

Chemical characterization and spatial distribution of PAHs and heavy hydrocarbons in rural sites of Campania Region, South Italy

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Abstract In this paper, the behaviour and distribution patterns of heavy hydrocarbons and several polycyclic aromatic hydrocarbon (PAH) priority pollutants, as listed by the US Environmental Protection Agency, were evaluated in 891 soil samples. The samples were collected in three expected polluted rural sites in Campania (southern Italy) as part of the LIFE11 ECOREMED project, funded by the European Commission, to test innovative agriculture-based soil restoration techniques. These sites have been selected because they have been used for the temporary storage of urban and building waste (Teverola), subject to illicit dumping of unknown material (Trentola-Ducenta), or suspected to be polluted by metals due to agricultural practices (Giugliano). Chemical analysis of soil samples allowed the baseline pollution levels to be determined prior to any intervention. It was found that these areas can be considered contaminated for residential use, in accordance with Italian environmental law (Law Decree 152/2006). Statistical analysis applied to the data proved that average mean concentrations of heavy hydrocarbons could be as high as 140 mg/kg of dry soil with peaks of 700 mg/kg of dry soil, for the Trentola-Ducenta site; the median concentration of analytical results for hydrocarbon (HC) concentration

for the Trentola-Ducenta and Giugliano sites was 63 and 73.4 mg/kg dry soil, respectively; for Teverola, the median level was 35 mg/kg dry soil. Some PAHs (usually benzo(a)pyrene) also exceeded the maximum allowed level in all sites. From the principal component analysis applied to PAH concentrations, it emerged that pollutants can be supposed to derive from a single source for the three sites. Diagnostic ratios calculated to determine possible PAH sources suggest petroleum combustion or disposal practice. Our sampling protocol also showed large dishomogeneity in soil pollutant spatial distribution, even at a scale as small as 3.3 m, indicating that variability could emerge at very short spatial scales.

Keywords Heavy hydrocarbons · PAHs · Soil pollution · Waste disposal · Small-scale sampling · Campania rural areas

Introduction

Even though disposal at landfills has steadily declined and the percentage of waste and energy recovery has significantly grown in recent years, in 2008 the EU-27 countries generated more than 2.6 billion tonnes of wastes, of which 98 million tonnes was hazardous (Eurostat 2011). This amounts to about 6 t of solid waste for every man, woman and child. Such a large production of waste inevitably feeds into illegal dumping and inappropriate practices (e.g. burning of agricultural residues). Recently, the European Commission, through the European Soil Data Centre, conducted a project to collect data on contaminated sites from national institutions in Europe using the European Environment Information and Observation Network for soil (EIONET-SOIL). There was estimated to be local soil contamination at 2.5 million potentially contaminated sites, of which about 342,000 have already

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been identified as contaminated, including several thousands in Italy (Panagos et al. 2013). In a more detailed study, it was estimated that there were as many as 2551 contaminated sites, 13 % of which were used as illegal landfills in the region of Campania (southern Italy) between 1996 and 2008 (Vito 2008).

Soil contamination usually poses significant environmental hazards for terrestrial and aquatic ecosystems, given the frequent involvement of potentially toxic metals, mineral oil, hydrocarbons and persistent organic pollutants (POPs), that is, highly toxic molecules, recalcitrant to degradation, most of which have carcinogenic or mutagenic activity (Fent 2004; Rushton 2003). Their origin, occurrence and fate in soils have been extensively studied. Due to their hydrophobic character, hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in environmental matrices are rapidly sorbed on particles and organic matter of sediments and soils, becoming their primary reservoirs (Latimer and Zheng 2003; Mai et al. 2002; Wilcke 2000). Consequently, soils and sediments are the ultimate repository for most of the hydrophobic organic contaminants. Their negative impact mainly results from their toxicity to biological processes catalyzed by soil microorganisms, inhibition of organic matter mineralization and root mycorrhizal infection (Máthé et al. 2012).

From 1994 to 2008, Campania was under a formal state of emergency, declared as a consequence of regional landfill saturation with severe consequences for public and environmental health. The local waste management policy was so inappropriate that waste continued to accumulate during the delay in constructing the waste incinerators (Senior and Mazza 2004). In that period, illegal waste disposal was very intensive, with waste being buried in agricultural areas, roads, construction sites and natural caves; it has been shown that illicit waste disposal still continues (D'Alisa et al. 2010). A recent editorial (Nature 2014) summarized the complex situation that has been forming over the years, due to widespread illegal use of rural land and which now, after years of reticence, has begun to receive the required attention.

PAH contamination in Campania has created an alarming scenario, as shown by the high concentration of carcinogenic and toxic PAH congeners in soil and *Quercus ilex* leaves in the densely populated Naples urban area (De Nicola et al. 2014). Albanese et al. (2014) evidenced the human health risks posed by PAH exposure in the metropolitan area of Naples and Caserta Provinces (Agro Aversano area).

To date, four National Interest Priority Sites (*Siti di Interesse Nazionale* (SINs), as defined by Italian Law DM 22/1997) have been identified, with different levels and sources of pollution, and the Regional Environmental Protection Agency (ARPA-Campania) has already worked on soil pollution characterization (Vito 2008). Some recent

scientific studies have started to show the relations between environmental pollution and damage to health for people living in two provinces of Campania, namely, Caserta and Naples (Esposito et al. 2010; Giovannini et al. 2014). Based on higher biomarker values within the SEBIOREC biomonitoring study (De Felip et al. 2014), several municipalities were tagged as possibly deserving attention for health-oriented interventions.

