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The occurrence of OCPs, PCBs, and PAHs in the soil, air, and bulk deposition of the Naples metropolitan area, southern Italy: Implications for sources and environmental processes

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ABSTRACT

I am often reminded of the famous saying of Goethe: "Vedi Napoli e poi muori! - See Naples and die!". Sadly, Naples is now confronted with a number of serious, ongoing problems with a need to alleviate pressure on the worsening environment. One serious problem facing the environment is the presence of the potentially hazardous persistent organic pollutants (POPs), although few systematic studies at regional scale have been conducted. In this study, samples of soil, air, and bulk deposition were collected in Naples metropolitan area (NMA) to characterize the status of POPs, including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). The results obtained showed that most of these compounds are pervasive in all the studied environmental matrices, especially in some hotspot areas, such as the Bagnoli Brownfield Site and the infamous "Triangle of the Death", where unwanted ecological risk conditions for PAHs and Endosulfan were determined, respectively. The interactional complexity between urban and the surrounding rural areas was also confirmed, as is the role that urban areas play in the migration and transformation process of POPs. High urban-rural gradients for atmospheric PAHs and PCBs were observed in the NMA, and the urban areas were identified as the emission source of these contaminants. Similarly, the OCP residues, historically originated from the nearby agricultural regions, experience long-term soil re-emission and continuously influence the connected urban environment via atmospheric transport processes.

1. Introduction

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), are well-known persistent organic pollutants (POPs) that resist degradation and exert toxic effects on the environment (Haddaoui et al., 2016; Pozo et al., 2006; Ravenscroft and Schell, 2018). For decades, the addition of POPs into the environment from anthropogenic sources has dropped sharply through the use of effective control methods, which has been greatly beneficial to lightening the pressure of POP pollution. However, a feature of many POPs is a moderate vapor pressure, and may revolatilize to the atmosphere from POP-contaminated soils, sediments, buildings, or equipment (Růžičková et al., 2008; Tao et al., 2008; Wang et al., 2011). In general, as the economy develops, cities experience tremendous pollution by POPs, which has attracted widespread attention (Diefenbacher et al., 2015; Harner et al., 2004; Wang et al., 2011). The presence of POPs in environmental matrices is driven, in large part, by their local historical application and atmospheric transport (Aichner et al., 2013; Wang et al., 2016). In reality, urban areas serve either as emission sources of PCBs (e.g., from discarded electrical equipment) and PAHs (e.g., from coal combustion and vehicle emissions), or receptors of OCPs (e.g., from agricultural activities) releasing from the

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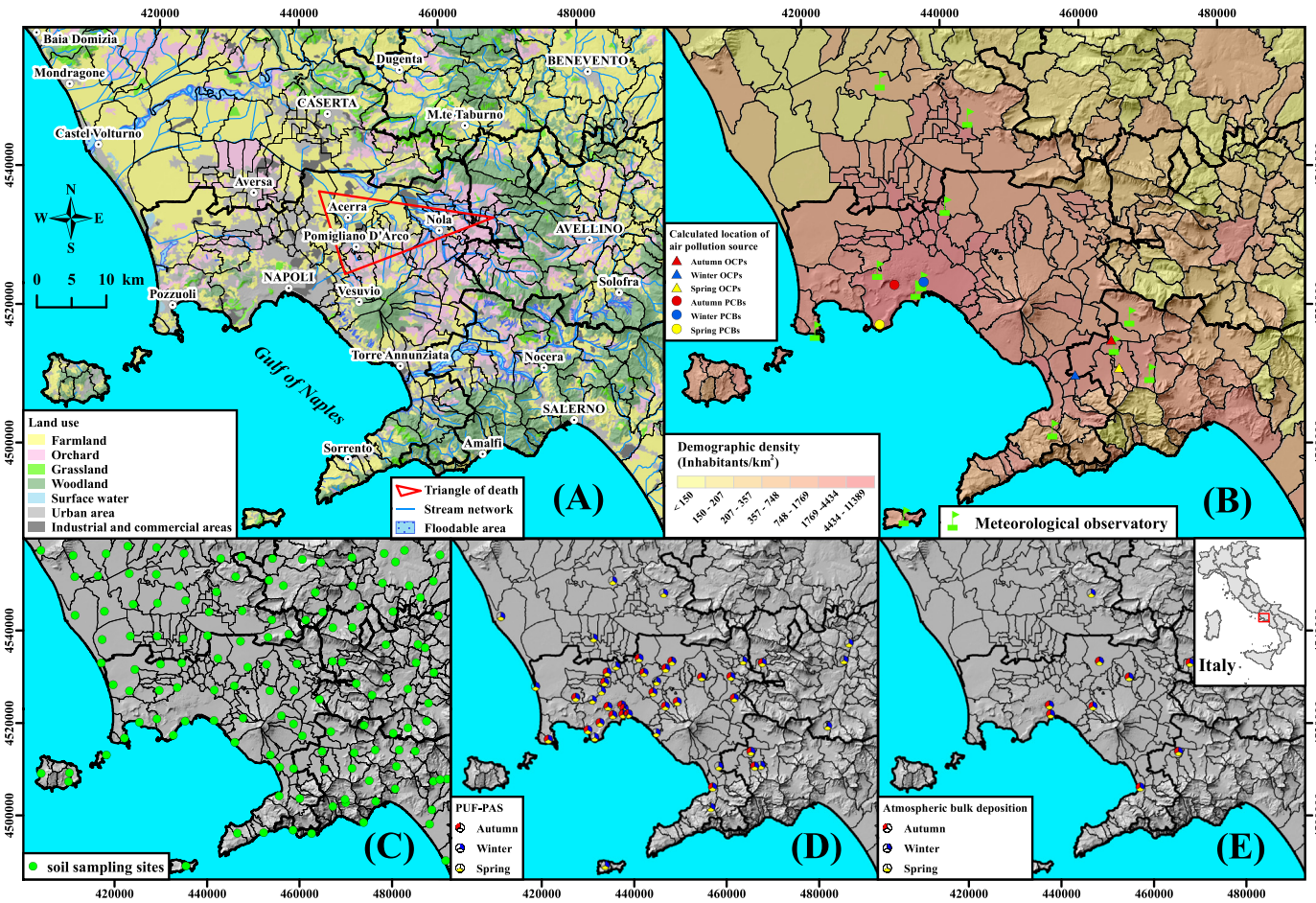

