



# Assessment of polycyclic aromatic hydrocarbons (PAHs) in soil of a Natural Reserve (Isola delle Femmine) (Italy) located in front of a plant for the production of cement

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## ABSTRACT

Isola delle Femmine Natural Reserve is a very little isle about 15 km from the centre of Palermo, in front of a plant for the production of cement and about 600 m from coast. In the present research, profiles soil PAHs were obtained for 16 sites within the reserve and for 8 stations on the rural soil taken as reference.  $\sum$ PAHs, in the soil of investigated area, ranged from 35 to 545  $\mu\text{g}/\text{kg}$ . With the aim to find the origin of PAHs in the soil of Isola delle Femmine, we compare the distribution of single analytes in the investigated area with those of the reference rural area (Monte Raffo Rosso), with those of atmospheric urban particulate collected at Palermo along with reported of emissions of some cement plants. The island's investigated area showed a high amount of 4- and 5-rings PAHs, whereas 3-ring PAHs are present mainly in the emission of cement plants (from literature). The percentage of 3-, 4-, 5- and 6-rings PAHs determined in samples of Isola delle Femmine are similar to those of the reference rural soils and to those of urban atmospheric particulate. Cement plant activity has a negligible weight on the presence of PAHs in the soil of Isola delle Femmine.

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## 1. Introduction

Isola delle Femmine is an island located at about 600 m from Sicilian coast, in front of a plant for the production of cement, between villages of Sferracavallo and Carini. In many cases, manufacturing of cement plays a significant role in the management of hazardous wastes. Pet coke, recently, has substituted for fuels and raw materials, incorporating through clinker emitting toxic components into the atmosphere [1].

The Isola delle Femmine area is a Natural Reserve since 2002. This area is a unique habitat for many species (birds, fishes, amphibious, etc.) and, despite to the ecological richness, there are urban inputs, especially from the city of Palermo and its sub-urban area and industrial activities, which are the most likely sources of the environmental degradation. Despite of those features, insignificant efforts are taken in order to monitor and minimize any anthropogenic harm on the studied environment.

Since there are no previous data concerning the concentrations of PAHs in the soils of the Natural Reserve Isola delle Femmine, important goals of this investigation are to establish if the area is affected by environmental pollution, establish the sources for PAHs in order to compare the present results with data obtained in future

surveys and, eventually, to allow the competent authorities to take any technical and policy decisions to protect the area. As a result of the fact that some environmental groups argue that the cement production, causes the deterioration of environmental quality of the small island, this study examine the influence of the cement plant on the level and distribution of PAHs in Natural Reserve Isola delle Femmine.

For this purpose, in the present study, investigations on soil of Isola delle Femmine were carried out for the 15 PAHs identified by the US-EPA as requiring priority-monitoring action within the framework of environmental quality control [2,3] and perylene (non-US-EPA listed PAHs) was also investigated in order to obtain further information on their origins. Perylene is included on the expanded scan of PAHs recommended by NOAA (National Oceanic and Atmospheric Administration) [4–6]. Perylene is not universally considered a pyrogenic or a petrogenic PAH; it has been said to be one of the few PAHs found in nature. In solid matrices perylene can be formed from early diagenesis of vegetal pigments; it is sometimes considered an important chemical marker for plant pigments such as chlorophyll a, so its presence in environmental matrices is not necessarily indicative of anthropogenic contamination [7,8].

In the present study, profiles soil PAHs were obtained for 16 sites within the Natural Reserve Isola delle Femmine and for 8 stations within a rural area (Monte Raffo Rosso) taken as reference. In addition, three sampling sites for analytes of the particulate in Palermo area were selected to investigate the PAHs fingerprints in

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urban and sub-urban ambient where highest commercial activities and traffic density occur.

In this paper, we have selected a limited set of PAHs ratios that exhibit the best potential to distinguish natural and anthropogenic sources.

Emission factors have long been a fundamental tool for air quality management. Data from direct emission tests or continuous emission monitors of specific sources are usually preferred for estimating a source emission, however, direct measurement data from individual sources are not always available and, even when they are, they may not reflect the variability of actual emissions over time. In spite of their limitations, emission factors are frequently the best or only method available for estimating air-pollutant emissions.

Together with PAHs, we analyzed organic contents because it has been demonstrated that the concentrations of PAHs in some environmental matrices were affected by physicochemical properties of the samples such organic matter content [9,10]. Generally, sediments with high organic content were characterized by high values of PAHs [10–12].

Polycyclic Aromatic Hydrocarbons (PAHs) are organic molecules made up of two or more fused aromatic rings [13]. Their production is favored by an oxygen-deficient combustion, temperatures in the range of 650–900 °C and fuels which are not highly oxidized in both natural (forest fires, volcanic emissions, etc.) and anthropogenic (burning of fossil fuels, asphalt and industrial waste, etc.) processes, with the latter now being the major contributor [14–18]. Some authors have shown that motor vehicle exhausts are probably the most important source of PAHs presently detected [19–23]. The quantities and proportion of PAHs emitted from industrial stacks will depend on several factors, for the same kind of industrial plant, the PAHs emission might not be the same because of the following influencing factors: type of input fuel, additives, the manufacturing process, etc. [1,24–27]. Combustion processes and, in particular, cement manufacturing have been pointed out as one of the most important sources of PAHs released into the atmosphere [1,26]. Under anaerobic conditions, some PAHs can also be derived from biogenic precursors [11,12,28].

Once produced, PAHs may be widely dispersed through the environment in the air, in water and they may accumulate in soils [29,30] and sediments [11,12,31–33]. Due to their hydrophobic character, PAHs in the environmental matrices rapidly bind with particles of sediments, soils becoming their primary reservoirs [31]. Consequently, soils and sediments [11,12] are the ultimate repository for most of the hydrophobic organic contaminants such as PAHs. So it is expected that most anthropogenic PAHs will be restricted to the top layer of the soil. It is estimated that more than 90% of the total burden of PAHs resides in the surface soils where they accumulate [33]. PAHs are retained in the soil matrix for a long time after adsorption to the soil organic matter [9]. However, soils and sediments contaminated with PAHs often contain high amounts of other pollutants such as heavy metals, which often derive from the same sources as PAHs [29,30].

PAHs may create toxicity in organisms, by interfering with cellular membrane function and the coupled enzyme systems, and metabolites of PAHs may bind to DNA which causes biochemical disruptions and cell damage in organisms [27,34–39]. Some of these compounds such as benzo[a]pyrene are known to be carcinogenic while others are suspected of being so. Several PAHs species have been classified into probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer (Agency for Toxic Substances and Disease Registry, 1995) [38–40].

The present work is focused on EPA-priority PAHs, among which only eight are recognized as both genotoxic and carcinogenic [2,39]. In addition, eight 4–6-rings PAH have been introduced in the EU-

priority PAH list. In addition, 11 out of the 16 PAHs listed by the US Environmental Protection Agency as priority pollutants were photo mutagenic [3]. Various PAHs-mixtures showed different carcinogenic potency [41]. Very mutagenic and carcinogenic is B[a]P and it has been accepted as a marker of carcinogenic PAHs in food and environmental samples. Since the ratio of the contents of B[a]P and the other carcinogenic PAHs is quite constant, the use of B[a]P as a marker for the contamination by PAHs may be justified. B[a]P is also regarded and recommended as a marker in Air Quality Standards. However, it is necessary to underline that in a recent report, the Commission of European Food Safety Authority (EFSA) concluded that there are some doubts about their relevance [42].