Currently, there are few papers published on soil pollution by hydrocarbons (HCs) and PAHs in Campania (Albanese et al. 2007, 2008, 2014; Caricchia et al. 1999; Esposito et al. 2010; De Nicola et al. 2014; Fedele et al. 2008) and in Italy (Fabiatti et al. 2010; Orecchio 2010).

Recently, ECOREMED, a LIFE11 project, has been funded by the European Commission. The objective of this project is to develop the validation of an assisted agriculture-based bioremediation protocol for different soil contamination levels (ECOREMED 2014). To this aim, the 'Litorale Domitio-Agro Aversano', one of the four SINs in the Campania region, has been selected to host the pilot-scale experiments linked to this project. This SIN includes a large part of potentially polluted agricultural areas, belonging to 77 municipalities in the provinces of Naples and Caserta, and high level of point contaminations is due to both legal and illicit industrial and municipal waste dumping and burning, with hazardous consequences also on the quality of drinkable water (Vito 2008). Recent analytical activity promoted by the Italian Government (DL 136/2013) on these sites, based on the database of the ECOREMED project, quantified the percentage of soils at risk at about 2 % of agricultural land (ECOREMED 2014).

Within this SIN, the Acerra-Marigliano-Nola conurbation has been called 'The triangle of death', after Senior and Mazza (2004), due to the significant above average mortality for colorectal and liver cancer, leukaemia and lymphoma. However, it is worth mentioning that the age-standardized incidence (any kind but melanoma) in the district of Naples during years 2005–2009 is in line with that recorded in Italy, 496.4 new cases every 100,000 inhabitants in the district of Naples against an average of 467.7 for all cancer registries in Italy for males and 315.6 in the district of Naples against 339.6 for females (AIRTUM 2014).

In this paper, we present the results concerning the analysis of heavy HCs and PAHs in different, but potentially polluted, areas in the 'Litorale Domitio-Agro Aversano' SIN. For the characterization of soil pollution levels, an experimental campaign was carried out to define the state of selected pilot sites before any intervention. Full characterization of medium/heavy weight ($C > 12$) HC concentrations and PAHs was carried out. HCs are the most frequently discovered contaminants in the environment (Wang and Fingas 2003), while PAHs are receiving increasing attention due to their carcinogenic and mutagenic properties.

Materials and methods

Study areas

The main objective of the ECOREMED project is to develop an operative protocol for the bioremediation of contaminated agricultural soils. To demonstrate the effects of this protocol, three expected polluted areas were selected in the municipalities of Trentola-Ducenta, Teverola and Giugliano. These comprised a 4500-m² area in Trentola-Ducenta with organic and heavy metal pollution and subject to unauthorized waste disposal, a 3000-m² public area in Teverola used as a site for temporary storage of urban waste (now disused) and a 1000-m² rural area in the municipality of Giugliano subject to unauthorized waste disposal. Figure 1 shows the land cover map, from the CORINE CLC2006 database (European Environment Agency 2014), of the 'Litorale Domitio-Agro Aversano' SIN and the position of the three monitoring sites. These three sites are all close to urban/industrial areas and were chosen because they represent different levels of expected soil pollution: Teverola was used as a legal, but poorly managed, landfill for the temporary storage of urban waste (now removed) during the waste management emergency in the Campania region. Waste, whose nature is not completely known, has also been illegally buried in Trentola-Ducenta. Giugliano is a heavily populated urban area, bordering the city of Naples, and the selected site, subjected to unauthorized waste disposal, was also influenced by other human activities, e.g. deposition of atmospheric pollutants, combustion of waste or agricultural residues and low-quality compost usage. This site belongs to a well-known polluted area; previous analyses of 190 wells in the Giugliano municipality evidenced high contents of tri- and tetrachloroethylene and organic pollutants with a cancerogenic potential (Balestri 2010). These compounds are bound, to some extent, to the dumping of about 1,300,000 Mg of waste close by RESIT and Scafarea dumping areas, including about 50 % of hazardous special waste (Balestri 2010).

Soils in the area are characterized by the presence of both detrital-alluvial sediments and the fall of pyroclastic material from the nearby Phlegrean Fields. Soils are known to be highly fertile soils. Accordingly, ancient Romans used to call the region Campania felix. The slopes are between 1 and 5 % and the elevation ranges from 42 to 150 m above sea level. Studied soils are sandy loam soils (from 54 to 71 % of the soil in the sand fraction), with a cation exchange capacity (CEC) ranging between 28 and 34 cmol+/kg. Soil pH is neutral to subalkaline (7.3–8.1), in agreement with the carbonate content (174 to 92 g/kg). Soil organic carbon is always below 2 %.

Sampling method

Samples were collected according to widely accepted procedures (Boudreault et al. 2012; Theocharopoulos et al. 2001). As a trade-off between economic constraints and the need for a detailed and adequate characterization of soil properties, a reasoned sampling criterion was defined, based on a two-level grid resolution. On the first level, a regular low-resolution grid was defined, which completely subdivides the three areas into 10×10-m cells (plots). On the second level, each grid plot was further subdivided into 3×3-m cells, so that, at the finer resolution level, each soil sampling point is about 3.3 m away from the next. Moreover, samples were collected from two soil layers: 'topsoil' layer (0–30-cm depth) and 'subsoil' layer (30–60-cm depth). An example of the sampling scheme, at the two levels, is shown in Fig. 2.