Fig. 1. (A) Map of the different land uses within the study area; (B) Map showing the calculated location of air pollution source based on a Gaussian diffusion model; (C) Location of soil sampling sites; (D) Location of passive air sampling sites; (E) Location of atmospheric bulk deposition sites.

surrounding farming areas (Harner et al., 2004; Heywood et al., 2006). Within urban areas, potential emission sources are diverse, and thus how they are characterized is problematic (Diefenbacher et al., 2015). High-density spatial sampling is an approach used to identify "hot spots" and possible sources. Until recently, the research into POPs with large sample sizes in a multimedia environment, but particular in the atmosphere, is regrettably scarce, with sample sizes often restricted by cost and logistics. To handle these problems, passive sampling has been an increasingly popular technology that contributes to the understanding of environmental significance and ultimate fate of POPs (Qu et al., 2018).

Naples is the capital of Campania region, and one of the largest municipalities in Italy. Today, the environmental deterioration in the Naples metropolitan area (NMA) is considerable and lamentable, and is closely correlated with increasing rates of cancer (Qu et al., 2016; Senior and Mazza, 2004). To the northeast of the NMA, for example, the long-term illegal dumping of waste, have spawned a high incidence of cancer, known as "Triangle of Death" (Senior and Mazza, 2004) and research on potentially toxic metals struggle to explain the "phenomenal rise in cases of cancer" in this area. Potentially toxic metal anomalies, such as Pb and Sb, have been linked to male infertility and cancer mortality in the NMA (Albanese et al., 2013; Giaccio et al., 2012). However, limited research performed to date in the NMA, has probed the cancer risk from the perspective of POP contamination (Albanese et al., 2015; Qu et al., 2016; Qu et al., 2017). Knowledge of the spatio-temporal distribution of POPs in the environment is a prerequisite for implementing an accurate assessment of the distribution of "hot spots", which contribute to the understanding of how these toxics influence health. With the exception of soil sampling campaigns, a regional monitoring network for the presence POPs had yet to be established in the NMA. This lead to the current project, a novel investigation into the occurrence of POPs in the soil, air, and bulk deposition of the NMA.

Polyurethane foam-based passive air samplers (PUF-PAS) are the most effective devices for monitoring POPs on a regional scale, and has been recently used to measure metal concentrations in air (Li et al., 2018). They are excellent for generating spatially and seasonally resolved data (Qu et al., 2018). Here, we established a network of PUF-PAS and bulk deposition samplers across the Campania region, and simultaneously collected surface soil samples. Our goals include to (i) provide a geochemical baseline database of OCP, PCB, and PAH concentrations in soil, air, and bulk deposition; (ii) illustrate their spatio-temporal trends, and potential local sources; (iii) assess possible factors contributing to pollutant concentrations; and (iv) gain insights into the environmental fate and transport of POPs. The complexity of an urban environment resulting from industrial and anthropogenic activities has caused difficulty in the understanding of the ultimate fate and potential influence of POPs in the neighboring and distant. To our knowledge, our work is the first systematic study of the metropolitan-scale monitoring of POPs in a multimedia environment using a high-density spatial sampling method. The sampling and interpretative methodology resulting from this study will become a reference for other similar studies in other metropolitan areas of the world.

2. Methodology

2.1. Sampling

A large-scale field campaign, managed by Istituto Zooprofilattico Sperimentale del Mezzogiorno (IZSM), Portici, under the scientific responsibility of Prof. B. De Vivo, has been implemented within the framework of Project Campania Trasparente. In this program, water, soil, air, and biological samples across the whole region, have been collected, and persistent toxic substances including OCPs, PCBs, PAHs, and potentially toxic metals, have been measured, with the purpose of characterizing the environmental conditions of the Campania region. This study is a product of the aforementioned program. Details regarding the sampling campaign are provided in Qu et al. (2018) with an outline of these procedures reported here.

2.1.1. Soil

A systematic soil sampling approach was implemented by employing a grid of 6 × 6 km. Within each sampling cell, samples were produced by mixing five subsamples at depths between 0 and 5 cm collected within a radius of 5–10 m. All samples were wrapped in aluminum foil, sealed in polyethylene-zipped bags, and stored at −20 °C prior to analysis. A total of 417 soil samples were collected across the whole regional territory between December 2014 and February 2015 (Fig. S1). In the study, 134 soil samples were extracted from the soil database, as illustrated in Fig. 1.

2.1.2. Passive air sampler

Details of the PUF-PAS described briefly here can be found in detail elsewhere (Qu et al., 2018). The monitoring network ultimately contained at approximately 150 sites, and the implementation of the project is divided into two stages: first pilot study in the NMA and its surrounding regions, and then investigation of atmospheric POPs in the territory of the greater Campania region. The sampling campaign lasted from July 2015 to April 2017 with 3 monthly integration periods, and the sampling period was an initial three seasons in the first stage, and four seasons in the second stage.

The first pilot study is presented in this study, involving data collected in autumn (July to October 2015), winter (October 2015 to January 2016) and spring (January to April 2016) (Fig. 1). 10 days before sampling, PUF disks were Soxhlet extracted with dichloromethane (DCM) for 48 h, dried in a clean desiccator, and subsequently spiked depuration compounds (DCs) (Moeckel et al., 2009). PCB congeners 54, 104, and 188 were used as the DCs to calibrate the site-specific sampling rate (R_s) in the first season of the first stage, and $^{13}C_{12}$-labeled PCB congeners 31, 70, 95, 153, and 180 were used in the subsequent sampling campaign. After retrieval, PUF samples were sent back to the laboratory for analysis.

