Heavy metal pollution and Pb isotopes in urban soils of Napoli, Italy

D. Cicchella [a, *], B. De Vivo [b], A. Lima [b], S. Albanese [b], R. A. R. Mc Gill [c], R. R. Parrish [c]

a - Dipartimento di Studi Geologici ed Ambientali, Università degli Studi del Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy
b - Dipartimento di Scienze della Terra, Università di Napoli "Federico II", Via Mezzocannone 8, 80138 Napoli, Italy
c - NERC Isotope Geosciences Laboratory, British Geological Survey, Nottingham, UK
** e-mail: cidom@unisannio.it*

published on: *Geochemistry: exploration, environment, analysis, vol. 8; p. 103-112, ISSN: 1467-7873, doi: 10.1144/1467-7873/07-148.*

ABSTRACT: Pb isotope analyses is an increasingly widespread tool in the study of environmental pollution as lead isotope compositions do not change during industrial and environmental processes, and always reflect their source origin. In this study we present the results of R-mode factor analysis for associations between chemical elements in Neapolitan soils, combined with the distribution of Pb concentrations and Pb isotope compositions in order to differentiate natural from anthropogenic metal sources. Results show Neapolitan urban soils to be significantly enriched in Pb, Hg, Zn, Sb, and to a lesser extent in Cu, Cd, Cr and Ni. Lead isotope measurements form a trend suggesting mixing between two end-member compositions, one of clear natural origin (geogenic) and another related to human activities (anthropogenic). Pb isotope investigations demonstrate that road traffic is one of the main sources of metal pollution.

KEYWORDS: Heavy metal, urban soil, environmental pollution, Pb isotopes, R-mode factor analysis.

INTRODUCTION

In recent years, many scientists have focused their interest on heavy metals in the soils of urban areas where pollution might have a direct influence on public health (Markus and McBratney, 2001; Fordyce *et al.*, 2005, Wong *et al.*, 2006). This is due to the frequent, close, juxtaposition of humans with soils either as suspended dust or by direct contact. Furthermore, the compilation of databases of trace metal concentrations have enabled informed decision making for setting soil protection guidelines and determining the suitability of a particular land use, by assessing potential risk to humans or the environment. Mapping contaminant distribution allows immediate appraisal of the variability of harmful elements in an area and enables rapid identification of areas that may contain excessive concentrations of toxic metals (Facchinelli *et al.*, 2001; Salminen *et al.*, 2005; Lee *et*

al., 2006). This is essential for site and subsequent risk assessment (Manta *et al.*, 2002; Cicchella *et al.*, 2005; De Vivo *et al.*, 2006).

In the Napoli metropolitan area it has already been shown (Cicchella *et al.*, 2005) that heavy metal compositions of soil are affected by a combination of two components: one natural, related to volcanic lithologies; and one anthropogenic, related to traffic and industrial activities. In this study we present the factor score distribution of elemental associations resulting from R-mode factor analysis, along with the distribution of Pb concentrations and Pb isotope compositions in order to differentiate natural from anthropogenic sources.

In the last 50-100 years, the natural geochemical Pb cycle has been completely overwhelmed by anthropogenic emissions in the atmosphere from industrial and vehicle contamination (Nriagu, 1989; Pacyna and Pacyna, 2001; USGS, 2002). Pb isotope analyses are widely used to study environmental pollution as the lead isotope composition does not change during industrial and environmental processes, but always reflects the source origin. In addition, Pb is relatively immobile in the surface environment and it is ubiquitous in many industrial processes.

The introduction of Pb into soils occurs by atmospheric deposition and by incorporation of Pb from underlying bedrock. Stable Pb isotope ratios, in combination with concentration data of Pb and other heavy metals, are an useful method of differentiating natural from anthropogenic sources (Erel *et al.*, 1997; Hansmann & Köppel, 2000; De Vivo *et al.*, 2001a; Charalampides & Manoliadis, 2002; Flament *et al.*, 2002; Tarzia *et al.*, 2002; Haack *et al.*, 2004; Ayuso *et al.*, 2004; 2005).

Lead isotopes used for this study are ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. ^{204}Pb is non-radiogenic and ^{206}Pb, ^{207}Pb and ^{208}Pb are formed by the radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively.

STUDY AREA

Geographical setting

Napoli is located in the Campania Region, along the Tyrrhenian coastline (Fig. 1), in one of the most densely populated and active volcanic areas of the Earth, with a density of about 7,700 inhabitants per km^2. The climate is typically Mediterranean with an average annual temperature of 15.4 °C and an average rainfall of 1026 mm/y.

The communication network has been expanded considerably in the last few decades, with the construction of motorways, for the increasing traffic that has now practically reached saturation level. In Napoli city between 1991 and 2001, the number of circulating cars grew from *c.* 700,000 to more than 1,500,000 and 30% of them are currently >14 years old.

The metropolitan area of Napoli has become a typical example of intensive human activities affected by various environmental hazards, such as hydrogeological degradation, soil and water pollution, as well as volcanic, seismic and bradyseismic activities.

Geological setting

The geology of the area is dominated by volcanics which erupted since Upper Pleistocene by Mt. Somma-Vesuvius to the east and the Campi Flegrei fields to the west (Fig. 2). The morphology of the metropolitan area of Naples can be subdivided into several flat areas, consisting of reworked pyroclastic terrains, and hills formed by the overlapping of different welded pyroclastic flows (i.e.: Campanian Ignimbrite and Neapolitan Yellow Tuff) (De Vivo *et al.*, 2001b; Rolandi *et al.*, 2003) intercalated with pyroclastic deposits of different origins and ages (i.e., Campi Flegrei, Mt. Somma-Vesuvius, Ischia) (De Vivo *et al.*, 1993; Spera *et al.*, 1998; De Vivo & Rolandi, 2001; De Vivo, 2006). Soils developed on these volcanics, which cover the greater part of the Neapolitan territory, are characterized by andic properties (di Gennaro and Terribile, 1999). The mineralogical assemblage consists mainly of biotite, sanidine, leucite, garnet and pyroxenes (Imperato *et al.*, 2003). In particular, leucite occurs only in the Vesuvian soils.

METHODS

Sampling

Soil samples were collected from 207 sites within a network of an area of about 120 km^2, with a grid of 0.5 x 0.5 km in the urbanized downtown and 1 x 1 km in the suburban areas (Fig. 1). About 3 kg of soil sample were taken at depths of 15 cm in each sampling location. Soil sampled at different points over an area of about 10 square meters was combined for each location.

The samples consist of 107 residual soils developed on pyroclastic bedrock collected in the suburban areas and 100 soils collected from flower-beds in the downtown area and referred to as non-residual soils. Information from Napoli City Park Authorities indicates that flower-beds have been in place from about 1992 and that they are not fertilized.

Chemical analysis

After being air-dried, the samples were sieved and the <100 mesh fraction (150 μm) was utilized for analyses. Analyses were carried out at the ACME Analytical Laboratories Ltd (Vancouver, Canada), accredited under ISO

9002, by ICP-MS and ICP-AES using Acme's Group 1F-MS package for Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, Os, P, Pb, Pd, Pt, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W, Zn by Aqua Regia digestion. Some elements were only determined by ICP-MS (Au, Ga, Hg, Os, Pd, Pt, S, Sc, Se, Te, Tl). Major elements (Al, Ca, Fe, K, Mg, Na, P, Ti) were determined by both instruments (ICP-AES and ICP-MS) but the reported values are from the ICP-AES. Remaining elements (Ag, As, B, Ba, Bi, Cd, Co, Cr, Cu, La, Mn, Mo, Ni, Pb, Sb, Sr, Th, U, V, W, Zn) were determined by both instruments. Trace and ultratrace levels (i.e., < 100 mg/kg) of these elements are reported from the ICP-MS whereas elevated concentrations (i.e., > 100 mg/kg) are reported from the ICP-AES.

Specifically, a 15 g split of powdered soil was digested in 45 ml of Aqua Regia at 95°C for 1 hour. The solution is taken to a final volume of 300 ml with 5% HCl. Aliquots of sample solution are aspirated into a Jarrel Ash Atomcomp 975 ICP-Emission Spectrometer and a Perkin Elmer Elan 6000 ICP-Mass Spectrometer.

Analysis of the same sample solution by both ICP-MS and ICP-AES allows greater accuracy through cross checking and better interference correction in addition to extending the upper range of major elements such as Ca, Fe, P, etc.. Calibration solutions were included at the beginning and end of an analytical run of 40 solutions. Spiking of the sample solution with a tracer element allowed internal standardization. Precision is $\pm$ 10% at concentrations of 50 times the detection limit or higher. Precision is calculated on three in-house replicates and two blind duplicates submitted by the authors. Accuracy is calculated on Acme's in-house reference material, DS3. Reference material DS3 was calibrated to an Aqua Regia digestion / ICP-MS determination against published values for a concentrated HCl and HNO_3 digestion of Canadian Certified Reference materials (CCRMP) TILL-4 and LKSD-2. The results obtained for these reference materials were consistent with the values obtained from the certification program (e.g., Cu, Pb, Zn, Mo, Ag etc.). The digestion by Aqua Regia is considered to be pseudo-total for the dissolution of metal bound as water soluble salts, in cation-exchange sites, statically bound to clay particles, in organic chelates in amorphous oxides and hydroxides of Mn and Fe, in carbonates, in sulphides and some sulphates. It also partially solubilizes metal in silicates (generally the darker coloured ferromagnesian-rich silicates) and some crystalline oxides of Fe, Ti and Cr.

Table 1 lists the elements analyzed, the instrumental detection limits, the accuracy and the precision of the geochemical data.

Isotope analysis

24 soil samples (Fig. 3) with Pb content > 100 mg/kg were analyzed at the British Geological Survey (BGS, Keyworth, UK) by UV microprobe laser ablation using a VG Elemental P54 Multi-Collector ICPMS (LA-MC-ICPMS) with a VG Elemental Microprobe II Laser system. Analysis of solid samples by LA-MC-ICPMS required minimal preparation: the powdered samples were pressed into pellets and placed in the laser ablation cell. Bulk lead isotope analyses were measured on each pellet comprising 50-100 integrations over a 5 x 3 mm raster grid using a repetition rate of 20Hz, 30-65% power and a spot size of 200-400 μm (depending sample heterogeneity and concentration). This avoids lengthy digestions and chemistry, which may be incomplete and can also potentially introduce sample contamination. Correction of instrumental mass bias was made by aspirating thallium solution through the laser cell during analyses, and ^{202}Hg was monitored during analyses to allow ^{204}Hg to be subtracted from ^{204}Pb measurements.

