Source patterns and contamination level of Polycyclic Aromatic hydrocarbons (PAHs) in urban and rural areas of Southern Italian soils

Matar Thiombane[1*], Marcello Di Bonito[2], Stefano Albanese[1], Annamaria Lima[1], Daniela Zuzolo[3], Roberto Rolandi[1], Shihua Qi[4], Benedetto De Vivo[5]

[1]. Department of Earth, Environment and Resources Sciences (DiSTAR), University of Naples "Federico II", Complesso Universitario di Monte Sant' Angelo, Via Cintia snc, 80126 Naples, Italy.

[2]. School of Animal, Rural and Environmental Sciences, Brackenhurst Campus Southwell NG25 0QF Nottingham Trent University, Unites Kingdom.

[3]. Department of Science and Technology, University of Sannio, via dei Mulini 59/A, 82100 Benevento, Italy.

[4]. State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 430074 Wuhan, People's Republic of China.

[5]. Pegaso University, Piazza Trieste e Trento 48, 80132 Naples & Benecon Scarl, Dip. Ambiente e Territorio, Via S. Maria di Costantinopoli 104, 80138 Naples, Italy

* Corresponding author: Matar Thiombane, thiombane.matar@unina.it

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants (POPs). They have been identified as a type of carcinogenic substance and are relatively widespread in environment media such as air, water and soils, constituting a significant hazard for human health. In many parts of the world, PAHs are still found in high concentrations despite improved legislation and monitoring, and it is therefore vital defining their profiles, and assessing their potential sources. This study focused on a large region of the South of Italy, where concentration levels, profiles, possible sources and toxicity equivalent quantity (TEQ) level of sixteen PAHs were investigated. The survey included soils from five large regions of the south of Italy: 80 soil samples (0–20 cm top layer) from urban and rural locations were collected and analysed by Gas chromatography-mass spectrometry (GC-MS). Total PAHs and individual molecular compounds from the US Environmental Protection Agency (EPA) priority pollutants list were identified and measured.

Results showed that 16PAHs varied significantly in urban and rural areas, and different regions presented discordant characteristics. Urban areas presented concentrations ranging from 7.62 to 755 ng/g (mean = 84.85 ng/g), whilst rural areas presented ranges from 1.87 to 11,353 ng/g (mean = 333 ng/g). Large urban areas, such as Rome, Naples and Palermo, exhibited high PAHs total concentration, but high values were also found in rural areas of Campania region. Different PAHs molecular ratios were used as diagnostic fingerprinting for source identification: LWMPAHs/HWMPAHs, Fluo/(Fluo

+Pyr), BaA/(BaA +Chr), Ant/(Ant +Phe), and IcdP/(IcdP +BghiP). These ratios indicated that PAHs sources in the study area were mainly of pyrogenic origin, i.e. mostly related to biomass combustion and vehicular emission. On the other hand, values in Sicilian soils seemed to indicate a petrogenic origin, possibly linked to emissions from crude oil combustion and refineries present in the region. Finally, results allowed to calculate the Toxicity equivalent Quantity (TEQ_{BAP}) levels for the various locations sampled, highlighting that the highest values were found in the Campania region, with 661 ng g^{-1} and 54.20 ng g^{-1}, in rural and urban areas, respectively. These findings, which could be linked to the presence of a large solid waste incinerator plant, but also to well-documented illegal waste disposal and burning, suggest that exposure to PAH may be posing an increased risk to human health in some of the studied areas.

Keywords: Southern Italy; PAHs; ratio diagnostic; soil pollution sources; Toxicity Equivalent Quantity (TEQ_{BAP}).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are diffuse persistent organic pollutants (POPs) that can be found in different environmental media, including air, water and soil. They are human carcinogens, mutagens and are toxic to all living organisms, making them a group of compounds of public concern, which are becoming increasingly studied and monitored in many areas of the world (IARC, 1983, Hwang et al., 2003; Nadal et al., 2004; Vane et al, 2014). PAHs are primarily formed through the incomplete combustion of carbon containing fuels such as wood, coal, diesel, fat, and tobacco, and most sources of PAHs are anthropogenic, arising from industrial emissions, solid waste incineration, and vehicular emissions among others (Dong and Lee, 2009). Sixteen U.S. Environmental Protection Agency (EPA) priority PAHs are classified in two main groups of compounds related to the number of aromatic rings: low molecular weights PAHs (LMWPAHs) with 2 to 3 aromatic rings (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene) and high molecular weight PAHs (HMWPAHs) with 4 to 6 aromatic rings such as fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]-pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthrancene, and benzo[g,h,i]perylene. PAHs from a petrogenic source are formed predominantly with those of low molecular weights, while the PAHs from a pyrogenic source generally have high molecular weights (Soclo et al., 2000).

Once formed by the mechanisms of partial combustion, PAHs can be found in different media. In particular, soil is considered an important media to quantify PAHs patterns due to its physico-chemical properties that allow PAH compounds to be held in soil matrices (Means et al., 1980). PAHs are slightly or completely insoluble in water and they are adsorbed on soil particles, particularly on soil organic matter. Hence, the physical–chemical properties of soils are responsible for the retention of PAHs in soil matrices. The organic carbon content, the hydrophobicity of soil organic matter, and soil texture were estimated to be the most significant parameters controlling the environmental availability of PAHs (Albanese et al., 2015a). Furthermore, some studies (Menzie et al., 1992; Nadal et al., 2004) have demonstrated that the amount of human exposure to PAHs through soils was higher than through air or water. As they exist in different forms with a different degree of toxicity, it is important to characterise individual PAHs compounds as much as possible. However, given their number and variety, often their ratios can be a more effective diagnostic tool to identify potential source patterns and quantify the amount of PAH pollution for a specific area (e.g., Pandey et al., 1999; Yunker et al., 2002; Hwang et al., 2003). One of the most widespread computations used is that involving the LMWPAHs/HMWPAHs ratio introduced by Budzinski et al. (1997) who fixed a value ≤ 1 for pyrogenic source and above 1 for a petrogenic PAHs fingerprint. Since the introduction of this method, other authors have developed alternative takes by using individual PAH compounds, in particular low and high molecular weight groups, to highlight their main source patterns (Hwang et al., 2003, Yunker et al., 2002; Tobiszewski and Namieśnik, 2012). Recent development of analytical techniques has seen an increase in the number of studies focusing on individual PAHs compounds, and several studies (Zhang et al., 2006; Albanese et al., 2015a; Islam et al., 2017) have focused on topsoil PAHs occurrence and concentration, helping to shape and informing government policy for human and ecological safety. For example, Italian environmental law (D. Lgs. 152/2006) establishes threshold values that regulate the mitigation of the PAHs in soil media. This legislation fixes different PAHs concentration values based on the type of PAHs and the land use (e.g. residential and industrial areas). Regulations can guide efforts and resources for reclamation and more detailed monitoring, contextualising interpretations in line with risk-based approaches. However, much needs to be done to establish baselines and understand the mechanisms of these contaminants' movement and availability in the environment. In particular, in southern Italy there exist several potential anthropogenic sources of PAHs such as petroleum exploitation districts, biomass combustion plants, vehicular emissions and residential wood combustion which can all constitute a source of PAHs compounds and contribute to their concentrations in soils and other media. These have been only recently studied, and mainly at a local, small scale, whilst a regional baseline approach has not been carried out yet.

The present study will focus on the 16 (EPA) PAHs priority compounds to carry out a regional survey in southern Italy. PAHs will be characterised in soils of several urban and rural locations to assess their spatial distribution, their potential sources and pathways their level of toxicity.

This study is important because it will constitute the first regional survey carried out in Italy and can be considered a first stepping stone towards a more detailed and meaningful investigation on potential sources and levels of PAHs in the region. It is anticipated that this study will contribute to build a baseline for PAHs characterisations in urban and rural areas of southern Italy. Follow up studies should be expected in areas where high PAHs concentration levels (i.e., contamination) were found, with a larger number and higher density of (soil and air) samples in each affected location.

2. Materials and Methods

2.1. Study areas

The survey area included five administrative regions (Latium, Campania, Basilicata, Calabria and Sicily) of the South of Italy. The total area extends to approximately 81,054 km^2 with 19.38 million inhabitants, mostly grouped in urban areas. The overall area is characterised by a principal mountain range, the Apennine chain, which presents very specific geological and morphological features (Fig. 1A).

[Figure 1. about here]

The main geological features of the study area are a result of the tectonic and orogenic activities related to the nearby boundary between the Eurasian and the African Plates. The area is characterised by active volcanism of different origin, such as that related to the Vesuvius, the Phlegraean Fields, Ischia island, Pontine Islands and Roccamonfina in the Campania region, and the Etna and Aeolian islands in the Northeast of Sicily. Such volcanism can be considered a potential (though limited) source of PAHs during volcanic eruptions (Kozak et al., 2017). From the land use point of view, the study region is devoted to intensive agriculture activities such vineyards, olive plantations - mostly in hilly areas – citrus fruits, seasonal crops, and greenhouse products (tomatoes, potatoes, aubergines, peppers and peas) which represent major resources for the local economy (Albanese et al., 2007). In addition to this, large industrial works are also present in the region, processing raw materials of various origins (e.g. petroleum plants, biomass, and alloy). Some of these industrial activities can be linked to 'petrogenic' sources of organic pollutants. Some good examples can be found in: 1) the Priolo and Gela districts (Sicily), where the largest petroleum field and refinery in Europe can be found (DPCM, 1990); 2) Alta Val d'Agri (Basilicata), which is the location of the largest Italian inland oil field; 3) Crotone (Calabria) and Milazzo (Sicily), the sites of two very large petroleum refineries. An industrial activity that can be linked to potential 'pyrogenic' sources of organic pollutants is that related to energy (and energy-from-waste) generation, which is widely diffused in the study area. Some good examples can be found in: 1) Latium, with the thermal and coal power plants in Civitavecchia and the solid municipal waste incinerator plant in Frosinone; 2) in Campania, with various large industrialized areas within the metropolitan area of Naples, and with the urban solid waste Incinerator plant of Acerra; 3) in Basilicata (Potenza and Melfi) and Calabria (Gioia Tauro), where other incinerators plants can be found (Fig. 2).

[Figure 2. about here]

2.2. Description of sampling locations

The sampling campaign took place from early April to end of September 2016, with the aim of taking the most representative soil samples in urban and rural areas throughout five administrative regions (Latium, Campania, Basilicata, Calabria and Sicily) of southern Italy. In each region the main urban areas and the nearest rural areas, where most of the land is devoted to agricultural activities, were selected. The sampling site characterisation and selection was performed using Geographical Information Systems (GIS) data of the industrial and agricultural activities and land use of the study area (ISPRA, 2014; ISTAT, 2016) as well as using satellite images (Google Earth® professional, 2016 version).