2.1.3. Atmospheric bulk deposition

Nine sets of atmospheric bulk deposition samplers were deployed synchronously with the sampling campaign of PUF-PAS in the first pilot stage (Fig. 1). Schematic of sampling apparatus is visually represented in Fig. S2. Samples of bulk deposition were achieved using a coating polyethylene funnels with an inner diameter of 20 cm. They were filtered *in situ* through pre-combusted (4 h at 450 °C) Whatman™ glass microfiber filters (GF/F, 90 mm diameter, 0.7 μm retention size), and the filtrated water were collected in a 10 L glass bottle wrapped with aluminum foil. A detailed description of the sampling process is referred to in previous literature (Li et al., 2010). After collection, all samples were preserved in a car refrigerator, immediately transferred to the laboratory, and stored at −20 °C until analysis.

2.2. Chemical analysis

Three types of POPs have been analyzed in each sample:

OCPs: HCHs (α-, β-, γ-, and δ-HCH), DDTs (*p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, *o,p′*-DDE, *o,p′*-DDD, and *p,p′*-DDT), HCB (Hexachlorobenzene), Endosulfans (α-Endosulfan, β-Endosulfan, Endosulfan sulfate), Chlordanes (cis-Chlordane, trans-Chlordane), Nonachlors (cis-Nonachlor, tran-Nonachlor), DRINs (Aldrin, Dieldrin, and Endrin), Heptachlor, Mirex, Methoxychlor.

PAHs: 16 USEPA priority PAHs [Acenaphthene (Ace), Acenaphthylene (Acy), Anthracene (Ant), Benz(a)anthracene (BaA), Benzo(a)pyrene (BaP), Benzo(b)fluoranthene (BbF), Benzo(ghi)perylene (BghiP), Benzo(k)fluoranthene (BkF), Chrysene (Chr), Dibenz (a,h)anthracene (DBA), Fluoranthene (Flu), Fluorene (Fl), Indeno (1,2,3-cd)pyrene (IcdP), Naphthalene (Nap), Phenanthrene (Phe), Pyrene (Pyr)], and DBPs [Dibenzo(a,e)pyrene (DBaeP), Dibenzo(a,h) pyrene (DBahP), Dibenzo(a,i)pyrene (DBaiP), Dibenzo(a,l)pyrene (DBalP)].

PCBs: Dioxin-like PCBs (DL-PCBs: PCB81, PCB77, PCB123, PCB118, PCB114, PCB105, PCB126, PCB167, PCB156, PCB157, PCB169, PCB189), and Marker PCBs (M-PCBs: PCB28, PCB52, PCB101, PCB153, PCB138, PCB180).

All analyses were accredited by ISO 17025 laboratory, and the Quality Assurance/Quality Control (QA/QC) followed protocols established in EPA 1668C and 1699. The details of the analytical procedures and QA/QC are described in Text S1 of the Supporting Information (SI).

In addition, soil physiochemical properties including total organic carbon (TOC), pH, and particle-size distribution, were also measured in all soil samples, and the detailed analytical methods are presented in Text S1.

2.3. Data processing and statistical analyses

For the purpose of data analysis, "non-detect" data points were designated as analyses with levels of one-half of the detection limit (DL). A probability of $p < 0.05$ was regarded as the significant level. The data deviated from a normal distribution (Kolmogorov-Smirnov test, $p < 0.05$), thus non-parametric statistics were performed using the SPSS 19.0. Spearman's correlation was used to measure the relationship between pairs of variables. Spatial and seasonal variations of POP concentrations were compared using Kruskal-Wallis and Mann-Whitney tests. Species sensitivity distribution (SSD) was generated using R 3.3.3 software (Qu et al., 2017). With the MATLAB R2012b software, the soil mass inventory of POPs was estimated, and Gaussian diffusion model was built. Spatial distribution maps of POPs in soils were produced by Multifractal Inverse Distance Weighted (MIDW) method, and subsequently, the concentration intervals were defined by means of the concentration-area (*C-A*) method (Qu et al., 2016).

3. Results and discussion

3.1. General comments regarding POP concentrations

3.1.1. Soil

The statistical results of the quantity of OCPs, PCBs, and PAHs in soils are tabulated in Tables S3–S5. All the target compounds were detected in soil. Levels of Σ_{24}OCPs, Σ_{18}PCBs and Σ_{16}PAHs greatly varied between locations, ranging by over roughly four to five orders of magnitude. The soil concentrations at all sampling sites were 0.076–193, < DL-23.7, and < DL-4191 ng/g for Σ_{24}OCPs, Σ_{18}PCBs, and Σ_{16}PAHs, with geometric mean (Gmean) values of 3.84, 0.73, and 73.3 ng/g, respectively.

Among the OCPs, ΣDDTs were the dominant OCPs contributing to 77.1% of the Σ_{24}OCPs, followed by ΣEndosulfans (9.91%), ΣDRINs (4.93%), and ΣHCHs (2.45%). In the soils of the Campania region, predicted no-effect concentrations (PNEC) were estimated to be 1.71 and 57.8 ng/g for ΣEndosulfans and ΣHCHs, respectively (Qu et al., 2017). In this study, almost one-fifth of samples exceeded the PNEC for Endosulfans, while all samples were located below the PNEC for HCHs

(Table S3). The potential ecological risk caused by Endosulfan here was also concluded by Qu et al. (2017).

Of the PCB congeners measured, higher molecular weight (HMW) congeners were abundant and mostly dominated by hexa-, hepta-, penta-PCB at ~35.0%, 29.3%, and 13.6% of the total PCBs (Table S4), respectively, of a similar proportion to previous studies (Heywood et al., 2006; Meijer et al., 2003). Concentrations of marker PCBs (ΣM-PCBs) contributed up to 85.9% of Σ_{18}PCBs. The profile of the individual marker PCBs was 37.4% PCB180, 27.6% PCB153, 26.9% PCB138, 6.57% PCB101, 0.98% PCB52, and 0.53% PCB28. This likely reflects the impact of the use of common technical PCB mixtures, such as Clophen A60 and Aroclors 1254 and 1268, since these commercial products mainly contain hexa-, hepta-PCB (PCB138, PCB153, and PCB180 as most abundant constituents) (Aichner et al., 2013).

