



Research article

Assessing contamination sources and environmental hazards for potentially toxic elements and organic compounds in the soils of a heavily anthropized area: the case study of the Acerra plain (Southern Italy)

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Abstract: Epidemiological and environmental studies demonstrated that the rate of cancer mortality in the Acerra area, better known as “Triangle of Death”, and, more in general, in the Neapolitan metropolitan territory are higher than the regional average values. In the “Triangle of Death” the higher rate of mortality has been mostly related to the presence of toxic wastes illegally buried in agricultural areas which have been contaminating soils and groundwater for decades. Thus, collecting a total of 154 samples over an area of about 100 km², a detailed study was carried out to assess the geochemical-environmental conditions of soils aiming at defining the environmental hazard proceeding from 15 potentially toxic elements (PTEs), 9 polycyclic aromatic hydrocarbons (PAHs) and 14 organochlorine pesticides (OCPs) related with soil contamination. The study was also targeted at discriminating the contamination sources of these pollutants. Results showed that 9 PTEs, 5 PAHs and 6 OCPs are featured by concentrations higher than the guideline values established by the Italian Environmental laws, especially in the proximities of inhabited centers and industrial areas. The contamination source analysis revealed that, as regards the concentrations of chemical elements, they have a dual origin due to both the natural composition of the soils (Co-Fe-V-Tl-Be) and the pressure exerted on the environment by anthropic activities such as vehicular traffic (Pb-Zn-Sb-Sn) and agricultural practices (Cu-P). As far as organic compounds are concerned, the source of hydrocarbons can be mainly attributed to the combustion of biomass (i.e., grass, wood and coal), while for pesticides, although the use of some of them has been prohibited in Italy since the 1980s, it has been found that they are still widely used by local farmers.

Keywords: inorganic contaminants; polycyclic aromatic hydrocarbons; organochlorine pesticides; anthropogenic pollution; potential hazards; urban areas; agricultural land

1. Introduction

Potentially toxic elements (PTEs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) are the most common soil contaminants, especially in highly industrialized and anthropized areas due to their use in various processes linked to human activities (e.g., agricultural practices, industrial processes, mining activities, vehicular traffic). These contaminants, although they can be often found in combination in the soils, may have different origins [1,2].

The source of PTEs (mainly Cu, Pb, Zn, Cd, Hg, Sn, Ni, V and Cr) and metalloids (such as As, Sb and Se) in the urban environment can depend on a wide range of different anthropogenic agents and processes, such as mining, smelting, industrial manufacturing, domestic activities, residential heating, incinerators, power plants, industrial boilers, petrol and diesel vehicles, cigarette smoke and the use of fertilizers and anti-cryptogams in agricultural practices, as well as natural causes [1]. The distribution of these elements in the environment is a cause for concern because, although many of them are essential for life, some natural elements are potentially harmful to plants and animals [3,4]. Once these elements have entered the food chain, they tend to accumulate in the human body, causing damages to organs and the nervous and immune systems; some of them are also carcinogenic and/or teratogenic [5]. Apart of the level of exposure and the dose received, the risk posed by these elements can depend on several factors such as the degree of sorption, the chemical form, the concentration, the mobility, the bioavailability and the specific properties of the matrix [1].

National governments and international agencies developed, in the years, policies to limit the amount and the impacts of PTEs in the environment, establishing threshold concentration to be used as intervention limits, and procedures to estimate geochemical background ranges and bioavailable concentrations values considered as key concepts for a reliable assessment of the related risks [6].

PAHs are ubiquitous organic pollutants, containing only carbon and hydrogen atoms in their structure; they are basically made of multiple benzene rings fused through covalently bonded carbon atoms. These compounds are primarily classified based on their molecular weight. Low molecular weight (LMW) (made of 2 or 3 aromatic rings) and high molecular weight (HMW) (made of 4 to 7 aromatic rings) PAHs can derive both from natural phenomena (i.e.: such as volcanic eruptions and the maturation of the organic substance) and anthropogenic processes mostly associated with the incomplete combustion of organic matter (pyrolysis) both of petrogenic and biological origin [7]. More in details, PAHs are emitted as complex mixtures, containing over a hundred different compounds, and the molecular concentration ratios are considered characteristic of a given emission source [8].

PAHs are carcinogenic and mutagenic substances, toxic for all organisms. They are considered the most carcinogenic contaminants in the environment [9]. Due to their high lipophilicity, which increases with the molecular weight, PAHs can be easily adsorbed by plants, and therefore potentially transferred to animals and humans through the food chain; they have a great aptitude to bioconcentrate and bioaccumulate in organisms, predominantly in the adipose tissues [10]. In 1980, the U.S. Environmental Protection Agency (USEPA) included sixteen PAHs in the list of priority pollutants [11].

OCPs are a category of chlorinated aromatic hydrocarbons, that is, molecules consisting of organic structures containing at least one aromatic ring and one covalently bonded chlorine atom.

These compounds represent a group of synthetic molecules widely used for decades in the agricultural field as insecticides and fungicides [12] and, subordinately, in the medical field [13]. There are different types of OCPs, grouped into families based on their structural characteristics, which can differ significantly in their chemical and biological properties [14] and they can have different origins and follow different pathways in the environment.

Compared to other synthetic organic pesticides on the market, OCPs show a greater environmental persistence and are generally characterized by a marked tendency towards bioaccumulation and biomagnification along the food chain due to their lipophilic character [15,16]. Due to both their attitude to accumulate in the food chain and their non-selective toxicity towards different living species including mammals (without excluding humans), some OCPs, such as dichloro-diphenyl-trichloroethane (DDT), hexachlorobenzene (HCB), dieldrin, hexachlorocyclohexane (HCH α and β) and lindane (HCH γ), are currently banned from the market [17,18]. Despite this, some compounds are still used in other fields than agriculture, such as the DDT (synthesized since 1873 and used as an insecticide and pesticide since the 1940s) which has been (and still is) used to combat malaria in some sensitive areas such as Africa, India and South America [13].

Following the Stockholm Convention, a certain number of OCPs, specifically aldrin, chlordane, DDT, HCB, HCH (α , β and γ), dieldrin, endrin, heptachlor, endosulfan (α and β), endosulfan sulfate and mirex, have been defined as Persistent Organic Pollutants (POPs) [19,20]. The International Agency for Research on Cancer (IARC) in 2015 has classified DDT and its metabolites DDD and DDE (dichloro-diphenyl-dichloroethane and dichloro-diphenyl-dichloroethylene, respectively) as probable carcinogenic substances for humans (class 2A) [21].

In recent years, Campania, a region of southern Italy, has been the subject of media attention for the alleged degradation of the agricultural territories in its northern Tyrrhenian coastal side. In October 2004, the British medical journal *The Lancet Oncology* published a work by the researchers Senior and Mazza in which the villages of Marigliano, Nola and Acerra (located in the same territory) were indicated as vertices of what was called “The Triangle of Death” [22]. In the area, which is densely populated and is featured by a relevant socio-economic development related with the huge presence of production activities, infrastructures and natural resources, the resident population resulted affected by a cancer incidence rate higher than the regional average. The increase in the mortality rate was associated by the authors with the presence of many toxic wastes illegally buried in agricultural areas, close to urban centers [23].

In the last two decades, a huge number of scientific studies have assessed the degree and the spatial distribution of inorganic and organic contaminants in different environmental media across the Campania plain which goes from the Mt. Somma-Vesuvius slopes to Mt. Roccamonfina including the “Terra dei Fuochi” [24–58]. Most of the above cited authors have hypothesized the existence of a significant spatial coincidence between the highest cancer incidence (and/or mortality) in the population of the metropolitan area of Naples with the presence of extremely high concentration of PTEs [59,60] and POPs [44,45,61] in soils and, subordinately, in air.

The purpose of this work has been the assessment of the geochemical-environmental conditions of the north-eastern sector of the metropolitan area of Naples, roughly corresponding to the Acerra-Marigliano conurbation. The work is based on selected PTEs, PAHs and OCPs and it considers their concentrations and distribution patterns in topsoils to determine the nature of their potential sources and the level of hazard to which the local population is exposed.

2. Study area

The study area is located in the central sector of the Campania Plain, a wide coastal belt roughly extending from the Garigliano River plain, in the northwest of the region (at the border with the Latium region), to the Sarno River Basin, southward of the volcanic complex of Mt. Somma-Vesuvius. The conurbation covers a total area of about 100 km² and includes 6 municipalities (Acerra, Pomigliano D'Arco D'Arco, Castello di Cisterna, Brusciano, Mariglianella and Marigliano) (Figure 1a).