2.3. Sample collection and materials

A total of 80 soil samples were collected for polycyclic aromatic hydrocarbons (PAHs) with a nominal density of 2 samples (in urban and rural areas) in each 2500 km^2 (Fig. 1B). The sampling procedure followed the Geochemical Mapping of Agricultural and Grazing Land Soils (GEMAS) sampling procedure described by Reimann et al. (2005). All the samples were collected using a stainless steel scoop and were kept in labelled glass bottles and directly stored in ice boxes to minimize the losses caused by volatilization and initial degradation of the organic compounds (Albanese et al., 2015a). Each topsoil sample (from 0-20 cm) was made by homogenizing 5 subsamples at the corners and the centre of a $100m^2$ square, collecting approximately 1.5 kg in total. The homogenized soil samples were sieved using a <2mm mesh sieve after removing stones, detritus and residual roots. Finally, composite samples were stored at −4 °C in the environmental geochemistry laboratory of the University of Naples Federico II (Italy) until instrumental analysis. For each sampling site pH, moisture content and electric conductivity of the soil were measured. Records of the land use, main industrial works and any other human activity observed in the proximity of the sampling locations were recorded at each site, where geographical coordinates were uploaded by global positioning systems (GPS). These attributes would form the dataset subsequently used for the spatial analysis and representation by GIS.

2.4. Sample preparation and analytical procedures

Samples were analysed for PAHs content at the Key Laboratory of Biogeology and Environmental Geology of Ministry of Education, China University of Geosciences, Wuhan, China. For this study, the target analytes were the 16 US EPA priority PAH compounds: naphthalene(Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene(Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]-pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthrancene(DahA), and benzo[g,h,i]perylene (BghiP). 10g of soil sample were weighed and injected with PAH surrogates (naphthalene-d8, acenaphthened10, phenanthrene-d10, chrysene-d12 and perylene-d12), and Soxhlet-extracted with dichloromethane (DCM) for 24h. The extracts were treated with activated copper granules to remove elemental sulfur, concentrated and solvent-exchanged to n-hexane and further reduced to 2–3 mL by a rotary evaporator (Heidolph 4000, Germany). A 1:2 (v/v) alumina/silica gel column (450° C muffle drying for 4 h, both 3% deactivated with H_2O before using) was used to clean up the extracts and PAHs were eluted with 70 mL of DCM/hexane (2:3). The eluate was then reduced to 0.2 mL under a gentle stream of nitrogen. A known quantity of hexamethylbenzene was added as an internal standard for PAHs analysis prior to instrumental quantitation for the PAHs.

PAHs were analysed using GC-MS (Agilent 6890N/5975 MSD) coupled with a HP-5972 mass selective detector operated in the electron impact mode (70 eV) installed with a DB-5 capillary column (30 m×0.25 mm diameter, 0.25um film thickness). Helium (99.999%) was used as the GC carrier gas at a constant flow of 1.5 mL/ min. An 1uL concentrated sample was injected with splitless mode. The chromatographic conditions were as follows: injector temperature 270 °C; detector temperature 280 °C; oven temperature initially at 60° C for 5 min, increased to 290 °C at 3 °C/ min, and held for 40 min. Chromatographic peaks of samples were identified by mass spectra and retention time.

2.5. Quality control

Procedure types used for quality assurance and quality control (QA/QC) were as follows: method blank control (procedural blank samples), parallel sample control (duplicate samples), solvent blank control, and basic matter control (US EPA, 2002). In order to ensure the validity of the analyses during the experiment, different reagents and procedures were used:

1. One thousand nanograms (ng) of naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12 were used as recovery surrogates, and 1000 ng hexamethylbenzene was added in extracts as the internal standard substance. The spiked recoveries of PAHs using composite standards were 79.9±14.5 % for naphthalene-D8, 74.2±9.4 % for acenaphthene-D10, 91.5±11.6 % for phenanthrene-D10, 87.1±8.5 % for chrysene-D12, and 89.2±11.0 % for perylene-D12, respectively.
2. An internal standard method was used for quantification: a six-point calibration curve was established according to the results from the PAH-16 standard reagents with concentration of 10, 5, 2, 1, 0.5, and 0.2 mg.l^{-1}. For PAHs, the target compounds were identified on the basis of the retention times and selected quantitative ion.
3. During the pre-treatment, a procedural blank and a parallel sample consisting of all reagents was run to check for interference and cross contamination in every set of samples (about 16 samples). Only low concentrations of few target compounds can be detected in procedural blank samples. For more than 96 % of target compounds in parallel samples, the relative error (RE, %) of concentrations are less than 50 %, which is acceptable for Specification of Multi-purpose Regional Geochemical Survey and Guidelines for sample analysis of Multi-purpose Regional Geochemical Survey recommended by China Geological Survey (DD2005-1 and DD2005-3);
4. During the GC-MS analysis period, a solvent blank sample and a PAH-16 standard reagent with concentration of 5 mg l^{-1} and 100μg l^{-1} were injected every day before analysing the soil samples. The target compounds were not detectable in the solvent blank samples.
5. Multi-injections were used for precision or accuracy. The samples of different concentrations were injected continually for ten times, and the relative standard deviation was calculated. RSD for all the target compounds ranged from 3.2 to 7.9 %. The final concentrations of PAHs in all samples were corrected according to the recovery of the surrogates and the results of blank samples were subtracted.

2.6. Statistical computations

Univariate and multivariate analyses were carried out on the 16 PAHs through descriptive statistics and compositional principal factor analysis modelling, which helped displaying the variation of these compounds and their main correlations in the survey area. Computations and graphical representations were implemented by mean of the open source statistical software R (Templ et al., 2011).

2.7. Source apportionment

2.7.1. PAHs diagnostic ratios

Whilst several PAHs diagnostic ratios are available in the literature, (e.g., Katsoyiannis et al., 2007; Ravindra et al., 2008), in this study, four specific PAH molecular ratios were used for the identification of PAHs pollution sources: LMWPAHs/HMWPAHs, Fluo/(Fluo+Pyr), IcdP/(IcdP+BghiP), and BaA/(BaA+Chr) (Figs. 5, 6; Table 1). In particular, the reasons why these were chosen are that: the ratio LMWPAHs/HMWPAHs ≤ 1 corresponds to pyrogenic sources, and > 1 for petrogenic sources (Budzinski et al., 1997); the ratio Fluo/(Fluo + Pyr) < 0.4 has been shown to indicate petroleum source, between 0.4 and 0.5 implies fossil fuel combustion, and a ratio > 0.5 is the characteristic of biomass and coal combustion (Yunker et al., 2002). IcdP/(IcdP+ BghiP) < 0.2 is an indication of petroleum sources, while that between 0.2 and 0.5 indicates that the PAHs usually derive from petroleum combustion (liquid fossil fuel, vehicle, and crude oil combustion) and IcdP/(IcdP + BghiP) > 0.5 strongly indicates the contribution of coal, grass, and wood combustion (Tobiszewski and Namieśnik, 2012). Yunker et al. (2002) implemented the BaA(BaA+Chr) ratio and the value <0.2 to mark a petroleum/petrogenic source, while that between 0.20 to 0.35 is linked to a combustion and >0.35 is related to a traffic emission.

[Table 1 about here]

2.7.2. Compositional multivariate computation: Factor analysis

R-mode factor analysis, a type of multivariate statistics, was chosen to explain the correlation structure of the 16 EPA PAHs compounds (variables) using a smaller number of factors (Reimann et al., 2002). This methodology has been shown to successfully correlate the PAHs distribution to their main hypothetical origins (Albanese et al., 2015a; Islam et al., 2017). To minimize and/or eliminate the presence of outliers and spurious correlation (Pawlowsky-Glahn and Buccianti, 2011), isometric log-transformed data (ilr) are recommended in this type of multivariate analysis (Filzmoser et al., 2009). In order to facilitate the interpretation of results, varimax rotation was used, since it is an orthogonal rotation that minimises the number of variables that have high loadings on each factor, simplifying the transformed data matrix and assisting interpretation (Reimann et al., 2002). The different factors obtained were studied and interpreted in accordance with their presumed origin (petrogenic, pyrogenic or mixed) (Table 4, Fig. 7). The factor score values were mapped at each sample site using GIS software GeoDAS (Cheng et al. 2001) and ArcGIS (ESRI, 2012). GeoDAS™ was used to produce interpolated geochemical maps of the factor scores by means of the multifractal inverse distance weighted (MIDW) algorithm (Cheng et al., 1994; Lima et al., 2003). MIDW is one of the most widely used interpolation method on geochemical data because it preserves high frequency information, retain local variability taking into consideration both spatial association and local singularity (Cheng et al., 1994, 2001; Lima et al, 2003). Singularity is an index representing the scaling dependency from multifractal point of view, which characterizes how the statistical behaviour of a spatial variable changes as the measuring scale changes (Cheng et al., 1994). Spatial association represents a type of statistical dependency of values at separate locations, and its indexes (e.g. covariance, autocorrelation and semivariogram) have been used to characterize the local structure and variability of surfaces (Cheng et al., 1994). During interpolation and mapping of geochemical variables, both spatial association and scaling are taken into account. Despite the low density, interpolation is still a valid tool at regional level, as shown, for example, by the production of European geochemical atlases, which have used similar techniques (Reimann et al. 2012; Ottesen et al. 2013; Albanese et al. 2015b). The concentration–area (C–A) fractal method (Cheng et al., 1994) was applied to set the factor score intervals (Thiombane et al., 2017) in interpolated surface images generated by the MIDW method, and ArcGIS™ software was used for the graphical presentation of the results (Figs. 8, 9, 10).

2.8. Characterisation and toxicity assessment of PAHs

For each PAH compound, the Toxicity Equivalency Factor (TEF) was established to allow measuring its relative carcinogenicity (EPA, 1984; Nisbet and Lagoy, 1992). Among the 16 EPA PAHs, seven of them, including BaA, Chr, BaP, BbF, BkF, IcdP and DahA, present high toxic and carcinogenic effects. In particular, Benzo[a]-pyrene (BaP) is considered as one of the most toxic PAHs and it has been used to quantify the relative toxicity of others PAHs (Nisbet and Lagoy, 1992), also because it's the only compound with sufficient toxicological data to derive carcinogenic factors among all other potentially carcinogenic PAHs. The toxicity of soil can be measured using the BaP toxic equivalent quantity (TEQ_{BaP}) (Nadal et al., 2004) for each sampling site using the equation described below:

$$TEQ_{BAP} = \sum_{i=1}^{7} \mathrm{TEF} \times \mathrm{C_{PAHi}} \qquad \text{equation 1} \;,$$

where TEQ_{BAP} is the toxic equivalent quantity of ith PAH, the TEF of BaA, Chr, BaP, BbF, BkF, IcdP and DahA correspond to 0.1, 0.01, 1, 0.1, 0.1, 0.1 and 1, respectively, and C_{PAHi} is the concentration of the ith PAH in the soil.