Σ_{16}PAHs in soils were dominated, similarly to PCBs, by HMW PAHs (4, 5 and 6 rings); more specifically, Flu, BbF, Pyr, and Chr were abundant and contributed on average for ~16.5%, 11.5%, 11.2%, and 9.70% of the Σ_{16}PAH, respectively (Table S5). This is consistent with previously reported studies in Britain, Germany and Hungary (Aichner et al., 2013; Degrendele et al., 2016; Heywood et al., 2006). By building the SSD model, the PNEC values of BaP were estimated to be 422 ng/g (Fig. S3). The BaP_{eq} concentrations of Σ_{16}PAHs in three sites, located near Bagnoli and Acerra, were above the aforementioned trigger limit value. The findings are well anticipated due to notorious reputation for serious pollution of those areas, so-called "Bagnoli Brownfield Site" and "Triangle of Death", respectively (Albanese et al., 2015; De Vivo and Lima, 2018).

A preliminary survey of OCP and PAH contamination in soils of the Campanian plain was completed in 2011 (Albanese et al., 2015; Qu et al., 2016; Qu et al., 2017). The concentrations of some OCPs and Σ_{16}PAH in this study were significantly correlated with the former study, including ΣDDTs ($r^2 = 0.18$, $p < 0.01$), ΣHCHs ($r^2 = 0.11$, $p < 0.01$), ΣEndosulfans ($r^2 = 0.076$, $p < 0.05$), ΣDRINs ($r^2 = 0.058$, $p < 0.05$), and Σ_{16}PAH ($r^2 = 0.30$, $p < 0.01$) (Fig. S4). This reflected the consistency of hotspot identification, which high levels of OCPs and PAHs occurred in the Bagnoli, Acerra, and Sarno (Fig. 2). In addition, the abundance of HCB, ΣEndosulfans were similar to those reported in the survey of 2011; however, the abundance of ΣDDTs, ΣHCHs, ΣChlordanes, Heptachlor, and Σ_{16}PAH were all significantly lower than the Gmean value of 2011. Different sampling strategies and analytical methodology may explain the reduced tendency between the two sampling campaign.

3.1.2. PUF-PAS

A volumetric air concentration (pg/m^3) for target compound was derived from the amount of compound sequestered in the PUF (pg/PUF) divided by R_s (m^3/day) and the sampling time (days). The R_s was estimated by the DC method, and the detailed information for this method is presented in Text S2. R_s and derived air concentrations are illustrated in Fig. S5. Previous studies have suggested that the R_s is approximately 3–4 m^3/day (Moeckel et al., 2009; Pozo et al., 2006). The site-specific R_s in this study was 3.58 ± 1.18, 3.13 ± 1.38, 3.72 ± 1.66 m^3/day in autumn, winter, and spring, respectively. This result was well correlated with the Global Atmospheric Passive Sampling (GAPS) study, which yielded the R_s of 3.90 ± 2.00 m^3/day (Pozo et al., 2006). Local factors (i.e., temperature, wind speed, and atmospheric particles) might conceivably be the source of variability in the site-specific R_s (Qu et al., 2018).

The air concentrations of Σ_{24}OCPs, Σ_{18}PCBs, and Σ_{16}PAHs during the entire sampling campaign were 40.4–2932, 8.53–707, and 4708–842,577 pg/m^3, with a GM value of 231, 46.6, and 33,634 pg/m^3, respectively. Compared with the GAPS study, levels of ΣHCHs, ΣChlordanes, Dieldrin observed here were similar to those recorded in the global atmosphere, and ΣEndosulfans were below the global average, conversely, ΣDDTs and Σ_{18}PCBs were higher than the global average (Pozo et al., 2009). Seasonal variability in atmospheric concentrations of most OCPs, PCBs, and PAHs were evident ($p < 0.05$). As shown in Fig. 2, the levels of Σ_{24}OCPs in autumn and winter were similar, but significantly higher than in spring; Σ_{16}PAH in winter and Σ_{18}PCBs in autumn were significant higher than that of the other two seasons ($p < 0.05$).

For all seasons, the levels of Σ_{16}PAHs and Σ_{18}PCBs in urban areas were significantly higher than those of rural areas ($p < 0.05$), with approximately twice the difference in abundance between areas. This is similar to previous research reporting high urban/rural gradients for PAHs and PCBs (Harner et al., 2004; Hong et al., 2016; Motelay-Massei et al., 2005). A large population may imply higher local PAH concentrations in the air as the result of energy consumption (Hafner et al., 2005). However, only spring air concentrations of PAHs displayed a significant negative correlation with local human population ($r^2 = 0.091$, $p < 0.05$) in this study. The finding is unintelligible, however, we hypothesize that this can be the result of the difference in spatial resolution between the population and air sampling density. This is supported by a clear positive correlation between soil PAHs and population ($r^2 = 0.25$, $p < 0.01$). Breivik et al. (2002) predicted that current global concentrations of PCBs in air originate mainly from emanations existing and disposed equipment containing PCBs. These findings corroborate the continuing role of urban areas as emission sources of PAHs and PCBs. Regional variations for Σ_{24}OCPs were not shown, however, the abundance of ΣDDTs, and winter and spring ΣEndosulfans showed a strong urban/rural gradient.

3.1.3. Atmospheric bulk deposition

Atmospheric bulk deposition fluxes of OCPs, PCBs, and PAHs are presented in Fig. S6. The deposition fluxes of Σ_{24}OCPs, Σ_{18}PCBs, and Σ_{20}PAHs showed no seasonal variation ($p > 0.05$). The deposition fluxes of Σ_{24}OCPs ranged from 0.52 to 3.48 ng/m^2/day, with an arithmetic mean (Amean) value of 1.42 ng/m^2/day. The most frequently observed OCPs were HCB, *p,p′*-DDT, *α*-HCH, *β*-HCH, and *o,p′*-DDT, whereas HCB, ΣDDTs, and ΣEndosulfans were the most abundant, contributing average ~89.7% of the Σ_{24}OCPs. The deposition fluxes of ΣHCHs and individual cyclodienes observed here have persisted at a low level compared with values reported in literature (Cindoruk and Tasdemir, 2014; Huang et al., 2014; Jakobi et al., 2015; Li et al., 2010), but the HCB deposition fluxes were much higher than those in three alpine areas, namely Zugspitze, Sonnblick, and Weissfluhjoch (Jakobi et al., 2015). The deposition fluxes of ΣDDTs were significantly lower than those reported in Zugspitze (Jakobi et al., 2015) and the Pearl River Delta (PRD) (Huang et al., 2014; Li et al., 2010), and higher than those in Sonnblick and Weissfluhjoch (Jakobi et al., 2015).