The origin, occurrence and destiny of the PAHs found in soils have been extensively studied [43]. For example, characteristic PAHs ratios and distributions (i.e., distributions of the relative amounts of the major PAHs ranked by molecular weight) can provide data about the sources of the PAHs in soils: whether they are natural (oil seeps, coal, plant debris, forest and grassland fires) or anthropogenic (combustion of fossil and other fuels) [14,44]. PAHs origin signatures of natural records have been used successfully to determine recent changes in anthropogenic vs. natural sources of the PAHs in lake and marine sediments [44] but, to the best of our knowledge, the occurrence and accumulation of PAHs in soils located near plants for the production of cement have been not investigated.

## 2. Materials and methods

### 2.1. Laboratory equipment

All glassware and sample containers were thoroughly washed with hot detergent solution followed by rinsing with purified water and acetone (analytical grade), respectively. These were finally kept in the oven at 110 °C overnight. To avoid contaminations of samples, different glassware and syringes were used for standards and for solutions extracted from samples. Our laboratory was designed and constructed to control airborne contamination using filtration and high air exchange rates.

### 2.2. Sampling sites

#### 2.2.1. Natural Reserve Isola delle Femmine

Isola delle Femmine (38°12'34"75N, 13°14'13"34E) is a very little isle (Fig. 1) separated from the north-west coast of Sicily from just 600 m, located in the Bay of Carini, about 15 km from the centre of Palermo (Italy) and 2–3 km from sub-urban area. Approximately 30 years ago, in Sicily, one of the largest cement manufacture plants was located about 1 km from Isola delle Femmine (Fig. 1). The island is almost oval in shape (Fig. 1). The area of approximately 13 ha consists of laminated limestone dating to Mesozoic Era, when it was probably linked to the Sicily. Isolation along with potential food availability of the surrounding environment, have made the island an ideal place both for nesting and for the pause during the long migration of several specimen of birds (gray herons, red herons, cormorants, etc.). The island is home to a large colony of Real Mediterranean Seagull. On the island there are slender traces of human presence in old ages. The island's coast, for its structure, is an uninhabitable place for many species of vegetables. This is due above all to high concentration of mineral salts and to inconsistency and high permeability of land. Nevertheless there are about 145 species of vegetables.

#### 2.2.2. Reference site Monte Raffo Rosso

The reference samples were collected from Monte Raffo Rosso (400–500 m above sea level) area in September, 2006. Monte Raffo

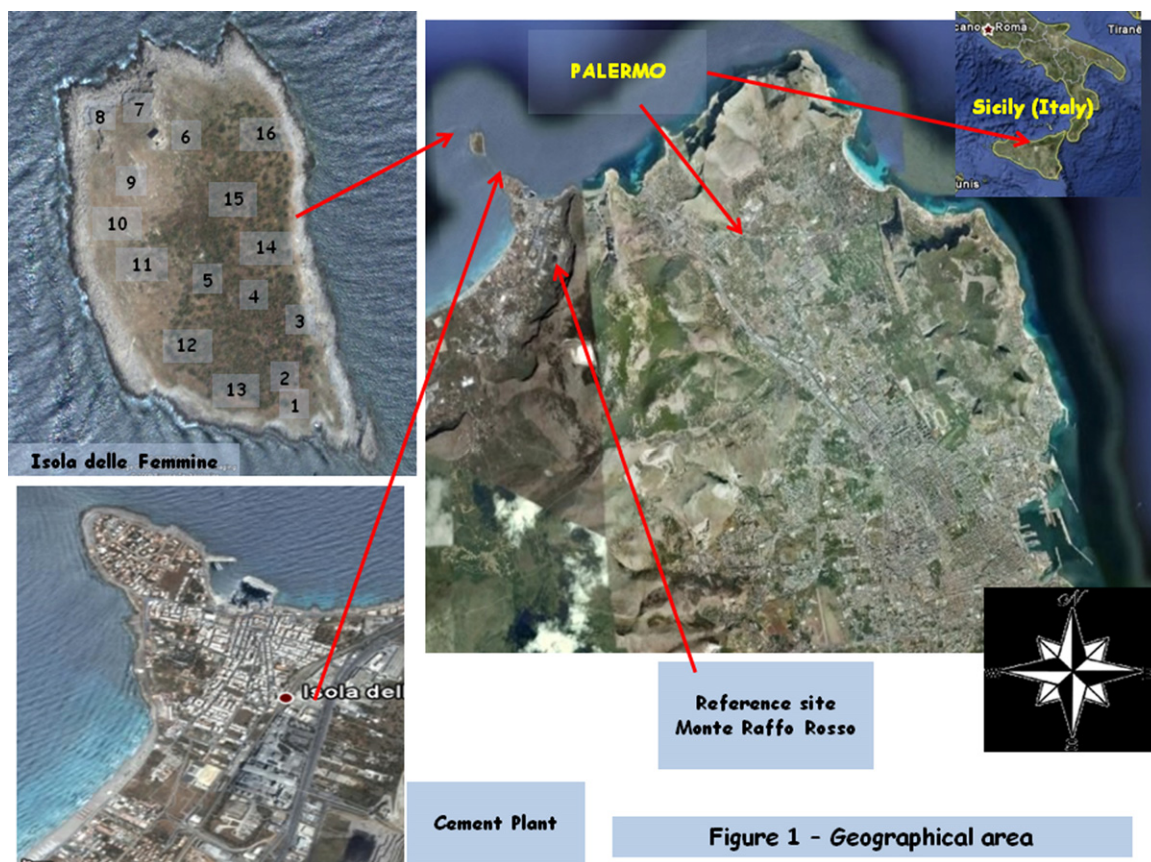


Fig. 1. Geographical area.

Rosso (Fig. 1) is located in a non-contaminated area on the west side of Isola delle Femmine, where there is no anthropic sources and the distance to nearby industrialized area is approximately 10 km.

Monte Raffo Rosso is an area of environmental protection (under the EEC Directive, adopted in Italy by Presidential Decree (no. 357, 8/09/1997)). This area is composed of limestone reliefs. The slopes with severe inclines are often uncultivated or without vegetation, or covered by recent artificial vegetable stands.

### 2.3. Samples collection

#### 2.3.1. Soils collection

Samples were taken with the help of a stainless steel auger up to a depth of 5 cm. The samples were transferred into polythene bags, transported to the laboratory and were preserved at  $-20^{\circ}\text{C}$  till further processing. At each sampling site 4–6 samples were collected within a distance of 50 cm. In the laboratory the samples for PAHs analyses were dried in desiccators in dark. Twigs and stones were removed. Those samples were mixed thoroughly to make a composite sample. After homogenization, the soil samples were sieved through 2 mm sieve. Representative samples were obtained after quartering.

The distribution of the sampling sites was as follows: 16 soil samples were collected in the island (Fig. 1) and 8 in rural area (Monte Raffo Rosso) (Fig. 2) far away from the area of influence of the suspected source of contamination.