Local geology reflects the geological history of the Campania Plain which has been generated by the surface levelling of a huge graben generated during the Pleistocene and filled by volcanic products [62] and by alluvial materials, mainly consisting of reworked pyroclastic deposits and weathered carbonatic rocks proceeding from the Apennine chain. According to the underlying geology, in the flat areas, soil developed on pyroclastic deposits is characterized by a coarse texture and a good availability of oxygen; soil developed on alluvial sediments has a medium texture at the surface and they become finer with the depth increase [63].

In the area two hydrogeological systems can be distinguished: a superficial unconfined aquifer and a deeper aquifer (ca. 5 m below ground level) [64–67], both located in the pyroclastic complexes and confined below by the Campanian Ignimbrite [68,69]. The tuffaceous complex, which separates the two aquifers, shows, in the north-western and south-eastern sectors of the Acerra area, a significant reduction in both the thickness and the degree of cementation. Therefore, the complex itself does not guarantee the net confinement of the deep aquifer, allowing vertical drainage and creating mixtures between the two water bodies [69]. This condition is also facilitated by the fact that in these areas there are numerous wells without adequate conditioning, necessary for the separation between the two aquifers. Due to the interconnections between the aquifers, the state of the groundwater of the area appears to be strongly compromised, both due to diffuse agricultural and industrial contamination phenomena [65,67,69].

The total population in the study area is about 160,000 and the most populous municipality is Acerra with more than 50,000 inhabitants. The average population density is about 1,600 inhabitants/km², if considering the total surface of the conurbation, which could be corrected to 6–7,000 inhabitants/km² if we take into account only the effective extension of the urbanised areas (18–20 km²).

Non-urbanized areas are mostly occupied by agricultural activities (Crops, orchards and vineyard) and, subordinately, by industries (Figure 1a). Three principal industrial settlements can be distinguished in the area: 1) a branch of the Italian automotive industries FIAT, which came into activity in the early 70's and nowadays counts about 6000 employees, is present between the town of Acerra and Pomigliano D'Arco D'Arco; 2) the Montefibre factory, closed almost two decades ago, which produced polyester fibers, and a joint thermoelectric power plant, equipped with diesel engines and fuelled with palm oil (operating since 2000) in the northern sector of the study area; 3) an incinerator for urban waste treatment inaugurated in 2009 (close to the Montefibre area), which was used to burn non-differentiated waste accumulated during the Campania region worldwide notorious waste crises (2004, 2008–2009) [70].

3. Soil sampling, samples preparation and analyses

A total of 121 surficial composite soil samples was collected across the study area, at an average sampling density of 3 samples/km² in urbanized areas and 1 sample/km² in suburban and

agricultural/uncultivated areas, to determine the content in PTEs (Figure 1b). In addition, a total of 33 surficial composite soil samples were collected with an average density of 1 sample/4 km², during the spring of 2011, to be analysed for their PAHs and OCPs contents (Figure 1b).

The samples were collected following the FOREGS procedures [71]. At each sampling location, the composite sample was made up by mixing five soil aliquots collected at the corners and the centre of a 10 × 10 m virtual square. The single aliquots were collected within a depth interval between 0 and 15 cm from the surface by using a scoop. Samples destined to PTEs analyses were stored in plastic bags and labelled after mixing. Samples destined to PAHs and OCPs were previously enveloped in an aluminum foil and subsequently stored in plastic bags, avoiding any contact of the samples with the bag surface. After the collection, all the collected samples were daily transported to the Environmental Geochemistry Laboratory (LGA) at University of Naples Federico II. During the transport, samples destined to the determination of organic compounds were kept at a temperature of 4 °C by means of a portable cooler; once at LGA, they were, finally, stored in a freezer until their expedition to the Key Laboratory of Biogeology and Environmental Geology of Ministry of Education at China University of Geosciences in Wuhan for analyses.

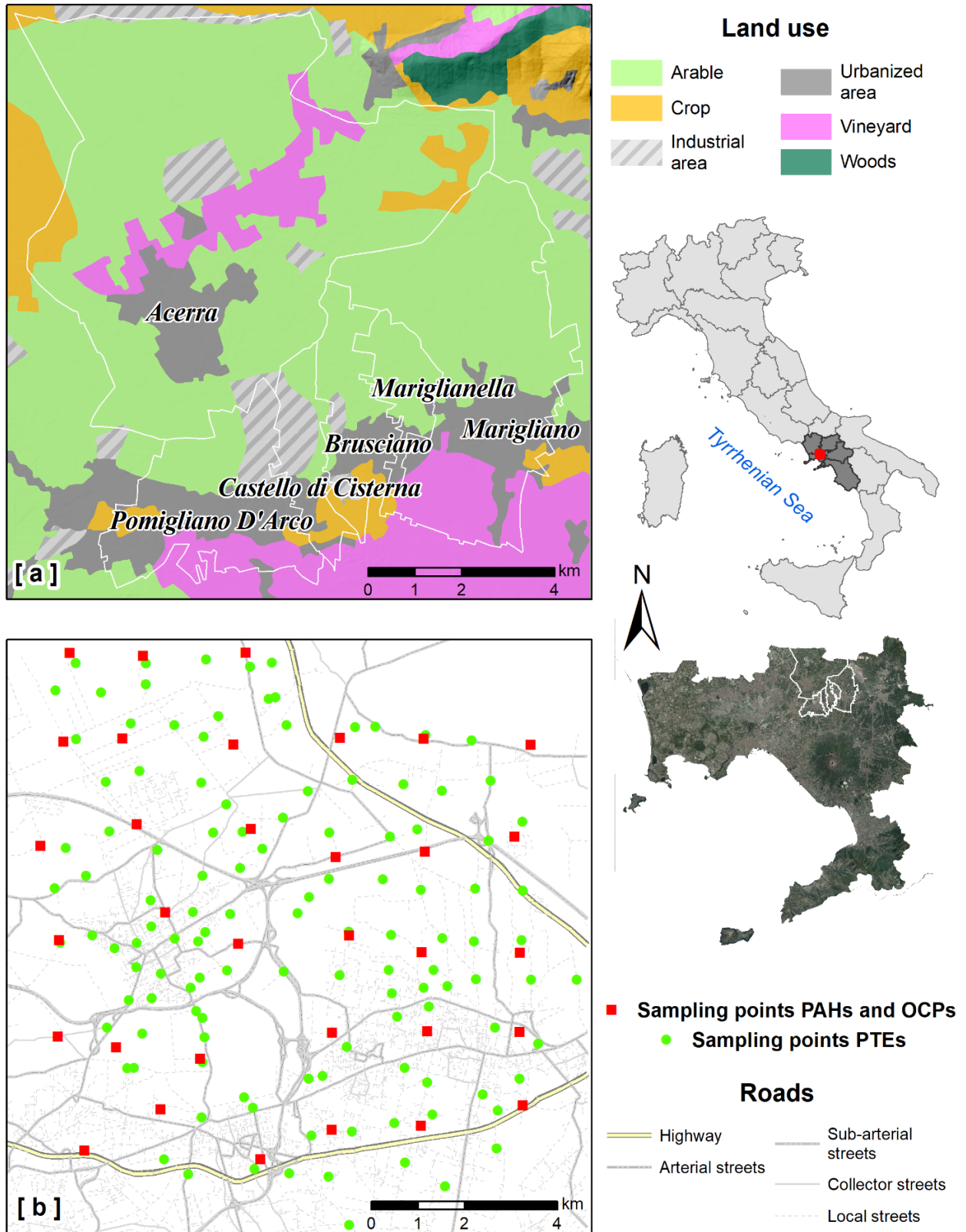
Each sampling site was regularly described for spatial coordinates, soil and air temperature, local geology, type and main properties of soils, land use, and any additional detail related to anthropic activities in the surroundings.

3.1. PTEs analyses

At the LGA, after being dried by means of infra-red lamps at a controlled temperature below 35 °C to avoid Hg volatilization, the samples were sieved to retain the 100 mesh (~150 µm) fraction. The obtained pulps were stored in small plastic bags containing at least 30 g of samples, and then sent to the ACME Analytical Laboratories Ltd (now Bureau Veritas) (Vancouver, Canada), accredited under ISO 9002, to be analysed for the concentrations of 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).

At the ACME facility, each sample was digested in 90 ml of aqua regia and leached for 1 h in a hot (95 °C) water bath. After cooling, the solution was made up to a final volume of 300 ml with 5 % HCl. The sample weight to solution volume ratio is 1 g per 20 ml. The solutions were analyzed combining a Spectro Ciros Vision emission spectrometer for ICP-AES (inductively coupled plasma atomic emission) and a Perkin Elmer Elan 6,000/9,000 for ICP-MS (inductively coupled plasma mass spectrometry).

The quality of all data was assessed by estimations of the error of both accuracy and precision, calculated using an international standard as reference in accordance with De Vivo et al. [33], which resulted to be always in the range of 10–15% for both parameters (Table S1: supplementary materials).