The deposition fluxes (ng/m^2/day) of Σ_{20}PAHs varied between 18.8 and 278 (Amean = 88.8), and this levels were much lower than those in the PRD (Li et al., 2009; Li et al., 2010), Hong Kong (Liu et al., 2013a), and Turkey (Esen et al., 2008). Flu, Phe, Pyr, Chr were the major compounds detected, accounting for 18.4%, 18.3%, 14.0%, and 9.22% of the total PAH deposition fluxes, respectively. The deposition profile was similar to the finding of the aforementioned study (Esen et al., 2008; Li et al., 2009; Li et al., 2010). The deposition fluxes (ng/m^2/day) of Σ_{18}PCBs ranged from 0.075 to 1.22 (Amean = 0.33), and their pattern were dominated by PCB180 (20.1%), PCB153 (16.7%), PCB138 (16.6%), and PCB28 (16.6%). tetra-PCB contributed ~63.4% of the total PCB deposition fluxes, followed by hexa-PCB (9.49%), tri-PCB (8.75%), and hepta-PCB (6.74%). The levels of PCBs, PAHs, and HCB deposition fluxes in this study were all lower than those reported around the industrial district of Porto Marghera, northern Italy (Rossini et al., 2005).

3.1.4. Source identification

Molecular indices based on ratios of selected OCP and PAH concentrations might yield insight regarding source apportionment. Scatterplots of the ratios used to identify OCP and PAH sources are presented in Fig. S7. The principles behind the use of molecular indices

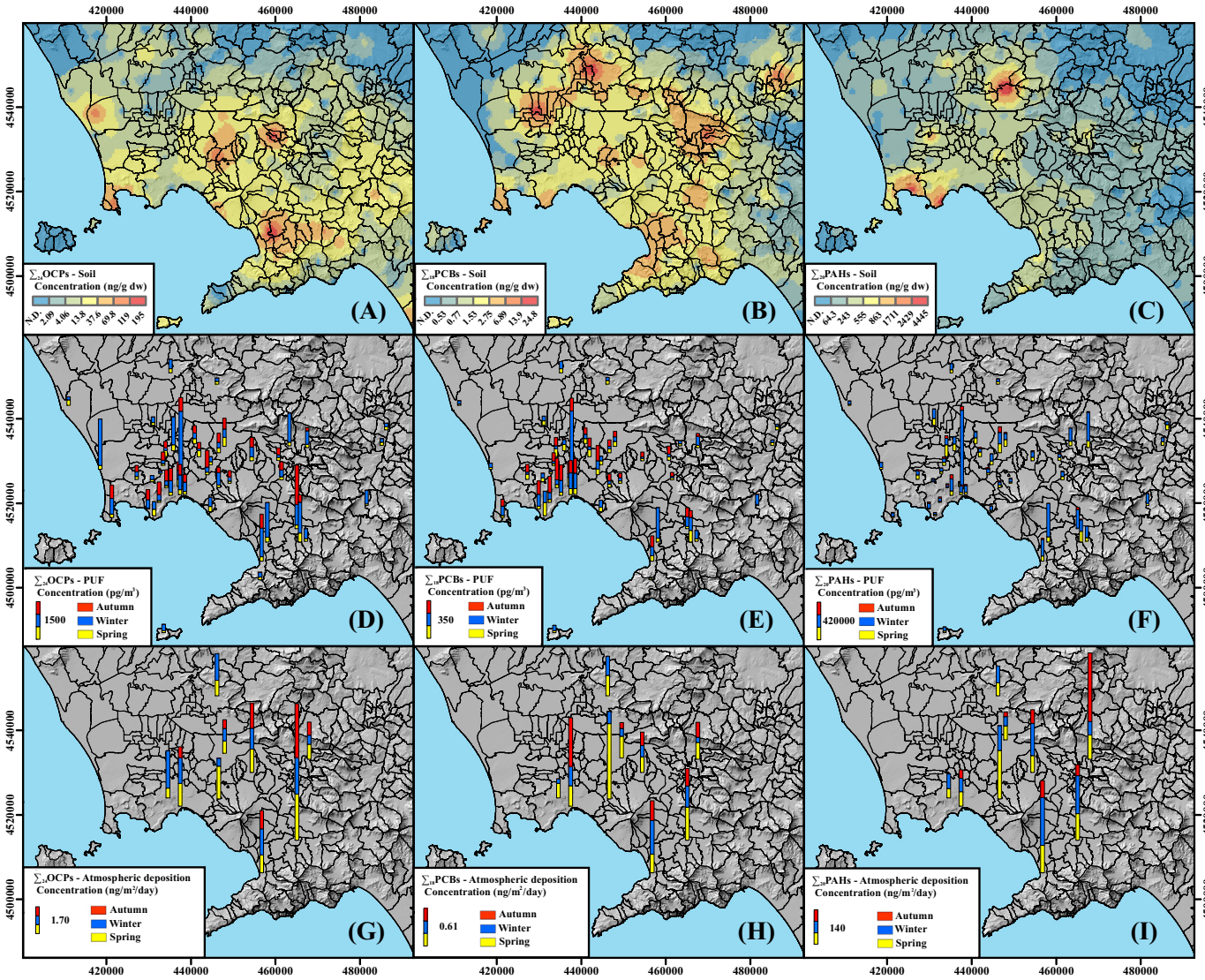

Fig. 2. Map showing the Multifractal IDW results for the geochemical data of POPs in the soils: (A) Σ_{24}OCPs, (B) Σ_{18}PCBs, and (C) Σ_{20}PAHs; Spatial distribution of Σ_{24}OCPs, Σ_{18}PCBs and Σ_{20}PAHs in the air (D, E, F, respectively), and bulk deposition (G, H, I, respectively) of the Naples metropolitan area, southern Italy in autumn, winter, and spring, respectively.

as tracing signatures is described in detail elsewhere in the literature (Qu et al., 2016; Qu et al., 2017; Qu et al., 2015).