The reproducibility of the sampling was preliminarily checked by analyzing for PAHs five different samples of soil collected at different points of the same area ( $3\text{ m} \times 3\text{ m}$ ). The standard deviation on sampling (about 8%) with respect to that of the analytical process was similar.

#### 2.3.2. Particulate collection

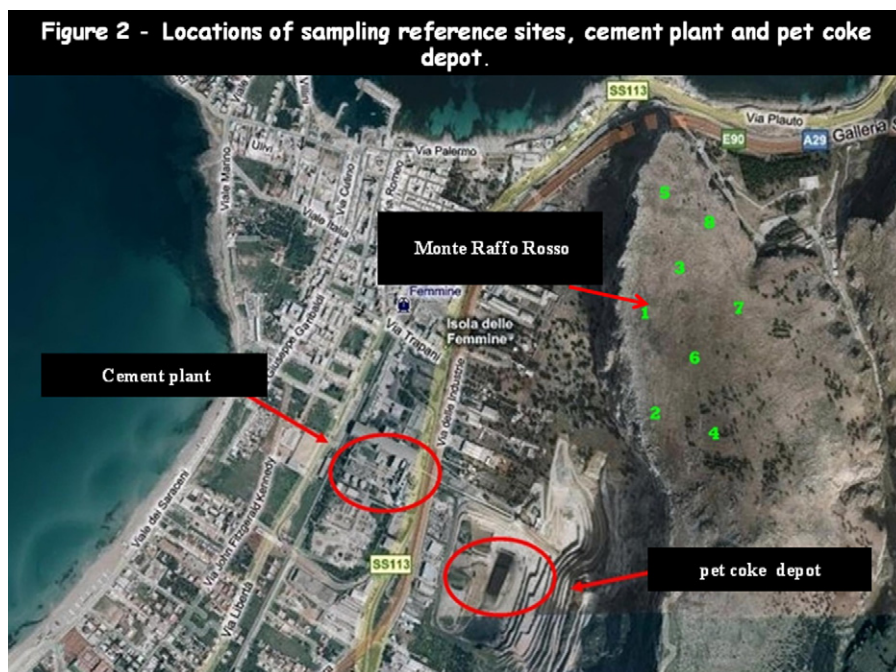
In this study, ambient PAHs profiles were obtained for the atmospheric urban particulate ( $\text{PM}_{10}$ ) of three sites within the urban and sub-urban area of Palermo that is the city closest to the investigated area (about 2–3 km from sub-urban area). Palermo ( $38^{\circ}6'43''56\text{N}$ ,  $13^{\circ}20'11''76\text{E}$ ) (30 m above sea level) is the largest urban area of Sicily with 860,000 inhabitants. The town is situated on the north-western coast of Sicily along the wide bay *Piana di Palermo* overlooked by *Mt. Pellegrino* (600 m above sea level). It is delimited at NE by the Tyrrhenian Sea and it is surrounded by *Monti di Palermo* elevated 500–1000 m above sea level. Potential local pollutants are limited to emission from vehicular traffic, house heating and very small manufacturing industries [15,22,23,45,46].

A total of 27 particulate samples were collected, in a range of several days at sampling stations belonging to the municipal air quality monitoring network [47], characterized by varying traffic density [45,46]. The three selected stations were: an urban site, characterized by lower traffic density relative to the other stations; a large square in the centre of town, exposed to heavy traffic, composed by cars and urban and extra-urban buses; an sub-urban site, characterized by high traffic flow, located close to a crossroad with traffic lights at pedestrian crossings.

To meet the requirements of the Directive 1999/30/CE, particulate sampling was performed according to European Standard EN12341 [48], using a low-volume system (Explorer or mod. ZB1, Zambelli, Italy), equipped with a sampling inlet head (Zambelli) with a quartz fiber filter (47 mm in diameter, Ref. FQT, Albet) operating at constant sampling rate of about 38 L/min ( $2.3\text{ m}^3/\text{h}$ ), giving a total volume of air sampled over 24 h of about  $55\text{ m}^3$ .

Fiber filters were weighed before and after sampling to determine the amounts of particulate collected. Prior to sampling, quartz fiber filters were cleaned with dichloromethane and a mixture of





**Fig. 2.** Locations of sampling reference sites, cement plant and pet coke depot.

n-hexane/acetone (50/50, v/v) for 24 h each, and finally dried at 105 °C.

#### 2.4. Chemicals

Analytical-reagent grade n-pentane, dichloromethane, cyclohexane and acetone (Fluka, Milano) were used as solvents. A PAHs standard solution containing 16 PAHs compounds (100–2000 mg/L) (Mixture SS EPA 610, Supelco, Milano) and perylene standard solution (Supelco, Milano) (2000 mg/L) were used. Solutions in methylene chloride of surrogates PAHs (anthracene- $d_{10}$  and benz[a]anthracene  $d_{12}$ ) and of internal standards (acenaphthene  $d_{10}$ , phenanthrene  $d_{10}$ , chrysene  $d_{12}$  and perylene  $d_{12}$ ) were supplied by Supelco, Milano.

#### 2.5. Determination of water

About 2 g of homogenized sample of soil were dried at 180 °C for one night. The water content was determined by weight loss and was utilized to correlate all the results with dry weight.

#### 2.6. Determination of organic matter

An aliquot (2–3 g) of dried sample was weighed and placed in a platinum crucible. Total organic matter in the soil was measured by determining the loss of weight after combustion at 450 °C for 4 h.

#### 2.7. Quality control and quality assurance

All the analyses of PAHs were repeated three times and the relative standard deviation results ranged from 3 to 16%. Quantification limits for PAHs in the soil tests, calculated on the basis of 10 determinations of the blanks as ten times the standard deviation of the blank, are shown in Table 1 and ranged from 0.057 to 3.1  $\mu\text{g}/\text{kg}$  d.w.

The compound-specific coefficient of variation (as a measure of analytical precision) was within 6%, based on three injections of the standard solution. A blank (cartridge without sample) was run up every five samples. All reported data were blank corrected. Four deuterated PAHs standards (acenaphthene  $d_{10}$ , phenanthrene  $d_{10}$ ,

chrysene  $d_{12}$  and perylene  $d_{12}$ ) were added as internal standard to each extract prior to the GC–MS measurements and recoveries of the surrogate standards (anthracene- $d_{10}$  and benz[a]anthracene  $d_{12}$ ), added prior to the extraction procedure, were calculated. For all analyzed samples they ranged from 75 to 106%. Mean relative standard deviation (RSD) (%) of recovery efficiencies were up to 14%. The calibration was performed once every week.

#### 2.8. Extraction and analysis

All analytes were quantified from a Soxhlet extract of each soil sample. In brief, 5 g each of soil sample was mixed with 15 g of anhydrous sodium sulphate, spiked with 250  $\mu\text{L}$  of a solution containing two surrogate PAHs (anthracene- $d_{10}$  and benz[a]anthracene- $d_{12}$ ) in cyclohexane and placed in pre-extracted Whatman extraction thimbles. The thimbles were placed into a 250 mL Soxhlet unit and extracted for 24 h with 150 mL of n-pentane-dichloromethane (1:1, v/v). Extracts were then reduced to near dryness on a rotary evaporator (Buchi R-124) ( $T=35 \pm 0.5$  °C), taken up in 10 mL and transferred into pre-washed and baked glass vials.

