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RESEARCH ARTICLE

Assessing persistent organic pollutants (POPs) in the Sicily Island atmosphere, Mediterranean, using PUF disk passive air samplers

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Abstract In this study, PUF disk passive air samplers were deployed at eight sites, during two sampling periods, on the Island of Sicily in the Mediterranean basin. Samples were screened for a number of persistent organic pollutants (POPs) including polychlorinated biphenyls (PCBs) (n = 28 congeners), organochlorine pesticides (OCPs) (n = 16 compounds), and polybrominated biphenyl ethers (PBDEs n = 28) using GC-MS. PCB concentrations in air ranged ~10–300 pg m^{-3}. The PCB pattern was dominated by lower to middle molecular weight PCBs (Cl_{3-5}) and PCB-28 and PCB-52 were the most abundant congeners. α- and γ-Hexachlorocyclohexanes (HCHs) concentrations in air were relatively high ~420 ± 320 (50–1000) and 460 ± 340 (30–1000) pg m^{-3}, respectively, with an average α/γ ratio of 1 ± 0.5, indicating a tendency of higher use of lindane than of technical HCH. Among DDTs, only p,p'-DDT 90 ± 15 (~10–800) and p,p'-DDE 60 ± 60 (20–400) were frequently detected. DDT/DDE = 0.4–3.0 (1.0 ± 0.7 for both periods) suggesting past and fresh inputs of DDT at the sampling sites. α-Endosulfan, recently included in Annex A of the Stockholm Convention, fluctuated between 120 ± 50 (50–1000) pg m^{-3}. In contrast, PBDE levels were very low (0.2–2 pg m^{-3}). Back trajectories of advection suggest that POP levels are mainly related to local sources (primary or secondary) from Sicily (50–70 % contribution of air masses), Southern Italy, and Sardinia (20 %). This study provides new information for POP levels in the atmosphere of the Mediterranean region.

Keywords POPs · Passive samplers · PUF disks · The Island of Sicily · Air back trajectories · Mediterranean

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Introduction

The Mediterranean basin is a fairly uniform biogeographic region because of the climatic conditions across a small range of latitudes under the influence of the North Atlantic (Lejeusne et al. 2009). The basin has a diversity of ecosystems, providing a variety of climate and landscape, particularly favorable for human settlements, which has increased human activities leading to ecosystem impacts (Report GREAT Med Study Areas 2015). Persistent organic pollutants (POPs) are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and to the environment (UNEP 2011). In Europe, two international regimes for the protection of human health and the environment from these substances came into force, the global Stockholm Convention (SC) on POPs (UNEP 2011) and the regional 1998 Aarhus Protocol on Persistent Organic Pollutants under the 1979 Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP). Recently, under the SC, a new set of compounds has been included in the POPs list, including polybrominated biphenyls ethers (PBDEs), endosulfans, and its related isomers (UNEP 2011).

All European countries are parties to the SC, except Italy and Malta, which have both signed but have not been yet ratified (Stockholm Convention 2011). To assist parties in assessing the effectiveness of their mitigation efforts, UNEP Chemicals published a guidance document for the global monitoring of POPs (UNEP 2007). Of the media that are recommended for monitoring, the atmosphere is especially important, because it responds relatively quickly to changes in emissions of POPs. The UNEP Guidance document further promotes the use of passive air samplers (PAS) as a cost-effective approach for conducting air sampling of POPs. Over the last decade, polyurethane foam (PUF) disks have been successfully used as PAS for numerous spatial studies at local, regional, and continental scales. For instance, levels of polychlorinated biphenyls (PCBs) and PBDEs in Europe have been reported by Jaward et al. (2004) and Halse et al. (2011), from southern UK to northern Norway by Gioia et al. (2006), in eastern Europe and in Africa by Klánová et al. (2009), and in Estonia by Roots et al. (2010).