The NBS-981 standard value obtained (after the above corrections were applied) during repeated runs was: $^{206}Pb/^{204}Pb$ = 16.938, $^{207}Pb/^{204}Pb$ = 15.491, $^{208}Pb/^{204}Pb$ = 36.691 with a precision of about 0.05% (2σ). Accepted values for NBS 981 are $^{206}Pb/^{204}Pb$ = 16.9356, $^{207}Pb/^{204}Pb$ = 15.4891, $^{208}Pb/^{204}Pb$ = 36.6996 (Todt *et al*, 1996). Internal reproducibility is given by a matrix matched soil pellet which was also used as an in-house standard giving $^{206}Pb/^{204}Pb$ = 18.373, $^{207}Pb/^{204}Pb$ = 15.620, $^{208}Pb/^{204}Pb$ = 38.291 with a precision of circa 0.05% (2σ) for the first two ratios but nearer 0.15% (2σ) for $^{208}Pb/^{204}Pb$ possibly due to a transient organic interference. The Pb isotopic composition of analyzed samples are reported in Table 2.

Statistical analysis

Univariate and multivariate analyses were carried out in order to show the single-element geochemical distribution and the distribution of factor scores of the elemental associations resulting from R-mode factor analysis. The statistical parameters of the univariate analysis are reported in table 3. For statistical computation, the data below the instrumental detection limit (IDL) was assigned a value corresponding to 50% of the detection limit. The data distribution was generally positively skewed, so, to normalize it, we converted the data into their logarithm values.

Factor analysis was used to develop different groups of chemical elements with approximately the same geochemical pattern. Factor analysis is a statistical method that extracts the most important information from the data because it is based on the concept of communality (for each variable, communality is defined as the common variance explained by the factors). In order to facilitate the interpretation of results, varimax rotation

was used because it is an orthogonal rotation that minimizes the number of variables that have high loading on each factor, simplifying the interpretation (Reimann *et al.*, 2002). The different factors obtained were studied and interpreted in accordance with their hypothetical origin (natural, anthropogenic or mixed).

R-mode factor analysis has been performed using GRFAC software (Miesh, 1990) on a matrix containing 35 elements. The chemical elements with an elevated percentage (>5%) of analytical determinations below the instrumental detection limit were not considered for factor analysis. The four-factor model, accounting for 78.5 % of the data variability, deemed appropriate for Neapolitan volcanic soil data is shown in Table 4. Elements with loadings over |0.5| are considered as representative members of each association that results from the chosen factor model. The element association **F1** (Pb-Sb-Ag-Au-Cd-Cr-Zn-P-Hg-Ni-Cu-Ca-Mo-Ba) accounts for 51.6% of total data variability while the **F2** association (Ga-La-Al-Ti-Tl-Th-U-Sc-Co) accounts for 28.6% of total data variability; **F3** (Na-Sr-K-B-Mg-Ca-Mo-V-Ba) and **F4** (As-Mn-Fe-W-Bi-Te-V) account for 12.4 % and 7.4 % of total data variability respectively. In each association, elements are listed with decreasing loadings (Table 4).

Geochemical mapping

Maps showing Pb and the four association factor score distributions have been obtained using GeoDAS and ArcView GIS software. Multifractal Inverse Distance Weighted (IDW) is the interpolation method used with a search distance of 1 km and map resolution of 150 m (for more details about this methodology see Cheng, 2000; Lima *et al.*, 2003a; Cicchella *et al.*, 2005).

RESULTS AND DISCUSSION

Heavy metal distribution

For the sake of conciseness, only distribution maps of Pb (Fig. 3) and the factor scores for the four element associations (Fig. 4), obtained by R-mode factor analysis, are presented here. Geochemical maps showing concentration distribution of all the analyzed elements are published in De Vivo *et al.* (2006).

The interpolated Pb distribution map (Fig. 3) shows that the highest values (>325 mg/kg) are mostly located in the central and eastern part of Napoli city. These areas are highly urbanized and more industrialized compared with the western part. Pb concentrations decreased gradually from the centre to the city boundary. Corresponding background values, obtained from uncontaminated soils of volcanic and non-volcanic origin (Cicchella *et al.*, 2005), vary in the range 40 - 80 mg/kg.

Maps of the factor score distributions are very useful to correlate lithologies with physico-chemical and pollution processes of the surface environment at each sampled site. Figure 4 shows, for each association identified by the factor model 4, an interpolated distribution map of factor scores. These maps fit well with the distribution of the single elements that have a high loading in this association. This can be seen comparing the Pb interpolated map (Fig. 3) with F1 factor scores (Fig. 4) map, where Pb has a very high loading (0.9). The association F1 (Pb-Sb-Ag-Au-Cd-Cr-Zn-P-Hg-Ni-Cu-Ca-Mo-Ba), accounting for 51.6% of total data variability, is explained by elements introduced in the environment by human activities. The factor scores distribution (Fig. 4) is, hence, clearly dominated by anthropogenic sources. The very high values (between 1 and 2.2) coincide exactly with the international airport area, the eastern industrial area and Napoli city centre, characterized by heavy daily traffic jams (Fig.1).

The western portions of the urban area, with least industrial and commercial influence, are practically uncontaminated. They are characterized by negative factor scores which means that the sampled sites are depleted in the elements of the association. In this western area, the concentration values of the single harmful elements of F1 association (e.g., Fig. 3) do not exceed the local geochemical backgrounds (Cicchella *et al.*, 2005).

The F1 association includes most of the harmful elements (Pb, Sb, Cd, Cr, Zn, Hg, Ni and Cu) which have national intervention levels fixed by the Italian environmental Law 471/1999 (Table 5). Figures 5 and 6, show cumulative frequency curves for each element listed in Table 5, and for comparison a range of background values are marked with the grey shading from Cicchella *et al.* (2005) and De Vivo *et al.* (2006). In these figures, the cumulative percent value (a) is corresponding to the residential/recreational intervention limit; the cumulative percent value (b) is corresponding to the commercial/industrial intervention limit. Many of the samples collected in this study are characterized by harmful element concentrations exceeding the limit recommended for residential and recreational area. This is true particularly for Pb and Zn. Figure 5F shows that 62% of sampled soils have Pb concentrations greater than 100 mg/kg (residential/recreational intervention limit) and 2% exceed 1000 mg/kg (Pb commercial/industrial intervention limit). The majority of sampled soils (73%) have a Pb content that exceed the local background values. For Zn, 55% of samples (Fig. 5H) have concentrations greater than 150 mg/kg (residential/recreational intervention limit) and about 70 % exceed the local background values. With exception of Cr and Ni (Figs. 5B and 5E), the concentration of the other harmful elements of F1 association: Cd, Cu, Hg and Sb (Figs. 5A, 5C, 5D, 5G) also exceed the Italian intervention limits for residential/recreational areas. On the basis of the percentage of samples that exceed background values (Fig. 5

and Table 5) for all the harmful elements which contribute to this factor association, urban surface soils are most significantly enriched in Pb, Hg, Zn, Sb, and to a lesser extent in Cu, Cd, Cr and Ni. Leaded petrol is the most probable source for the Pb enrichment, whereas tyre wear may be the main source for Zn (Muschack, 1990).

Factor scores distribution for the F2 association (Ga-La-Al-Ti-Tl-Th-U-Sc-Co), accounting for 28.6% of total data variability, clearly divides Napoli city area in two sectors: the eastern one with high factor scores (from 0.9 to 2.3) and the western one with negative values (Fig. 4). The local geology controls the covariation between the elements of this association with Mt. Somma-Vesuvius volcanics outcropping in the eastern part of Neapolitan area, whereas Ignimbrites and Campi Flegrei volcanics occur to the west. These lithological differences are also defined by the factor score distribution of the F3 association. Tl, however, is an important element of the association (F2), and 65% of sampled soils (Fig. 6C) have concentration values above the residential/recreational limit (1 mg/kg). But, as shown by Cicchella *et al.* (2005) and De Vivo *et al.* (2006), the Tl background values (0.5-1.5 mg/kg), obtained from uncontaminated Neapolitan volcanic soils, are higher than the residential/recreational intervention limits fixed by the Law 471/1999 (Fig. 6C). This finding indicates that intervention limits fixed by the legislation should be modified to take into account the elevated background values found in volcanic areas such as the “Neapolitan Province”.

The factor score distribution for the F3 association (Na-Sr-K-B-Mg-Ca-Mo-V-Ba), accounts for 12.4% of total data variability, and clearly differentiates the soils developed on the Mt. Somma-Vesuvius volcanics as opposed to those that develop on Campi Flegrei volcanic field. This element association could be used as a lithological marker since high factor scores values (from 0.5 to 2.6) distinctly characterize the Mt. Somma-Vesuvius lithologies, whereas low values (from 0.5 to –1.9) characterize the Campi Flegrei volcanics and other lithologies (Fig. 2). The only exceptions to this generalisation are the high factor scores (from 0.5 to 2.6) occurring on the western sector of the territory, in the Bagnoli area, where the influence of the hydrothermal activity plays an important role (Tarzia *et al.*, 2002).

The F4 association (As-Mn-Fe-W-Bi-Te-V), accounts for 7.4% of total data variability, and shows higher factor scores (> 0.8) in the Bagnoli area. The elevated concentrations of elements from this association in the Bagnoli soils are derived from a natural origin and can be explained by the occurrence of Fe and Mn hydroxides which can adsorb and co-precipitate with of metallic elements, such as As, W, Bi, Te and V. Arsenic concentrations in Bagnoli soils (Cicchella *et al.*, 2005) reach 164 mg/kg (Fig. 6A) well above the background value of 18 mg/kg, the residential/recreational intervention limit of 20 mg/kg, and the commercial/industrial intervention limit of 50 mg/kg. The existence of this natural As-enrichment is due, to the hydrothermal activity

in the Bagnoli area, as discussed before, where many active fumaroles and springs occur. High concentrations of As and other metallic elements (e.g. As up to 8000 μg/l) are reported in thermal waters from spas of the Campi Flegrei by other authors (Dall'Aglio *et al.*, 1970; Celico *et al.*, 1992; Tarzia *et al.*, 2002). Thermal activity has resulted in enrichment of As, Mn and other elements that are mobile under hydrothermal conditions. This metal enrichment is typical of spring and spas active in volcanic geothermal systems (Mc Kibben & Elders, 1985; Goff *et al.*, 1994). This is also confirmed in the waters of spas of the volcanic area of Ischia island (e.g., As average = 155 μg/l, with values up to 1500 μg/l; Lima *et al.*, 2003b).