An aliquot (about 200 g) from each, previously homogenized, discrete high-resolution soil sample was used to make two 'mean composite samples' (MCSs): the first made up by the nine discrete topsoil samples taken within each 3×3-m plot and the second MCS from discrete subsoil samples taken within each 3×3-m plot, such that the two MCSs are representative of the topsoil and subsoil of each 10×10-m plot.

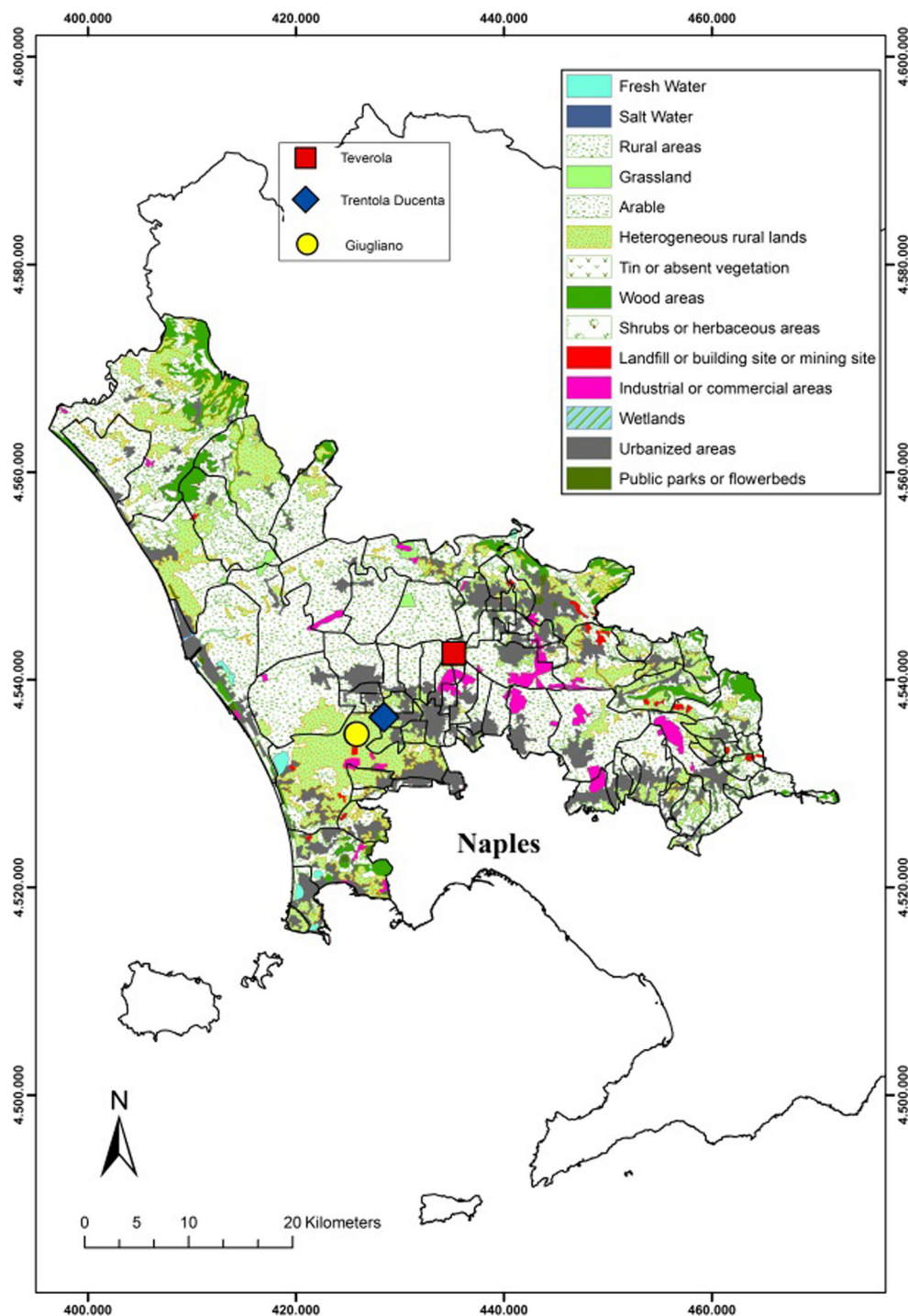
Analyses were made on all MCSs; if a topsoil or subsoil MCS was tagged as 'polluted', as specified below, analyses were extended to all discrete samples within that plot. We collected 16 MCSs and 144 discrete samples from Giugliano, 56 MCSs and 504 discrete samples from Trentola-Ducenta, and 27 MCSs and 243 discrete samples from Teverola. A hydraulic rotating drilling probe, MK 420 GEL (CMV, Italy), was used without the aid of drilling fluids, to preserve samples from contamination.

Each grid cell (plot) was named according to a unique criterion for all sites under investigation. Encoding follows the scheme 'XXYY/Z-K', where XX is a two-letter code and identifies the municipality of the site to be sampled (GI for Giugliano, TE for Teverola and TD for Trentola-Ducenta); YY is the low resolution (10×10 m) plot number; Z is a one-letter code indicating the sampling layer, where A stands for topsoil (0–30 cm) and B for subsoil (30–60 cm); K is a digit between 1 and 9 and identifies the discrete sample number within the 3×3-m plot. For example, GI02/A-1 indicates the first discrete topsoil sample from the second plot of the Giugliano site. In the case of an MCS, the sample number within the plot is missing and it is denoted merely by the code 'XXYY/Z'.