3. Results and discussions

3.1. Variety PAHs concentrations in the survey area

Table 2 shows the descriptive statistic of the 16 EPA PAHs compounds in soils found on the sample locations of the studied area.

[Table 2. about here]

The total concentration of the 16PAHs in urban and rural area ranged from 7.62 to 755 ng/g with a mean value of 84.85 ng/g, and from 1.87 to 11,353 ng/g with a mean of 333 ng/g, respectively. The spatial distribution of the ∑16PAHs concentrations in the survey areas can be seen in Fig. 3, which compares urban and rural areas using proportional thematic mapping.

[Figure 3. about here]

The Figure 3A shows high total PAHs values (ranging from 59.52 to 755 ng g^{-1}) in correspondence with urban towns such as Rome (755 ng g^{-1}), Naples (715 ng g^{-1}) and Palermo (303 ng g^{-1}). These areas are also the most densely populated and urbanised cities of the southern Italy. In a recent study, Albanese al. (2015a) highlighted that the principal source of the PAHs pollutants in the Neapolitan (Campania) soils is related to pyrogenic combustion (vehicular emission). When considering the variation of total PAHs in rural areas (Fig. 3B), the highest values ranged from 33.30 to 11,353 ng g^{-1}, and are found mostly in the sampling sites of the Campania (Sarno Basin with 11,353 ng g^{-1}, Acerra with 917 ng g^{-1}, and Battipaglia with 276 ng g^{-1}), and the Sicily countryside (Acireale with 74.25 ng g^{-1}, Trapani with 56.56 ng g^{-1} and Milazzo with 52.45 ng g^{-1}). When compared to other studies of PAHs in urban and rural soils worldwide, the ranges reported in our study present similar concentrations ranges, though with some noticeable differences (Table 3). Morillo et al. (2007) found total PAHs values ranging from 148 to 3,410 ng g^{-1} in the Turin (Italy) urban area; these values are 4 times greater than those found in urban areas of this survey study. The total 16PAHs found in others European urban cities such in Seville (ranging from 89.5 to 4,004 ng g^{-1}; Morillo et al., 2008), London (ranging from 400 to 67,000 ng g^{-1}; Vane et al., 2014), Glasgow (ranging from 48 to 51,822 ng g^{-1}; Morillo et al., 2007) and Moscow (208 to 3,880 ng g^{-1}; Agapkina et al., 2007) are all higher than the values displayed in the urban areas of this study. Similarly, though at a larger scale, the ranges shown in the urban areas of Beijing (China) (Tang et al., 2005) and Delhi (India) (Bhupander et al., 2012) went from 219 to 27,825 ng g^{-1} and from 81.6 to 45,017 ng g^{-1}, respectively. On the other hand, the rural areas of the southern Italy showed higher total concentration of PAHs compared to the values displayed in Hong Kong (China) (Zhang et al., 2006) and Delhi (Agarwal et al., 2009), ranging from 42.3 to 410 ng g^{-1}, and from 830 to 3,880 ng/g, respectively. Many studies revealed that PAHs pollution sources are usually related to fuel combustion from traffic vehicle which is mostly occurring in urban areas. These studies are confirmed by the findings on some urban areas of the present study (e.g high 16PAHs in urban areas of Latium, Naples and Palermo). However, this survey also highlighted some unexpected higher values outside of the urban areas, perhaps due to the presence of industrial activities such as incinerator plants, oils refineries as well as and illegal activities (e.g., wood and solid waste burning in the Acerra district and in the Naples wider metropolitan area). Even though such large industrial activities are actually forbidden in urban areas by the most recent Italian environmental legislation, their influence on the distribution of PAHs on rural areas remained, until now, largely unexplored.

[Table 3. about here]

These findings are confirmed by the Tukey's box-and-whiskers plots (Fig. 4), which display how all 16 PAHs compounds showed higher concentration values in the rural sampling sites compared to the urban ones. On the other hand, Flo, Phe, Ant, Fluo, BaA, BbF, BkF, BaP, IcdP, DahA, and BghiP, which are all HMWPAHs, displayed higher median concentration values in urban areas (Table 2). Since the median is a good, intuitive metric of centrality representing a 'typical' or 'middle' value (Reimann et al., 2008), it is reasonable to infer that HMWPAHs are therefore more likely to be related to those pollution sources that are occurring mostly in urban areas, such as vehicular emission and fuel combustion, whereas LMWPAHs could be more strongly related to biomass and oil combustion sources which are more likely to be occurring in rural areas (Chen et al., 2005; Aichner et al., 2007).

[Figure 4. about here]

3.2. Diagnostic ratios and source apportionment of PAHs compounds

The LMWPAHs/HMWPAHs ratios (Fig. 5) were interpreted in terms of source apportionment. Soils from rural Sicilian areas displayed a higher mean value compared to those from urban areas, with ratios ranging from 0.12 to 2.48 (mean value of 1.14) compared to 0.08 to 1.35 (mean value of 0.56). These values also indicate that the most likely sources of PAHs in Sicilian rural areas may be related to 'petrogenic' emissions. As mentioned earlier, in Sicily there are some of the most important Italian oil fields and refineries (e.g., Priolo, Gela, Ragusa and Milazzo - Bevilacqua and Braglia, 2002). These industrial activities can give rise to ‘petrogenic’ emissions of PAHs, and are found in sub-urban or nearby rural areas.

[Figure 5. about here]

In Calabria, the ratios are ranging from 0.11 to 1.37 (mean value 0.73) and from 0.25 to 1.11 (mean value 0.80) in urban and rural areas, respectively. In comparison, in Basilicata the ratios are ranging from 0.49 to 1.11 (mean value 0.59) and from 0.25 to 1.55 (mean value 0.71) in urban and rural areas, respectively. From these values it seems that Calabria displays some similar or slightly higher average values of LMWPAHs/HMWPAHs ratios compared to those in Basilicata. A potential explanation is that in Calabria there may be more sources of LMWPAHs (petrogenic, e.g. the large Crotone oil refineries) than in Basilicata. However, the highest measured ratios in Basilicata were found in the urban (ratio = 0.99) and rural (ratio = 1.55) areas of Viggiano municipality, in proximity of the most important Italian inland petroleum exploitation (Alta Val d’Agri oil field) (ISPRA, 2014).

Campania and Latium presented lower ranges of LMWPAHs/HMWPAHs in urban areas, from 0.08 to 1.02 (mean value of 0.29) and from 0.08 to 0.52 (mean value of 0.27), respectively, and, from 0.08 to 0.14 (mean value of 0.10) and from 0.16 to 0.96 (mean value of 0.42) in rural areas, respectively. Given that most of the sites (but one) show a LMWPAHs/HMWPAHs ratio < 1, it seems that in these two areas the most likely sources of PAHs may be related to pyrogenic activities.

Individual molecular compound ratios were used to evaluate their potential sources (Hwang et al., 2003, Yunker et al., 2002). Fluo/(Fluo+Pyr) ratios ranged from 0.39 to 0.64, and 0.40 to 0.61 in urban and rural areas, respectively (Fig. 6A). When considering sources characterisations ranges, it appeared that none of the sampling sites, neither urban nor rural areas, presented ratios characteristic of petrogenic sources (ratio <0.4). Similarly, very limited sites displayed BaA/(BaA+Chr) ratio below 0.2. On the other hand, about 48.3% and 34.5% of the urban and rural sampling sites, respectively, presented a ratio that could be linked to a fuel combustion source (ratios from 0.4 to 0.5). This is also backed up by looking at two other diagnostic ratios: 1) the IcdP/(IcdP+BghiP) ratio, for which the results showed that the majority of the urban (58.2%) and rural (52.8%) areas fall in the range (<0.5) characterised by fuel combustion sources; 2) the BaA/(BaA+Chr ratio (Fig 6B), for which results indicated that the majority of the samples sites, in urban and rural areas, presented ratios >0.35, corresponding to the same traffic combustion sources. Besides, Fluo/(Fluo+Pyr) ratios highlighted that 51.7% and 65.5% of urban and rural areas are displayed in the plot (ratios above 0.5) where sources of PAHs are more likely to be related to coal and biomass combustion. These measurements seem to suggest that the most likely sources of PAHs compounds in the studied areas may be related to fuel (vehicular and biomass) combustion (pyrogenic).

[Figure 6. about here]

To summarise, by using different molecular diagnostic ratios, it can be highlighted that:

- LHMPAHs/HWMPAHs ratios -> dominant pyrogenic sources ($r < 0.1$)
- LHMPAHs/HWMPAHs ratios -> some petrogenic sources ($r>1$ – Sicily).
- Fluo/(Fluo+Pyr) ratio -> no petrogenic source ($r < 0.4$)
- BaA/(BaA+Chr) ratio -> dominant pyrogenic sources ($0.4 < r < 0.5$)

3.3. Factor score maps for sources patterns

The total variance expressed by the 16PAHs variables was 73.05 % through three-factor models, F_1, F_2 and $F_{3,}$ accounting for 46.65%, 15.05% and 11.35% of the variance, respectively (Table 4). Variables with loadings >0.50 were considered to describe the main composition of each factor. All variables hold communalities >0.5 (50% of variability), which means that they were all well correlated to one another. The associations of PAHs compounds for the three factor models, sorted in descending loading values, were:

F_1: Fluo, Pyr, BaA, Chr, - (Nap, Acy, Flo)
F_2: BkF, BbF, BaP, - (Nap, Acy, Ace)
F_3: BghiP, DahA, IcdP, - (Ant)

[Table 4. about here]

The 16 PAHs variables were organised in two groups by using the log-transformed data and a varimax rotation in the factor analysis (Table 4), allowing to distinguish between positive and negative correlations within the three-factor models: G_1=Fluo, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, DahA, and BghiP (positive correlation) and G_2= Nap, Acy, Flo, Nap, Acy, Ace and Ant (negative correlation). These compound associations actually matched the main two groups of PAHs, where G_1 corresponds to the high molecular weight PAHs (HMWPAHs) and G_2 to the low molecular weight PAHs (LMWPAHs). In addition to this, each of the three factor models displayed variables associations which can be used to further investigate and reveal the potential sources of the 16 PAHs contaminants in the survey area (Fig. 7).