Isotopic signatures of Pb sources

Table 2 shows measured Pb isotope ratios for the selected soil samples (with Pb content > 100 mg/kg). Values range between 0.852 - 0.883 for $^{207/206}$Pb and 2.064 - 2.120 for the $^{208/206}$Pb. In fig. 7A $^{207/206}$Pb ratios have been plotted against $^{208/206}$Pb ratios, and show a linear trend with a significant regression coefficient ($R^2 = 0.91$).

In the simplest interpretation, this suggests mixing has occurred between two end-member Pb sources of different Pb isotope composition; one of clear natural origin (geogenic) and another of anthropic nature. In figure 7B $^{207/206}$Pb ratios, plotted against $^{208/206}$Pb ratios, show the studied Neapolitan soil data, the European gasoline Pb isotope data (Monna *et al.*, 1999; Teutsch *et al.*, 2001), representing a possible anthropogenic component, the Neapolitan volcanic Pb isotope signature (Ayuso *et al.*, 1998; Gilg *et al.*, 2001; Somma *et al.*, 2001) and Pb isotope values for the Neapolitan Yellow Tuff (NYT) (D'Antonio *et al.*, 1995), which represent the natural component (geogenic). This figure (7B) clearly confirms that Neapolitan soil data (field B) form a mixing line between two components: geogenic (field A) and anthropogenic (field C), with the anthropogenic component dominated by petrol Pb. Soil compositions also show an overlap with the anthropogenic field indicating that the latter component is dominant compared with the geogenic (natural) one, as one would expect for higher Pb concentrations. Fig. 8 showing $^{207/206}$Pb versus $^{206/204}$Pb also demonstrates that Neapolitan soils have mixed Pb isotope compositions. They fall between the Pb isotope compositions of geological materials (bedrocks) (Ayuso *et al.*, 1998; Gilg *et al.*, 2001; Somma *et al.*, 2001) and an anthropogenic end member dominated by Pb from motor vehicle emissions (Keinonen, 1992). Overlap of the Neapolitan soil Pb isotope trend with anthropogenic compositions indicate that the anthropogenic isotope contribution prevails in a mixing pattern of the two Pb sources. This is further demonstrated by plotting ^{207}Pb/^{206}Pb ratios versus Pb log-concentrations (Fig. 9). The plot shows a strong correlation between elevated concentrations of Pb and high $^{207/206}$Pb isotope ratios, which are

typical of the Pb added to the European gasoline (Monna *et al.*, 1999; Teutsch *et al.*, 2001). This indicates that a large part of the Pb, present in excess in the Neapolitan soils, is derived from leaded gasoline combustion.

In the last 10 years levels of Pb pollution have certainly decreased because of the elimination of leaded gasoline, but new pollutants have been introduced in urban areas: the platinum elements related to the use of catalytic exhausts. It has been, in fact, demonstrated that Pd and Pt concentrations in the Neapolitan soils are already high (Cicchella *et al.*, 2003).

CONCLUSIONS

The main conclusion of this research is that Pb concentrations and the distributions of metal associations factor scores, resulting from R-mode factor analysis, combined with Pb isotope data, are powerful indicators for monitoring the pollution of urban soils. Neapolitan urban soils are significantly enriched in Pb, Hg, Zn, Sb, and to a lesser extent in Cu, Cd, Cr and Ni.

Pb isotope investigation demonstrates that road traffic is one of the main sources of metal pollution. Pb isotope compositions for the Neapolitan urban area soils form a trend indicative of mixing between two end-members, one of clear natural origin (geogenic) and another related to human activities (anthropogenic). The latter component is dominant and increases with increasing Pb concentration. Uncontaminated samples fall in the geogenic field for Pb isotope ratios and are characterized by high F4 (As-Mn-Fe-W-Bi-Te-V) association factor scores. Enrichment of these elements is controlled by natural sources (Fe and Mn hydroxides absorption and co-precipitation phenomena) and are closely related to the existence of natural As-pollution due to hydrothermal activity. This was particularly demonstrated in the Bagnoli brownfield site where many active thermal springs occur (Tarzia *et al.*, 2002).

The concentration levels of many of the investigated elements are well above the intervention limit fixed by the Italian environmental Law 471/1999 (Cicchella *et al.*, 2005; De Vivo *et al.*, 2006). The levels of these pollutants are not of concern in the suburban areas, but in some places, particularly in the historic center and in the eastern industrialized area, concentrations are above the maximum acceptable limits, for residential/recreational land use and in some instances for industrial/commercial land use. This means, as dictated by Law 471/1999, that some of the areas we have identified through this study should be delimited and closed for safety purposes in order to guarantee the health of the people who live there. Remediation of these soils should be carried out by the local Authorities to eliminate the source of the harmful pollutants.

Acknowledgments

This research was supported by PON fund to Prof. B. De Vivo (Project PETIT-OSA; OR10). We wish to express many thanks to the reviewers of the manuscript for their helpful comments.

REFERENCES

AYUSO, R. A., DE VIVO, B., ROLANDI, G., SEAL II, R. R., PAONE, A. 1998. Geochemical and isotopic (Nd-Pb-Sr-O) variation bearing on the genesis of volcanic rocks from Vesuvius, Italy. *In:* Spera, F.J., De Vivo, B., Ayuso, R. A., Belkin, H. E. (Eds.), *Vesuvius,* Special issue of Journal of Volcanology and Geothermal Research, **82**, 53-78.

AYUSO, R. A., FOLEY, N. K., ROBINSON, G. R. JR., WANDLESS, G., DILLINGHAM, J. 2004. Lead Isotopic compositions of common arsenical pesticides used in new England. *U.S. Geological Survey. Open file report series 2004*, 1:342, pp. 14.

AYUSO, R. A., FOLEY, N. K., WANDLESS, G., DILLINGHAM, J., COLVIN, A. S. 2005. Lead Isotopic compositions of soil and near surface till profiles from a watershed containing arsenic-enriched groundwater in coastal Maine. *U.S. Geological Survey. Scientific investigations report 2005*, 5112, pp. 23.

CELICO, P., DALL'AGLIO, M., GHIARA, M. R., STANZIONE, D., BRONDI, M., PROSPERI, M. 1992. Geochemical monitoring of the thermal fluids in the phlegraean fields from 1970 to 1990. *Bollettino della Società Geologica Italiana*, **111**, 409-422.

CHARALAMPIDES, G., MANOLIADIS, O. 2002. Sr and Pb isotopes as environmental indicators in environmental studies. *Environment International*, **28**, 147-151.

CHENG, Q. 2000. *GeoData Analysis System (GeoDAS) for Mineral Exploration: User's Guide and Exercise Manual.* Material for the training workshop on GeoDAS held at York University, Nov. 1-3, pp. 204.

CICCHELLA, D., DE VIVO, B., LIMA, A. 2003. Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: possible effects of catalytic exhausts. *The Science of the Total Environment*, **308 (1-3)**, 121-131.

CICCHELLA, D., DE VIVO, B., LIMA, A. 2005. Background and baseline concentration values of elements harmful to human health in the volcanic soils of the metropolitan and provincial area of Napoli (Italy). *Geochemistry: Exploration-Environment-Analysis,* **5**, 29-40.

D'ANTONIO, M., TILTON, G. R., CIVETTA, L. 1995. Petrogenesis of Italian alkaline lavas deduced from Pb-Sr-Nd isotope relationships. *In:* Basu, A., & Hart, S. R. (Eds.), *Isotopic studies of crust-mantle evolution*, American Geophysical Union Monograph, 253-267.

DALL'AGLIO, M., MARTINI, M., TONANI, F. 1972. Rilevamento geochimico delle emanazioni vulcaniche dei Campi Flegrei. *Quaderni de "La Ricerca Scientifica", CNR*, **83**, 152-181.

DE VIVO, B., SCANDONE, R., TRIGILA, R. (Eds.) 1993. *Mount Vesuvius*. Special issue of Journal of Volcanology and Geothermal Research, **58**, pp. 381.

DE VIVO, B., ROLANDI, G. 2001. *Mt. Somma-Vesuvius and volcanism of the Campanian Plain*. Special Issue of Mineralogy and Petrology, **73**, pp. 233.

DE VIVO, B., SOMMA, R., AYUSO, R. A., CALDERONI, G., LIMA, A., PAGLIUCA, S., SAVA, A. 2001a. Pb isotopes and toxic metals in floodplain and stream sediments from the Volturno river basin, Italy. *Environmental Geology*, **41**, 101-112.

De VIVO, B., ROLANDI, G., GANS, P. B., CALVERT, A., BOHRSON, W. A., SPERA, F. J., BELKIN, H. E. 2001b. New constraints on the pyroclastic eruptive history of the Campanian volcanic Plain (Italy). *Mineralogy and Petrology*, **73**, 47-65.

DE VIVO, B., LIMA, A., ALBANESE, S., CICCHELLA, D. 2003. *Atlante geochimico-ambientale della Regione Campania.* De Frede Ed., Napoli, pp. 214.

DE VIVO, B. 2006. Volcanism in the Campania Plain: Vesuvius, Campi Flegrei, Ignimbrites. *Developments in Volcanology*, **9**, Elsevier Ed., pp. 324.

DE VIVO, B., CICCHELLA, D., LIMA, A., ALBANESE, S. 2006. *Atlante geochimico-ambientale dei suoli dell'area urbana e della Provincia di Napoli / Geochemical Environmental Atlas of the urban and provincial soils of Napoli*. Aracne Editrice, Roma, ISBN 88-548-0563-7, pp. 324.

DI GENNARO, A., TERRIBILE, F. 1999. *I suoli della Provincia di Napoli. Carta 1:75.000 e Legenda*. Camera di Commercio Industria Artigianato e Agricoltura di Napoli. GE.PRO.TER. Ed. S.EL.CA., Firenze, pp. 63.