The samples were then reduced under a gentle stream of  $\text{N}_2$  to dryness and 250  $\mu\text{L}$  of a solution containing four deuterated PAHs (acenaphthene  $d_{10}$ , phenanthrene  $d_{10}$ , chrysene  $d_{12}$  and perylene  $d_{12}$ ) in cyclohexane were added.

One microliter of each sample extract was injected into a Shimadzu gas chromatograph (mod. GC-17A) fitted with a 30 m Equity-5 fused silica capillary column (0.25 mm  $\times$  0.25  $\mu\text{m}$  film thickness) and connected to a mass selective detector (GCMS-QP5000) operating with acquisition data (Shimadzu, CLASS 5000 system). The carrier gas was helium, maintained at a flow rate of 1.4 mL/min by electronic pneumatic control. The injection port temperature was 280 °C. The quadrupole temperature was 325 °C. The instrument was tuned on PFTBA every week. The oven program for standards and samples (soil and particulate) was as follows: 60 °C for 2 min, 14.5 °C/min up to 325 °C for 13 min respectively.

Calibration for PAHs was with 16 external standards over the concentration ranges 1–200  $\mu\text{g}/\text{L}$ . The mass spectrometer was operated in selective ion monitoring mode (SIM) using separate ions to identify and confirm compounds (Table 1).

**Table 1**  
List of groups of PAHs formed for analysis, the deuterated internal and surrogate standards employed (underlined), the quantification ion, the confirmation ion for SIM GC–MS mode and quantification limits ( $\mu\text{g}/\text{kg}$  d.w.).

Group	Analytes	Quantification ion	Confirmation ions	Quantification limits ( $\mu\text{g}/\text{kg}$ d.w.)
1	Acenaphthylene	152	76, 151	0.057
	Acenaphthene	154	152, 76	0.090
	Fluorene	166	164, 165	0.75
	<u>Acenaphthene d<sub>10</sub></u>	<u>164</u>		
2	Phenanthrene	178	188, 89	2.0
	Anthracene	178	188, 89	0.28
	<u>Anthracene d<sub>10</sub></u>	<u>188</u>	188	
	Fluoranthene	202	101, 200	3.1
	Pyrene	202	101, 200	2.3
	Benz[a]anthracene	228	114, 226	1.2
	Benzo[a]anthracene d <sub>12</sub>	240	240	
	<u>Phenanthrene d<sub>10</sub></u>	<u>188</u>		1.4
	Chrysene	228	114, 226	1.4
	Benzo[b]fluoranthene	252	126, 250	0.62
	Benzo[k]fluoranthene	252	126, 250	
3	Benzo[a]pyrene	252	126, 250	1.6
	Chrysene d <sub>12</sub>	240		
4	Perylene	252	126, 250	0.14
	Indeno[1,2,3-cd]pyrene	276	277, 138	0.35
	Dibenz[a,h]anthracene	278	279, 139	0.27
	Benzo[g,h,i]perylene	276	138, 124	0.65
	<u>Perylene d<sub>12</sub></u>	<u>264</u>		

For PAHs analysis of the samples of particulate collected in quartz filters, after final weighting, all quartz filters were placed in ultrasound bath and extracted, for three times, with cyclohexane (8 mL) for 20 min. The extracts were filtered through  $\text{Na}_2\text{SO}_4$ , and concentrated in a rotary evaporator with thermostatic bath at  $T = 35 \pm 0.5^\circ\text{C}$ . The final volume was around 2 mL. The last stage in the procedure involved drying the solution containing PAHs under a weak nitrogen flow at room temperature. The dry residue was dissolved in 250  $\mu\text{L}$  solution containing the perdeuterated internal standards. All extracts were analyzed using a GC–MS.

### 3. Results and discussion

The mean water content in the 16 samples collected in the area of Natural Reserve Isola delle Femmine was 11% and ranged from 2.4 to 22% while the mean content of organic matter was 9.9% and ranged from 4.1 to 18%. The wide range of organic contents (relative standard deviation was 42%) found in the soil samples indicates heterogeneous physical chemistry characteristics of the investigated area.

In Table 2, we report the concentration of each individual PAH in the collected soils. The total concentrations (the averages of three analyses) of 16 investigated compounds, expressed as the sum of the concentrations,  $\sum\text{PAHs}$ , in the soil of Isola delle Femmine, ranged from 35 to 545  $\mu\text{g}/\text{kg}$  of dry matrix (Fig. 3). The wide range of PAHs concentrations (relative standard deviation is 93%) found in the soil samples indicates heterogeneous levels of contamination in the investigated area. The heterogeneity of the levels found in the island can be interpreted on the base of the spatial heterogeneity of the pedologic conditions (organic carbon content), density of vegetation and exposure. For example, binding of PAHs to humic matter influences their degradation in soil [49].

The highest concentrations of total PAHs were found in soils sampled in the station nos. 1 and 3, located in south coast of the investigated area, corresponding to those closest to Sicily. The station no. 2, even if located closer the Sicilian coast, shows concentrations of PAHs lower than the two previous one because there is some vegetation which impedes the deposition of pollutants into the soil. Plants, especially evergreen, may strongly influence deposition fluxes of contaminants to the soils [50,51].

The capacity of leaves to accumulate organic pollutants [15] and the extent of organic surface area [22,52] create the conditions for vegetation, in particular during the cold season, to be an important storage or retardation compartment for contaminants in the terrestrial environment. During the warm season, the volatilisation, photodegradation and oxidize degradation processes reduce the levels of contaminants in vegetation. In this mode, plant canopies are seen as cumulative compartments able to redirect PAHs, to the soil following different processes: rain washout, wax erosion, and transport due to litter fall. The quantity of contaminants direct from the plants to the ground is lower than those deposited directly into areas not covered by vegetation.

No statistically significant correlations were found between the distance of the sampling sites from the Sicilian coast and from the plant for the production of cement and the concentrations of PAHs in the different points of Natural Reserve.

Soils collected in the Isola delle Femmine showed generally the highest concentrations, being the sum of the 16 PAHs about 1.4 times higher than that corresponding to rural reference sites Monte Raffo Rosso (141  $\mu\text{g}/\text{kg}$  d.w. vs. 101  $\mu\text{g}/\text{kg}$  d.w. respectively) (Fig. 3). By Student *t*-test ( $p = 0.05$ ), the total PAHs concentrations measured in the Isola delle Femmine ( $n = 16$ ) was similar than those of Monte Raffo Rosso ( $n = 7$ ).

It is estimated that background levels for soils without point sources or influence from traffic are less than 50–100  $\mu\text{g}/\text{kg}$  [53,54]. Concentrations in tropical soils are in the range 12–380  $\mu\text{g}/\text{kg}$  [55]. There is some evidence that PAHs found in rural soils, remote from major anthropogenic sources, can be primarily attributed to biological activity and, only a negligible fraction to air pollution [55].

Considering our results, the average concentration of PAHs (101  $\mu\text{g}/\text{kg}$  d.w.), for references area, is in good agreement with those of literature reported background [55,57].