Analytical procedure

A hierarchical protocol for chemical analyses was designed. In the first stage of the analytical procedure, a screening analysis was carried out only on MCS. If an MCS was tagged as 'polluted', then a second stage was performed. We chose to

Fig. 1 Land use (from the Corine 2006 Land Use database) of the ‘Litorale Domitio-Agro Aversano’ SIN, as defined by Italian Law DM 80/2006. Symbols indicate the position of the three monitoring sites: *circle* Giugliano, *diamond* Trentola-Ducenta and *square* Teverola



tag an MCS as polluted if its hydrocarbon content exceeded a pre-defined threshold. Given the lack of a threshold for rural areas, we considered the limit established by Italian standards (defined by the Law Decree 152/2006) for HCs in residential or public green areas of 50 mg/kg of dry soil. Due to the dilution effect in the composite soil sampling procedure, we arbitrarily defined a limit for tagging an MCS as polluted at the value of 45 mg/kg, i.e. 90 % of the threshold for residential

or public green areas. This value was chosen because Italian Legislation does not define a limit for agricultural soil, so the limit of 50 mg/kg used for public green areas was reduced by 10 % for a more precautionary point of view.

Each MCS and discrete soil sample were prepared for the analysis according to the following procedure: air-dried and sieved at 2 mm, evaluation of dry residual at 105 °C and storage of samples in a dark room. Glassware and sample



Fig. 2 Sampling scheme for the Trentola-Ducenta site. *Red dots* represent low-resolution samples and *black dots* high-resolution samples

containers were washed with detergent solution followed by rinsing with purified water and acetone (analytical grade), respectively, and finally kept in an oven at 115 °C for one night. To avoid sample contamination, different glassware was used for standards and for solutions, and all the laboratory equipment was designed and constructed to control airborne contamination using air filtration at high exchange rates.

In the first stage, MCSs were analysed to determine heavy hydrocarbons (C>12) according to US-EPA method 8440 (1996) by Fourier transform infrared spectroscopy (FT-IR) and to determine PAHs according to US-EPA method 8270D (2007) by gas chromatograph coupled to a quadrupole mass spectrometer (GC/MS).

EPA method 8440 is based on extraction with 1,1,2-trichloro-1,2,2-fluoroethane (Freon 113) and FT-IR spectroscopy (PerkinElmer Spectrum One) of the extracted solution. This method is widely used for initial site investigation due to the relatively cheap price per sample, but the extraction efficiency is known to depend on the solvent, on the intrinsic variability of samples and on other sample properties (Schwartz et al. 2012). Because of these uncertainties, MCSs that showed a value close to the legal threshold (i.e. greater than 40 mg/kg of dry soil) were further analysed for HC content, according to the UNI EN ISO 16703 (2011) analytical method. According to this method, 20 g of soil sample was extracted with 80 mL of a mixture of acetone/*n*-heptane (60:20 v/v) and sonicated for 1 h. The extract was then shaken with water and purified by passing over a Florisil® clean-up column, reduced under a gentle stream of N₂ and analysed by GC-FID (Agilent Technologies 7890A) with a 30-m×0.25-mm capillary column, with a silicone-coated fused film 320 µm thick (J&W Scientific DB-5).

For every 15 samples, one sample was chosen and spiked with a standard of PAH and hydrocarbons for quality control determinations. For PAH, a mixture at 50 ng/mL was used and for heavy hydrocarbons a mixture of motor oil diesel (1:1 v/v) at 100 µg/mL. For PAH, the mean recovery range was from a minimum of 89 % to a maximum of 97 %. The mean recovery

for HCs ranged from 88 to 96 %, with worse precision for the more volatile and the last eluting compounds.

In the second stage, analyses were made on every discrete sample of each polluted plot, according to the MCS analyses, for both depths, such that each polluted plot was characterized by 18 samples. Measured analytical parameters were HCs (C>12) and 13 PAHs, many of which belong to the list of PAH priority pollutants defined by US-EPA (Yan et al. 2004). The list of analysed PAHs is reported in Table 1.

PAH analyses were made according to the EPA 8270D method (Wang and Fingas 2003), i.e. 10 g of soil sample was mixed with 5 g of anhydrous sodium sulphate, extracted with 25 mL of a mixture of acetone/cyclohexane (30/70 v/v), sonicated for 1 h, reduced to a few millilitres under a gentle stream of N₂ and purified passing over a silica clean-up column (according to EPA method 3620C). The reduced sample was then spiked with 1 mL of PAH surrogate standards and analysed by an Agilent GC (7890A) coupled to an Agilent Quadrupole Mass Spectrometer (5975 C) fitted with a 30-m×0.25-mm capillary column, with a silicone-coated fused film 250 µm thick (J&W Scientific DB-5MS).