EREL, Y., VERON, A., HALICZ, L. 1997. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. *Geochimica et Cosmochimica Acta*, **61,** 4495–4505.

FACCHINELLI, A., SACCHI, E., MALLEN, L. 2001. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environmental Pollution*, **114(3)**, 313-324.

FLAMENT, P., BERTHO, M. L., DEBOUDT, K., VE´RON, A., PUSKARIC, E. 2002. European isotopic signatures for lead in atmospheric aerosols: a source apportionment based upon $^{206}Pb/^{207}Pb$ ratios. *The Science of the Total Environment*, **296**, 35-57.

FORDYCE, F. M., BROWN, S. E., ANDER, E. L., RAWLINS, B. G., O'DONNELL, K. E., LISTER, T. R., BREWARD, N., JOHNSON, C. C. 2005. GSUE: urban geochemical mapping in Great Britain. *Geochemistry: Exploration-Environment-Analysis*, **5**, 325-336.

GILG, H. A., LIMA, A., SOMMA, R., BELKIN, H. E., DE VIVO, B., AYUSO, R. A. 2001. Isotope geochemistry and fuid inclusion study of skarns from Vesuvius. *Mineralogy and Petrology*, **73**, 145-176.

GOFF, F., STIMAC, J. A., LAROCQUE, A. C. L. & 9 OTHERS 1994. Gold degassing and deposition at Galeras Volcano, Colombia. *GSA Today*, **4 (10)**, 241-247.

IMPERATO, M., ADAMO, P., NAIMO, D., ARIENZO, M., STANZIONE, D., VIOLANTE, P. 2003. Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environmental Pollution*, **124**, 247-256.

HAACK, U., KIENHOLZ, B., REIMANN, C., SCHNEIDER, J., STUMPFL, E. F. 2004. Isotopic composition of lead in moss and soil of the European Arctic. *Geochimica et Cosmochimica Acta*, **68 (12)**, 2613-2622.

HANSMANN, W., KÖPPEL, V. 2000. Lead isotopes as tracers of pollutants in soils. *Chemical Geology*, **171**, 123-144.

KEINONEN, M. 1992. The isotopic composition of lead in man and the environment in Finland 1966-1987: isotope ratios of lead as indicators of pollutant source. *The Science of the Total Environment*, **113**, 251-268.

LEE, S. L., LI, X. D., SHI, W. Z., CHEUNG, S. C. N., THORNTON, I. 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. *The Science of the Total Environment,* **356**, 45-61.

LIMA, A., DE VIVO, B., CICCHELLA, D., CORTINI, M.**,** ALBANESE, S. 2003a. Multifractal IDW interpolation and fractal filtering method in environmental studies: an application on regional stream sediments of Campania Region (Italy). *Applied Geochemistry*, **18 (12)**, 1853-1865.

LIMA, A., CICCHELLA, D., DI FRANCIA, S. 2003b. Natural contribution of harmful elements in thermal groundwaters of Ischia island (southern Italy). *Environmental Geology*, **43**, 930-940.

MANTA, D., ANGELONE, M., BELLANCA, A., NERI, R., SPROVIERI, M. 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *The Science of the Total Environment*, **300**, 229-243.

MARKUS, J. A, MCBRATNEY, A. B. 2001. A review of the contamination of soil with lead II. Spatial distribution and risk assessment of soil lead. *Environment International*, **27**, 399-411.

MCKIBBEN, M. A., ELDERS, W. A. 1985. Fe-Zn-Cu-Pb mineralization in the Salton Sea geothermal system, Imperial Valley, California. *Economic Geology*, **80**, 539-549.

MIESCH PROGRAMS 1990. *G-RFac*. Grand Junction, CO, USA.

MUSCHACK, W. R. 1990. Pollution of street run-off traffic and local condition. *The Science of the Total Environment*, **93**, 419-431.

NRIAGU, J. O. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature*, **338**, 47-48.

PACYNA, J. M., PACYNA, E. G. 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environmental Reviews*, **9**, 269-298.

REIMANN, C., FILZMOSER, P., GARRETT, R. 2002. Factor analysis applied to regional geochemical data: problems and possibilities. *Applied Geochemistry*, **17 (3)**, 185-206.

ROLANDI, G., BELLUCCI, F., HEIZLER, M. T., BELKIN, H. E., DE VIVO, B. 2003. Tectonic controls on the genesis of ignimbrites from the Campanian Volcanic Zone, Southern Italy. *In:* De Vivo, B., Scandone, R., (Eds.), *Ignimbrites of the Campania Plain, Italy*. Mineralogy and Petrology, **79**, 3-31.

SALMINEN, R., BATISTA, M. J., BIDOVEC, M., & 27 OTHERS 2005. *Geochemical Atlas of Europe - Part 1 - Background information, methodology and maps.* Geological Survey of Finland, Espoo; 526 pp.

SOMMA, R., AYUSO, R. A., DE VIVO, B., ROLANDI, G. 2001. Major, trace element and isotope geochemistry (Sr-Nd-Pb) of interplinian magmas from Mt. Somma-Vesuvius (Southern Italy). *Mineralogy and Petrology*, **73**, 121-143.

SPERA, F. J., DE VIVO, B., AYUSO, R. A., BELKIN, H. E. (Eds.) 1998. *Vesuvius*. Special issue of Journal of Volcanology and Geothermal Research, **82**, pp. 247.

TARZIA, M., DE VIVO, B., SOMMA, R., AYUSO, R. A., MCGILL, R. A. R., PARRISH, R. R. 2002. Anthropogenic versus natural pollution: an environmental study of an industrial site under remediation (Naples, Italy). *Geochemistry: Exploration-Environment-Analysis*, **2**, 45-56.

TEUTSCH, N., EREL, Y., HALICZ, L., BANIN, A. 2001. Distribution of natural and anthropogenic lead in Mediterranean soils. *Geochimica et Cosmochimica Acta*, **65 (17)**, 2853-2864.

TODT, W., CLIFF, R. A., HANSER, A., HOFFMANN, A. W. 1996. Evaluation of a ^{202}Pb-^{205}Pb double spike for high-precision lead isotope analysis. In: Hart, S. R. & Basu, A., (eds), *Earth Processes: Reading the Isotopic Code.* Geophysical Monograph, American Geophysical Union, **95**, 429–437.

USGS 2002. Lead statistics. *In: Historical statistics for mineral commodities in the United States*, U.S.G.S. Open-File Report 01-006. U.S. Geological Survey, Reston.

WONG, C. S. C., LI, X. D., THORNTON, I. 2006. Review on urban environmental geochemistry of trace metals. *Environmental Pollution*, **142**, 1-16.

Table 1. *Detection limits, accuracy error and precision.**

**The laboratory accuracy error was been determined using the following formula:*

$$\text{Accuracy error} = (|X - TV| / TV) * 100$$

where
X = laboratory's analysis result for the performance sample (standard DS3)
TV = true value of the performance sample (standard DS3)

Precision was been calculated as Relative Percent Difference (%RPD) with following formula:

$$\%RPD = [(|SV - DV|)/(SV + DV) / 2] * 100$$

where
SV = the original sample value
DV = the duplicate sample value

Elements	Unit	Detection Limit	Accuracy (%)	Precision (% RPD)
Al	%	0.01	0	1.8
Ca	%	0.01	3.9	2.2
Fe	%	0.01	0.7	1.3
K	%	0.01	6.3	5.3
Mg	%	0.01	0	1.5
Na	%	0.001	3.6	2.9
P	%	0.001	0	3.6
S	%	0.02	30	11.9
Ti	%	0.001	0	5.7
Ag	mg/kg	0.002	0.4	7.9
As	mg/kg	0.1	0.3	3.0
Au	mg/kg	0.0002	4.8	28.9
B	mg/kg	1	0	11.0
Ba	mg/kg	0.5	0.3	1.5
Bi	mg/kg	0.02	1.8	3.2
Cd	mg/kg	0.01	1.4	5.6
Co	mg/kg	0.1	0	2.7
Cr	mg/kg	0.5	1.5	3.2
Cu	mg/kg	0.01	1.6	3.7
Ga	mg/kg	0.1	3.2	2.2
Hg	mg/kg	0.005	0	8
La	mg/kg	0.5	3.5	3.4
Mn	mg/kg	1	0.5	1.9
Mo	mg/kg	0.01	1.2	3.1
Ni	mg/kg	0.1	0.6	1.7
Pb	mg/kg	0.01	0.6	3.5
Sb	mg/kg	0.02	1.2	3.1
Sc	mg/kg	0.1	0	4.4
Se	mg/kg	0.1	0	28
Sr	mg/kg	0.5	5.3	2.4
Te	mg/kg	0.02	0.9	8.4
Th	mg/kg	0.1	5.1	3.6
Tl	mg/kg	0.02	1	3.6
U	mg/kg	0.1	1.6	3.7
V	mg/kg	2	1.3	2.4
W	mg/kg	0.2	2.7	4.4
Zn	mg/kg	0.1	0.5	2.6

Table 2. *Lead isotopic composition for 24 selected samples.*

sample	$^{206}Pb/^{204}Pb$	1σ%	$^{207}Pb/^{204}Pb$	1σ%	$^{208}Pb/^{204}Pb$	1σ%
NA15	18.000	0.025	15.606	0.026	37.928	0.057
NA15D*	18.008	0.019	15.607	0.023	37.948	0.049
NA16	18.074	0.056	15.609	0.015	38.056	0.054
NA17	18.116	0.026	15.612	0.025	38.100	0.051
NA20	18.215	0.020	15.629	0.025	38.271	0.050
NA30	18.000	0.027	15.603	0.027	37.893	0.122
NA33	17.994	0.024	15.600	0.013	37.973	0.044
NA34	18.180	0.025	15.620	0.015	38.227	0.047
NA38	18.161	0.038	15.611	0.019	38.153	0.070
NA43	18.074	0.022	15.618	0.024	38.098	0.050
NA45	17.826	0.024	15.586	0.025	37.700	0.085
NA47	17.624	0.075	15.573	0.026	37.359	0.360
NA49	18.050	0.025	15.611	0.024	38.028	0.052
NA54	18.204	0.024	15.623	0.024	38.230	0.061
NA55	18.029	0.023	15.613	0.022	37.997	0.025
NA80	18.372	0.018	15.660	0.022	38.485	0.025
NA81	18.021	0.024	15.609	0.023	38.044	0.031
NA84	17.955	0.028	15.599	0.026	37.926	0.042
NA84D*	17.950	0.025	15.595	0.024	37.915	0.031
NA85	18.094	0.021	15.614	0.025	38.112	0.028
NA87	17.974	0.027	15.597	0.023	37.925	0.032
NA100	17.812	0.025	15.585	0.023	37.630	0.116
NA123	18.190	0.046	15.618	0.023	38.192	0.035
NA137	18.008	0.010	15.603	0.021	37.974	0.013
NA140	17.953	0.043	15.598	0.026	37.902	0.057
NA149	18.160	0.118	15.603	0.064	38.105	0.255