[Figure 7. about here]

The F_1 association (Fluo, Pyr, BaA, Chr, - (Nap, Acy, Flo)) accounted for the highest total variance (46.65%) with good adequacy (Eigenvalues = 7.46 >1) between the factor and its variables. Factor scores distributions were processed in a GIS environment and interpolated to be displayed in maps to better visualise regional PAHs distribution (Lima et al., 2003; Thiombane et al., 2017). The F_1 factor scores interpolated map (Fig. 8) presented the highest values (from 1.13 to 2.77) in and around the largest urban sites (Rome, Naples and Palermo). These areas are characterised by substantial vehicular traffic and emission (Spaziani et al., 2008). The lowest factor scores loadings (from –2.52 to -0.84) are mostly distributed in and around the rural sites in Basilicata (Val d'Agri oil field, Viggiano municipality), Calabria and Sicily (near the Priolo, Gela and Ragusa districts). Some of the compounds part of this factor (Fluo, Pyr, BaA and Chr) are contaminants usually related to traffic and vehicle exhaust emissions (Sofowote et al., 2008; Li et al., 2012), which are obviously most likely to occur in urban areas. On the other hand, the other compounds part of this factor (Nap, Acy and Flo) are instead usually indicative of spilled-oil-related products at low-temperature combustion (Yunker et al., 2002; Hwang et al., 2003; Bucheli et al., 2004), and can be associated to similar 'petrogenic' sources (e.g., oil combustion from petroleum exploitation industries) in the Basilicata and Sicily regions.

[Figure 8. about here]

The F_2 association (BbF, BkF, BaP, - (Nap, Acy, Ace)) expressed 15.05% of the total variance with an eigenvalue of 2.41. The F_2 factor scores map (Fig. 9) presented the higher factor scores values (from 1.15 to 1.81) mostly distributed in and around the rural sites within the Campania region. In particular, the highest factor score values (from 1.81 to 2.23) were noted in the Acerra district. This municipality, which falls within the metropolitan/suburban area of Naples, is characterised by the presence of a large solid waste incinerator plant, but also by some illegal waste disposal and burning, and illegal practice of industrial toxic and solid urban waste dumping (Mazza et al., 2015; Marfe and Di Stefano, 2016). At the same time, a number of industrial activities are also present in the nearby rural areas of the Campania region, where it is also common practice to use biomass resources for the combustion in heating systems. These results confirmed the findings of other studies which pointed out that BbF, BkF, and BaP compounds were usually associated to biomass combustion (waste and wood combustion) in most rural areas in the Campania region (Arienzo et al., 2003; Albanese et al. 2015a). Similarly, Bixiong et al. (2006) suggested BbF and BkF as indicators of coal and wood combustions, whilst BaP has been used successfully as marker for biomass combustion (Simcik et al., 1999; Fang et al., 2004). The lower F_2

factor scores (from -2.55 to -1.0) were found in the same areas where F_1 (see Fig. 8) displayed its lower factor score values. These areas were identified in Calabria (e.g. nearby Nucleo Industrial areas, Cosenza), and in areas nearby the oil field in Sicily (Priolo, Ragusa and Gela). These results support the observation that Nap, Acy, and Ace compounds are usually related to oil combustion from petroleum exploitation industries (Masclet et al., 1987; Budzinski et al., 1997), which are present both in Basilicata and in Sicily.

[Figure 9. about here]

Factor 3, contributing to 13.36% of the total variance, is dominated by positively correlated IcdP, DahA, and BghiP and antithetic Ant. The factor score map (Fig. 10) presented high values (from 1.04 to 2.42) in and around most urban sites such as Naples, Vibo Valentia and Catania, and around the largest oil refineries in the study area (Milazzo and Val D'Agri). These finding are supported by the fact that IcdP, DahA, and BghiP compounds are usually considered as markers of gasoline engine and crude oil combustion sources (Khalili et al., 1995; Larsen and Baker, 2003).

[Figure 10. about here]

3.4. Potential soil toxicity

Using equation 1, potential toxicity levels of PAHs (in soils) were calculated and reported as TEQ_{BAP} (Nam et al., 2007; Agarwal et al., 2009). Results highlighted a significant variation of TEQ_{BAP} values in the five administrative regions studied (Fig. 11). TEQ_{BAP} values in Sicily ranged from 0.49 to 49.29 ng g^{-1} and from 0.20 to 7.228 ng/g in urban and rural areas with mean values of 5.56 and 2.04 ng/g, respectively, indicating that urban soils have higher TEQ_{BAP} toxicity levels compared to those in rural areas. Similarly, in Calabria and Latium average TEQ_{BAP} values were 3.40 ng/g and 23.87 ng/g in urban areas, and 1.79 ng/g and 2.12 ng/g in rural areas, respectively. The slightly higher mean value displayed by Latium (TEQ_{BAP} 23.87 ng/g) in urban areas can be associated with the prevalence of HWMPAHs in the TEQ computation. These compounds are usually related to vehicular emissions, where Rome (Latium region) is the Italian city with the highest motorisation rate (ISTAT, 2012; ISPRA, 2012).

[Figure 11. about here]

Interestingly, Campania and Basilicata presented instead higher mean TEQ_{BAP} values in their rural areas (661 ng/g and 2.71 ng/g, respectively), whilst the mean TEQ_{BAP} values for their urban areas were 54.93 ng/g and 1.19 ng/g, respectively.

Overall, Campania presented the highest toxicity average values in both its urban and rural areas. The values found in the present study are significant when compared to similar works published worldwide. In urban areas, variability is greater and depends on size of the city and urban fabric, For example, TEQ_{BAP} values found in Gwangju City (Korea) were 13.23 ng/g (Islam et al., 2017), which are comparable to those found in urban areas of Tarragona (Spain) with 64.0 ng/g (Nadal et al., 2007) and the present study, whilst those found in urban soils of a megacity such as Delhi (India) were an order of magnitude higher (218 ng/g - Agarwal et al., 2009), (Table 5). In rural soils studies, values found in the literature vary from 11.20 ng/g in agricultural soils in Poland (Maliszewska-Kordybach et al., 2009), 14.30 ng/g in some soils of Norway (Nam et al., 2008), to values of 83.12 ng/g found in rural soils in the UK (Nam et al., 2008) (Table 5). Several studies (Means et al., 1980; Agapkina et al., 2007; Bhupander et al., 2012) revealed that the occurrence of individual PAHs in soils depend on the land use and the settlement of main PAHs pollution sources. In fact, biomass burning is considered the major source of PAHs in rural soils, and urban soils are likely polluted by release of PAHs from vehicular emission around the heavy traffic roads (Khalili et al. 1995; Morillo et al., 2007; Albanese et al. 20015a). This study unveiled that urban areas of Sicily, Calabria and Latium displayed higher TEQBAP values than in their rural areas, but rural soils of Basilicata and Campania revealed the contrary.

Among all the findings, it is perhaps arguable that the most striking of all is that related to the metropolitan and rural areas around Naples, characterised by high toxicity levels. These results are partially confirmed by a more detailed study carried out by Albanese et al (2015a) and by a larger study (known as Campania Trasparente - still in progress), with sampling of soils and air matrices covering the entire regional territory (Qu et al., 2018).

[Table 5. about here]

4. Conclusions

This study carried out a regional survey of urban and rural topsoils (80 samples) in five administrative regions of the south of Italy, in an attempt to shed light to the main potential sources and patterns of pollution for 16 PAHs compounds (US EPA priority compounds). Measuring molecular PAHs diagnostic ratios allowed to identify and clearly show the main areas of concern, as well as giving an indication of the most likely sources for the PAHs compounds in the various regions. Results strongly pointed to the direction of pyrogenic sources (e.g., vehicular emission, fuels, and biomass combustions) for some areas (urban areas of Latium and rural areas of Campania regions). In particular, these areas were found to have high BAP concentration levels, which in turn indicated high levels of toxicity equivalent quantity (TEQ_{BAP}). The highest level of TEQ (661 ng g^{-1}) was found in metropolitan and rural areas of the Campania region, which could be related to the presence of a large solid waste incinerator plant, illegal waste disposal and burning, and illegal practice of industrial toxic and solid urban waste dumping (both known in the area). Results from this study can represent a fundamental step to understand the distribution, sources and toxicity levels of PAHs in the soils of these regions, giving an impetus to follow up with more detailed surveys. Given the carcinogenic and mutagenic properties of these contaminants, it is envisaged that the findings from this study will help initiate an assessment of human health risks from to PAH exposures in rural and urban areas in this Mediterranean region.

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Table and figure captions

Table 1. Compilation of PAH ratios and molecular markers for source diagnosis.

Table 2. Descriptive statistic of the 16 US EPA PAHs compounds from the survey area. Minimum (Min), mean, median, maximum (Max) concentration values are expressed in ng/g.

Table 3. Total PAH concentrations (ng/g dry weight) in the survey area topsoil compared to those found in other studies in the recent literature.

Table 4. Varimax-rotated factor (three-factor model) of isometric logratio clr back-transformed variables for 80 topsoil samples from the survey area; bold entries: loading values over |0.50|.

Table 5. Means TEQ_{BaP} values in the 5 studied regions compared to other selected survey studies.

Figure 1. (A) Simplified Geology of the study area, modified after Doglioni and Flores (1997). (B) Survey area with samples sites.

Figure 2. Land use and main industrial activities in the study area. This industrial repertory is based on the ISPRA 2014 annual report.

Figure 3. Dots maps of the 16PAHs concentration in urban (A) and rural (B) soils.

Figure 4. Tukey's box-and-whiskers plot of individual PAH concentration (ng/g) in the survey area.

Figure 5. LWPAHs/HWPAHs ratios scatter diagram of each sample site location. The different symbology (dots) reflects whether the sites were urban or rural nature.

Figure 6. Cross plots for the isomeric ratios: (Fig. 6A) displays the IcdP/(IcdP+BghiP) versus Fluo/(Fluo+Pyr) and (Fig. 6B) shows the BaA(BaA+Chr) ratio against Fluo/(Fluo+Pyr).

Figure 7. Flow chart displaying the possible pollution sources of PAHs in the south of Italy throughout factor analysis. Each factor is characterized by antithetic variables association (marked by - and + symbols) which reveal the possible sources of PAHs in the survey area.

Figure 8. Interpolated factor score map of the factor 1 (F1). Factor score values ranges are created by means of fractal concentration–area plot (C-A method).

Figure 9. Interpolated factor score map of the factor 2 (F2). Highest factor scores are correlated with BbF, BkF, and BaP compounds, and are displayed in the metropolitan area of Naples (Campania).

Figure 10. Interpolated factor score map of the third factor (F3). High factor score values corresponding to IcdP, DahA, and BghiP variables, are displayed in Naples, Vibo Valentia, Catania, and around the largest oil refineries in the study area (Milazzo and Val D'Agri).

Figure 11. Variation of the BaP toxicity equivalent quantity (TEQ_{BaP}) values in the survey area; logarithmic scale is applied on the Y axis.

Figure 1.