In the Campania region, the residues of HCHs, DDTs, Endosulfan, and Chlordane in soil, sediment, bird, and marine species are ultimately dependent on their historical use (Naso et al., 2003; Naso et al., 2005; Qu et al., 2016). This conclusion is supported by the current soil research as well as the air, and bulk deposition results. The use of Endosulfan in Campania was briefly permitted for mite control on hazelnut trees in 2008 and 2009 (Qu et al., 2017). As illustrated in Fig. S7, lower α/β-Endosulfan ratios (~2.3) in air suggests the more recent usage of technical Endosulfan (Qu et al., 2015). This relatively low level of *o,p′*-DDT/*p,p′*-DDT ratio precluded the possibility of the "dicofol-type DDT" pollution (Fig. S7), which was also determined in previous studies (Qu et al., 2016).

PAH congener ratios in air and soil are clustered together, although the ratios did fluctuate in atmospheric deposition results presumably due to low sampling density (Fig. S7). This, in fact, reflects the relative stability of source patterns of PAHs. This finding illustrated that Italy, like other early-industrialized countries (e.g., Germany and United Kingdom), is now strongly affected by stable, non-point source, diffuse legacy PAH contamination (Liu et al., 2013b). The patterns of atmospheric PAHs, which were independent of concentration, support this inference (Fig. S8). The ratios of Flu/(Flu + Pyr), BaA/(BaA + Chr), and IcdP/(IcdP + BghiP) for all samples were concentrated in 0.5–0.7, 0.2–0.6, and 0.2–0.5, respectively, suggesting combustion of petroleum and biomass/coal. The ratios of Ant/(Ant + Phe) in soil samples distributed bilaterally to the distinguishing value of 0.1 (Amean = 0.16), and they were generally below 0.1 in air and atmospheric disposition samples. This implied that petrogenic sources exist widely, and pyrogenic sources continue to contribute to soil PAHs. Ant may undergo direct or indirect photolysis during atmospheric transport, thus, the ratios of Ant/(Ant + Phe) would deviate and should be used with caution (Kamens et al., 1988).

3.2. The potential role of soil as POP sources or sinks

3.2.1. Soil mass inventory

The soil mass inventory of POPs were calculated using Monte Carlo method described in detail by Qu et al. (2016), and also provided in Text S3. The results of POP inventory are displayed in Figs. 3 and S9–S11. Overall, the Gmean inventory of Σ_{24}OCPs, Σ_{18}PCBs, and Σ_{20}PAHs was 2.05, 0.21, and 25.6 metric tons, respectively. DDTs

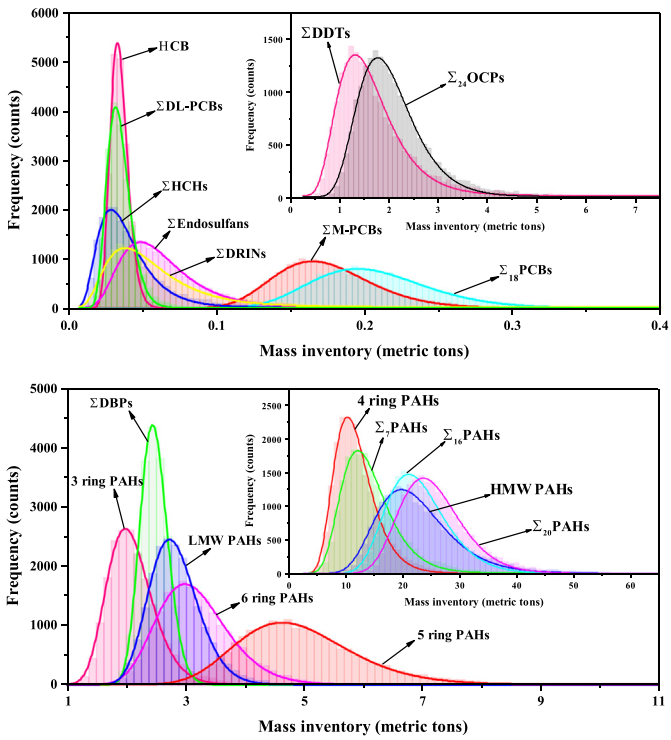

Fig. 3. Frequency distributions of OCP, PCB, and PAH inventory (metric tons) in the soils of the Naples metropolitan area, based on the results of 20,000 Monte Carlo simulations. Note: ΣDL-PCBs: ΣDioxin-like PCBs, ΣM-PCBs: ΣMarker PCBs, LMW PAHs: low molecular weight 2–3 ring PAHs, HMW PAHs: high molecular weight 4–6 ring PAHs, Σ_7PAHs: Σ7 carcinogenic PAHs, and Σ_{16}PAHs: Σ16 USEPA priority PAHs.

contributed over 80% to the total OCP inventory, and the finding agrees with previous studies (Qu et al., 2016; Qu et al., 2017). The Gmean inventory of ΣM-PCBs was approximate five times higher than ΣDL-PCBs, with values reaching up to 0.17 and 0.034 metric tons, respectively. The Gmean inventory of HMW PAHs and LMW PAHs was 22.6 and 2.82 metric tons, respectively, and 4 ring PAHs was the dominant contributing to 53.0% of the Σ_{16}PAHs inventory.

3.2.2. Air–soil exchange direction

Fugacity modeling is used to evaluate the air-soil exchange. Detailed calculation and evaluation criteria of the fugacity fraction (*ff*) were presented in Text S4. The variability in soil concentrations of POPs was postulated to be insignificant (Cetin et al., 2017; Wang et al., 2016), and thus, we generated soil POP database corresponding to the three air sampling campaigns by extracting value from their geochemical maps, as depicted in Figs. S12–S14. The results of the *ff* calculations are presented in Fig. S15.