Table 3. *Statistical parameters of 207 soil samples from Napoli.*

Element		Minimum	Maximum	Mean	Median	Geometric mean	25° percentile	75° percentile	Standard deviation
Al	%	1.57	5.97	3.38	3.19	3.28	2.87	3.83	0.84
Ca	%	0.51	15.34	2.64	1.73	2	1.14	3.47	2.28
Fe	%	1.1	15.46	2.2	2.06	2.1	1.85	2.34	1.1
K	%	0.36	4.2	1.52	1.32	1.41	1.07	1.69	0.67
Mg	%	0.18	1.13	0.47	0.4	0.43	0.32	0.56	0.2
Na	%	0.16	1.55	0.5	0.44	0.46	0.36	0.56	0.22
P	%	0.02	0.63	0.18	0.15	0.15	0.10	0.24	0.11
S	%	<0.02	0.54	0.05	0.04	0.03	0.02	0.07	0.05
Ti	%	0.05	0.18	0.11	0.1	0.1	0.09	0.12	0.03
Ag	mg/Kg	0.002	8.13	0.42	0.25	0.26	0.14	0.52	0.64
As	mg/Kg	6.6	164	13.4	11.9	12.2	10.3	14.5	11.9
Au	mg/Kg	0.0002	1.28	0.067	0.031	0.026	0.009	0.079	0.123
B	mg/Kg	4	56	15	13	14	11	17	6.7
Ba	mg/Kg	140	1476	437	436	411	343	506	166
Bi	mg/Kg	0.21	11.8	0.66	0.48	0.52	0.4	0.6	1.04
Cd	mg/Kg	0.05	6.93	0.58	0.37	0.37	0.19	0.66	0.78
Co	mg/Kg	2.9	36.6	7.3	6.3	6.7	5.2	8	3.7
Cr	mg/Kg	0.8	149	15.3	11.2	10.8	6.1	18.7	16.7
Cu	mg/Kg	4	433	94	74	72	43.6	120	72
Ga	mg/Kg	4.1	12.6	7.4	7.1	7.2	6.2	8.4	1.7
Hg	mg/Kg	0.01	2.66	0.31	0.18	0.19	0.10	0.40	0.34
La	mg/Kg	13.8	58.1	36	34	35	30.6	41	7.4
Mn	mg/Kg	363	5923	683	635	645	576	697	436
Mo	mg/Kg	0.8	18.6	2	1.7	1.8	1.3	2.4	1.4
Ni	mg/Kg	0.8	101	11.6	8.9	8.9	5.4	14.5	10.7
Pb	mg/Kg	20	2052	204	141	141	69	270	219
Sb	mg/Kg	0.2	40.6	2.9	2.0	1.9	1	3.7	3.7
Sc	mg/Kg	0.5	2	1.19	1.20	1.15	1	1.4	0.28
Se	mg/Kg	<0.1	1.7	0.29	0.30	0.23	0.2	0.3	0.21
Sr	mg/Kg	83	551	193	175	180	138	231	74
Te	mg/Kg	0.02	0.56	0.06	0.05	0.05	0.04	0.07	0.04
Th	mg/Kg	3.8	24.2	11.4	10.9	10.8	8.5	13.9	4
Tl	mg/Kg	0.47	2.47	1.14	1.06	1.1	0.91	1.31	0.33
U	mg/Kg	1.3	7.8	3.3	3	3	2.6	3.6	1
V	mg/Kg	31	187	58	52	55	46	62	20
W	mg/Kg	0.4	12.2	1.1	1	1	0.8	1.2	0.9
Zn	mg/Kg	35	3211	223	158	163	93	267	274

Table 4. *Varimax-rotated factor (four-factor model) for 207 samples from metropolitan Neapolitan soils.*

	FACTORS			
	F1	F2	F3	F4
Elements	Pb-Sb-Ag-Au-Cd-Cr-Zn-P-Hg-Ni-Cu-Ca-Mo-Ba	Ga-La-Al-Ti-Tl-Th-U-Sc-Co	Na-Sr-K-B-Mg-Ca-Mo-V-Ba	As-Mn-Fe-W-Bi-Th-V
Ag	**0.881**	0.044	0.067	0.117
Al	0.029	**0.914**	0.319	0.034
As	0.003	0.303	-0.129	**0.848**
Au	**0.880**	-0.003	-0.051	-0.173
B	0.408	0.183	**0.721**	0.128
Ba	**0.544**	0.253	**0.514**	0.001
Bi	0.309	-0.119	-0.191	**0.736**
Ca	**0.601**	-0.067	0.579	0.298
Cd	**0.851**	-0.214	0.158	0.249
Co	0.448	**0.519**	0.354	0.488
Cr	**0.833**	0.001	0.194	0.331
Cu	**0.721**	0.035	0.124	0.267
Fe	0.372	0.208	0.219	**0.776**
Ga	0.038	**0.925**	0.256	0.050
Hg	**0.781**	0.087	-0.028	0.129
K	0.041	0.418	**0.807**	-0.144
La	-0.036	**0.918**	0.078	-0.079
Mg	0.455	0.339	**0.642**	0.389
Mn	0.269	0.224	0.091	**0.814**
Mo	**0.578**	-0.108	**0.579**	0.235
Na	-0.120	0.218	**0.856**	-0.070
Ni	**0.748**	0.227	0.307	0.345
P	**0.786**	0.118	0.121	0.025
Pb	**0.898**	-0.128	0.092	0.168
Sb	**0.887**	-0.240	0.114	0.152
Sc	0.112	**0.686**	0.320	0.269
Sr	0.238	0.288	**0.844**	0.096
Te	0.023	0.030	0.190	**0.632**
Th	-0.267	**0.829**	0.080	0.152
Ti	-0.006	**0.859**	0.022	0.297
Tl	-0.095	**0.856**	0.035	0.130
U	-0.035	**0.714**	0.409	0.234
V	0.273	0.499	**0.519**	**0.526**
W	0.358	0.292	0.050	**0.768**
Zn	**0.813**	-0.226	0.243	0.307
Variance % (total data)	51.6	28.6	12.4	7.4

Table 5. Background concentration values for harmful elements in Neapolitan volcanic soils (Cicchella *et al.*, 2005; De Vivo *et al.*, 2006b) and Italian intervention criteria for soils (D.M. 471/1999).

Elements	Background values in Neapolitan soils (mg/Kg)	Residential/recreational intervention limits (mg/Kg)	Industrial/commercial intervention limits (mg/Kg)
Antimony	0.2 – 1.1	10	30
Arsenic	6 - 18	20	50
Cadmium	0.1 – 0.5	2	15
Cobalt	3 - 17	20	250
Chromium	1 - 16	150	800
Mercury	0.01 – 0.10	1	5
Nickel	1 – 19	120	500
Lead	20 - 80	100	1000
Copper	4 – 100	120	600
Selenium	0.1 – 0.4	3	15
Thallium	0.5 – 1.5	1	10
Vanadium	30 – 75	90	250
Zinc	35 - 100	150	1500

FIGURE CAPTIONS

Figure 1. Traffic flow and sample sites map.

Figure 2. Schematic geological map of metropolitan area of Napoli

Figure 3. Pb interpolated data distribution

Figure 4. Factor scores association maps from soils of metropolitan area of Napoli.

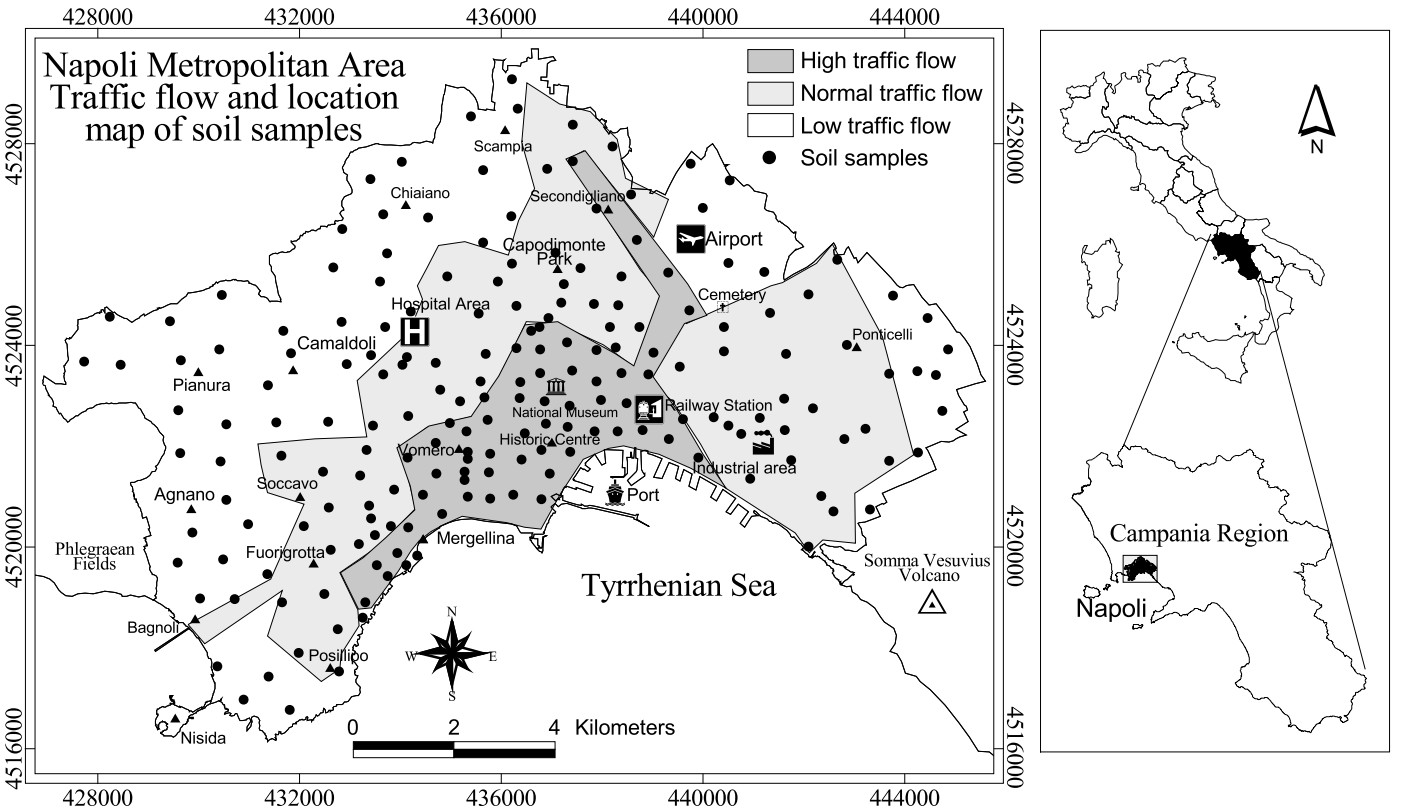
Figure 5. Cumulative frequency curves for Cd, Cr, Cu, Hg, Ni, Pb, Sb, Zn,. The graphs also report the range of background values marked with the grey bands. The percent cumulative value (a) corresponding to the residential/recreational intervention limit; the percent cumulative value (b) corresponding to the commercial /industrial intervention limit.