In literature, four classes of soil contamination with PAHs were proposed: not contaminated when the  $\sum\text{PAHs}$  is lower of 200  $\mu\text{g}/\text{kg}$ ; weakly contaminated when  $\sum\text{PAHs}$  is in the range 200–600  $\mu\text{g}/\text{kg}$ ; contaminated when  $\sum\text{PAHs}$  is in the range 600–1000  $\mu\text{g}/\text{kg}$ ; heavily contaminated if  $\sum\text{PAHs}$  is higher than 1000  $\mu\text{g}/\text{kg}$ . The proposed threshold values which were expressed as the absolute sum of the content of 16 PAHs compounds in the soil samples ( $\sum\text{PAHs}$ ), disregarded PAHs composition and soil

**Table 2**

Concentration ( $\mu\text{g}/\text{kg d.w.}$ ) of single polycyclic aromatic hydrocarbons (mean of three analyses)<sup>a</sup> in soil samples (from 1 to 16) collected on Natural Reserve Isola delle Femmine and on Reference site Monte Raffo Rosso (from R1 to R8).

Compounds	Stations												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Acenaphthylene	1.1	0.81	0.88	1.4	0.25	1.8	0.25	0.25	1.7	0.25	0.79	0.25	0.25
Acenaphthene	0.31	1.6	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31
Fluorene	3.0	1.7	1.1	1.6	1.3	3.4	1.3	0.67	2.8	1.2	2.3	2.2	1.1
Phenanthrene	33	14	18	6.2	5.3	13	7.3	2.2	10	6.2	16	8.8	5.4
Anthracene	2.7	2.0	4.2	1.3	1.1	0.86	1.0	0.57	0.98	1.3	1.5	1.0	1.6
Fluoranthene	96	24	37	4.4	5.3	18	7.0	2.7	6.8	4.5	17	10	7.2
Pyrene	88	23	32	5.2	5.0	23	6.0	3.4	11	3.9	16	9.3	6.9
Benzo[a]anthracene	38	7.4	14	3.2	3.0	6.2	3.5	2.5	2.9	2.1	4.4	4.9	2.8
Chrysene	67	19	32	6.5	5.7	15	7.8	4.4	4.1	7.2	15	8.2	5.2
Benzo[b]fluoranthene	55	18	53	8.3	9.2	13	10	2.9	4.4	10	16	9.5	4.0
Benzo[k]fluoranthene	29	5.8	16	2.3	2.0	5.7	2.6	1.6	1.8	4.7	5.9	2.0	1.2
Benzo[a]pyrene	39	8.7	35	5.6	5.2	9.1	5.7	3.2	3.5	3.2	9.8	6.9	2.1
Perylene	0.16	14	15	9.0	17	0.16	12	2.7	0.16	0.16	0.16	19	0.84
Indeno[1,2,3-cd]pyrene	35	11	30	3.4	4.8	7.9	6.8	1.9	3.2	6.1	17	5.6	0.37
Dibenz[a,h]anthracene	13	0.27	8.7	0.27	2.5	4.6	0.86	0.27	2.3	0.27	4.6	0.27	0.27
Benzo[g,h,i]perylene	44	16	44	7.4	14	16	9.2	5.0	5.3	8.1	5.8	16	0.62

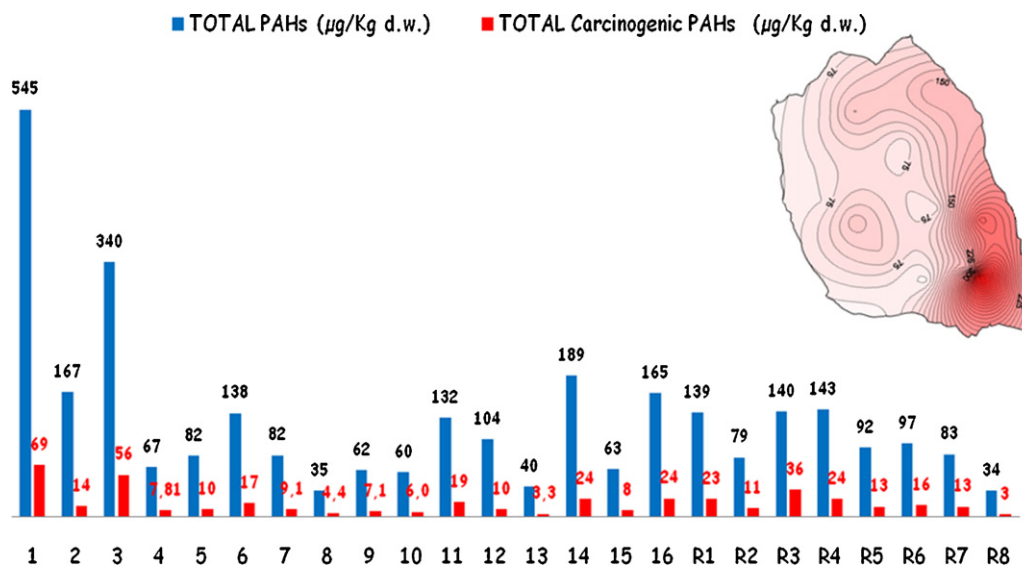
  

Compounds	Stations										
	14	15	16	R1	R2	R3	R4	R5	R6	R7	R8
acenaphthylene	1.2	0.25	0.25	0.94	0.25	0.77	0.25	0.25	0.25	1.9	0.25
acenaphthene	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31	0.31
fluorene	2.1	1.3	1.0	2.2	1.1	2.5	3.1	1.7	1.5	2.4	0.77
phenanthrene	13	5.4	15	9.9	7.6	12	12	7.7	7.7	9.1	2.1
anthracene	1.2	0.80	1.6	2.1	1.1	2.4	2.3	1.4	1.6	1.4	0.55
fluoranthene	30	6.5	23	12	6.4	6.3	7.4	7.2	7.1	5.4	8.0
pyrene	32	6.0	21	13	6.3	8.2	9.6	6.9	7.9	6.3	6.8
benzo[a]anthracene	14	3.4	7.7	8.3	4.6	5.3	8.4	4.4	6.7	3.5	2.3
chrysene	21	5.5	16	11	6.6	10	9.7	7.0	9.0	6.8	1.6
benzo[b]fluoranthene	19	6.1	16	13	9.5	12	15	11	9.1	7.5	1.6
benzo[k]fluoranthene	9.0	2.9	9.0	5.1	9.2	3.0	2.6	2.1	3.3	2.4	0.69
benzo[a]pyrene	13	2.7	13	11	5.0	13	12	6.3	6.7	5.9	1.9
perylene	0.16	1.9	7.0	2.4	3.7	11	9.4	7.1	2.8	7.8	4.1
indeno[1,2,3-cd]pyrene	11	5.6	11	14	3.3	6.8	9.9	8.0	5.7	5.0	0.59
dibenz[a,h]anthracene	5.0	3.7	5.8	7.9	3.5	20	7.9	3.7	6.1	5.1	0.27
benzo[g,h,i]perylene	16	11	17	26	11	25	34	17	22	12	2.1

<sup>a</sup> Relative standard deviation of three analyses of PAHs ranged from 3 to 16%.

characteristics. These values (200, 600 and 1000  $\mu\text{g}/\text{kg d.w.}$ ) were derived from the results of determinations of PAHs content of soils in Europe [54,56], as well as from an estimation of the risk of human exposure (the possibility of PAHs transfer into the food chain) and the average intake rates [7,8,10,11].