The *ff* values of most POPs stretched across two or three categories (Fig. S15). Most of the PCB congeners are largely at air-soil equilibrium, with the trend toward deposition to soil as the temperature falls. The *ff* values of PCBs did not significantly reduce with increasing degree of chlorination (corresponding to volatility decreases), which differentiates it from previous results (Růžičková et al., 2008). However, in fact, the impact of physicochemical properties on chemical flux direction is still observed for OCPs and PAHs. For example, those more volatile OCPs and LMW PAHs, such as α-, and γ-HCH, HCB, Ace, Acy, etc., undergo net volatilization from soil, and other compounds are largely at equilibrium or deposition to soil. The finding was also observed in other studies (Qu et al., 2015; Růžičková et al., 2008; Wang et al., 2011). Almost all the *ff* values showed significant seasonal differences, except for PCB114, Dieldrin ($p < 0.05$). More specifically, the AM of *ff* values of almost all selected POPs were particularly higher in autumn than the other seasons (Fig. S15). The seasonal pattern of *ff* values was consistent with previous studies (Růžičková et al., 2008; Wang et al., 2011). This reveals that high temperature circumstances facilitated the volatilization and escape of POPs present in soils.

3.2.3. Air-soil exchange flux

The soil's ability to absorb or release POPs is quantified by estimating air-soil exchange flux, which can be calculated as eq9 in the SI. A single flux direction representing all chemicals is difficult to derive, but generally, the soil as a reemission source of Σ_{18}OCPs and Σ_{15}PAHs, and as a sink for Σ_{18}PCBs (Fig. S16). These results support the conclusions of our other recent studies (Qu et al., 2016; Qu et al., 2017) which postulated a secondary distribution pattern for some legacy pollutants, such as DDTs and HCHs. Maximum evaporation occurs in autumn, with fluxes reaching up to 7.39 ng/m^2/day for Σ_{18}OCPs, and 130 ng/m^2/day for Σ_{15}PAHs, respectively. A relatively large flux of OCPs and PAHs during warm seasons agrees with previous studies (Tao et al., 2008; Wang et al., 2011). Moreover, a shift from volatilization to deposition for the 4-ring PAHs, including Flu, Pyr, BaA, and Chr, was observed from autumn to winter and spring. Seasonal temperature variations may be instrumental in the shift of these 4-ring PAHs fluxes (Wang et al., 2011). The deposition fluxes of Σ_{18}PCBs were 0.016, 0.069, and 0.029 ng/m^2/day in autumn, winter, and spring, respectively.

Mackay (1979) hypothesized that the air-soil exchange process of gaseous POPs obeyed a first-order behavior. Thus, the first-order rate constant (k_v, h^{-1}) is obtained by dividing the air-soil exchange flux by the mass of POPs in a block soil of 1 m × 1 m × 0.05 m. The calculated k_v values of selected POPs ranged from 8.47×10^{-7} to 5.18×10^{-5} h^{-1}, which corresponds to a volatilization half-life ($t_{1/2} = \ln 2/k_v$) from 1.53 to 93.3 years (Fig. S17). This means that long-term soil emission of some POPs, such as *o,p′*-DDT and *p,p′*-DDT, are expected. In theory, the k_v value is dependent on temperature, and POPs tend to be adsorbed by soil organic matter. A $t_{1/2}$ value of approximately 80 years for *p,p′*-DDE was recorded in untilled soils in the southern United States (Scholtz and Bidleman, 2007), and 220 years for ΣDDTs was found in agricultural soil in southern Ontario, Canada (Kurt-Karakus et al., 2006). The ranges of annual temperature and soil TOC recorded here were similar to those reported in the southern United States (10–20 °C and 0.13–3.01%) but differed from that found in Canada (2–12 °C and 42%). This reinforces that high temperatures and low soil TOC may facilitate the volatilization of POPs from soils to atmosphere.

3.3. Influence of soil properties and anthropogenic factors

The soil concentrations of Σ_{24}OCPs, Σ_{18}PCBs, and Σ_{16}PAHs correlated well with each other ($r^2 = 0.19$–0.44, $p < 0.01$). Long-term accumulation of these compounds in soils is dependent on their physicochemical properties and soil characteristics while considering great spatial and seasonal variability of source contributions (Degrendele et al., 2016). As shown in Tables S6–S8, a single critical factor in retaining all individual POPs cannot be identified among the soil properties. This supports the difficulty in using a single soil-geochemical factor to predict the environmental fate of POPs at a regional scale (Qu et al., 2016).

The soil TOC did not significantly influence OCP distribution ($p > 0.05$); however, they significantly correlated with the distribution of PAHs and PCBs ($p < 0.05$). The correlations are stronger particularly for the HMW PCBs, as opposed to the LMW PAHs. This finding is the opposite of what Meijer et al. (2003) observed, that is, a stronger correlations between TOC and the LMW PCBs. The propensity of stronger correlation with lighter POPs may reveal that the more volatile POPs are moving toward equilibrium with soil organic matter. Significantly, almost all POPs were strongly influenced by population density ($p < 0.01$). Thus, given the influences of anthropogenic

activities, this more localized study has difficulty reflecting the signature of global fractionation observed by Meijer et al. (2003) and Yang et al. (2013). The stronger correlations for the HMW PCBs and LMW PAHs were found in British soils (Heywood et al., 2006), which support this conclusion.

The concentrations of some POP groups decreased significantly with the increase of soil pH ($p < 0.05$). This reflects the effect of pH on the structure of humus, and thus, their binding capacity to hydrophobic substances (Aichner et al., 2013). In this study, soil pH varies from moderately acidic to alkaline with an overall trend of alkalescent, which is favorable to the bio-degradation of POPs (Awasthi et al., 2000). The perception is supported by significant negative correlations between soil pH and the ratios of selected parent compounds and their metabolites, such as *p,p′*-DDT/*p,p′*-DDE ($p < 0.05$).