Results and discussion

The most extensive area investigated was Trentola-Ducenta (TD) with 57 MCS samples, while the smallest area was Giugliano (GI), with only eight MCS samples; for the

Table 1 List of the detected PAHs

PAH	Rings	TEF ^a	Carcinogenic group ^b
Pyrene (Pyr)	4	0.001	3
Benzo(a)anthracene (BaA)	4	0.1	2B
Chrysene (Chr)	4	0.01	2B
Indeno(1,2,3-c,d)pyrene (IcdP)	6	0.1	2B
Benzo(b)fluoranthene (BbF)	5	0.1	2B
Benzo(k)fluoranthene (BkF)	5	0.1	2B
Benzo(a)pyrene (BaP)	5	1	1
Dibenzo(a,h)anthracene (BahA)	5	1	2A
Benzo(g,h,i)perylene (BghiP)	6	0.01	3
Dibenzo(a,e)pyrene (BaeP)	6	1	2B
Dibenzo(a,h)pyrene (BahP)	6	10	2B
Dibenzo(a,l)pyrene (BalP)	6	100	2A
Dibenzo(a,i)pyrene (BaiP)	6	10	2B

The number of aromatic rings, toxic equivalent factors (TEF) and carcinogenic groups are also reported

^a List by Nisbet and LaGoy (1992), Malcolm and Dobson (1994) and Bergvall and Westerholm (2007)

^b Group 1: carcinogenic to humans; group 2A, probably carcinogenic to humans; group 2B, possibly carcinogenic to humans; group 3, not classifiable as to its carcinogenicity to humans (IARC Working Group 2010)

Teverola (TE) site, the low-resolution sampling allowed 27 MCS samples to be collected. Figure 3 shows the boxplot of analytical results for HC MCS concentrations for the three sites. It can be noted that values often exceed the limit established by Italian environmental legislation (50 mg/kg of dry soil, also written as mg/kg dry weight (d.w.)) for the residential use of soils; the median concentration of analytical results for HC concentration for the Trentola-Ducenta (exploited for unauthorized waste dumping) and Giugliano sites (also subjected to unauthorized waste disposal and close to a heavily populated urban area) is 63 and 73.4 mg/kg d.w., respectively. For Teverola (the site used for the temporary storage of urban waste, now removed and dismissed), the median level is 35 mg/kg d.w., but several samples show an HC concentration well above the maximum allowed limit (outlier values in Fig. 3). Moreover, the experimental HC concentration in MCS samples spans a wide range of values (from 25 to 153 mg/kg d.w. for the Giugliano site, from 24 to 92 mg/kg d.w. for the Teverola site and from 12 to 170 mg/kg d.w. for Trentola-Ducenta, respectively). Taking into account the limited spatial extent of the study sites, such large variability implies strong spatial dishomogeneity.

The MC samples were used to estimate a large-scale mean value and to test for the null hypothesis of significantly different intersite mean levels. Since the samples did not show a Gaussian distribution because the values for all three sites were distributed in an asymmetric manner, the standard *t* test (Carter and Gregorich 2008) could not be applied. Instead, we resorted to the simple but effective bootstrap method (Efron 1979; Efron and Tibshirani 1994). The mean, median (assumed to be less sensitive to outliers) and skewness factor, together with their corresponding confidence intervals, were

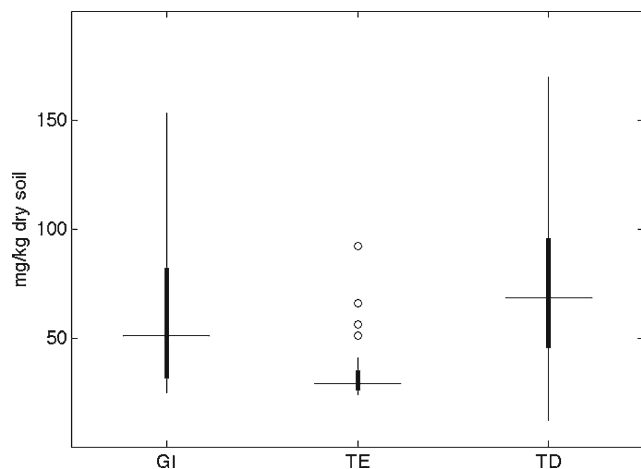


Fig. 3 Boxplot of heavy hydrocarbon concentration in SMC samples for the three sites (topsoil and subsoil samples merged). The horizontal line denotes the median value, while the thick black line spans the 25th–75th percentile and the thin lines (whiskers) cover the distance between 1.5 times below and above the interquartile range. Outliers (values outside whiskers) are plotted as circles. The plotted whiskers are truncated to the adjacent value, i.e. the most extreme data value that is not an outlier

estimated for the three sites and sampling depths. The basic bootstrap method was used to estimate the confidence intervals. Results are reported in Table 2.

Due to the small number of values, especially for the Giugliano site, the lower and upper limits extend across a wide range. Despite the limited number of values, the estimated skewness is always positive, suggesting the presence of right tails for the probability density functions of MCS values, though there is a slight probability of zero or even negative values in several cases. Moreover, apart from the Teverola site, skewness tends to be greater for subsoil samples, i.e. larger dishomogeneity is expected for subsoil samples, while pollutants are more homogeneously mixed in topsoil samples; for the Teverola site, the estimated mean (or median) values are close together for both the topsoil and subsoil samples. In rural sites, topsoil homogenization through ploughing and digging likely favours the incorporation of pollutants in the soil (Zampella et al. 2010).