As can be seen from Fig. 3, in 14 of soil samples of Isola delle Femmine Natural Reserve, the content of the sum of PAHs was below 200  $\mu\text{g}/\text{kg d.w.}$ . These soils were considered to be non-contaminated. In two soils the content of PAHs ranged from 200 to 600  $\mu\text{g}/\text{kg d.w.}$  and they were considered to be weakly contam-



**Fig. 3.** Total and carcinogenic PAHs concentrations (average of three analysis) in  $\mu\text{g}/\text{kg d.w.}$  in soils of Isola delle Femmine Natural Reserve and in reference sites and geographical distribution.

**Table 3**  
Toxic equivalency factors (TEFs) [56].

Compound	TEF	Compound	TEF
Acenaphthene	0.001	Benzo[k]fluoranthene	0.1
Acenaphthylene	0.001	Benzo[b]fluoranthene	0.1
Anthracene	0.01	Indeno[1,2,3-cd]pyrene]	0.1
Benz[a]anthracene	0.1	Perylene	0.001
Fluoranthene	0.001	Dibenz[a,h]anthracene	1
Fluorene	0.001	Benzo[a]pyrene	1
Phenanthrene	0.001	Chrysene	0.01
Pyrene	0.001	Benzo[g,h,i]perylene	0.01

inated. In all samples of Monte Raffo Rosso (reference area) the content of the sum of PAHs was below 200  $\mu\text{g}/\text{kg}$  d.w. (Fig. 3).

The total PAHs concentrations in the Natural Reserve soil are also lower than the maximum concentrations allowed by the Italian legislation for villas, public gardens and green areas uses of soils [57].

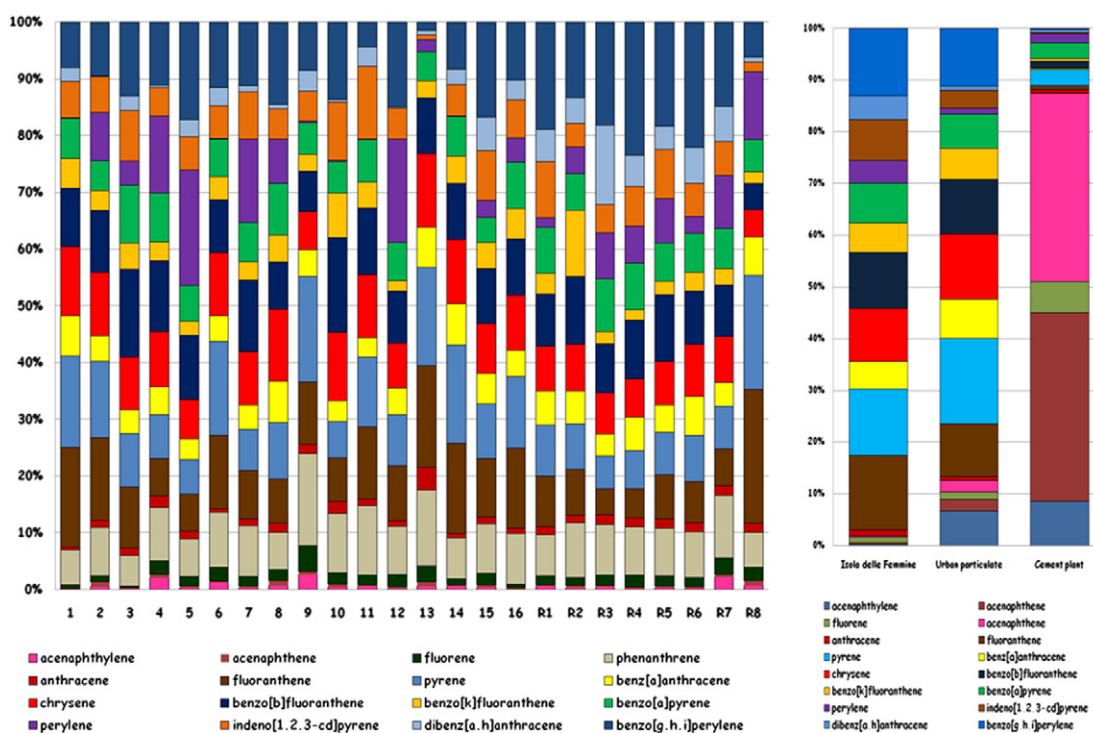
Several PAHs specimen including B[a]P, the most carcinogenic, have been classified into probable (2A) or possible (2B) human carcinogens by IARC [38]. Carcinogenic potency associated with exposure of a given PAH compound can be obtained by calculating its B[a]P equivalent concentration B[a]P<sub>eq</sub>. To calculate the B[a]P<sub>eq</sub> of individual species, toxic equivalent factor (TEF) of the given species relative to B[a]P was used. The list of TEFs compiled by Tsai et al. [58] was adopted in this study (Table 3). B[a]P has been assigned a TEF of one, which is highest among all PAHs. To compare the carcinogenic potencies associated with the total PAHs concentrations in the reference and Isola delle Femmine soils, sum of each individual BaP<sub>eq</sub> was used. Calculated total B[a]P<sub>eq</sub> concentrations at different sampling sites of Isola delle Femmine varied from 3.3  $\mu\text{g}/\text{kg}$  (site 13) to 69  $\mu\text{g}/\text{kg}$  (site 1) with an arithmetic mean of 18  $\mu\text{g}/\text{kg}$  (Fig. 3). The carcinogenic potency of the Isola delle Femmine sites was similar than the reference sites (mean = 17  $\mu\text{g}/\text{kg}$ ).

In most of the sampling sites of the Isola delle Femmine, the same distribution of 16 PAHs (expressed as weight percentage) was

observed (Fig. 4). Despite the difference between the total concentrations of PAHs in Natural Reserve Isola delle Femmine and in the reference area Monte Raffo Rosso, patterns in the soils from the two sites were similar suggesting common contamination sources.

The most abundant compounds in the soils here investigated were fluoranthene, pyrene, benzo[b]fluoranthene and chrysene. The relatively abundance reflect their low water solubility and low vapor pressures. Perylene, was found at all stations. The most polluted station (no. 12) shows the maximal absolute concentration (19  $\mu\text{g}/\text{kg}$  d.w.) and is followed in decreasing order by station nos. 5 and 3. However, on a relative basis, perylene accounts from 0.03 to 20 % of total PAHs. The origin of perylene is controversial, some authors argue that the marked abundance precludes its pyrogenic origins, in fact, a perylene contribution of more than 10% indicates a diagenic process [7,8]. Perylene is not present or occurs only in small amount in the products of combustion processes, probably due to its thermal instability or reactivity, but there is also significant evidence that it can be produced biologically under anaerobic conditions [28]. Several authors reported PAHs formation through plant and microbial metabolism [59], showed that wood from forest contained naphthalene, phenanthrene and perylene. Thiele and Brummer [28] reported that biological formation of 3-, 4-, 5- and 6-rings PAHs was observed after incubation of fresh plant material and of soil mixed with fresh plant material under reducing conditions. When only soil material was incubated, anaerobic biodegradation of 3-rings was observed. Perylene quinones (pigments found in several animal and vegetable organisms) are suspected to be degraded to perylene by anaerobic microbial metabolism. Another theory postulates production via biosynthesis, independent of special precursors [28].