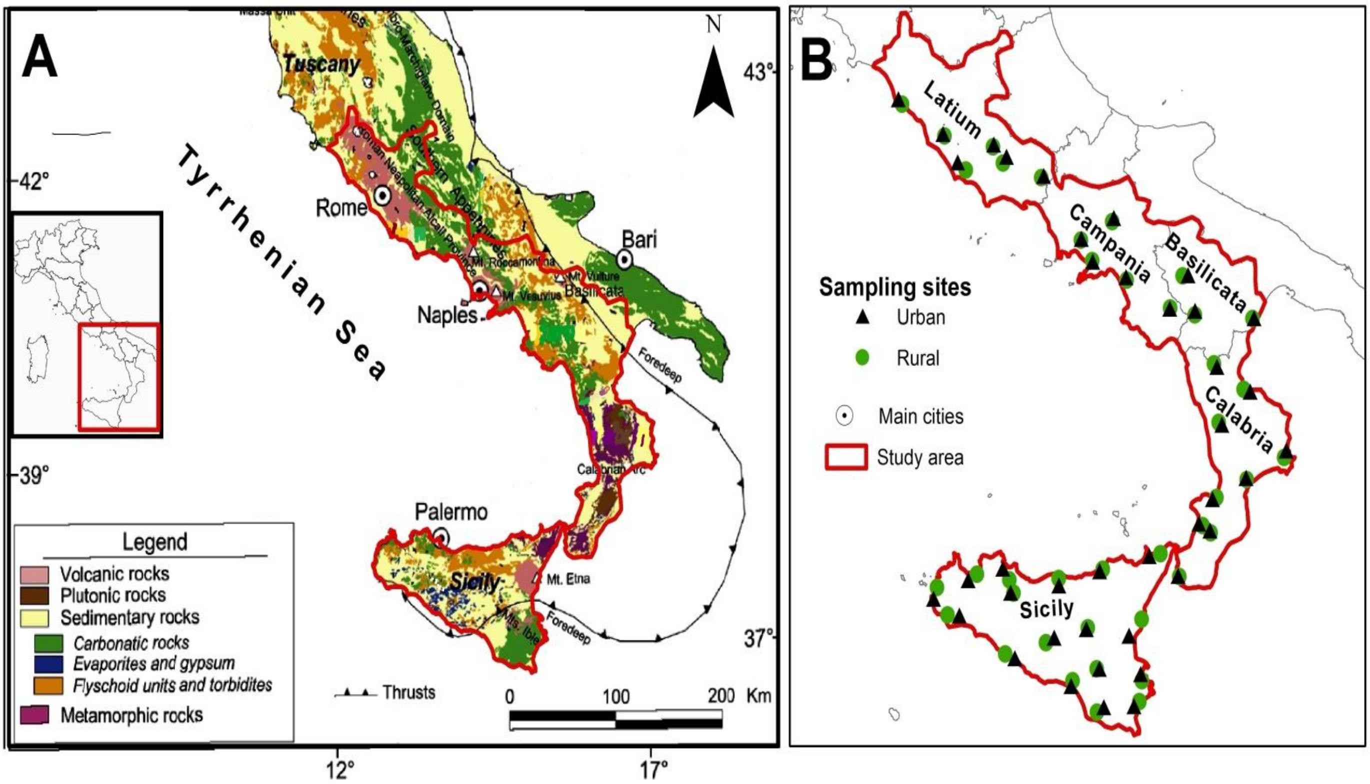
A
Tuscany
Rome
Naples
Bari
Palermo
Sicily
Tyrrhenian Sea
Basilicata
Mt. Roccamonfina
Mt. Vesuvius
Mt. Vulture
Mt. Etna
Mts. Iblei
Calabrian Arc
Foredeep
Foredeep
N
43°
42°
39°
37°
12°
17°
Legend
Volcanic rocks
Plutonic rocks
Sedimentary rocks
Carbonatic rocks
Evaporites and gypsum
Flyschoid units and torbidites
Metamorphic rocks
Thrusts
0
100
200 Km
B
Latium
Campania
Basilicata
Calabria
Sicily
Sampling sites
Urban
Rural
Main cities
Study area

Figure 2.


N
Thermal Power Station
Melfi incinerator Plant
Roma
Colleferro incinerator
Potenza incinerator
Napoli
Potenza
Acerra incinerator
Val d'Agri oil field
Gioia Tauro incinerator plant
Messina incinerator plant
Catanzaro
Milazzo oil refinery
Palermo
Crotone oil refinery
Priolo oil field and refinery
Gela oil field
0 25 50 100 Km
Urbanized areas
Agricultural areas
Forest and semi natural areas
Wetlands and water bodies
Main cities
Main contamination sources
Main roads
Survey area

Figure 3.

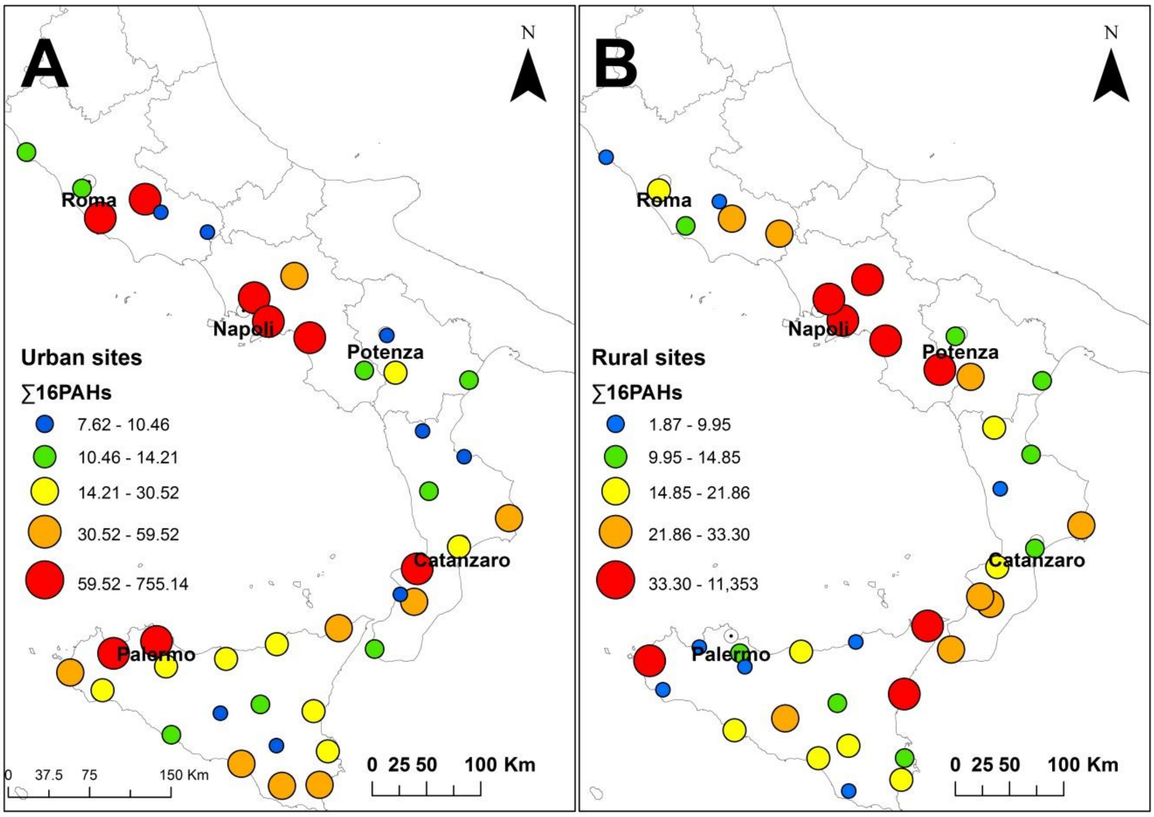
A
N
Roma
Napoli
Potenza
Catanzaro
Palermo
Urban sites
∑16PAHs
7.62 - 10.46
10.46 - 14.21
14.21 - 30.52
30.52 - 59.52
59.52 - 755.14
0 37.5 75 150 Km
0 25 50 100 Km
B
N
Roma
Napoli
Potenza
Catanzaro
Palermo
Rural sites
∑16PAHs
1.87 - 9.95
9.95 - 14.85
14.85 - 21.86
21.86 - 33.30
33.30 - 11,353
0 25 50 100 Km

Figure 4.

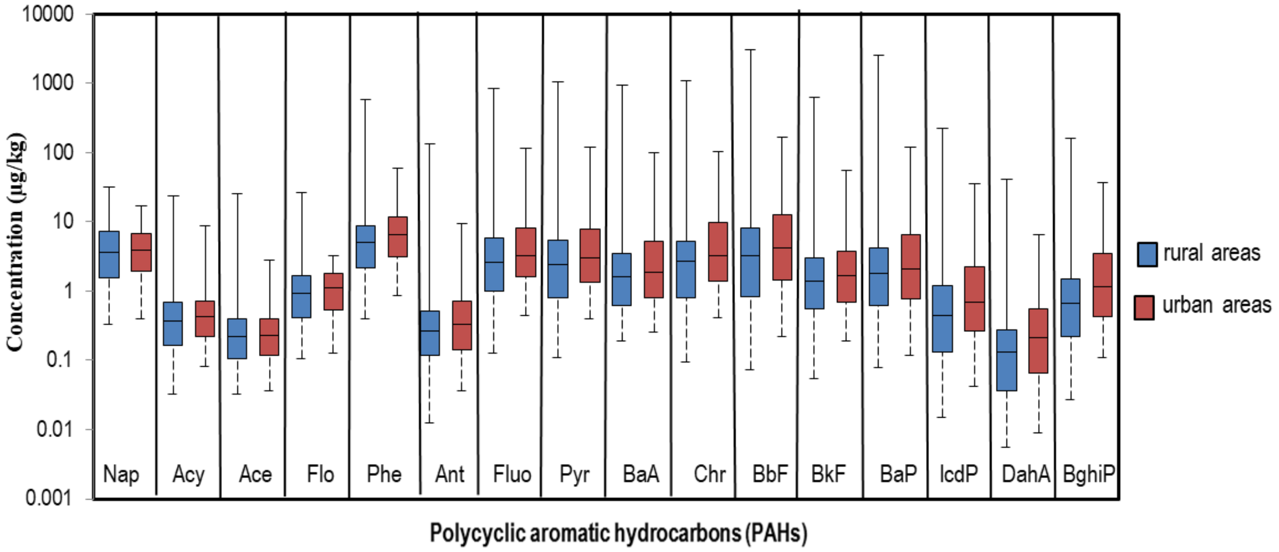
10000
1000
100
10
1
0.1
0.01
0.001
Concentration (μg/kg)
Nap
Acy
Ace
Flo
Phe
Ant
Fluo
Pyr
BaA
Chr
BbF
BkF
BaP
IcdP
DahA
BghiP
rural areas
urban areas
Polycyclic aromatic hydrocarbons (PAHs)