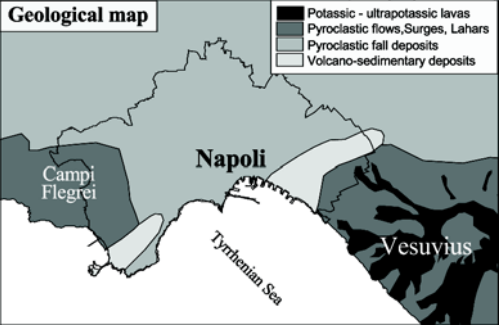
Figure 6. Cumulative frequency curve for As, Co, Tl and V.

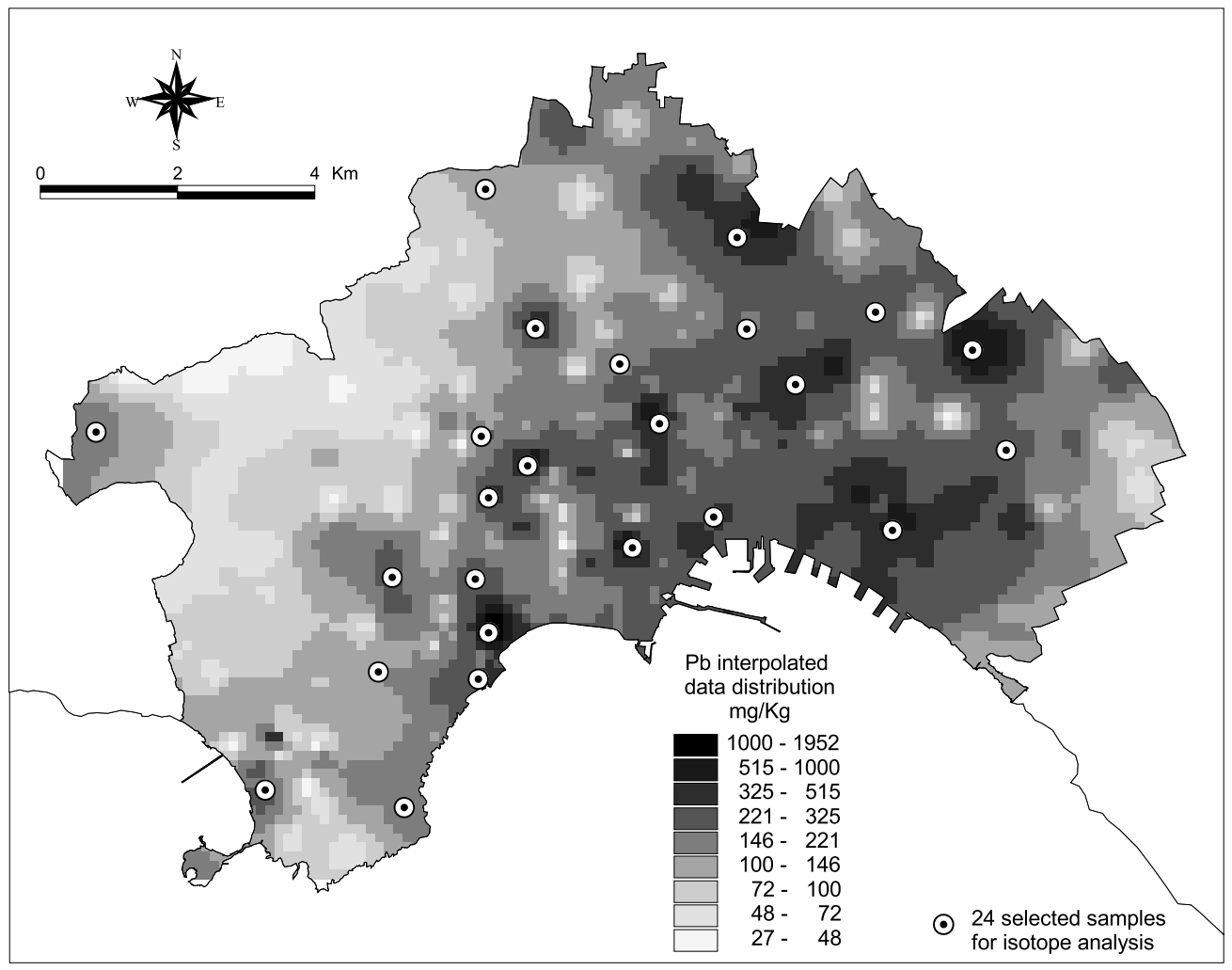
Figure 7. ***A*** - Plot of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$. In the diagram are also reported the 2 σ errors and the regression coefficient (R^2). ***B*** - $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ isotopic composition of samples collected in this study and data reported in literature. Data sources: Monna *et al.*, 1999; Teutsch *et al.*, 2001; Ayuso *et al.*, 1998; Gilg *et al.*, 2001; Somma *et al.*, 2001, D'Antonio *et al.*, 1995.

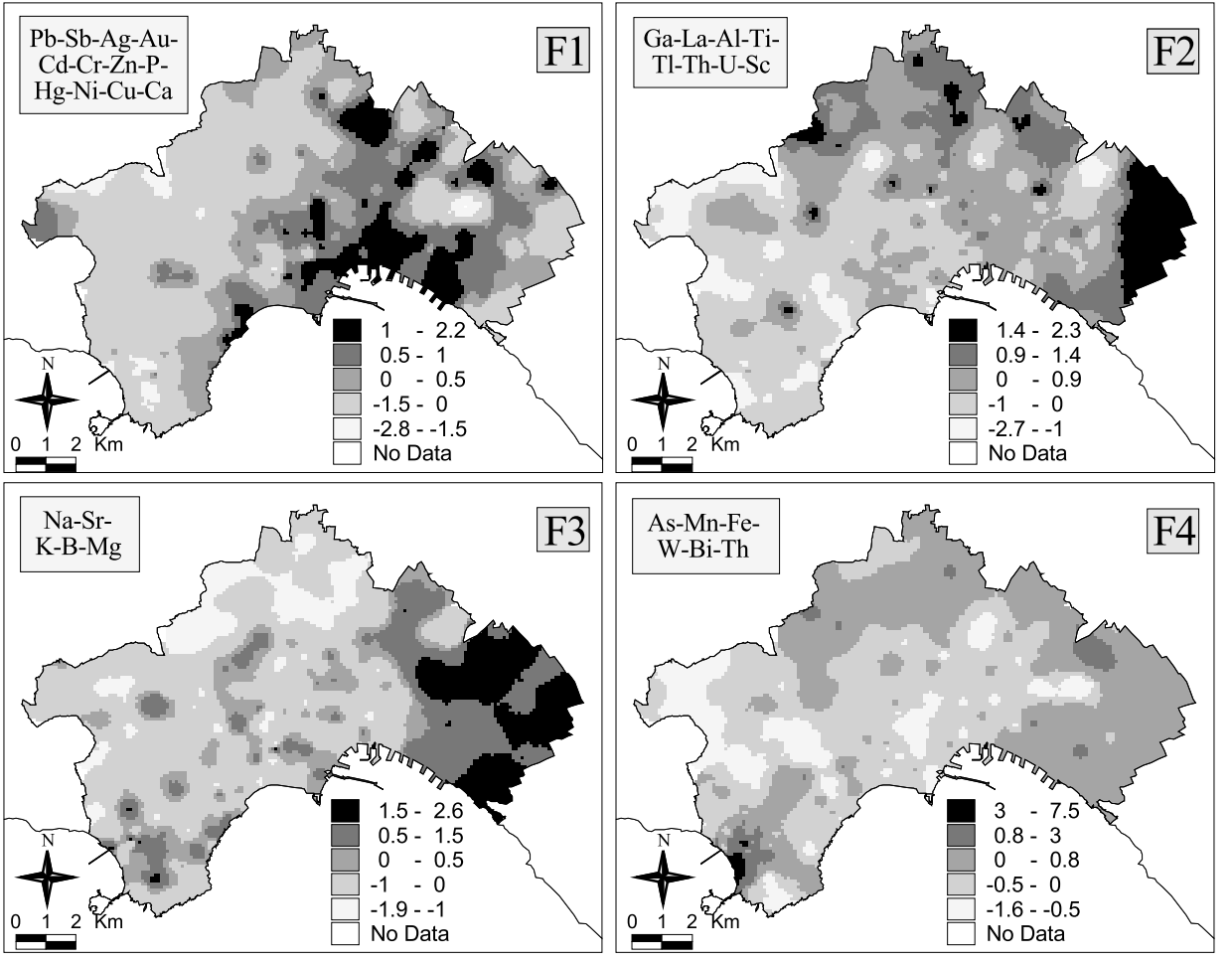
Figure 8. Plot of $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{206}Pb$. In the diagram are reported isotopic composition of samples collected in this study and data reported in literature. Data sources: Keinonen, 1992; Ayuso *et al.*, 1998; Gilg *et al.*, 2001; Somma *et al.*, 2001.