3.2. PAHs analyses

At the Key Laboratory of Biogeology and Environmental Geology, 10 g of homogenized and freeze-dried soils from each sample were spiked with 1000 ng (5 μ l of 200 mg/l) of recovery surrogates (naphthalene-D8; acenaphthene-D10; phenanthrene-D10; chrysene-D12 and perylene-D12) and were Soxhlet-extracted (4–6 cycles/h) with dichloromethane for 24 h. Elemental sulfur was removed by adding activated copper granules to the collection flasks.

The sample extract was concentrated and solvent-exchanged to hexane and further reduced to 2–3 ml by a rotary evaporator (Heidolph 4000). A 1:2 (v/v) alumina/silica gel column (both 3% deactivated with H₂O) was used to clean up the extract and PAHs were eluted with 30 ml of dichloromethane/hexane (3:7). The eluate was then concentrated to 0.2 ml under a gentle nitrogen stream and 1000 ng (5 μ l of 200 mg/l) of hexamethylbenzene were added as an internal standard prior to gas chromatography- mass spectrometry (GC- MS) analysis.

A HP6890N gas chromatograph equipped with a mass selective detector (5975MSD) operating in the electron impact mode (EI mode, 70 eV) and a DB-5MS (30.0 m \times 250 mm \times 0.25 mm film thickness) capillary column were used for detecting the levels of fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene in collected soils. The chromatographic conditions were as follows: injector and detector temperatures were of 270 °C and 280 °C, respectively; oven temperature program started at 60 °C for 5 min and increased to 290 °C at a rate of 3 °C/min and then was kept at 290 °C for 40 min. The carrier gas was highly pure helium at a constant flow rate of 1.5 ml/min. The mass spectrometer operated in the selected ion monitoring (SIM) mode and was tuned with perfluorotributylamine (PFTBA) according to the manufacturer criteria. Mass range between 50 and 500 m/z was used for quantitative determinations. Data acquisition and processing were made by a HP Chemstation data system. Chromatographic peaks of samples were identified by mass spectra and by comparison with the standards. An aliquot of 1 μ l of the purified sample was injected into the GC-MSD for the analysis, conducted in splitless mode with a solvent delay of 5 min. A six-point response factor calibration was established to quantify the target analyses.

3.3. OCPs analyses

The analytical method for OCPs was carried out based on the method of US-EPA 8080A. At the Key Laboratory of Biogeology and Environmental Geology, 10 g of dried soil from each sample, after being homogenized and freeze-dried, were spiked with 20 ng (4 μ l of 5 mg/l) of TCmX and PCB209 as recovery surrogates and were Soxhlet-extracted with dichloromethane for 24 h. Elemental sulfur was removed by adding activated copper granules to the collection flasks.

The sample extract was concentrated and solvent-exchanged to hexane and further reduced to 2–3 ml by a rotary evaporator (Heidolph4000). A 1:2 (v/v) alumina/silica gel column (both 3% deactivated with H₂O) was used to cleanup the extract and OCPs were eluted with 30 ml of dichloromethane/hexane (2:3). The eluate was then concentrated to 0.2 ml under a gentle nitrogen stream. 20 ng (4 μ l of 5 mg/l) PCNB was added as an internal standard prior to gas chromatography-electron capture detector (GC-ECD) analysis.

An HP7890A gas chromatograph equipped with a ⁶³Ni electron capture detector (GC-ECD)

was used for detecting the levels of p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, o,p'-DDE, α -HCH, β -HCH, γ -HCH, δ -HCH, HCB, aldrin, dieldrin, endrin, α -endosulfan, β -endosulfan, trans-chlordane, cis-chlordane, endosulfan sulfate, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, trans-Nonachlor, cis-Nonachlor and methoxychlor in the soil samples. The capillary column used for the analysis was a HP-5 (30.0 m \times 320 μ m \times 0.25 μ m film thickness). Nitrogen was used as the carrier gas at 2.5 ml/min under the constant flow mode. Injector and detector temperatures were maintained at 290 °C and 300 °C, respectively. The temperature program is used as follows: the oven temperature began at 100 °C (equilibrium time 1 min), rose to 200 °C at 4 °C/min, then to 230 °C at 2 °C/min, and at last reached 280 °C at a rate of 8 °C/min, held for 15 min. A 2 μ l sample was injected into the GC-ECD for analysis. A six-point response factor calibration was established to quantify the target analyses.

4. Data processing

For the purposes of the work, we considered only the geochemical data of the analytes (PTEs, PAHs, OCPs) for which the Italian Environmental laws (IELs), that are the Legislative Decree 152/2006 (shortly D.Lgs. 152/06) and the Ministerial Decree 46/2019 (shortly D.M. 46/19), establish guideline concentration values to be used as a reference for soils according to land uses (i.e., residential/recreational, industrial/commercial, agricultural) (Tables 2,3 and 4) [72,73]. In detail, the IELs identify as potentially harmful and therefore define guideline values for 15 elements (i.e., As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V and Zn), 9 HMW PAHs among the ones considered as priority pollutants by the USEPA (i.e., pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene), and 14 OCPs among the ones considered as POPs (i.e., α -HCH, β -HCH, γ -HCH, o,p'-DDT, p,p'-DDT, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, Dieldrin, Aldrin, Endrin, Trans-Chlordane, cis-Chlordane).

With the aim of characterizing the geochemical conditions of the area, cartographic elaborations were created to have a clear view of the spatial distribution patterns of the analysed contaminants. Before mapping, a univariate statistical analysis was carried out on the selected variables aimed at identifying the main indices that characterize the distribution of the data.

The interpolated maps were produced by means of the Inverse Distance Weight (IDW) spatial interpolation method, associated with a methodology that uses the fractal geometry (Multifractal - IDW) [74–80]. The method, largely used in the field of environmental geochemistry [24,81,82], was implemented by means of the add-in ArcFractal developed by Zuo and Wang [83] which was made available for the ArcMap software produced by ESRI™.

For the selected variables, the potential hazard raster maps were obtained by using the guideline concentration values (CSC) established by the D.Lgs. 152/06 for residential and industrial land use and by the D.M. 46/19 for agricultural land use, respectively, to classify the pixels of the interpolated maps. For the sake of brevity, in the present work, we have reported only the maps of the contaminants for which at least one sample presented values exceeding the aforementioned guideline values.

Subsequently, an analysis was carried out to establish the emission source of the analyzed contaminants, following a different method for each group of contaminants considered.

Since multivariate statistic has been widely used to discriminate metals contamination sources [84–86], a factor analysis was performed on the 15 PTEs with, in addition, Fe and P (given

the close relationship of these elements with agricultural practices). The main goal of factor analysis, a method of multivariate statistics, was to find associations of elements which could be used to determine the existence of latent sources (or processes) which are capable of influencing their behaviors in the environment [24,87]. The factor analysis, conducted with the SPSS software, was carried out on the log-normalized data (Log10), using the “varimax” as a rotation method with Kaiser normalization and the principal component analysis (PCA) as an extraction method [87]. Elements that showed communalities <0.5 were eliminated from the data matrix and the 3-component factor model, responsible for 82.1% of the total data variability, was chosen as a reliable solution. For the determination of the 3 associations of elements (F1, F2 and F3) the elements with a weight (eigenvalue) $> |0.7|$ were considered suitable (Table 1) [88,89]. Once the sets of elemental associations were defined, a factor score based on the relevance of each component was assigned to each sample in the dataset.

Table 1. Factor loadings of individual variables for each component obtained from the factor analysis.

Elements	Components		
	1	2	3
Cu	0.396	0.317	0.767
Pb	0.035	0.932	-0.044
Zn	0.138	0.804	0.334
Co	0.929	0.019	0.270
Fe	0.980	0.011	0.017
As	0.570	0.540	-0.377
Cd	-0.106	0.675	0.475
Sb	-0.077	0.759	0.144
V	0.930	-0.055	0.262
P	0.142	0.246	0.901
Tl	0.925	-0.045	0.235
Sn	-0.026	0.807	0.118
Be	0.781	0.015	-0.458

As regard PAHs, in order to discriminate the emission sources, as suggested by Tobiszewski and Namiesnik [90], diagnostic ratios were taken into consideration. The use of these ratios is based on the thermodynamic stability of the PAHs molecules, since during low temperature (petrogenic) processes (e.g., wood burning) LMW PAHs are usually formed, while high temperature (pyrogenic) processes (e.g., combustion of fuels in engines) emit HMW compounds [91]. For the determination of the source of origins of PAHs, we used several diagnostic ratios: $\Sigma\text{LMW}/\Sigma\text{HMW}$ [92]; anthracene/(anthracene + phenanthrene) [93]; benzo(a)anthracene/(benzo(a)anthracene + chrysene) [94]; fluoranthene/(fluoranthene + pyrene) [95]; indeno(1,2,3-cd)pyrene/(indeno(1,2,3-cd)pyrene + benzo(ghi)perylene) [96]; benzo(a)pyrene/benzo(ghi)perylene [97].