Table 2 Results from the bootstrapping procedure for heavy hydrocarbon MC concentrations

Site	Parameter	Sampling depth	C_l	θ	C_u
GI	Mean	0–30 cm	43	70	94
	Median		26	63	94
	Std. dev.		20	36	56
	Skewness		−0.6	0.6	1.6
GI	Mean	30–60 cm	25	57	79
	Median		12	43	58
	Std. dev.		14	37	63
	Skewness		0.0	1.1	2.5
TE	Mean	0–30 cm	26	33	37
	Median		26	29	31
	Std. dev.		4	10	18
	Skewness		0.3	1.7	3.3
TE	Mean	30–60 cm	26	38	47
	Median		23	32	36
	Std. dev.		6	17	29
	Skewness		0.3	1.5	2.8
TD	Mean	0–30 cm	67	80	92
	Median		62	79	96
	Std. dev.		25	33	41
	Skewness		−0.2	0.3	1.0
TD	Mean	30–60 cm	45	62	77
	Median		39	57	77
	Std. dev.		21	36	50
	Skewness		−0.1	0.9	2.1

θ is the estimated MCS value, while C_l and C_u are the corresponding lower and upper levels encompassing an $\alpha=0.05$ significance level. The mean, median, standard deviation and skewness of each site and sampling depth are reported. All values are given as milligram per kilogram d.w.

For the Giugliano and Trentola-Ducenta sites, pollution levels are greater for topsoil samples, as inferred from both the mean and median values, while for the Teverola site, the estimated mean and median values for topsoil and subsoil samples are close together, and their confidence intervals are largely superposed, denoting increased spatial uniformity in the vertical column.

As already described in the “Analytical procedure” section, a hierarchical protocol was devised. If a plot was tagged as ‘polluted’, i.e. its topsoil or subsoil MCS value is greater than 45 mg/kg d.w. (90 % of the legal limit), a thorough analytical procedure was applied to every sample in that plot. At the second hierarchical level, analyses were made at a nesting ratio of 1:3, i.e. at 3×3 regularly spaced points for each plot. The screening procedure on MCS detected eight polluted plots out of 16 in the Giugliano site, four polluted plots out of 27 for Teverola and eight polluted plots out of 56 in Trentola-Ducenta.

These samples gave us the possibility to estimate the intra-plot variance at this small-scale spatial resolution. To this aim, the bootstrapping procedure was applied to estimate the variance between discrete soil samples belonging to the same plot.

Data presented in Table 2 for concentrations of heavy hydrocarbon in MCS show that values are higher in the topsoil than in the subsoil for GI and TD sites, while a converse trend was exhibited by the low polluted Teverola site (TE). Taking into account the high similarity in soil chemical properties among the studied soils, the converse trend exhibited in TE could be only related to a different disposal style in this site, which was interested by legal urban waste disposal. Likely, in this site, wastes were buried and covered by soil instead of being piled up on soil surface. Nevertheless, more information is needed to better explain this observation.

Results are reported in Table 3: the bootstrapping procedure was used to resample the analytical values of each plot and the mean and standard deviation (with respect to each plot mean) were estimated. For the Giugliano and Trentola-Ducenta sites, a large proportion of spatial variability already emerges at the smaller spatial scale, pointing out the dishomogeneity of pollutant spatial distribution. These two sites also show the highest intra-plot standard deviations and hydrocarbon concentrations, well above the Italian legal limit, especially for topsoil samples, achieving values as large as 140 and 134 mg/kg for Giugliano and Trentola-Ducenta topsoil samples, respectively. The deviations from each plot mean are of the same order of magnitude of mean concentrations. For the Teverola site (used for the temporary storage of urban waste for several years), the intra-plot spatial variability is about one order of magnitude lower than the average mean. Due to the high-resolution sampling scheme, such a large spatial variability is likely to imply strong horizontal gradients and dishomogeneously distributed pollutants, even within each plot.

Table 3 Average mean and intra-plot standard deviation for polluted heavy hydrocarbon concentrations from the bootstrapping procedure

Area	Parameter	Sampling depth	C_l	θ	C_u
GI	Mean	0–30 cm	75	140	220
	Std. dev.		17	111	236
GI	Mean	30–60 cm	33	61	108
	Std. dev.		4	62	162
TE	Mean	0–30 cm	31	34	39
	Std. dev.		4	6	7
TE	Mean	30–60 cm	53	60	66
	Std. dev.		3	11	18
TD	Mean	0–30 cm	105	134	168
	Std. dev.		14	48	116
TD	Mean	30–60 cm	63	75	89
	Std. dev.		4	21	41

θ is the estimated parameter (averaged over all polluted plots), while C_l and C_u are the corresponding lower and upper levels encompassing an $\alpha=0.05$ significance level. All values are given as mg/kg d.w.

Analysis was extended to selected PAHs (see Table 1). If a plot was tagged as ‘polluted’, based on results from HC concentrations, MCS PAH concentrations were determined, too; moreover, several plots were selected (the two most polluted plots from each site, according to MCS HC concentration) to test the effectiveness of bioremediation protocol within the Ecoremed project.

The bootstrapping procedure was applied to PAH concentrations as well. First, we tested the possibility of significant intersite or sub/topsoil differences between sample PAH concentrations, but for none of the selected PAHs, significant differences were detected. Table 4 shows synthetic statistics for each PAH. Heavy weight PAHs, i.e. dibenzo-pyrenes (see Table 1), were found at a negligible level, e.g. under the minimum detection level, since they are usually associated with contamination by heavy weight petroleum by-products, and results are not reported in Table 4 for them.