Figure 5

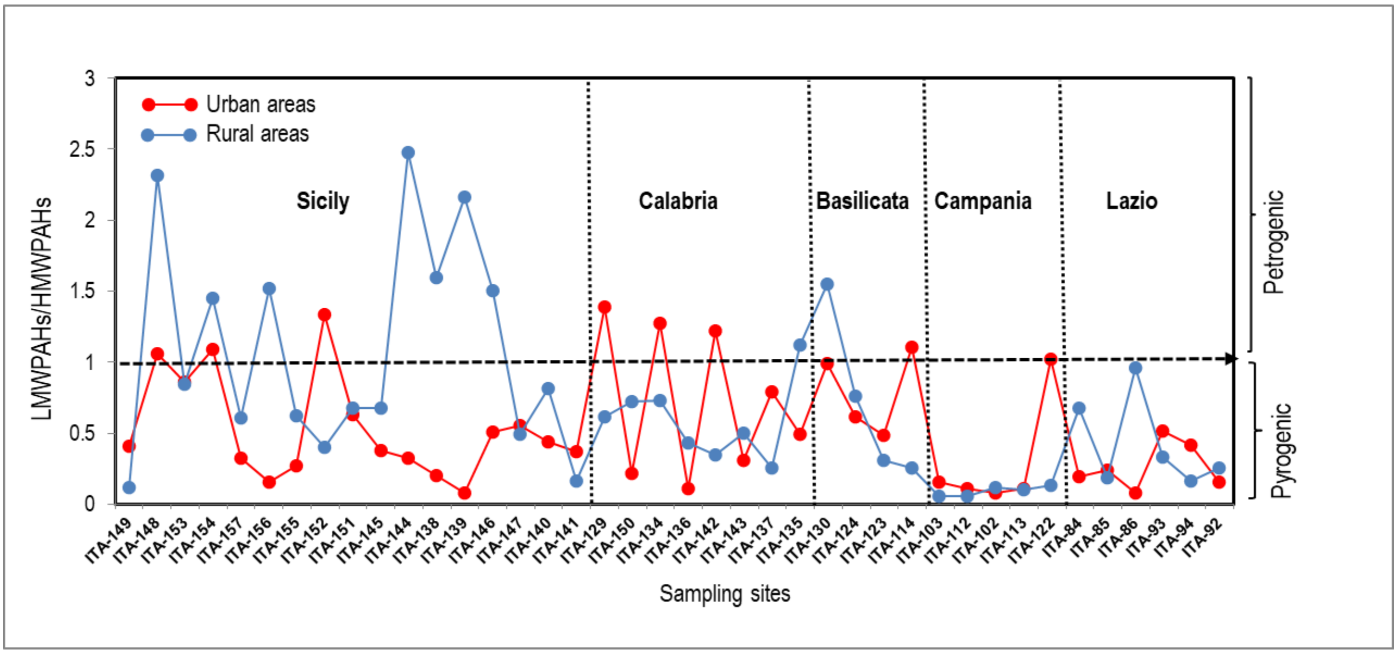
LMWPAHs/HMWPAHs
3
2.5
2
1.5
1
0.5
0
Urban areas
Rural areas
Sicily
Calabria
Basilicata
Campania
Lazio
Petrogenic
Pyrogenic
ITA-149
ITA-148
ITA-153
ITA-154
ITA-157
ITA-156
ITA-155
ITA-152
ITA-151
ITA-145
ITA-144
ITA-138
ITA-139
ITA-146
ITA-147
ITA-140
ITA-141
ITA-129
ITA-150
ITA-134
ITA-136
ITA-142
ITA-143
ITA-137
ITA-135
ITA-130
ITA-124
ITA-123
ITA-114
ITA-103
ITA-112
ITA-102
ITA-113
ITA-122
ITA-84
ITA-85
ITA-86
ITA-93
ITA-94
ITA-92
Sampling sites

Figure 6.

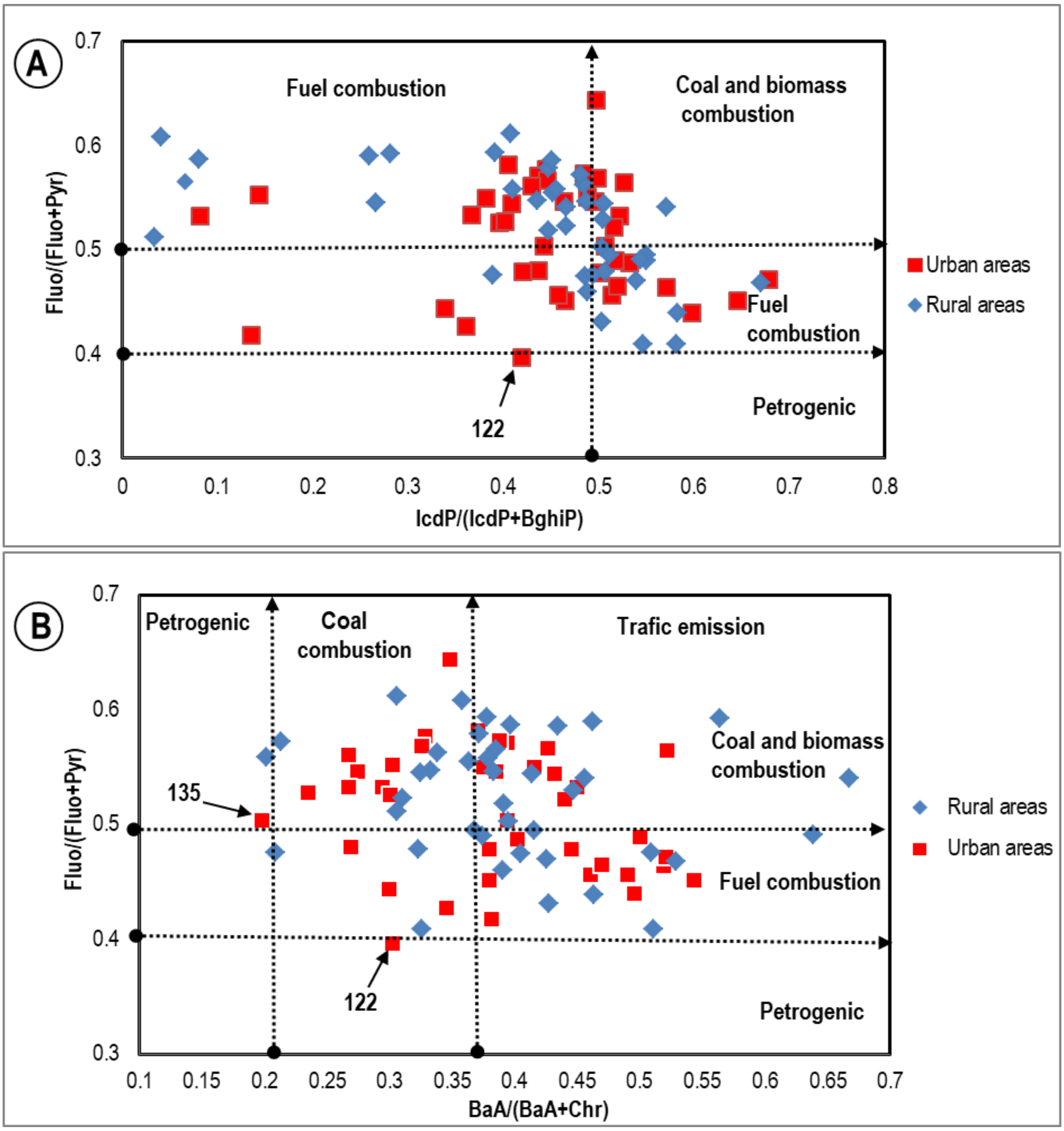
A
Fuel combustion
Coal and biomass combustion
Fuel combustion
Petrogenic
122
0.7
0.6
0.5
0.4
0.3
Fluo/(Fluo+Pyr)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
IcdP/(IcdP+BghiP)
Urban areas
Rural areas
B
Petrogenic
Coal combustion
Trafic emission
Coal and biomass combustion
Fuel combustion
Petrogenic
135
122
0.7
0.6
0.5
0.4
0.3
Fluo/(Fluo+Pyr)
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
0.7
BaA/(BaA+Chr)
Rural areas
Urban areas

Figure 7.

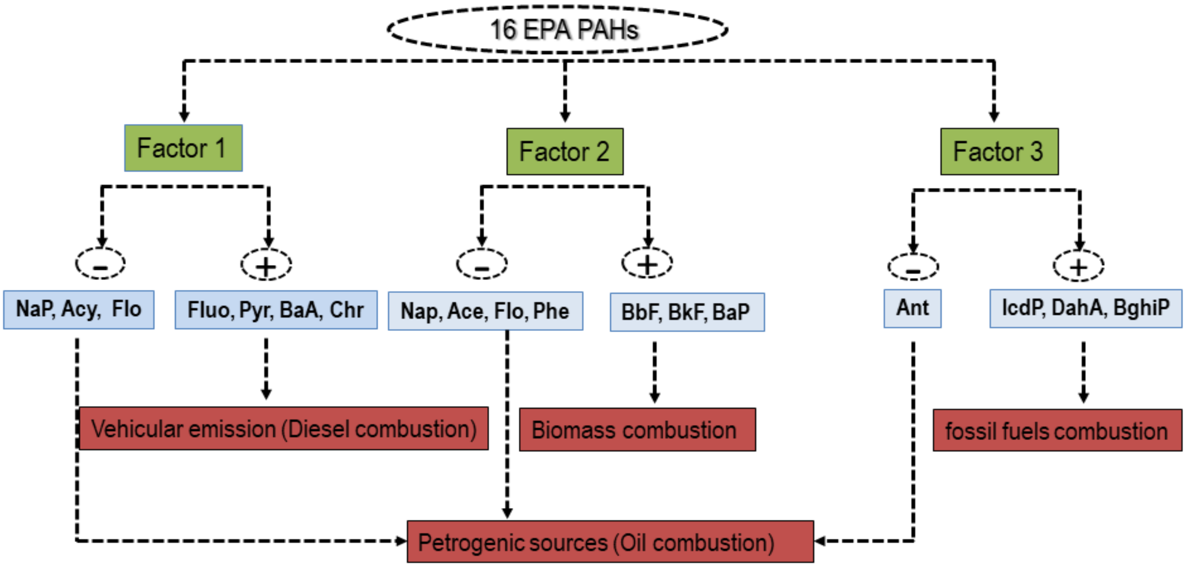
16 EPA PAHs
Factor 1
Factor 2
Factor 3
-
+
-
+
-
+
NaP, Acy, Flo
Fluo, Pyr, BaA, Chr
Nap, Ace, Flo, Phe
BbF, BkF, BaP
Ant
IcdP, DahA, BghiP
Vehicular emission (Diesel combustion)
Biomass combustion
fossil fuels combustion
Petrogenic sources (Oil combustion)

Figure 8.

