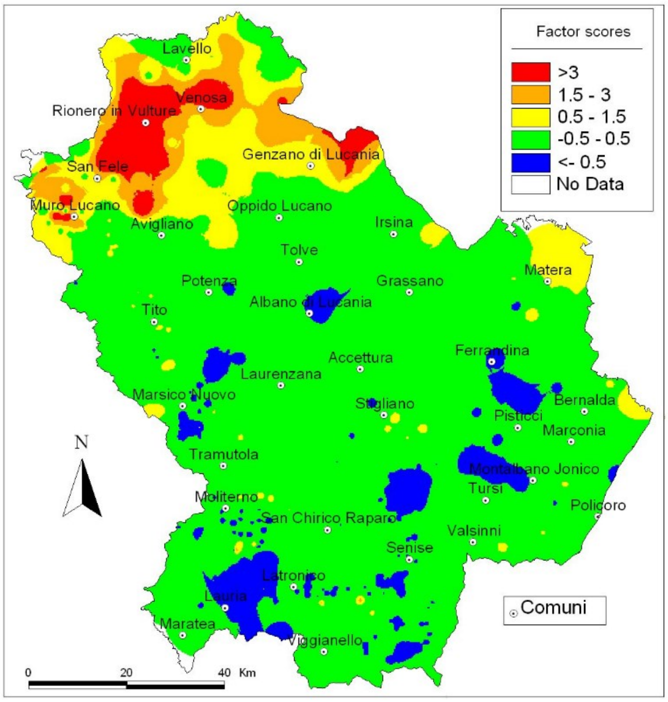


Figure 19 factor scores association map (F1)

Carta dell'associazione fattoriale F2
Factor scores association map
(Zn, Cu, Fe, Sb, Ag, Bi, Mo)

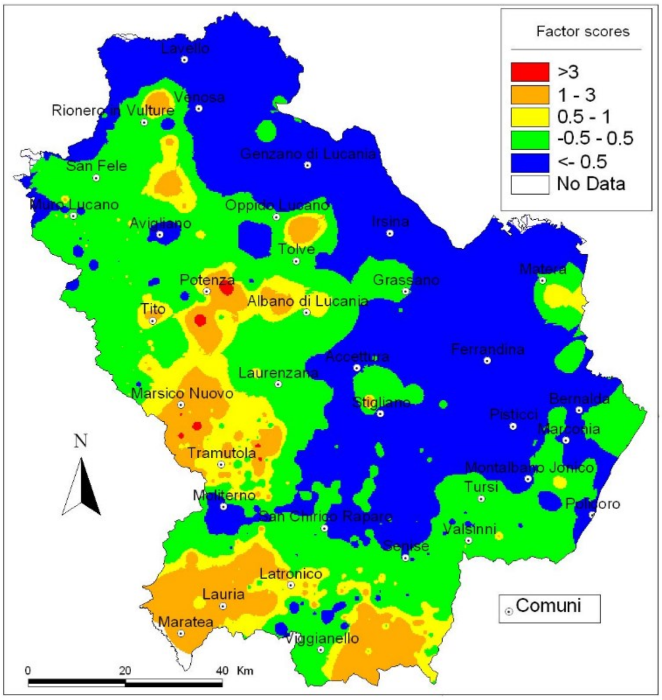


Figure 20 Factor scores association map (F2)

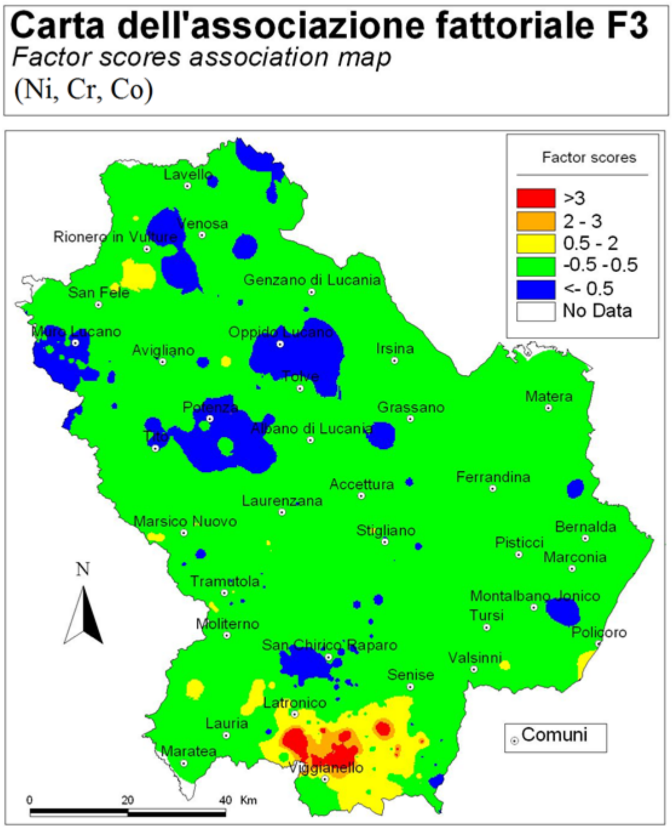


Figure 21 Factor scores association map (F3)

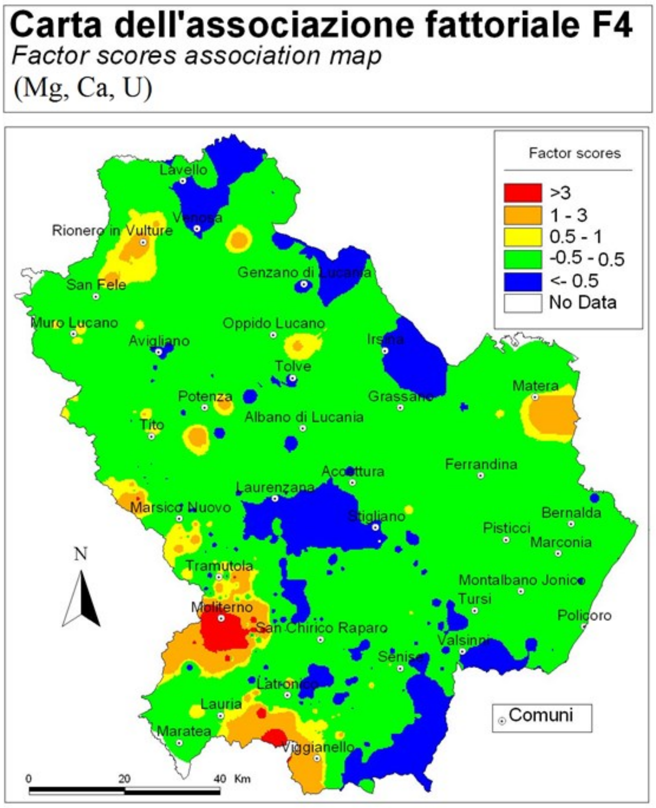


Figure 22 Factor scores association map (F4)

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