In order to assess specific inputs of perylene to the Isola delle Femmine, the distribution patterns (%) of PAHs were evaluated for the soils and compared with those of the atmospheric particulate sampled at several monitoring stations in Palermo area and with those of two cement plant reported in literature [1,26]. Fig. 4 shows the relative percentages of single PAHs in the samples of



**Fig. 4.** Distribution (%) of single compounds in soil samples collected in Natural reserve Isola delle Femmine (from 1 to 16), in reference site (from R1 to R8) and in different samples (soils particulate and cement plant).



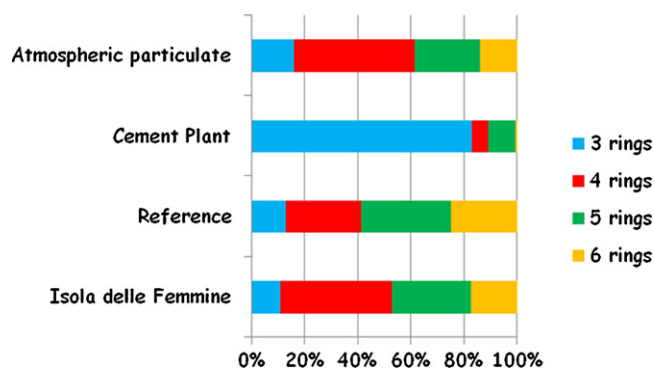


Fig. 5. Relative percentage of 3-, 4-, 5- and 6-rings PAHs.

soil collected at Isola delle Femmine. The percentages of perylene, apparently, no matches with those of atmospheric particulate and with those of emissions of cement plants obtained from literature data. Hence, the presence of perylene in the soils of Isola delle Femmine must be not related to vehicular traffic and to cement plant. There is no correlation between total PAHs concentration and perylene content. These evidences suggest that the perylene identified in the samples does not originate from the same type of emission which contains most of the other PAHs. We can suppose that a fraction of perylene is produced by biological activities of microorganism using organic matter of the soil.

With the aim to find the origin of PAHs in the soil of Isola delle Femmine, we compare (Fig. 4) the distribution of singles analytes in the investigated area with those of the reference area, those of atmospheric particulate (mean concentrations of single PAHs determined by us on filters aspirating a known volume of air in the various stations) and those of emission of some cement plants obtained from literature data because it was not possible to take samples of particulate or other matrix in the vicinity of cement plant located in Sicilian coast.

Investigated soil (Isola delle Femmine) showed (Fig. 5) a high amount of 4- and 5-rings PAHs, whereas 3-ring PAHs are present mainly in the emission of cement plants (about 80%). The relative (percentage) of 3-, 4-, 5- and 6-rings PAHs determined in samples of Isola delle Femmine are similar to those of the reference soils and those of urban atmospheric particulate. On the other hand, according to their physical and chemical characteristics (low molecular weight, high vapor pressure, etc.), 3-rings PAHs are mainly in gaseous form and their presence would be more related with long-range transport than with emissions from a local source.

Taking into account the percentage of compounds with different number of rings, in the soil of Isola delle Femmine Reserve, the distribution results different from those of some cement plants [26].

Four-, five- and six-ring PAHs are those with a higher molecular weight, and consequently, they would fall down more easily near those points where they are emitted. In our case they would probably be accumulated in an area immediately adjacent to the cement industry.

This has also been observed in studies investigating PAHs concentrations in soils depending on the proximity to highways [60].

A linear correlation between total PAHs concentration and single compounds content was calculated. The values of  $r$  for the most representative compounds ranged from 0.88 to 0.98. These results suggest that most of the PAHs identified in the samples of Isola delle Femmine soil, originate from the same type of emissions.

In Fig. 3 the geographical distributions of total PAHs in the soil of Isola delle Femmine is shown which is almost anywhere comparable and well reflect the position of the points nearest to Sicilian Coast and of the density of vegetation. Site nos. 1, 3, 14,

and 16 located on a border area of the island, show the highest level of PAHs, while the inner area, far from the coast, of the island, shows the lowest concentrations of PAHs which are about two times lower than mean value ( $142 \mu\text{g}/\text{kg d.w.}$ ). This result is presumably explained considering the distance from the anthropized area, the major wind directions and the density of vegetation.

Another method can evaluate the sources of PAHs whether coming from the mainland of Palermo. The ratio of BaA/Chr could be used to evaluate the origin of PAHs [60,61]. The lower ratio of BaA/Chr implied longer distance of transport, while the higher ratio would suggest that those PAHs might be mostly from the emission of the local sources. Since BaA is photodegraded and oxidize degraded more easily than its isomer Chr during their atmospheric travel, the ratio of BaA/Chr can be used as a tracer for the degree of photodegradation and oxidize degradation, in addition to being used as source discriminators. If the ratios are small, the sources might be far away from the urban areas because of the photodegradation and oxidize degradation of most BaA, while the big ratio is referred to local source. The mean values of BaA/Chr is 0.5 for the soil of the isle and 0.7 for particulate collected at Palermo, respectively, indicating that PAHs in soil of Isola delle Femmine Natural Reserve might be transported from Palermo. The conclusion from the reported data was that PAHs loadings in the Isola delle Femmine Natural Reserve are strongly affected by proximity to Sicilian coast (in particular to Palermo) and the likelihood of enhanced atmospheric deposition. In other words, this implies that the soil burden is primarily a reflection of cumulative atmospheric deposition. Cement plant activity has a negligible influence on the presence of PAHs in the soil of Isola delle Femmine Natural Reserve.

These evidences can be attributed to the fact that, prevailing wind directions are from East and West. The movement of the local air masses is strictly linked to topography. Normally, during daytime sea breeze drives the pollutants produced in the city of Palermo and in the cement plant towards the surrounding mountains. During evening and night a reversal in the breeze takes place, which drives back the contaminants (quantitatively reduced by degradation), toward the sea. Thermal inversion is commonly observed phenomena and, in these periods, warning levels of other air pollutants ( $\text{NO}_x$ , CO,  $\text{O}_3$ , etc.) may be reached.

The organic matter content has been implicated as the key properties influencing PAHs content in contaminated soils [61]. It is therefore appropriate to investigate the influence of this variable further. Generally, analysis of the organic matter in environmental matrices (sediments, soils, etc.) showed that concentrations of PAHs increase with an increase of organic matter content. This trend has already been observed by a number of authors [11,12,61]. With the aim of identifying a relationship between the organic matter content and PAHs concentrations determined in the investigated soils, we carried out a linear regression analysis. The total PAHs had a weak positive correlation ( $r=0.60$ ) with organic matter content for reference samples. When low regression coefficients for the organic matter vs. contamination level relationship are found, other elements probably play a major role in determining the level of contamination (e.g. proximity to sources, soil characteristics, vegetation type, altitude or latitude) [50].

We can hypothesized that the soils of the Isola delle Femmine Natural Reserve are mainly influenced by deposition from particulate matter, suggesting that the partitioning between organic matter and PAHs is not a dominant process in the soils.