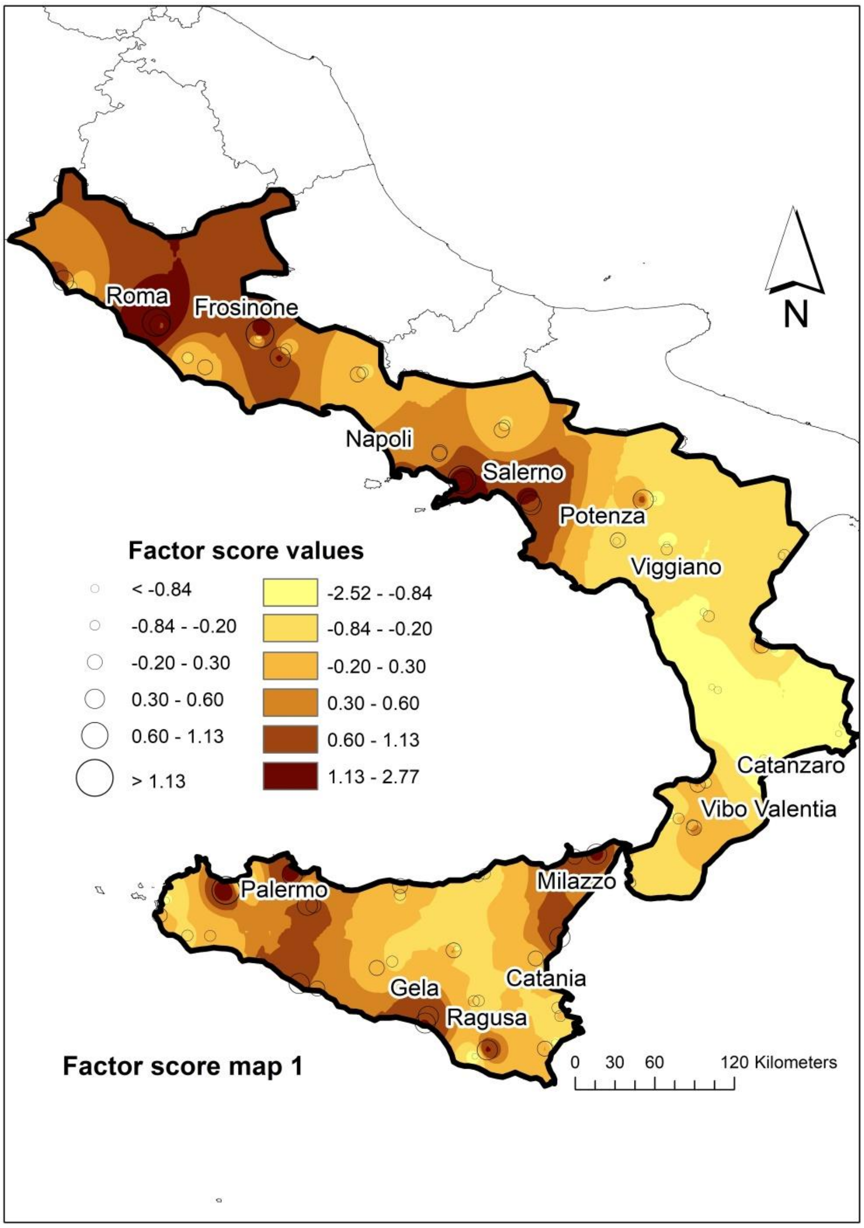
N
Roma
Frosinone
Napoli
Salerno
Potenza
Viggiano
Catanzaro
Vibo Valentia
Milazzo
Palermo
Catania
Gela
Ragusa
Factor score values
< -0.84
-0.84 - -0.20
-0.20 - 0.30
0.30 - 0.60
0.60 - 1.13
> 1.13
-2.52 - -0.84
-0.84 - -0.20
-0.20 - 0.30
0.30 - 0.60
0.60 - 1.13
1.13 - 2.77
Factor score map 1
0 30 60 120 Kilometers

Figure 9.

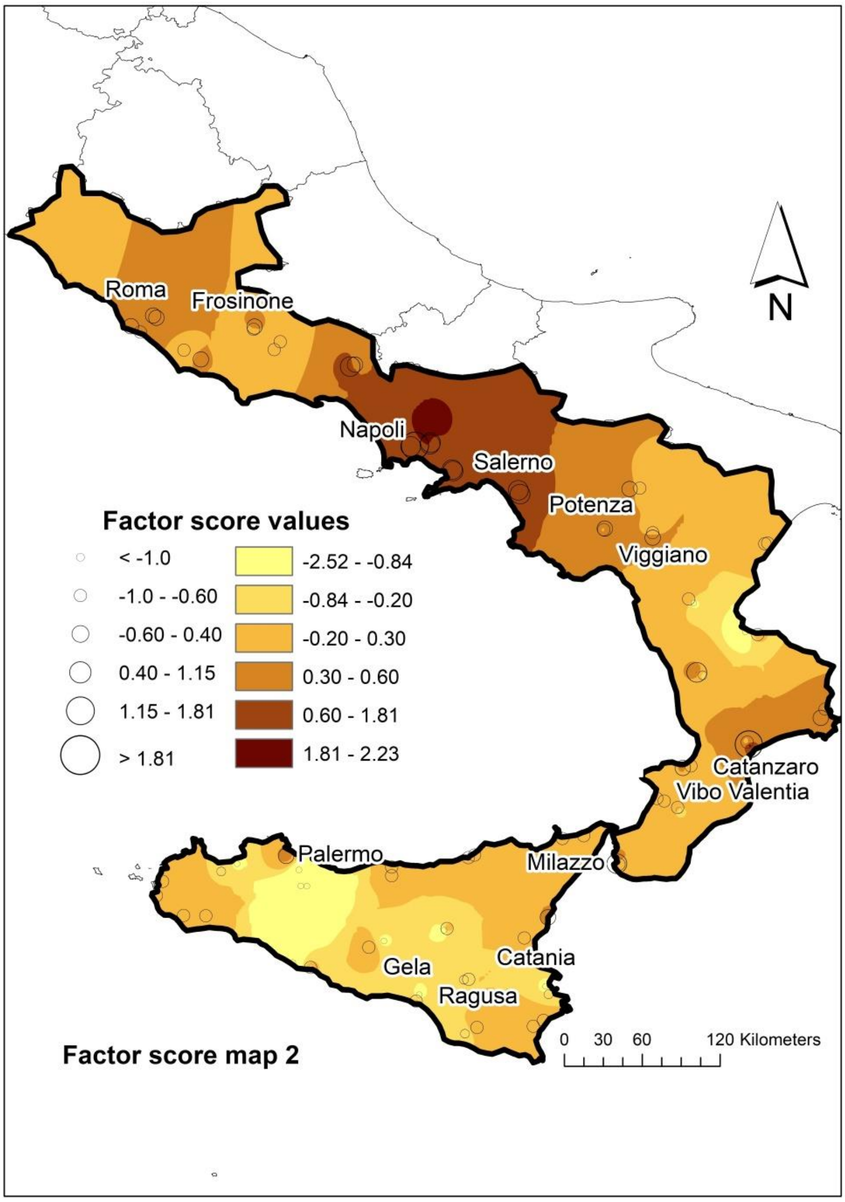
N
Roma
Frosinone
Napoli
Salerno
Potenza
Viggiano
Catanzaro
Vibo Valentia
Palermo
Milazzo
Catania
Gela
Ragusa
Factor score values
< -1.0
-1.0 - -0.60
-0.60 - 0.40
0.40 - 1.15
1.15 - 1.81
> 1.81
-2.52 - -0.84
-0.84 - -0.20
-0.20 - 0.30
0.30 - 0.60
0.60 - 1.81
1.81 - 2.23
Factor score map 2
0 30 60 120 Kilometers

Figure 10.

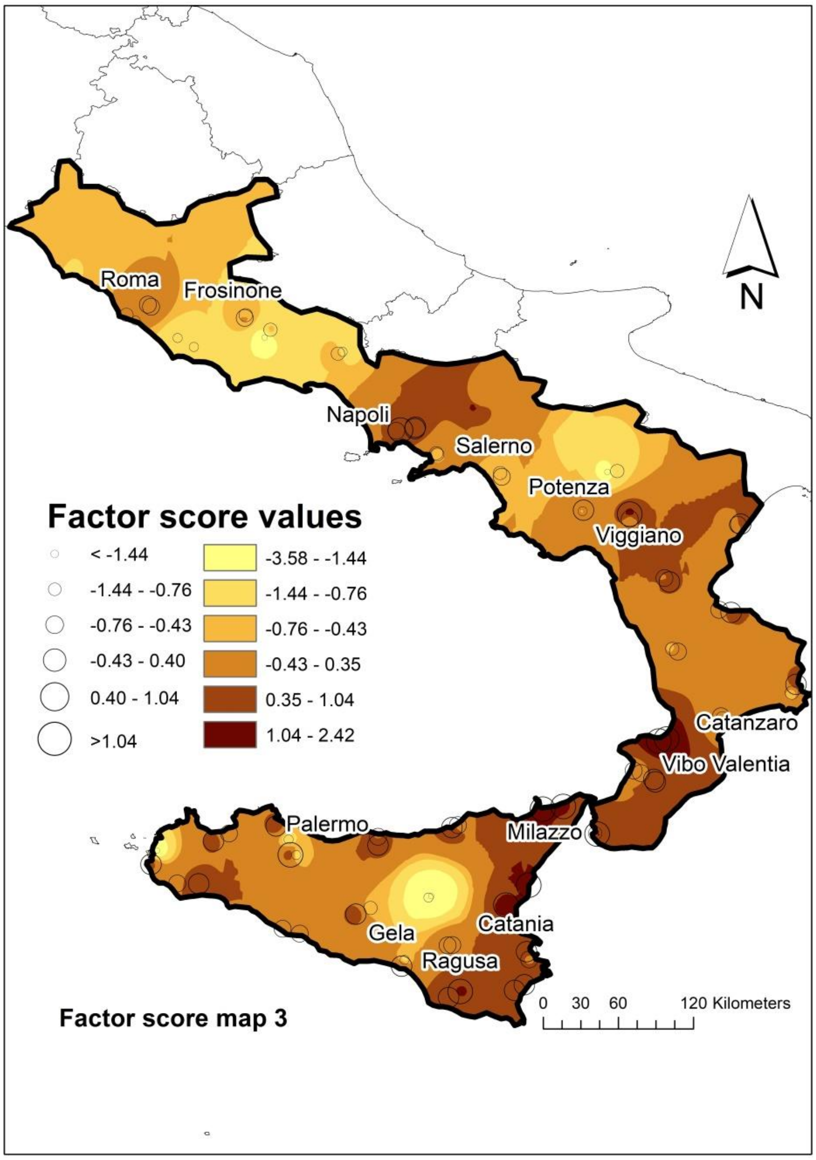
Roma
Frosinone
Napoli
Salerno
Potenza
Viggiano
Catanzaro
Vibo Valentia
Milazzo
Palermo
Catania
Gela
Ragusa
N
Factor score values
< -1.44
-1.44 - -0.76
-0.76 - -0.43
-0.43 - 0.40
0.40 - 1.04
>1.04
-3.58 - -1.44
-1.44 - -0.76
-0.76 - -0.43
-0.43 - 0.35
0.35 - 1.04
1.04 - 2.42
Factor score map 3
0 30 60 120 Kilometers

Figure 11.