The soil texture varied from sandy to clay (Fig. S18). Soil sand content was positively correlated with several compounds, whereas clay and silt content were negatively correlated. This is consistent with results of previous measurements, as reported by Qu et al. (2017). However, this is indeed a perplexing relationship. For example, Guggenberger et al. (1995) reported the highest aromaticity of the organic matter in the silt-size fraction. Clay minerals have a strong absorption capacity for nonionic organic compounds (Degrendele et al., 2016). Based on these factors, clay and silt content are expected to promote the storage of POPs, as observed by Degrendele et al. (2016) and Jin et al. (2014). We speculate that the enrichment mechanism of POPs is mainly affected by TOC, which was predicted by the fact that TOC correlated positively with sand content and negatively with clay/silt content (Table S6).

3.4. The modeling of atmospheric POPs

With a Gaussian diffusion model, the atmospheric concentration of POPs at location i (C_i) as a function of distance from its source (d_i) is given by Qiu and Hites (2007):

$$C_i = a_0 d_i^{-(a_1+a_2)}$$

The source location, the constant a_0, and the exponent $(a_1 + a_2)$ were derived by the least-squares method (Du et al., 2009; Qiu and Hites, 2007). The atmospheric transport of PAHs is not discussed here because of a lack of significant correlation ($p > 0.05$). This is acceptable due to the presence of local non-point source PAH inputs, as mentioned earlier. The simulation results of Σ_{24}OCPs and Σ_{18}PCBs are visualized in Fig. 4, and the source locations are presented in Fig. 1.

In theory, the exponent $(a_1 + a_2)$ is dependent on atmospheric stability, with its expectation ranged from 1.1 to 2.3 (Klug, 1969). In this study area, the exponent $(a_1 + a_2)$ were less than the expected range of values (Fig. 4). The lower values of $(a_1 + a_2)$ implied the typical stability of the atmosphere during the sampling period, and our data sets do not satisfy the major assumptions of the currently used model. For metropolitan areas, however, the presence of multiple primary sources and secondary emission sources may result in the lessening of spatial gradients. For example, relatively low levels of $(a_1 + a_2)$ were recorded in Philadelphia metropolitan area, with values ranging from 0.39 to 0.66 (Du et al., 2009). The role of Campanian soil as a reemission source for some OCPs and PCBs has been validated. The "urban fractionation" of PCBs in air has also been observed (Harner et al., 2004), but multiple primary sources may still potentially affect the exponent $(a_1 + a_2)$. The source location of OCPs and PCBs occurred in Sarno River Basin and the urban area of Naples, respectively (Fig. 1). These areas are unquestionably recognized as the critical source areas for these compounds, respectively (Qu et al., 2016; Qu et al., 2017). Moreover, the model used here explains 31%–93% of the variation in the data set (Fig. 4), although they do not meet some of the basic assumptions of the model. Despite the minor inconsistencies, the model is still interpreted as a reasonable empirical method of reproducing the spatial variation of POP concentrations in the metropolitan area.

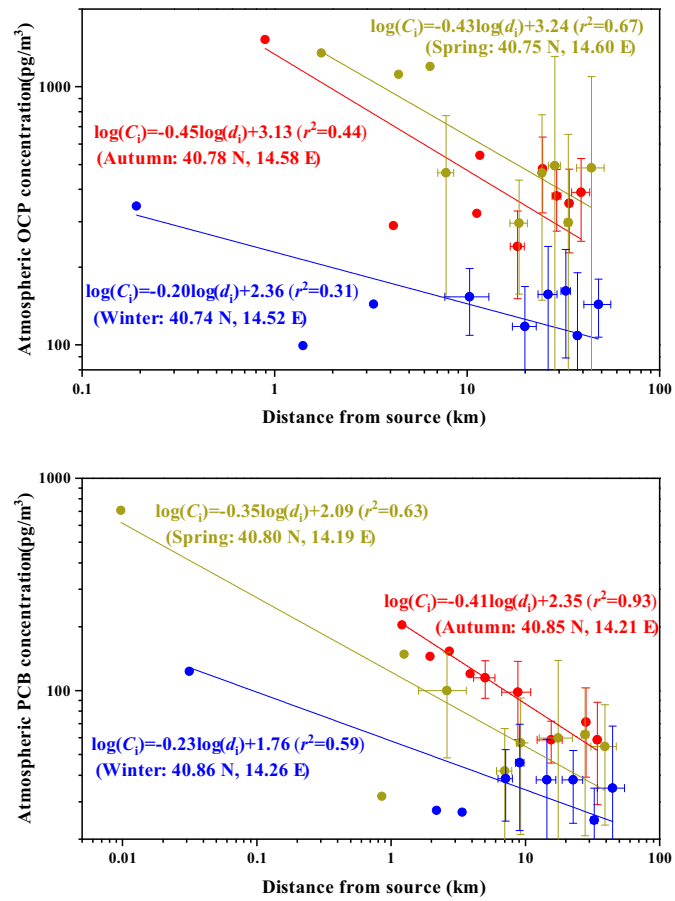

Fig. 4. Concentrations of Σ_{24}OCPs and Σ_{18}PCBs in passive air samples (pg/m^3) as a function of spherical Euclidian distance (km) from their sources.

4. Implications

This study presented the results of a novel investigation to explain the occurrence of POPs in the soil, air, and bulk deposition of Naples metropolitan area. This is taking a toll on the worsening environment here. Considering the contamination of POP, some notorious "hotspots" were validated yet again, such as the "Bagnoli Brownfield Site", the "Triangle of Death" and the "Sarno River Basin". In these areas, POPs persist for long time periods, and may cause lasting environmental damage from soil secondary release. So far, Italy still has no ratified the Stockholm Convention, although it was one of the first signatories. The potential ecological risks of some Stockholm Convention POPs, such as Endosulfan, and their ongoing detection in Italian soils are clear, and thus, their neglect in Italian policy and regulations should attract attention. In addition, the geochemical baseline database of POPs, set up by this study, encourages further research on links between the incidence of specific diseases and the distribution of POPs on a regional scale.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2018.12.031.

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