Recently, Halse et al. (2011) reported levels of POPs using PAS at background sites (n = 86) in 34 countries under Co-operative Programme for Monitoring and Evaluation of the Long-range Transmissions of Air Pollutants in Europe (EMEP). However, less research has been dedicated to the Mediterranean than in central and northern Europe. Italy, in particular, is clearly understudied in regard to POP atmospheric levels. A few studies have shown rather high levels (using active air sampling; Sbrilli et al. 2003; Manodori et al. 2006; Mosca et al. 2011; Castro-Jiménez et al. 2012) and PAS data determined the POPs levels in Italy (Halse et al. 2011; Pozo et al. 2009). Recently, Estellano et al. (2012, 2014) reported POP concentrations in the air at sites of various land use, using PAS in Tuscany (central Italy) and Puglia (southern Italy).

In the Mediterranean region, PCBs have been used throughout urban and industrial areas in the Mediterranean region. In Italy, PCBs were widely used as insulating fluids in electrical equipment, such as transformers and capacitors, and for many other uses. Italian production of PCBs began in 1958 and ended in 1983 with a cumulative production of approximately 3192 t (Breivik et al. 2007).

According to the European and the Italian legislation, a preliminary inventory of equipment containing PCB oils was carried out in Italy in the year 2000 and had to be updated every 2 years. Equipment containing insulating oils with more than 500 mg/kg of PCBs had to be decontaminated or eliminated by December 2010. As a result, a constant decrease in PCB-contaminated equipment was achieved (PEN 2015).

Organochlorine pesticides (OCPs) are synthetic chemicals commonly used for agricultural activities. In Italy, the agricultural usage of most OCPs was prohibited in the 1970s. Nevertheless, there is very limited data on the remaining levels of OCPs in the atmosphere in Italy. In 2009, both the technical mixture of HCH and the lindane formulations were banned under the SC, at least in agriculture (UNEP 2011). Technical HCH is a mixture of eight isomers, of which five do persist in the environment, i.e., 60–70 % α-HCH, 4–12 % β-HCH, 10–12 %, γ-HCH, 9–10 %, δ-HCH, and 3–4 % ε-HCH (Shen et al. 2004). α-HCH is highly volatile, degrading slowly in the atmosphere (Brubaker and Hites 1998) and is therefore transported globally, reaching fairly uniform concentrations in the air on a regional scale (Li et al. 2007). However, a specific exemption allows lindane to continue to be used as a pharmaceutical treatment (UNEP 2011). In Europe, lindane usage has been estimated at 287,160 t between 1950 and 2000, representing 63 % of the total world consumption (Vijgen et al. 2011). Endosulfan has been banned or withdrawn in 55 countries worldwide, mostly in Europe, Western Asia, and East Asia since recently (Stockholm Convention 2011). However, several corporations around the world still continue to produce endosulfan. Endosulfan in the European Union was not included in the list of authorized active ingredients, Annex I to Directive 91/414/EEC, by the Commission decision 2005/864/EC. Therefore, all of its uses in agriculture have been prohibited since 2005. In Italy, it was used until December 2007; however, Italian government gave especial authorization in 2008 and 2009 for hazelnut cultivation in the Campania Region.

PBDEs are a class of compounds extensively used, in Europe and North America, as flame retardants in a wide array of everyday products, including building materials, electronics, furnishing foams, motor vehicles, aircrafts, plastics, textiles, and others (Prevedouros et al. 2000; Jaward et al. 2004). This

widespread use coupled with their physical chemical properties has resulted in their distribution throughout the environment with the atmosphere serving as an important transport and deposition pathway (Besis and Samara 2012). The use of PBDEs has been regulated in recent years due to concerns over their toxicity, their potential to bioaccumalate, and their persistence in the environment (Kohler et al. 2008). Because of this, they are now listed under the SC (UNEP 2011). Three major PBDE commercial mixtures commonly used are deca-BDE, octa-BDE, and penta-BDE. The PBDEs used in Europe during 2001 were deca-BDE 7600, octa-BDE 610, and penta-BDE 150 t (Law et al. 2006). Based on comprehensive risk assessments, the European Union (EU) decided to ban the penta- and octa-BDE products in August 2004 (Directive 2003/11/EC).