On the average (extended over all analysed top/subsoil samples and sites), we found a mean concentration for total PAH of 665 µg/kg d.w. and a median concentration of 459 µg/kg d.w. encompassing (with a 95 % probability density mass) the intervals [493, 928] and [355, 630] µg/kg d.w., respectively (see Table 4). The most represented components were pyrene and benzo(b)fluoranthene; it should also be noted that the average mean concentration for benzo(a)pyrene (88 µg/kg d.w.), the most extensively measured PAH around the world due to its proved carcinogenic property, is close to the Italian law limit (100 µg/kg d.w.) and exceeds this limit in nine cases (out of 38 MCS plots analyzed), of which two samples were in Giugliano, three in Teverola and four in Trentola-Ducenta.

Methods for PAH emission source identification include various multivariate statistical methods and complementary

Table 4 PAH ($\mu\text{g}/\text{kg}$ of dry weight) results for samples in polluted MCSs of Giugliano, Teverola and Trentola-Ducenta

Acronym	Mean	Median	Std. dev.	Skewness
Pyr	115 [85, 159]	80 [60, 100]	112 [24, 182]	2.9 [0.5, 5.0]
BaA	85 [62, 123]	57 [50, 70]	92 [13, 158]	3.3 [0.6, 5.4]
Chr	86 [62, 123]	61 [45, 85]	89 [14, 147]	2.9 [0.4, 5.1]
IcdP	45 [38, 55]	38 [30, 40]	25 [7, 39]	2.7 [0.5, 4.6]
BbF	117 [86, 163]	80 [60, 105]	113 [24, 184]	2.9 [0.8, 5.0]
BkF	57 [42, 80]	39 [30, 50]	55 [11, 91]	3.0 [0.7, 5.1]
BaP	88 [62, 129]	58 [45, 75]	99 [15, 168]	3.2 [0.6, 5.3]
BahA	19 [12, 27]	6 [5, 18]	23 [13, 31]	1.7 [0.4, 3.0]
BghiP	50 [39, 66]	36 [30, 40]	40 [12, 63]	2.7 [0.6, 4.6]
Sum of PAHs	665 [493, 928]	459 [355, 630]	638 [117, 1047]	2.9 [0.4, 5.0]

Data have been aggregated for each site and sub/topsoil sample. Lower and upper levels encompassing an $\alpha=0.05$ significance level are given in square brackets. For the meaning of PAH acronyms, see Table 1

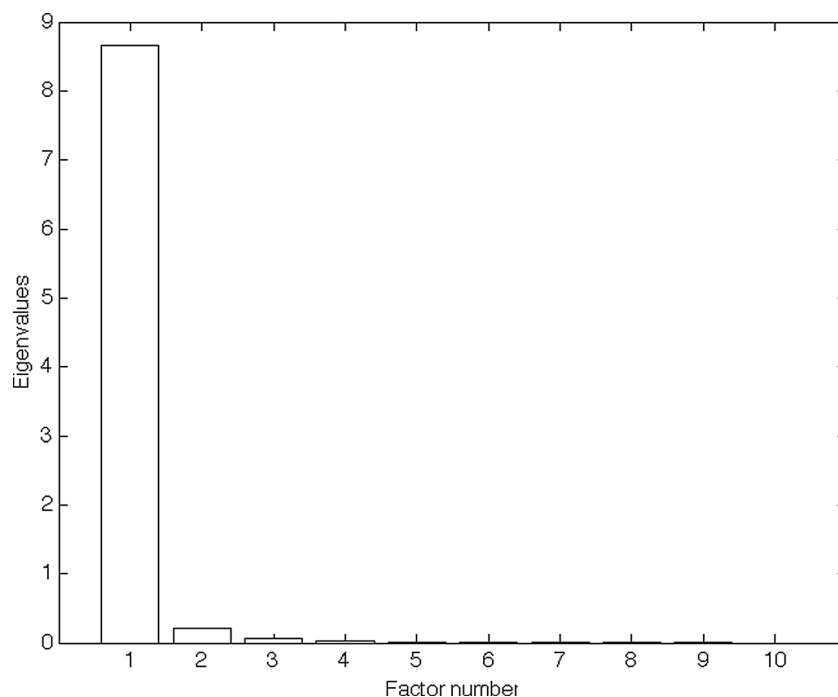
and alternatively to them the use of specific markers and diagnostic ratios of selected individual PAHs (Dvorská et al. 2011).

In this paper, principal component analysis (PCA, (Jolliffe 2005)) was performed to explain the total variability of the original PAH data. In order to determine the number of factors to retain, the simple Cattell scree test (Cattell 1966) and more sophisticated Horn's parallel analysis test (Horn 1965; Ledesma and Valero-Mora 2007) were undertaken. Cattell's scree test plots the eigenvalues of principal components onto the Yaxis and looks for an elbow towards a less steep decline. Horn's parallel analysis is a Monte-Carlo-based simulation method that compares the observed eigenvalues with those obtained from uncorrelated normal variables; a factor or

component is retained if the associated eigenvalue is greater than the 95th of the distribution of eigenvalues derived from the random data. Both tests indicated a variance almost totally (>96 %, see Fig. 4) explained by the first principal component, since neither the elbow was not located on the very left side of the scree plot with no doubts nor did all other components pass Horn's test. This suggests a unique source for all PAHs in the three investigated sites.