For OCPs the ratios between the parent compound and its metabolites have been used, where possible, as pollution sources indicators [98]. Because some OCPs tend to degrade over time in other metabolites and since the technical pesticides (i.e., DDT, HCH, chlordane, endosulfan) used, mainly in agricultural practices, are composed by a precise percentage of the different molecules, the ratio

between the parent compound and its metabolites can help identify whether the concentrations found in soil are attributable to fresh or historical use of these substances. The ratio used were: *o,p'*-DDT/*p,p'*-DDT [99]; *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) [98]; α -HCH/ γ -HCH [100,101]; α -HCH/ β -HCH [102]; *cis*-chlordane/*trans*-chlordane [103]; α -endosulfan / β -endosulfan [98,104].

All the variables resulting from the analyses conducted (i.e., factor scores, PAHs and OCPs ratios) were interpolated, again with the MIDW method, to generate a further set of distribution maps.

5. Results and discussion

5.1. PTEs distribution and sources

Table 2 shows the statistic of PTEs and the guideline values for different land uses. Cadmium, Co, Hg, Ni, Sb and Se do not show concentration values exceeding the guideline values established by the D.Lgs. 152/06, neither for the residential land use nor for the industrial use, and by the D.M. 46/19 for agricultural land use (Table 2).

Table 2. Summary statistics of PTEs and guideline values for different land uses according to Italian Environmental laws.

Element	Unit	Statistical parameters						D.M. 46/19 D.Lgs. 152/06		
		DL	Min	Max	Mean	St.Dev	Median	Agr.	Res.	Ind.
As	mg/kg	0,1	6,4	60,9	13,8	6,1	13,2	30 (2)	20 (4)	50 (1)
Be	mg/kg	0,1	1,9	12,2	4,7	1,3	4,6	7 (2)	2 (119)	10 (1)
Cd	mg/kg	0.01	0,18	1,38	0,51	0,16	0,51	5	2	15
Co	mg/kg	0,1	5,3	17,4	12,0	2,9	12,5	30	20	250
Cr	mg/kg	0,5	4,0	177,8	19,5	19,4	15,8	150 (1)	150 (1)	800
Cu	mg/kg	0,01	17,90	329,58	144,87	52,53	140,21	200 (18)	120 (81)	600
Hg	μ g/kg	5	28	563	136	100	109	1000	1000	5000
Ni	mg/kg	0,1	5,6	25,4	15,5	2,9	15,8	120	120	500
Pb	mg/kg	0,01	35,94	1099,09	85,95	133,83	64,22	100 (13)	100 (13)	1000 (2)
Sb	mg/kg	0,02	0,38	5,41	0,88	0,58	0,73	10	10	30
Se	mg/kg	0,1	0,2	1,6	0,7	0,2	0,6	3	3	15
Sn	mg/kg	0,1	2,4	18,9	4,9	2,6	4,1	–	1 (121)	350
Tl	mg/kg	0,02	0,87	2,91	2,12	0,50	2,21	1 (119)	1 (119)	10
V	mg/kg	2	36	117	85	21	89	90 (57)	90 (57)	250
Zn	mg/kg	0,1	42,8	627,9	119,2	66,1	109,6	300 (2)	150 (11)	1500

Note: Where present, the values in parenthesis associated to the guideline value represent the number of samples overcoming the guideline itself. (DL = detection limits; Min = minimum value; Max = maximum value; St.Dev = standard deviation; Agr./Res./Ind. = land use guideline according IELs).

Arsenic (Figure 2a), Pb (Figure 2e) and Zn (Figure 2i) show concentrations that overcome the guidelines both for residential and agricultural land use (20 and 30 mg/kg for As, 150 and 300 mg/kg for Zn and 100 mg/kg in both cases for Pb, respectively) across the urban center of Acerra. As for As and Pb, they even exceed guidelines for industrial land use (of 50 mg/kg and 1000 mg/kg,

respectively). Urban centers of Pomigliano D'Arco, Brusciano and Marigliano are also featured by values of Pb exceeding both the guideline values set for residential and agricultural land use (both equal to 100 mg/kg); in this latter area also Zn concentrations result to be over the values set for the residential land use (150 mg/kg).

Beryllium (Figure 2b), Sn (Figure 2f) and Tl (Figure 2g) show throughout the whole study area concentrations exceeding the guideline values established for residential land use (2 mg/kg for Be and 1 mg/kg for both Sn and Tl). In addition, considering that D.M 46/19 also sets the guideline for Tl to 1 mg/kg, hazard also could be given by an agricultural land use. Exception is made for Be in one sample (Table 2) located in the north of the municipality of Acerra (for which there are no exceedances at all) and two samples, one in the municipality of Pomigliano D'Arco and the other in the municipality of Acerra, overcoming the guidelines for agricultural land use of soil (7 mg/kg) (Table 2), as well. As for Tl, two sample, located in the northern area of the municipality of Acerra, do not show concentrations overcoming any of the guidelines considered (Table 2).

Chromium (Figure 2c) is, generally, featured by values below any of the guidelines considered. More in detail, its concentrations overcome both the guidelines for residential and agricultural land use (150 mg/kg) only in one sample (Table 2) located in the northernmost area of the municipality of Acerra.

Copper (Figure 2d) appears to overcome the guidelines values for residential land use (120 mg/kg) and, in some limited cases, for agricultural land use (200 mg/kg), in the southern and the eastern sectors of the study area. The area between Pomigliano D'Arco and Acerra and most of the northern sector of the study area are totally free from any hazard (Figure 2d).

Vanadium (Figure 2h) overcomes the guidelines values for residential and agricultural land use of 90 mg/kg in the southern and the eastern sectors of the study area, which roughly correspond to the slopes of the volcanic complex of Mt. Somma-Vesuvius. Also in the case of V the northern sector of the study area, mostly including the territory of the Acerra municipality, is not affected by hazards.

As reported above, the results of the factor analysis led to the identification of three factor association (F1, F2 and F3) responsible for the 82.1% of the total variability of data.

The F1 association, based on Co, Fe, V, Tl and Be, is responsible for the 36.1% of the total variability of the data. The map of the distribution of the factor scores (Figure 3a) show that positive values are recorded throughout the eastern part of the study area and close to the urban centers of Acerra and Pomigliano D'Arco while the association is less strong in the north-western sector of the municipality of Acerra (where negative values are present). The association can be easily related to the compositional features of local volcanic soils. In fact, it is stronger in correspondence of the slopes of the volcanic complex of Mt. Somma-Vesuvius, source of alkaline volcanic materials which are naturally enriched in these elements [32,105]. On the other hand, in the area north of Acerra the association is less strong probably due to the frequent rising of the water table to the ground level, which could cause the mobilization and partial depletion of some elements in the upper part of the soil profile (topsoil).

The F2 association, based on Pb, Zn, Sb and Sn, is responsible for the 28.13% of the total data variability, and its positive scores are mostly spatially associated with urbanized areas with intense vehicular traffic (Figure 3b). In fact, Pb derives mainly from the heritage of leaded gasoline use, whereas Zn, Sb and Sn are mainly related to non-exhaust car emissions such as the decay of tires and the consumption of brake pads [1,106]. Sn and Sb are also linked to some anthropogenic residential activities and to rail transport [107].