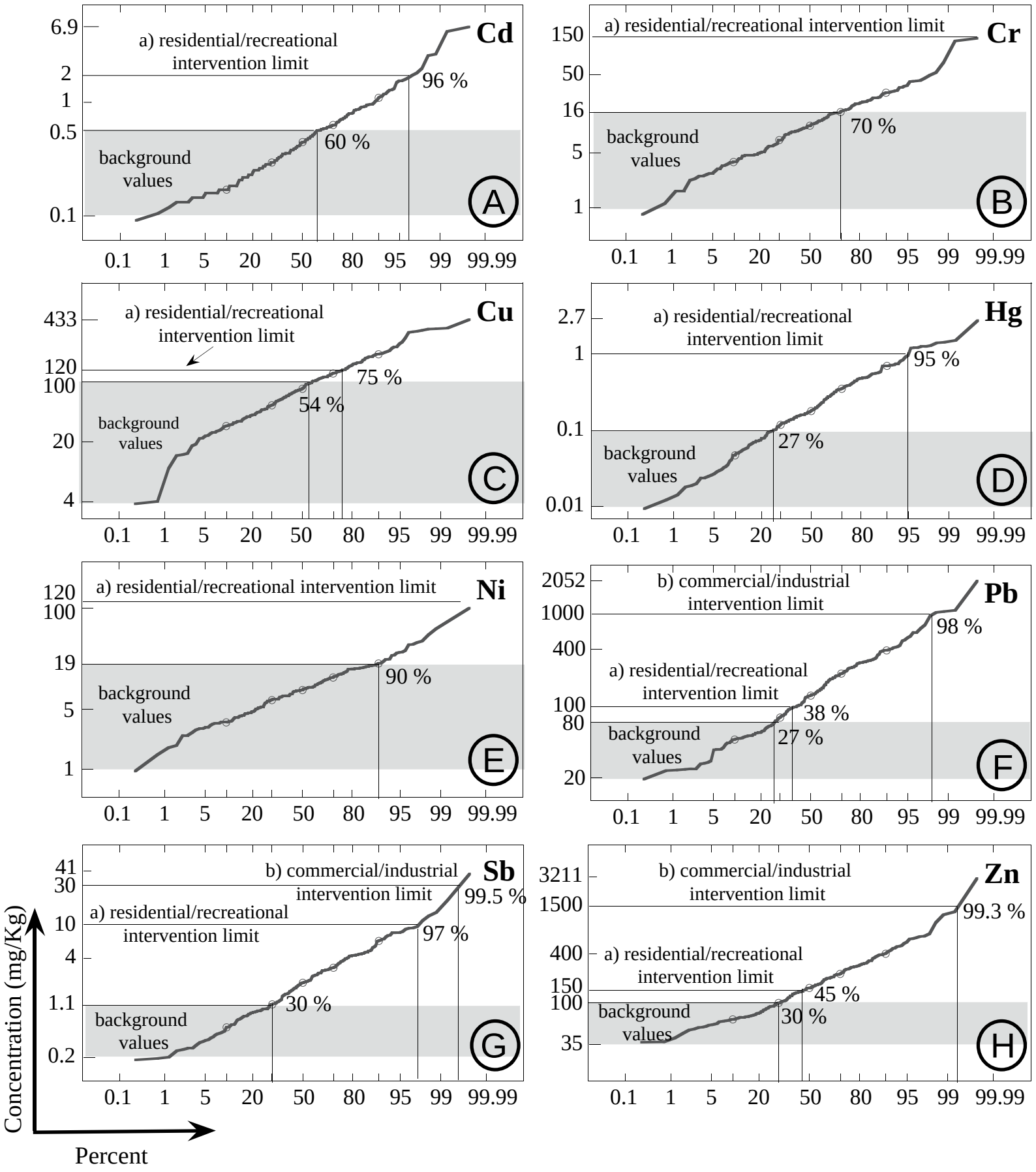
Figure 9. Pb Log-concentration plotted against $^{207}Pb/^{206}Pb$ isotopic ratio of samples collected in this study and in south-western area of Napoli (Bagnoli) (from Tarzia *et al.*, 2002).

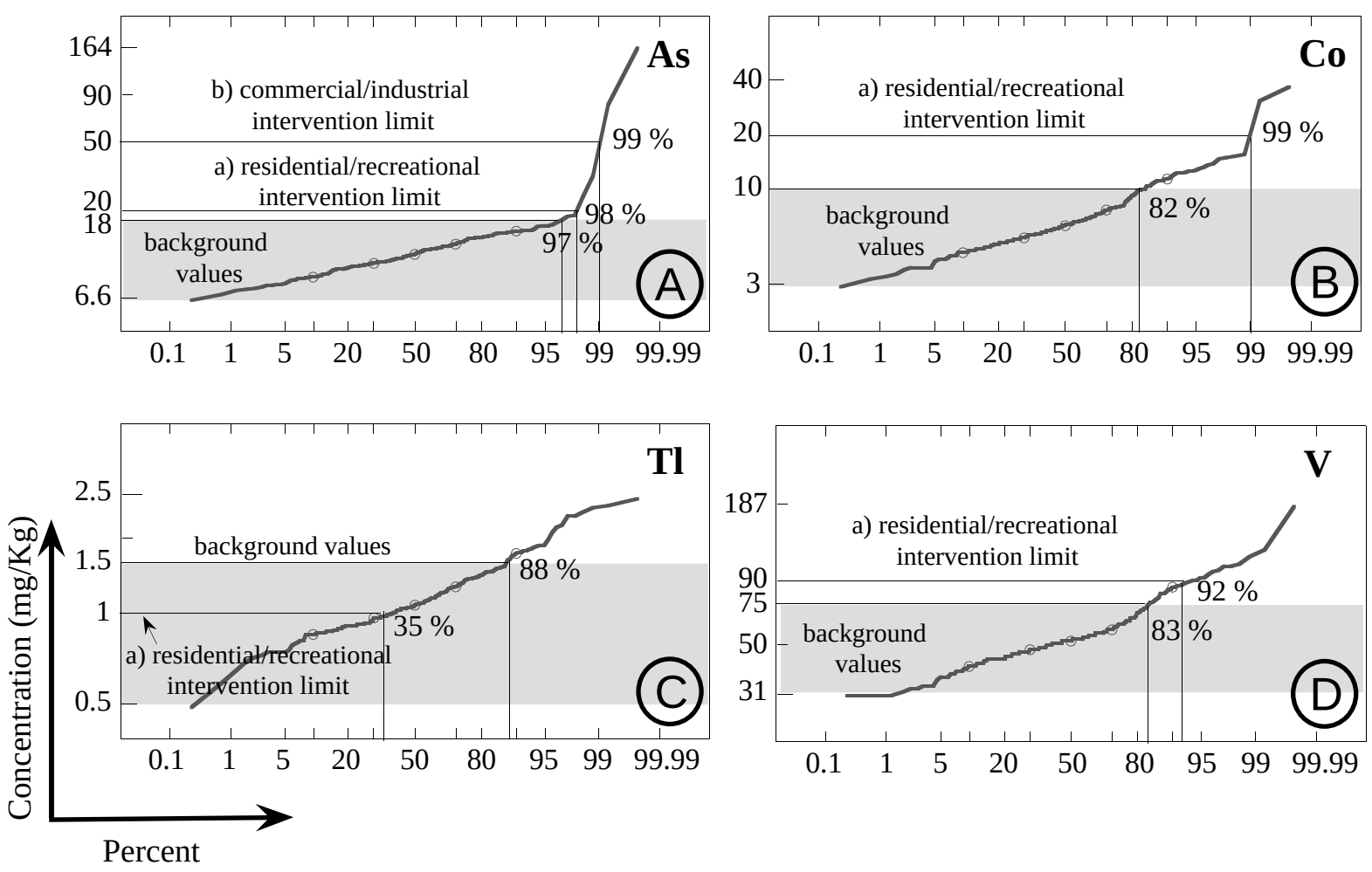

Napoli Metropolitan Area
Traffic flow and location
map of soil samples
High traffic flow
Normal traffic flow
Low traffic flow
Soil samples
428000
432000
436000
440000
444000
4528000
4524000
4520000
4516000
Scampia
Chiaiano
Secondigliano
Airport
Capodimonte
Park
Hospital Area
Cemetery
Camaldoli
Ponticelli
Pianura
National Museum
Railway Station
Historic Centre
Vomero
Industrial area
Agnano
Soccavo
Port
Phlegraean
Fields
Fuorigrotta
Mergellina
Somma Vesuvius
Volcano
Tyrrhenian Sea
Bagnoli
Posillipo
N
W
E
S
0
2
4
Kilometers
Nisida
N
Campania Region
Napoli

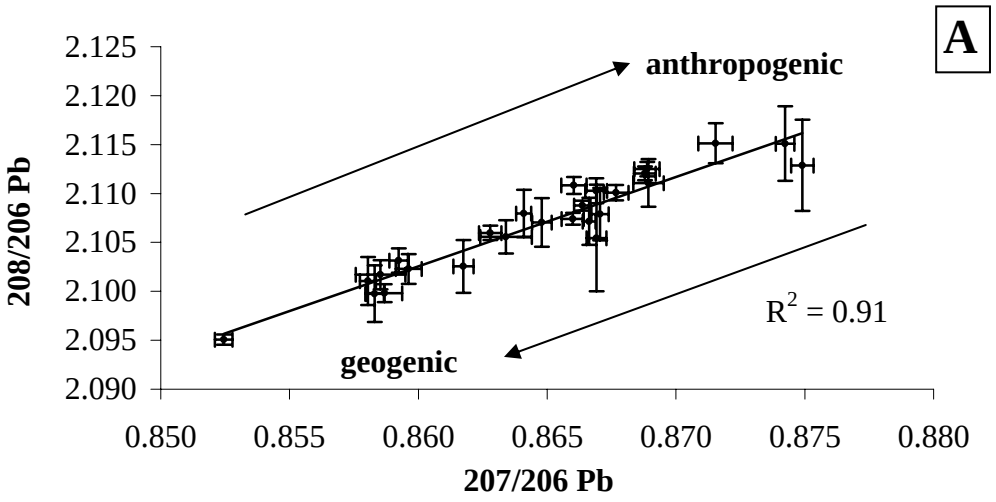

Geological map
Potassic - ultrapotassic lavas
Pyroclastic flows,Surges, Lahars
Pyroclastic fall deposits
Volcano-sedimentary deposits
Napoli
Campi
Flegrei
Vesuvius
Tyrrhenian Sea