### 3.1. Determination of PAH sources

Sources of PAHs pollution in the soil under investigation were established by comparing some indexes calculated by ratios of



**Table 4**  
Isomeric ratios.

Isomeric ratios/stations	1	2	3	4	5	6	7	8	9	10	11	12
An/(An + Ph)	0.08	0.13	0.19	0.18	0.18	0.06	0.12	0.20	0.09	0.17	0.08	0.10
Fl/(Fl + Py)	0.52	0.52	0.53	0.46	0.51	0.44	0.54	0.44	0.37	0.54	0.51	0.52
B[a]/(B[a] + Cr)	0.36	0.28	0.31	0.33	0.34	0.29	0.31	0.36	0.41	0.23	0.23	0.37
IP/(IP + B[g,h,i])	0.44	0.40	0.41	0.31	0.25	0.33	0.43	0.27	0.38	0.43	0.75	0.27
Total index	6.1	6.0	6.8	6.2	6.1	4.8	6.2	6.3	5.8	6.4	7.0	5.5
Isomeric ratios/stations	13	14	15	16	R1	R2	R3	R4	R5	R6	R7	R8
An/(An + Ph)	0.23	0.08	0.13	0.10	0.17	0.12	0.16	0.16	0.16	0.17	0.14	0.21
Fl/(Fl + Py)	0.51	0.48	0.52	0.53	0.50	0.51	0.44	0.43	0.51	0.47	0.46	0.54
B[a]/(B[a] + Cr)	0.35	0.39	0.38	0.32	0.43	0.41	0.34	0.46	0.39	0.43	0.34	0.58
IP/(IP + B[g,h,i])	0.37	0.40	0.35	0.40	0.34	0.24	0.21	0.23	0.32	0.21	0.29	0.22
Total index	7.2	6.0	6.2	5.9	6.8	5.7	5.5	6.1	6.4	6.1	5.6	7.5

concentrations of some PAHs. Phenanthrene/anthracene and fluoranthene/pyrene ratios have commonly been used as a means of determining the main origins of PAHs [11,14–17,23,26,44].

The values of isomeric ratios for the different samples of the soil considered in the present paper are reported in Table 3. The An/(An + Ph) ratio for soils is greatly variable (0.060–0.23), only five samples are below 0.10. The highest ratios are observed for the sample no. 16 (0.23). The mean value for Isola delle Femmine Natural Reserve is 0.12, while in reference soil (Monte Raffo Rosso) is 0.16. Based on the 0.10 transition [44] An/(An + Ph) ratios suggest combustion sources in the investigated and reference areas.

For the samples collected in Isola delle Femmine Natural Reserve, ratios Fl/(Fl + Py) ranged from 0.46 to 0.54 while for reference samples from 0.37 to 0.54. In agreement to the values of ratios Fl/(Fl + Py) reported in literature [44] the PAHs in the investigated area can be considered of pyrolytic origin.

For Isola delle Femmine stations, B[a]A/(B[a]A + Cr) ranged from 0.23 to 0.41 with an average value of 0.33, while for reference stations they ranged from 0.34 to 0.58 with an average of 0.42. The literature data [38] suggest that BaA/(BaA + Chr) ratios from 0.20 to 0.35 indicate either petroleum or combustion and >0.35 imply combustion. The analytical data indicate that PAHs found in most stations is of pyrolytic origin as the major source of PAHs.

Accordingly to literature data [44], IP/(IP + B[g,h,i]) ratios of 0.20 likely imply petroleum, between 0.20 and 0.50 liquid fossil fuel (vehicle and crude oil) combustion, and ratios >0.50 imply grass, wood and coal combustion. In our case, the mean values are 0.39 for reserve and 0.26 for references.

In some cases, the values of four ratios are not in agreement among them. Considering that, generally, the sources of PAHs in a matrix can result different and occasional, we calculate a total index [46] as the sum of single indices (previously discussed) respectively normalized for the limit value (low temperature sources-high temperature sources) reported in literature [44]: Total index = Fl/(Fl + Py)/0.4 + An/(An + Ph)/0.1 + B[a]A/(B[a]A + Chr)/0.2 + IP/(IP + B[g,h,i])P/0.2.

We consider PAHs prevalently originating by high temperature processes (combustion) when the total index is >4 while lower values indicate prevalently low temperature sources (petroleum product). The results (Table 4) confirm that all the PAHs identified in the soil samples originate from combustion processes.

#### 4. Conclusions

The present study allowed optimizing the extraction and analytical conditions for the determination of PAHs in soils. Under these conditions, the recoveries are very good; in every case they are

greater than 75% and in most cases near 100%. Relative standard deviation is less than 12%. The reproducibility and detection limits are also satisfactory, and the detection limits ranged from 0.057 to 3.1 µg/kg d.w.

Sixteen PAHs were quantitatively analyzed in the soils of two areas near a cement plant and we show their spatial distribution (Fig. 3) to consider the potential sources.

The results reported in this work represent the first quantitative investigations of PAHs of Natural Reserve Isola delle Femmine area. Mean concentration of total PAHs in the soils of the Isola delle Femmine was 1.4 times higher than the reference stations. Treating statistically the data, concentrations of total PAHs in the soils of the investigated area were similar than those of reference stations. However, the concentrations of PAHs are remarkably lower or similar than those found in a number of investigations from different regions and countries: for example, Jones [56] determined the typical range of 14 PAHs in Welsh soils to be 108–54500 µg/kg. PAHs levels differ among sites, but the contamination fingerprint is often similar. This finding is related to the *weathering* process of the mixtures in the atmosphere.

The distribution patterns of 16 PAHs from the two selected areas are comparable. Their patterns, however, are different from that of the emission of cement plants (obtained from literature) and are similar to that of urban particulate.

Negligible differences in the total carcinogenic PAHs concentrations referred to as benzo[a]pyrene among the stations were measured and the mean values are 18 and 17 µg/kg d.w. respectively for Isola delle Femmine and for the reference samples.

The mean values of BaA/Chr for the analyzed samples indicate that PAHs in soil of Isola delle Femmine Natural Reserve might be transported from Palermo.

This evidence shows that the entire area of Natural Reserve Isola delle Femmine is affected by anthropic emissions of contaminants due to vehicular traffic taking place in Palermo and in the nearby Sicilian coastal area, which may represent a potential hazard of bioaccumulation into the plants and animals. Cement plant activity has a negligible weight on the presence of contaminants in the soil of Isola delle Femmine Natural Reserve.

The larger presence of PAHs with high molecular weight found in all samples and the values of isomeric ratios, as PAHs distribution indexes, has demonstrated that the most samples owe their PAHs in investigated soils to a predominant single mode of origin, i.e. anthropogenic combustion or pyrolysis processes, but a negligible quantity of PAH can be derive by biogenic sources because all samples contain traces of perylene.

Total PAHs content in nearly all samples are correlated with the concentrations of many single compounds. This evidence indicates that during the process of production a characteristic mixture of PAHs is produced and consequently for routine analyses only a minor number of compounds could be analyzed.

According to the results of this study, a continuous environmental monitoring of the chemical composition of the soil of Natural Reserve Isola delle Femmine is recommended.

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