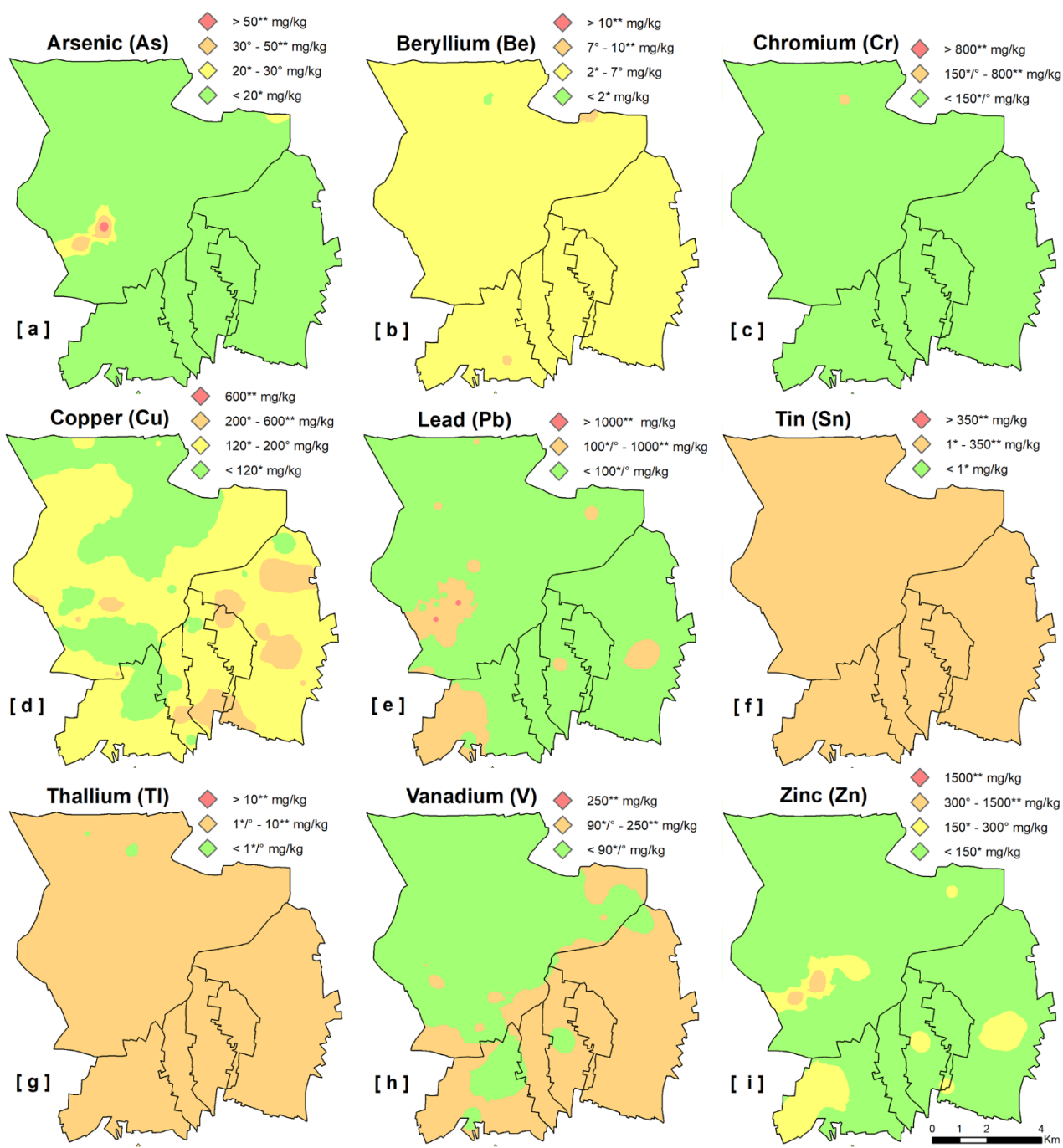


Figure 2. Potential hazard maps of PTEs. (* and ** are the guideline values established by the D.Lgs. 152/06 for residential and industrial land use, respectively; ° are the ones established by the D.M 46/19 for agricultural land use).

The F3 association, responsible for 17.87% of the total variability of the model, is featured by the high loadings of Cu and P. Positive factor scores for this association are found in the south-eastern area, close to the Vesuvius slopes, while negative values characterize urban centers (Figure 3c). Since Cu is a component of cupric fungicides and P is used in soil conditioners and phosphate fertilizers [108], this association was attributed to the predominantly agricultural use of the soil.

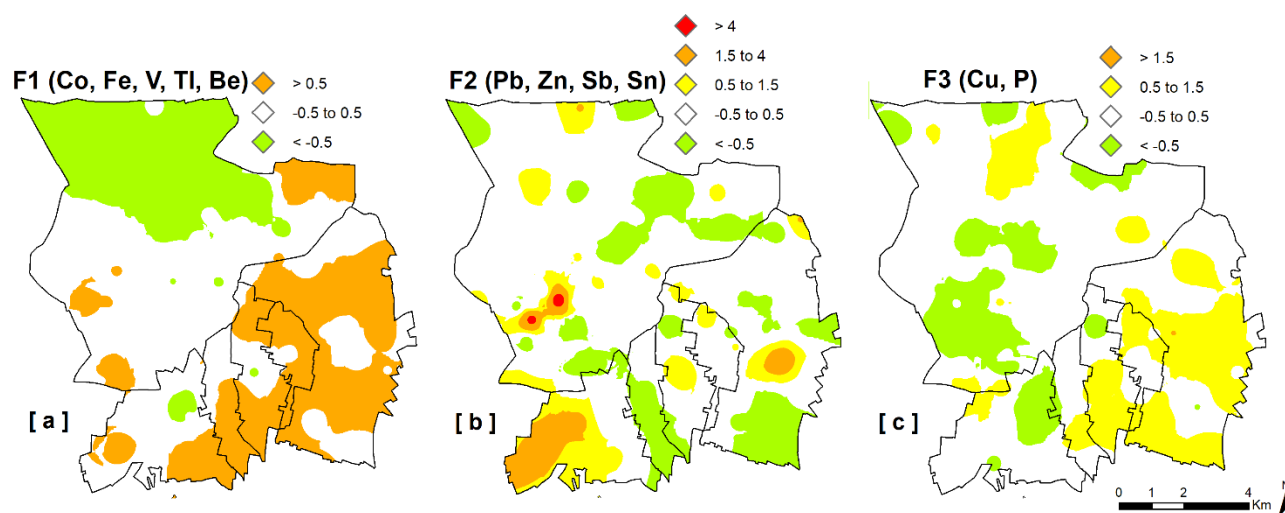


Figure 3. Maps of the factorial association found for PTEs.

5.2. PAHs distribution and sources

Table 3 shows the statistic of PAHs. Benzo(a)anthracene, benzo(k)fluoranthene, chrysene and pyrene did not show concentration exceeding neither the guideline values established by the D.Lgs. 152/06, for residential and industrial land use, nor the ones established by the D.M. 46/16 for agricultural land use (Table 3).

Table 3. Summary statistics of PAHs and legislative guideline values for different land uses according to Italian Environmental laws.

Compound	Unit	Statistical parameters						D.Lgs. 152/06		
		DL	Min	Max	Mean	St.Dev	Median	Agr.	Res.	Ind.
Pyrene	ng/g	0,10	4,02	396,7	79,88	77,83	55,21		5000	50000
Benzo[a]anthracene	ng/g	0,20	3,34	424,9	70,58	79,66	51,26	1000	1000	10000
Chrysene	ng/g	0,16	19,74	780,6	234,1	181,4	174,2	1000	5000	50000
Benzo[b]fluoranthene	ng/g	0,16	15,76	878,8	224,1	205,5	172,0	1000	500 (2)	10000
Benzo[k]fluoranthene	ng/g	0,08	6,48	381,8	108,1	93,3	73,7	1000	1000	10000
Benzo[a]pyrene	ng/g	0,16	18,98	1131,6	302,5	263,7	234,6	100 (25)	100 (25)	10000
Dibenzo[a,h]anthracene	ng/g	0,04	0,02	181,1	40,68	40,92	28,01	100 (3)	100 (3)	10000
Indeno[1,2,3-cd]pyrene	ng/g	0,14	13,85	1078,7	254,6	244,3	171,0	1000 (1)	100 (24)	5000
Benzo[g,h,i]perylene	ng/g	0,17	8,37	615,4	162,2	146,5	108,5	5000	100 (18)	10000

Note: Where present, the values in parenthesis associated to the guideline value represent the number of samples overcoming the guideline itself. (DL = detection limits; Min = minimum value; Max = maximum value; St.Dev = standard deviation; Agr./Res./Ind. = land use guideline according IELs).

Benzo(a)pyrene (Figure 4a) and indeno(1,2,3-cd)pyrene (Figure 4e) show values exceeding the guidelines for residential land use of 100 ng/g for both (which for benzo(a)pyrene corresponds to the guideline established by the D.M. 46/19 for agricultural land use) almost in all the study area, except

for small portion in the municipality of Acerra and Marigliano. Indeno(1,2,3-cd)pyrene also shows values exceeding the guideline for agricultural land use (1000 mg/kg) near the town of Brusciiano.

Dibenzo(a,h)anthracene (Figure 4b) and benzo(b)fluoranthene (Figure 4d) overcome the guidelines values for residential land use of 100 ng/g (which for dibenzo(a,h)anthracene corresponds also to the guideline established by the D.M. 46/19 for agricultural land use) and 500 ng/g, respectively, in correspondence of the industrial area between the towns of Acerra and Brusciiano.

Benzo(g,h,i)perylene has values not exceeding the guidelines for residential land use of 100 ng/g around the towns of Acerra and Pomigliano D'Arco and in the north-eastern sector of the study area, while it overcomes it in the remaining portions (Figure 4c).