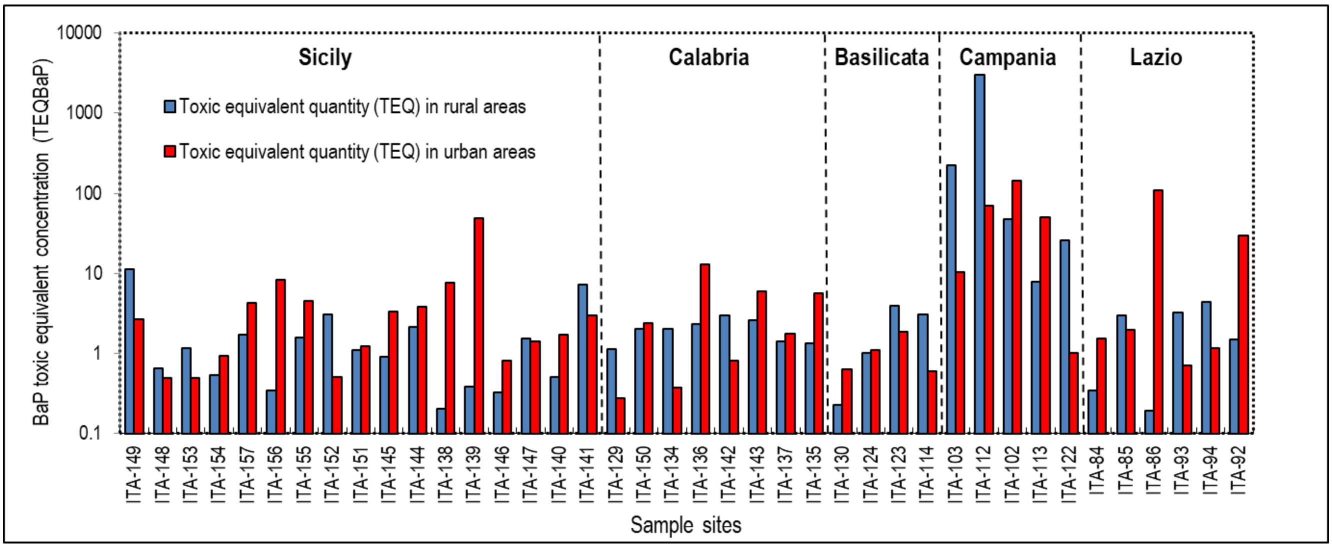
Sicily
Calabria
Basilicata
Campania
Lazio
Toxic equivalent quantity (TEQ) in rural areas
Toxic equivalent quantity (TEQ) in urban areas
BaP toxic equivalent concentration (TEQBaP)
10000
1000
100
10
1
0.1
ITA-149
ITA-148
ITA-153
ITA-154
ITA-157
ITA-156
ITA-155
ITA-152
ITA-151
ITA-145
ITA-144
ITA-138
ITA-139
ITA-146
ITA-147
ITA-140
ITA-141
ITA-129
ITA-150
ITA-134
ITA-136
ITA-142
ITA-143
ITA-137
ITA-135
ITA-130
ITA-124
ITA-123
ITA-114
ITA-103
ITA-112
ITA-102
ITA-113
ITA-122
ITA-84
ITA-85
ITA-86
ITA-93
ITA-94
ITA-92
Sample sites

Table 1.

Compounds, compounds ratios	Values, ranges	Sources	References
LMWPAHs/HMWPAHs	≤ 1	Pyrogenic combustion	Budzinski et al., (1997)
	≥ 1	Petrogenic source	Budzinski et al. (1997)

	< 0.40	Petroleum/petrogenic source	Yunker et al. (2002)
Fluo/(Fluo + Pyr)	0.4 - 0.5	Fossil fuel combustion	Yunker et al. (2002)
	> 0.5	Biomass and coal combustion	Yunker et al. (2002)

	< 0.20	Petroleum/petrogenic source	Yunker et al. (2002)
BaA(BaA+Chr)	0.2-0.35	Coal combustion	Yunker et al. (2002)
	> 0.35	Traffic emission	Yunker et al. (2002)

	< 0.20	Petrogenic source	Tobiszewski and Namieśnik (2012)
IcdP/(IcdP+ BghiP)	0.20 - 0.50	Fuel combustion	Tobiszewski and Namieśnik (2012)
	> 0.50	Coal and biomass combustion	Tobiszewski and Namieśnik (2012)

Table 2.

PAHS (ng/g)	Abbreviation	DL*	TEF**	Urban				Rural			
				Min	Mean	Median	Max	Min	Mean	Median	Max
Naphthalene	Nap	0.013	0.001	0.39	2.49	2.01	9.83	0.33	3.21	2.05	25.13
Acenaphthylene	Acy	0.028	0.001	0.08	0.60	0.20	8.07	0.03	1.41	0.21	22.78
Acenaphthene	Ace	0.047	0.001	0.04	0.24	0.11	2.40	0.03	0.79	0.11	25.20
Fluorene	Flo	0.009	0.001	0.12	0.61	0.57	1.49	0.11	1.21	0.53	25.05
Phenanthrene	Phe	0.001	0.001	0.85	6.74	3.34	47.32	0.40	17.87	2.80	570
Anthracene	Ant	0.005	0.01	0.04	0.77	0.19	8.57	0.01	3.78	0.14	131
Fluoranthene	Fluo	0.003	0.001	0.44	10.43	1.68	108	0.13	25.22	1.57	829
Pyrene	Pyr	0.003	0.001	0.40	10.74	1.60	113	0.11	30.98	1.61	1,059
Benz[a]anthracene	BaA	0.002	0.1	0.25	7.27	1.04	93.30	0.19	26.86	0.98	950
Chrysene	Chr	0.004	0.01	0.41	8.58	1.84	93.15	0.10	33.04	1.85	1,101
Benzo[b]fluoranthene	BbF	0.004	0.1	0.22	15.05	2.75	151	0.07	86.58	2.43	3,055
Benzo[k]fluoranthene	BkF	0.004	0.1	0.19	5.09	0.99	51.38	0.05	19.38	0.84	633
Benzo[a]pyrene	BaP	0.001	1	0.12	10.47	1.32	112	0.08	70.14	1.14	2,510
Indeno[1,2,3-c,d]pyrene	IcdP	0.003	0.1	0.04	2.64	0.42	33.51	0.01	7.91	0.31	226
Dibenzo[a,h]anthracene	DahA	0.003	1	0.01	0.50	0.15	6.09	0.01	1.45	0.09	41.23
Benzo[g,h,i]perylene	BghiP	0.001	0.01	0.11	2.65	0.71	33.38	0.03	6.28	0.44	161
∑16PAHs				7.62	84.85	18.65	755	1.87	336	18.81	11,353

*Detection Limit of the 16PAHs compounds

**Toxicity Equivalency Factor (TEF) Nisbet and Lagoy, 1992

Table 3.

Study areas	**Type of study area**	**∑PAHs in soils (ng/g)**	**Authors**
Southern Italy	Urban areas	7.62 - 755	this study
Southern Italy	Rural areas	1.87 - 11,353	this study
Turin, Italy	Urban areas	148 - 3,410	Morillo et al. (2007)
Hong Kong, China	Rural areas	42.3 - 410	Zhang et al. (2006)
Delhi, India	Urban areas	81.6 - 45,017	Bhupander et al. (2012)
Delhi, India	Rural areas	830 - 3,880	Agarwal et al. (2009)
Beijing, China	Urban areas	219 - 27,825	Tang et al. (2005)
Moscow, Russia	Urban areas	208 - 9,604	Agapkina et al. (2007)
Glasgow, UK	Urban areas	48 - 51,822	Morillo et al. (2007)
London, UK	Urban areas	400 - 67,000	Vane et al. (2014)
Seville, Spain	Urban areas	89.5 - 4,004	Morillo et al. (2008)

Table 4.

Variables	Factors			Communalities
	F1	F2	F3	
Nap	**-0.72**	**-0.58**	-0.03	0.86
Acy	**-0.51**	-0.13	-0.42	0.51
Ace	-0.32	**-0.66**	-0.47	0.75
Flo	**-0.55**	**-0.74**	-0.27	0.93
Phe	-0.29	**-0.73**	-0.27	0.69
Ant	0.10	-0.07	**-0.74**	0.56
Fluo	**0.92**	-0.08	0.03	0.86
Pyr	**0.92**	0.27	-0.06	0.92
BaA	**0.81**	0.41	-0.10	0.83
Chr	**0.71**	0.30	0.28	0.67
BbF	0.30	**0.79**	0.21	0.75
BkF	-0.13	**0.82**	-0.05	0.69
BaP	0.44	**0.76**	-0.02	0.78
IcdP	0.24	0.38	**0.69**	0.68
DahA	-0.19	0.31	**0.69**	0.61
BghiP	0.25	-0.22	**0.73**	0.65
Eigenvalues	7.464	2.408	1.816	
Total variance in %	46.652	15.05	11.348	
Cum. of total variance (%)	46.652	61.703	73.051	

Table 5.

Regions	Type of area	TEQ_{BaP} (ng/g)	References
Sicily	Urban	5.56	this study
	Rural	2.04	this study
Calabria	Urban	3.40	this study
	Rural	1.79	this study
Basilicata	Urban	1.19	this study
	Rural	2.71	this study
Campania	Urban	54.93	this study
	Rural	661	this study
Latium	Urban	23.87	this study
	Rural	2.12	this study
Gwangju City (Korea)	Urban	14.30	Islam et al. (2017)
Tarragonain (Spain)	Urban	64	Nadal et al. (2007)
Delhi (India)	Urban	218	Agarwal et al. (2009)
Rural soils in Norway	Rural	14.3	Nam et al. (2008)
Agriculture soils in Poland	Agriculture soil	11.9	Maliszewska-Kordybach et al. (2009)
Rural soils in the UK	Rural	83.5	Nam et al. (2008)