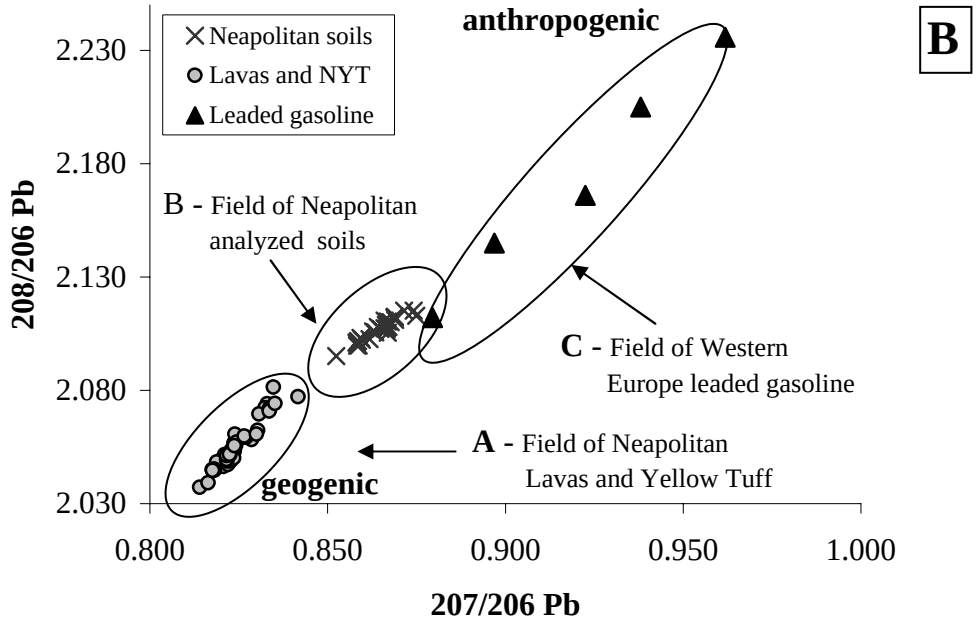

N
W
E
S
0
2
4 Km
Pb interpolated
data distribution
mg/Kg
1000 - 1952
515 - 1000
325 - 515
221 - 325
146 - 221
100 - 146
72 - 100
48 - 72
27 - 48
24 selected samples
for isotope analysis

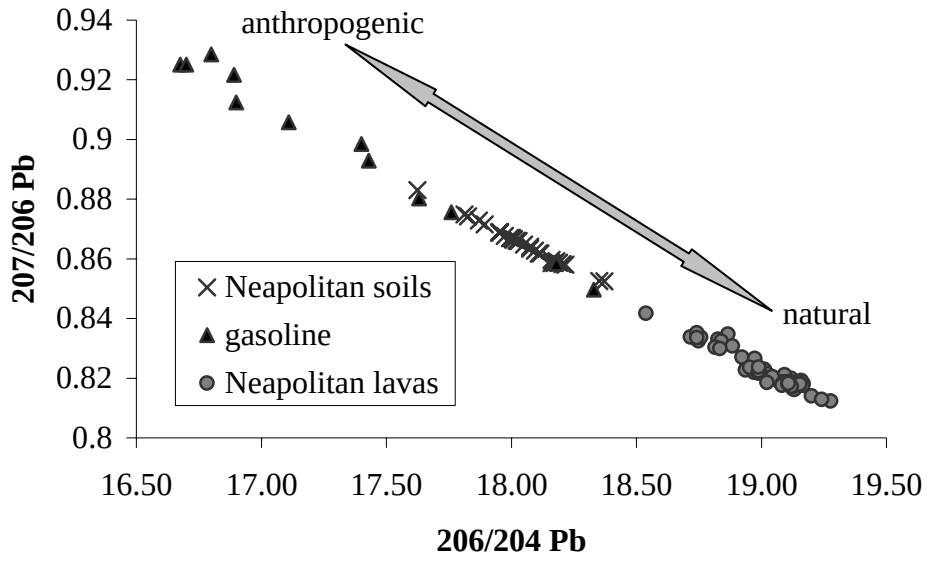

Pb-Sb-Ag-Au-
Cd-Cr-Zn-P-
Hg-Ni-Cu-Ca
F1
1 - 2.2
0.5 - 1
0 - 0.5
-1.5 - 0
-2.8 - -1.5
No Data
N
0 1 2 Km
Ga-La-Al-Ti-
Tl-Th-U-Sc
F2
1.4 - 2.3
0.9 - 1.4
0 - 0.9
-1 - 0
-2.7 - -1
No Data
N
0 1 2 Km
Na-Sr-
K-B-Mg
F3
1.5 - 2.6
0.5 - 1.5
0 - 0.5
-1 - 0
-1.9 - -1
No Data
N
0 1 2 Km
As-Mn-Fe-
W-Bi-Th
F4
3 - 7.5
0.8 - 3
0 - 0.8
-0.5 - 0
-1.6 - -0.5
No Data
N
0 1 2 Km

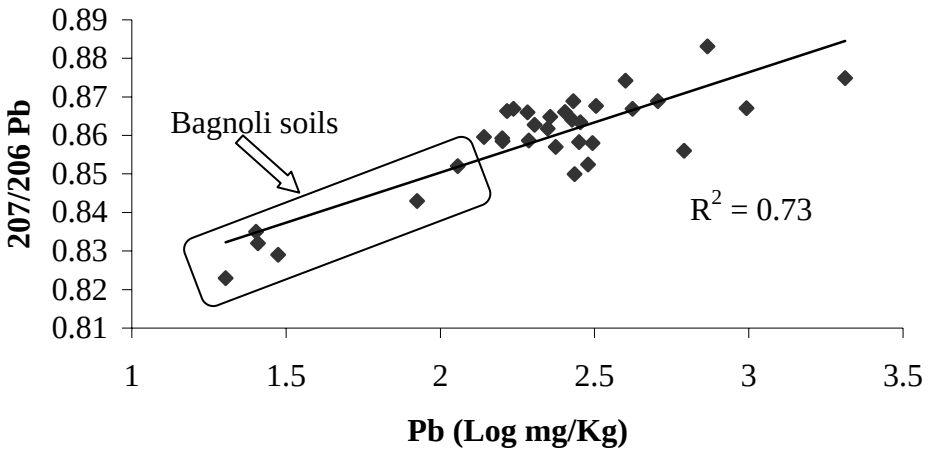

Cd
a) residential/recreational intervention limit
6.9
2
1
0.5
0.1
96 %
60 %
background values
A
0.1 1 5 20 50 80 95 99 99.99
Cr
a) residential/recreational intervention limit
150
50
16
5
1
70 %
background values
B
0.1 1 5 20 50 80 95 99 99.99
Cu
a) residential/recreational intervention limit
433
120
100
20
4
75 %
54 %
background values
C
0.1 1 5 20 50 80 95 99 99.99
Hg
a) residential/recreational intervention limit
2.7
1
0.1
0.01
95 %
27 %
background values
D
0.1 1 5 20 50 80 95 99 99.99
Ni
a) residential/recreational intervention limit
120
100
19
5
1
90 %
background values
E
0.1 1 5 20 50 80 95 99 99.99
Pb
b) commercial/industrial intervention limit
2052
1000
400
100
80
20
98 %
a) residential/recreational intervention limit
38 %
27 %
background values
F
0.1 1 5 20 50 80 95 99 99.99
Sb
b) commercial/industrial intervention limit
41
30
10
4
1.1
0.2
99.5 %
a) residential/recreational intervention limit
97 %
30 %
background values
G
0.1 1 5 20 50 80 95 99 99.99
Zn
b) commercial/industrial intervention limit
3211
1500
400
150
100
35
99.3 %
a) residential/recreational intervention limit
45 %
30 %
background values
H
0.1 1 5 20 50 80 95 99 99.99
Concentration (mg/Kg)
Percent


As
164
90
50
20
18
6.6
b) commercial/industrial
intervention limit
a) residential/recreational
intervention limit
background
values
99 %
98 %
97 %
A
0.1 1 5 20 50 80 95 99 99.99
Co
40
20
10
3
a) residential/recreational
intervention limit
background
values
99 %
82 %
B
0.1 1 5 20 50 80 95 99 99.99
Tl
2.5
1.5
1
0.5
background values
a) residential/recreational
intervention limit
88 %
35 %
C
0.1 1 5 20 50 80 95 99 99.99
V
187
90
75
50
31
a) residential/recreational
intervention limit
background
values
92 %
83 %
D
0.1 1 5 20 50 80 95 99 99.99
Concentration (mg/Kg)
Percent


A
anthropogenic
geogenic
R^2 = 0.91
208/206 Pb
207/206 Pb
2.125
2.120
2.115
2.110
2.105
2.100
2.095
2.090
0.850
0.855
0.860
0.865
0.870
0.875
0.880


B
Neapolitan soils
Lavas and NYT
Leaded gasoline
anthropogenic
B - Field of Neapolitan analyzed soils
C - Field of Western Europe leaded gasoline
A - Field of Neapolitan Lavas and Yellow Tuff
geogenic
208/206 Pb
207/206 Pb
2.230
2.180
2.130
2.080
2.030
0.800
0.850
0.900
0.950
1.000


anthropogenic
natural
Neapolitan soils
gasoline
Neapolitan lavas
207/206 Pb
206/204 Pb
0.94
0.92
0.9
0.88
0.86
0.84
0.82
0.8
16.50
17.00
17.50
18.00
18.50
19.00
19.50


0.89
0.88
0.87
0.86
0.85
0.84
0.83
0.82
0.81
207/206 Pb
Bagnoli soils
R2 = 0.73
1
1.5
2
2.5
3
3.5
Pb (Log mg/Kg)