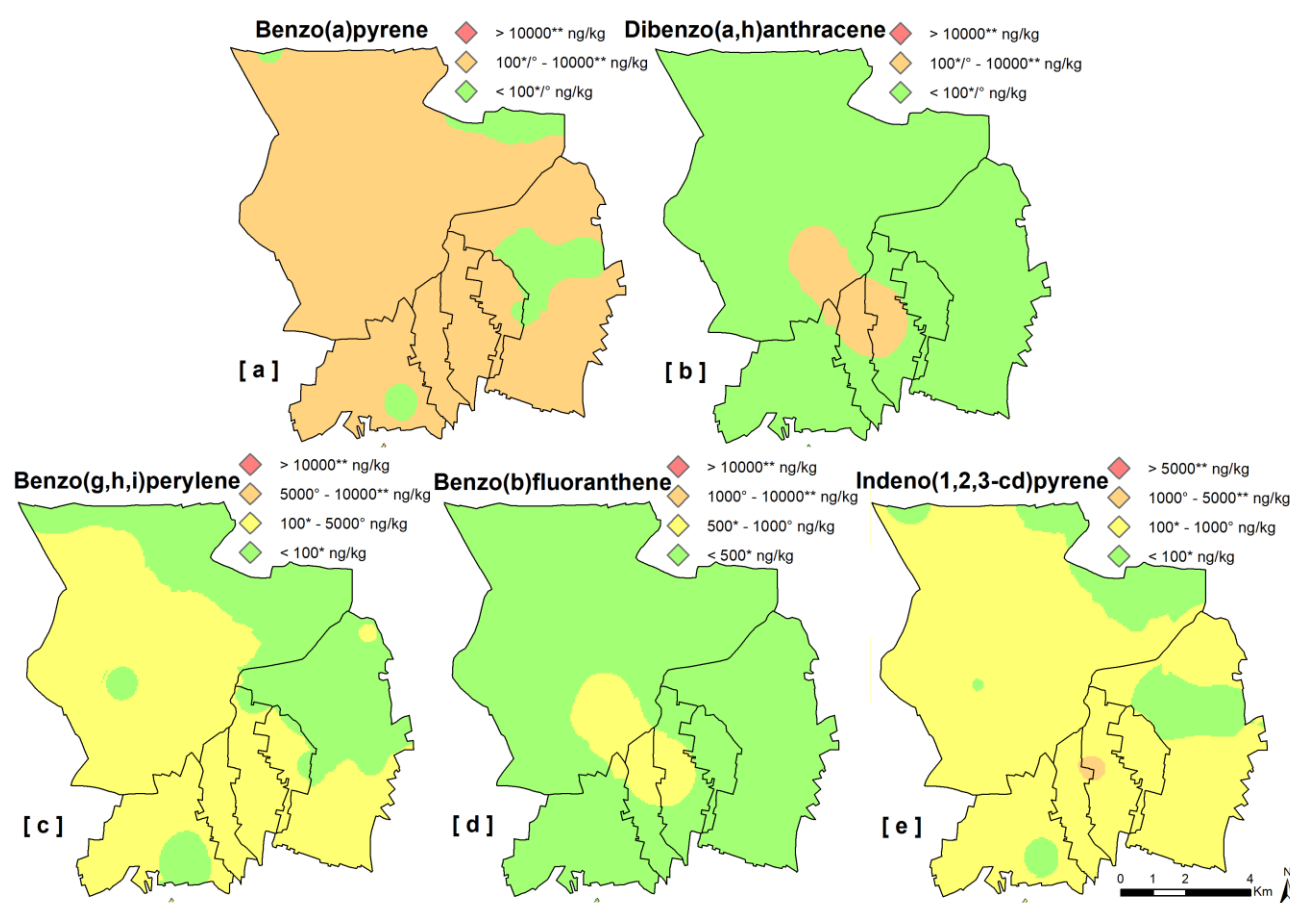


Figure 4. Potential hazard maps of PAHs. (* and ** are the guideline values established by the D.Lgs. 152/06 for residential and industrial land use, respectively; ° are the ones established by the D.M 46/19 for agricultural land use).

Generally, LMW compounds derive from petrogenic processes, i.e. produced by slow processes at low temperatures, while HMW compounds derive from pyrogenic processes associated to anoxic conditions and high temperatures [109]. The ratio between low and high molecular weight PAHs suggests a pyrogenic origin of these compounds, since in all the area values are <1 [92] (Figure 5a). This is confirmed also from the ratio between anthracene and phenanthrene, which, almost in the whole area except for three sample, assumes values >0.1 [93] (Figure 5b).

Both the ratios between fluoranthene and pyrene (Figure 5e) and the one of

indeno(1,2,3-cd)pyrene and benzo(ghi)perylene (Figure 5f) also show that the origins are linked to pyrogenic processes. In fact, in almost the whole area the values are, for both, >0.5 suggesting that the origin of these PAHs is attributable to the combustion of biomasses [95,96] and, only in small portions of the area, to the pyrolysis of fossil fuels.

The ratio between benzo(a)anthracene and chrysene shows that in almost the half of the study area the origin of these compound is attributed to petrogenic processes (values <0.2) while the rest to coal combustion (values from 0.2 to 0.35) [94] (Figure 5c).

The ratio between benzo(a)pyrene and benzo(ghi)perylene assumes values >0.5 in the whole study area, which means that the origin of these compounds is linked to traffic emission [97] (Figure 5d).

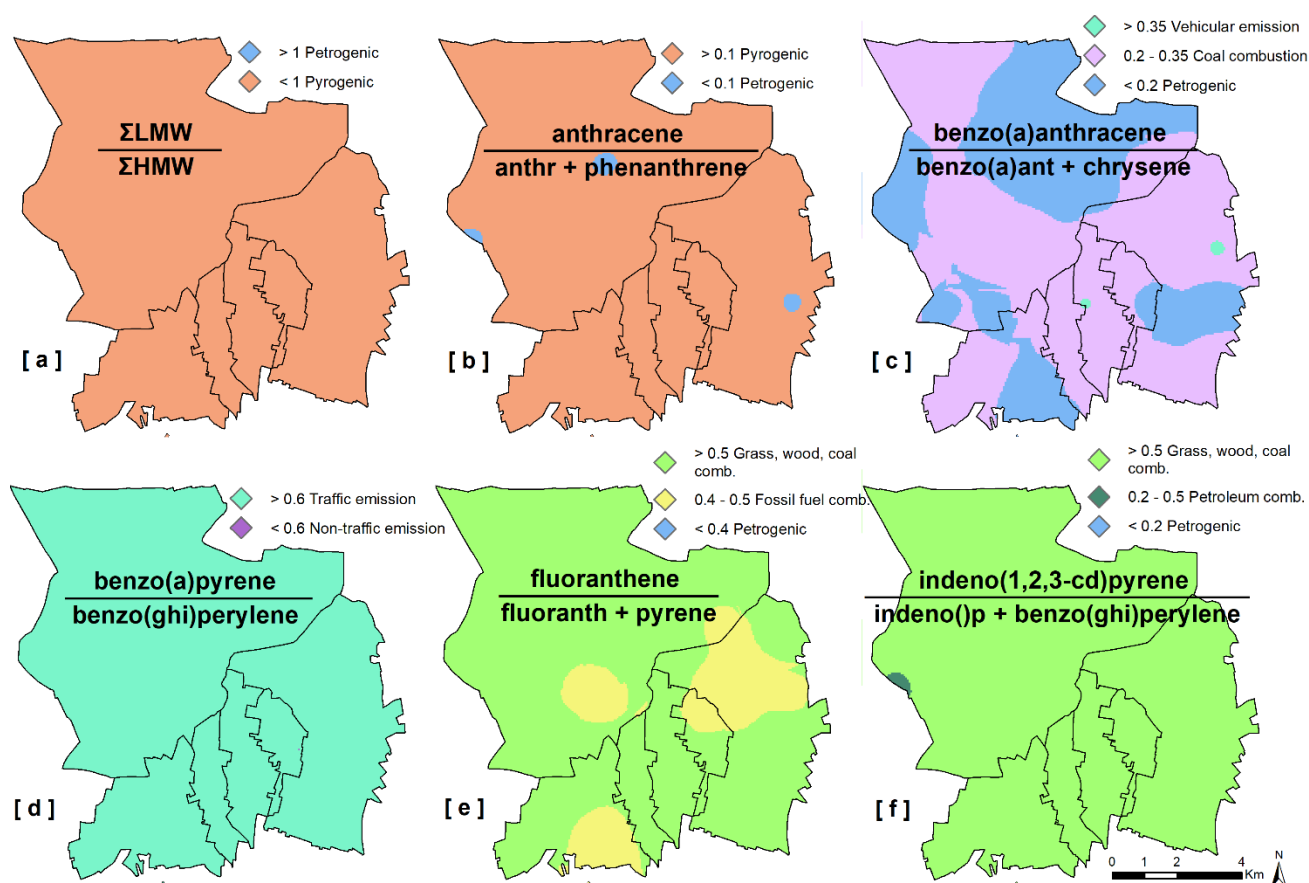


Figure 5. Maps of the diagnostic ratios of PAHs.