De Nicola et al. (2014) investigated the PAH contamination of the Naples urban area from soil and *Quercus ilex* leaves, showing a total PAH concentration ranging from 90 to 7700 $\mu\text{g}/\text{kg}$ d.w., with a median concentration of 890 $\mu\text{g}/\text{kg}$ d.w., i.e. a much higher concentration than that found in our three sites. In their paper, the authors identified fossil fuel

Fig. 4 Eigenvalues (sorted in decreasing order) of the correlation matrix for PAHs. Each eigenvalue represents the variance explained by the corresponding factor



combustion and vehicle traffic as prevailing PAH sources in the urban area and wood combustion and bush fires in areas furthest from the city centre.

Even if, across the Domizio-Flegreo Littoral and the Agro Aversano, several illegal waste dumps and the fallout of the soot produced by uncontrolled burning of agricultural and industrial waste have contributed to many degradation processes, the values of PAHs are still lower than those measured by De Nicola et al. (2014) in the urban area of Naples. Our analytical values are comparable to those of rural areas, as reported by Albanese et al. (2014). These findings highlight diffuse PAH contamination in the area examined and point to the leakage/spillage of storage tanks, during their use or transport, or their illegal abandonment and burial as a plausible cause of contamination. Our results indicate an exceedance of the legal concentration limit for benzo(a)pyrene (9 of 38 analysed cases).

Some PAH diagnostic ratios were calculated and compared to discriminating values reported in the literature (Table 5). The indeno(1,2,3-c,d)pyrene (IcdP)/(IcdP + benzo(g,h,i)perylene (BghiP)) ratio is in all three sites about 0.5, and the BbF/BkF ratio is about 2. These values indicate as preferential source a petroleum-diesel contamination. The benzo(a)anthracene (BaA)/(BaA + Chr) ratio suggests an anthropogenic source, and the BaP/BghiP ratio excludes the vehicle traffic sources in accordance with the previous diagnostic ratios that suggest a petroleum combustion/disposal. This interpretation is reinforced by the observation, during the sampling phase, of numerous barrels and heaps of waste burned. However, PAH diagnostic ratios should be used with prudence because chemical and natural processes can alter the PAH member pattern during their transport from the emission source to the sampling point (Krumal et al. 2013).

While De Nicola et al. (2014) suggest vehicular traffic as a PAH source in urban areas and wood combustion in remote areas, our diagnostic ratio suggests that activities related to petroleum use (combustion or disposal) can be considered as significant sources. According to Albanese et al. (2014), little

could be done to clean up a so large area with a so high spatial variability.

Conclusions

This study allowed characterization of soil pollutant distribution in three sites in the so-called Land of Fires area in the southern Italian region of Campania. Soil samples were analysed to survey pollution levels for both HC and PAH concentrations.

The results of our investigation, on one of the most controversially debated polluted regions in Italy, showed a worrying scenario for rural areas subject to known unauthorized waste disposal and burning. In all cases, the dumping of waste contaminated the sites considered here, above Italian legal limits. In most cases, the maximum admissible Italian law limit for HCs (50 mg/kg d.w., according to Law Decree 152/2006) was exceeded, such that these areas can be considered contaminated for residential or recreational use.

Our hierarchical sampling protocol, based on ‘topsoil’ layer (0–30-cm depth) and ‘subsoil’ layer (30–60-cm depth), showed large dishomogeneity in soil pollutant spatial distribution, even at a scale as small as 3.3 m. As a consequence, it is reasonable to imagine a leopard-spot distribution of soil pollutants, whose detection and health hazard diagnosis suggests the importance of more detailed soil surveys and samplings than those performed so far.

Due to extensive wide area involved (about 2400 km²), it is reasonably unworkable to use our hierarchical sampling protocol to evaluate the soil pollution level at such a high sampling density and the application of industrial processes for soil restoration. To reduce population exposure, combat unemployment and boost the local economy, the location and control of contaminant source emissions will be decisive, starting with a large programme of bio- and phyto-depuration compatible with the contamination condition.

Table 5 Diagnostic ratios of MCS mean values

	Value range	Source	GI (mean)	TD (mean)	TE (mean)
IcdP/(IcdP + BghiP) ^a	>0.5	Grass, wood, coal combustion	0.50	0.50	0.46
	0.2–0.5	Petroleum combustion			
	0.1–0.5	Petroleum disposal			
BbF/BkF ^b	>0.5	Diesel	2.06	1.96	2.00
BaA/(BaA + Chr) ^c	<0.2	Petrogenic	0.50	0.51	0.51
BaP/BghiP ^b	<0.5–0.6	Vehicle traffic	1.60	1.81	1.73
	>1.25	Coal			

^aYunker et al. (2002)

^bKozielska and Koniecznyński (2015)

^cDvorská et al. (2011)

Comparing all available data in the scientific literature, it is not yet possible to ascertain the soil pollution situation in these provinces mainly due to the lack of a regional soil database and comparable data, especially trend data, from which evidence of change can be found. In addition to these reasons, there is the need to raise awareness of the extremely high spatial variability of contamination even at a scale of a few metres. The high-resolution sampling scheme, applied in this work, allows to put in evidence a large short-range spatial variability of organic pollution, which could not be detected by low-resolution sampling schemes as those used in previously published papers.

Based on data in this study, the levels of pollutants are still high in the sampling soil to a depth of 60 cm. It is hard to answer to what depth of soil had been polluted in the studied region; more investigation on deeper depths is recommended in future soil pollution studies. Further evidence of the bio-availability of the pollutants and their role in the food chain will also be necessary.

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