5.3. OCPs distribution and sources

Table 4 shows the statistic of OCPs. For all the OCPs for which exist guideline values established by the D.Lgs. 152/06 and by the D.M. 46/19 (i.e., p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, o,p'-DDE, α -HCH, β -HCH, γ -HCH, aldrin, dieldrin, endrin, trans-chlordane, cis-chlordane), the values for residential land use correspond to the ones set for agricultural land use, which is equal to 10 ng/g for all of them.

Table 4. Summary statistics of OCPs and legislative guideline values for different land uses according to Italian Environmental laws.

Compound	Unit	Statistical parameters						D.M. 46/19	D.Lgs. 152/06	
		DL	Min	Max	Mean	St.Dev	Median	Agr.	Res.	Ind.
α -HCH	ng/g	0,070	0,035	0,91	0,16	0,19	0,10	10	10	100
β -HCH	ng/g	0,067	0,034	15,40	1,74	3,16	0,65	10 (1)	10 (1)	500
γ -HCH	ng/g	0,105	0,053	3,17	0,41	0,62	0,19	10	10	500
o,p'-DDT	ng/g	0,075	0,038	36,73	5,67	7,91	2,04	10 (8)	10 (8)	100
p,p'-DDT	ng/g	0,162	0,081	492,7	70,37	100,1	25,53	10 (23)	10 (23)	100 (10)
o,p'-DDE	ng/g	0,055	0,028	3,89	0,75	0,96	0,33	10	10	100
p,p'-DDE	ng/g	0,079	0,040	337,9	75,94	92,08	31,02	10 (25)	10 (25)	100 (9)
o,p'-DDD	ng/g	0,063	0,059	4,39	1,44	1,25	1,21	10	10	100
p,p'-DDD	ng/g	0,065	0,033	21,19	6,24	5,95	3,66	10 (7)	10 (7)	100
Dieldrin	ng/g	0,207	0,104	14,45	1,67	3,57	0,25	10 (3)	10 (3)	100
Aldrin	ng/g	0,092	0,046	1,52	0,54	0,39	0,45	10	10	100
Endrin	ng/g	0,183	0,092	2,43	0,49	0,63	0,09	10	10	2000
Trans-Chlordane	ng/g	0,061	0,031	0,44	0,06	0,08	0,03	10	10	100
cis-Chlordane	ng/g	0,036	0,018	0,55	0,05	0,10	0,02	10	10	100

Note: Where present, the values in parenthesis associated to the guideline value represent the number of samples overcoming the guideline itself. (DL = detection limits; Min = minimum value; Max = maximum value; St.Dev = standard deviation; Agr./Res./Ind. = land use guideline according IELs).

Trans-chlordane, cis-chlordane, o,p'-DDD, o,p'-DDE, α -HCH, γ -HCH, aldrin and endrin did not show concentration values exceeding the guideline values established by the D.Lgs. 152/06, neither for the residential land use nor for the industrial use, and by the D.M. 46/19 for agricultural land use.

Dieldrin (Fig. 6f) and β -HCH (Figure 6e) overcome the guideline of 10 ng/g just in one sample (Table 4), in the municipality of Acerra β -HCH and in the one of Marigliano dieldrin.

O,p'-DDT (Figure 6b) and p,p'-DDD (Figure 6c) overcome the guideline of 10 ng/g around the urban centres of Marigliano and Brusciano and in some samples in the municipality of Acerra.

P,p'-DDT (Figure 6a) and p,p'-DDE (Figure 6d) overcome the guidelines in almost all the study area, except for a few scattered samples, and show even values exceeding the guideline set for industrial land use of 100 ng/g in the municipality of Acerra and Marigliano both, and in the area between the urban centres of Castello and Mariglianella p,p'-DDE.

The ratio o,p'-DDT/p,p'-DDT was used to discriminate between technical DDT and dicofol contamination, since high values (>1.3) indicates dicofol sources while small values (<0.3) technical DDT [99]. The values have a median of 0.06, suggesting that more of the half of the values found are attributable to the use of technical DDT, while, just in a small area west to the town of Acerra, is linked to dicofol use (Figure 7a).

Since DDE and DDD are the main degradation products of DDT dechlorination [110], the ratio between p,p'-DDT, p,p'-DDE and p,p'-DDD can be used as indicator of the input of this compound in the environment because high values (>1) indicate fresh application while small values (<1) can be a sign of an historical DDT inputs [98]. The ratio calculated for the study area assumed a median value of 0.77 suggesting for almost the half of the territory a recent input of DDT (Figure 7d).

Furthermore, considering that the sequence of degradation of HCHs is α -HCH > γ -HCH > δ -HCH > β -HCH, both the ratio α -HCH/ γ -HCH (Figure 7b) and α -HCH/ β -HCH (Figure 7e) indicate that the contamination from OCPs is not linked to the use of technical mixture of hexachlorocyclohexane; in fact, the assessed values for α -HCH/ γ -HCH are always <2 [100,101], and those for α -HCH/ β -HCH are <11.8 [102].

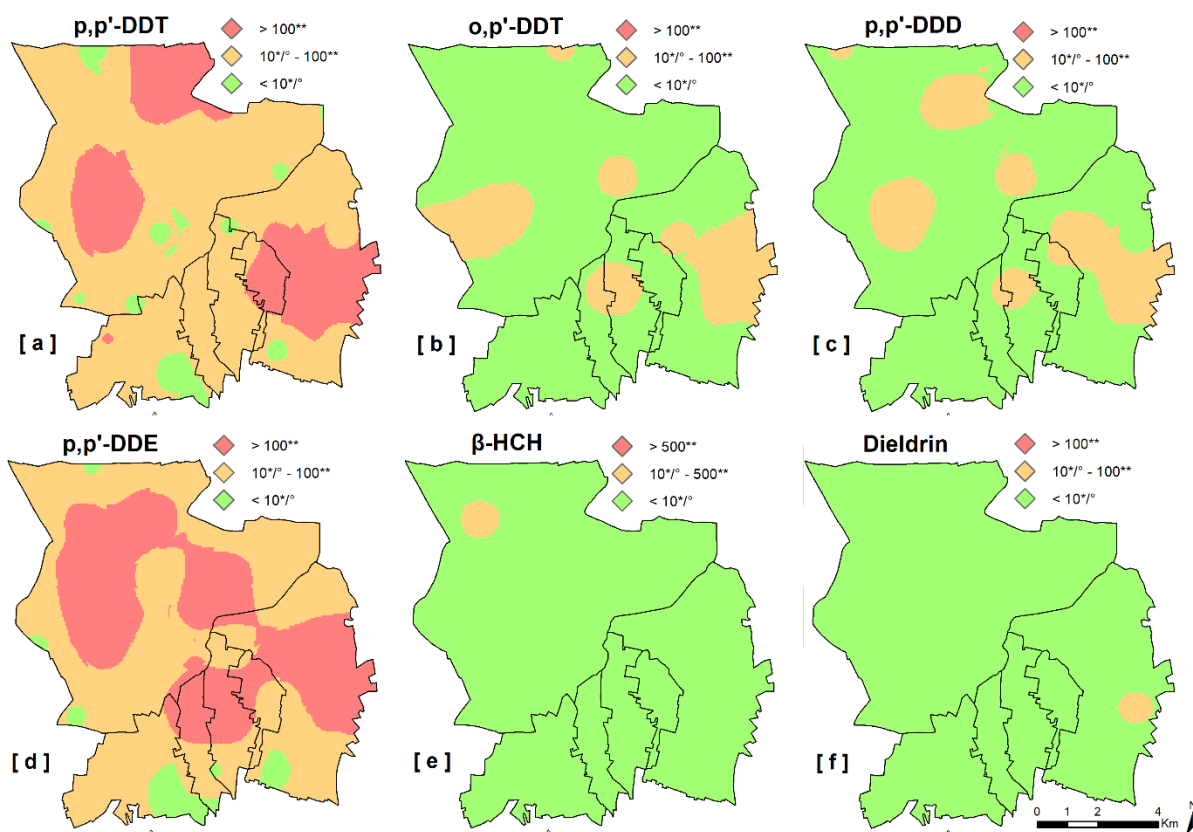


Figure 6. Potential hazard maps of OCPs. (* and ** are the guideline values established by the D.Lgs. 152/06 for residential and industrial land use, respectively; ° are the ones established by the D.M 46/19 for agricultural land use).

On the other hand, considering that trans-chlordane degrades more easily than cis-chlordane, and a value of the ratio cis-chlordane/trans-chlordane >1 indicate the presence of aged chlordane in soils [103], the areas around the city centers and in the north-eastern sector of the study area with values of the ratio <0.77 have been probably treated with technical mixtures, while the values are indicative of aged chlordane in the case of the remaining cultivated areas (Figure 7c).

The ratio α -endosulfan/ β -endosulfan was finally used to define the age of the mixture for these OCPs. In technical mixtures the ratio among the two isomers is about 2.33 [104,98] and values above this value are indicative of fresh inputs. The observation of the ratio map (Figure 7f) indicates that there have been recent applications of technical endosulfan, mostly in the central sector of the investigated area (Figure 7f).

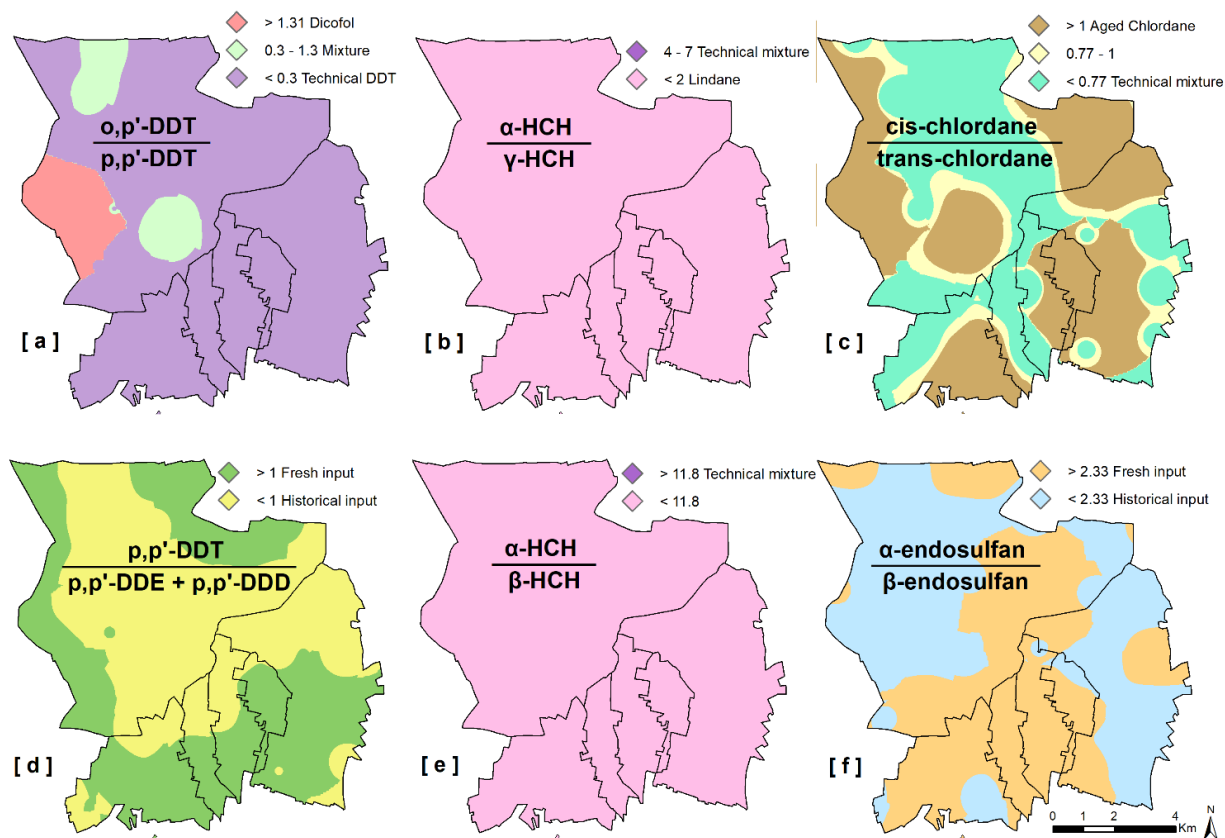


Figure 7. Maps of the isomeric ratios of OCPs.

6. Conclusions

From the analyses carried out for soils collected in the urban area of Acerra and neighboring municipalities it emerged that several PTEs, PAHs and OCPs have concentrations exceeding the guideline values set by the D.Lgs. 152/06 and the D.M. 46/19.

Specifically, over the entire investigated area Tl, Be, Sn and, limited to the south-eastern sector, V show exceedances of the guideline values even if the reasons are attributable to the volcanic origin of the pedological matrix. In the south-eastern sector, the surplus of Cu can be associated with the use of copper-based pesticides in agricultural practices set on volcanic soils destined for the cultivation of vines and, near urban centers, the high concentrations of Zn and Pb can mainly refer to motor vehicle traffic (current and past).

Benzo(a)pyrene, benzo(ghi)perylene and indeno(123-cd)pyrene showed high concentration values, above the guideline limits, in the whole study area, with the exception of the north-eastern portion of the territory analyzed, free from industrial activities. Dibenzo(a,h)anthracene and benzo(b)fluoranthene were found to be characterized by high values, higher than the CSCs for residential use, in the industrial area between the municipalities of Acerra and Brusciano.

The results obtained from the analysis of the contamination sources of PAHs showed that, in almost the entire area, most of the hydrocarbons derive from combustion processes, mostly biomass, and this is in line with the intense agricultural activity and the presence a power plant fueled with palm oil in the area.

The OCPs that showed the highest concentration, higher than the guidelines established by the D.Lgs. 152/06 and the D.M. 46/19, were p,p'-DDT, o,p'-DDT, p,p'-DDD and p,p'-DDE. The highest values were found mainly in the urban and industrial areas around the urban centres of Acerra, Brusciiano and Marigliano.

The analysed isomeric ratios showed that, despite the use of most OCPs is banned, there still is a present contribution to the high concentrations in soil due to fresh application of mixtures of pesticides in some portions of the study area.

Given the huge number of people residing in the area, and the presence of numerous productive activities, the results obtained are not surprising. It is clear, however, that it is necessary to implement new studies aimed above all at assessing health risk in probabilistic terms and also, due to the superficiality of the water table, perform a detailed study on the possible influence that soil contamination could have on groundwater geochemistry. A detailed analysis could help better identify the areas to which address the highest priority for intervention, and the use of more advanced multivariate statistical techniques could help to discriminate the sources of pollutant emissions with greater precision.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Supplementary

Table S1. Detection limits (DL), accuracy and precision of the analyses.

Element	Ag	Al	As	Au	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr
Unit	µg/kg	%	mg/kg	µg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	mg/kg
DL	2	0.01	0.1	0.2	1	0.5	0.1	0.02	0.01	0.01	0.1	0.1	0.5
Accuracy	4,3	4,5	2,6	5,0	0,4	4,3	6,9	8,5	4,1	5,2	9,2	5,5	5,2
Precision	7,0	3,8	2,7	8,7	8,2	5,6	11,1	16,2	3,3	6,9	7,1	8,9	4,6
Element	Cs	Cu	Fe	Ga	Hf	Hg	In	K	La	Li	Mg	Mn	Mo
Unit	mg/kg	mg/kg	%	mg/kg	mg/kg	µg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg	mg/kg
DL	0.02	0.01	0.01	0.1	0.02	5	0.02	0.01	0.5	0.1	0.01	1	0.01
Accuracy	3,4	4,8	2,6	5,0	18,8	9,0	-	3,1	10,1	4,3	2,7	2,7	6,0
Precision	4,3	8,4	4,5	5,2	7,5	17,7	-	1,5	6,2	5,2	3,6	3,8	4,4
Element	Na	Nb	Ni	P	Pb	Pd	Pt	Rb	Re	S	Sb	Sc	Se
Unit	%	mg/kg	mg/kg	%	mg/kg	µg/kg	µg/kg	mg/kg	µg/kg	%	mg/kg	mg/kg	mg/kg
DL	0.001	0.02	0.1	0.001	0.01	10	2	0.1	1	0.02	0.02	0.1	0.1
Accuracy	7,2	15,4	3,5	3,7	4,8	6,1	5,8	3,8	-	2,8	14,7	7,2	4,3
Precision	4,2	14	3,7	6,8	3,3	16	14	2,5	-	6,2	3,5	4,2	10,4
Element	Sn	Sr	Ta	Te	Th	Ti	Tl	U	V	W	Y	Zn	Zr
Unit	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
DL	0.1	0.5	0.05	0.02	0.1	0.001	0.02	0.1	2	0.1	0.01	0.1	0.1
Accuracy	5,7	6,9	-	5,1	6,2	6,8	3,6	6,9	4,6	5,6	8,4	3,6	11,5
Precision	4,7	5,1	-	9,1	5,6	7,9	3,5	2,2	10,0	4,8	5,4	4,7	18,0



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