In this pilot study, passive air samplers PUF disks were deployed at eight sites on the Sicilian coast with the aim to determine POP levels and to identify the long-range transportation influence, using air back trajectories from various parts of Italy that are potentially acting as a source (northern, central, southern, and the islands of Sardinia and Sicily). This study will contribute to new monitoring data in the central Mediterranean region, insights into potential sources, and help specify needs related to the implementation of the international chemicals regimes.

Materials and methods

Sample collection

Sicily is the largest island of the Mediterranean Sea: it has an area of 25,710 km^2 and is situated between 36 and 38° N and 12–15° W. Samples were taken at eight sites with different land use (urban, rural, and background areas) along the northern and southern coast of the Island (see Supplementary Material (SM), Fig. S1). PUF disks were deployed for 2 to 3 months during two sampling periods in 2007, summer season (period 1 = July to October; average temperature 24 °C) and autumn (period 2 = October to December; 16 °C). Detailed information of each sampling site is given in Table S1.

Chemical analysis and sample preparation

PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}; PacWill Environmental, Stoney Creek, ON), one per site, were housed inside a stainless steel chamber. The chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm. Air is allowed to flow over the sampling surface through a 2.5 -cm gap between the two domes and through holes in the bottom surface of the lower dome. Information regarding sample preparation, extraction, and cleanup procedures have been reported previously (Pozo et al. 2009; Estellano et al. 2012).

PUF disk samples were extracted in a Soxhlet apparatus for 24 h using petroleum ether. The necessary clean-up procedure was achieved on a silica gel column with activated albumin and sodium sulfate. Extracts were concentrated by rotary evaporation, and a mirex solution (10 μl) was added as an internal standard to correct the volume difference. Moreover, the extract was transferred with isooctane to 1 ml and then blown down under a gentle stream of nitrogen to about 1 ml (Estellano et al. 2012, 2014).

Air sample extracts were quantified for 20 OCPs, 28 PCBs congeners, and 27 PBDEs congeners (Text SM1). These target compounds were analyzed by gas chromatography-mass spectrometry (GC-MS) on a GC-Trace™ GC 2000 (equipped with auto sampler AS3000), and MS *Polaris*Q ionic trap (ThermoFinnigan). PCB analysis was carried out using positive electron impact-selected ion monitoring (EI-SIM). OCPs and PBDEs were analyzed in negative chemical ionization (NCI) mode. Detailed information of target/qualifying ions and instrumental conditions is presented elsewhere (Pozo et al. 2006; Estellano et al. 2012, 2014).

Quality assurance/quality control (QA/QC)

Surrogate recoveries were determined for all samples by spiking ^{13}C-PCB-105 (99 %, Cambridge Isotope Laboratory) prior to extraction. Surrogate recoveries ranged from 70 to 85 %. Recoveries of PCBs were assessed further by spiking PUF disks (n = 2) with the calibration solution and treating them as real samples. Average recoveries for all PCBs were satisfactory (75 % ± 4 %), and no recovery correction was applied to the samples. Blank levels were assessed from six field blanks and six laboratory blanks. All blank levels were below the detection limit. Method detection limits (MDL) in air samples were defined as the average blank (n = 6) plus three standard deviations (SD). When target compounds were not detected in blanks, 2/3 of the instrumental detection limit (IDL) was used as the MDL (See Table 1). All qualified data (i.e., exceeding the MDL) has been blank corrected.

Calculations of air concentrations

Information on sampler performance and methods to derive air concentrations were published previously (Shoeib and Harner 2002; Estellano et al. 2012, 2014). Briefly, air concentration for the target chemicals were derived from the amount accumulated in the PUF disk (ng $sampler^{-1}$) during the whole period of deployment, and divided by the effective air volume (EAV). For the estimation of the EAV, Eq. 2 from Shoeib and Harner (2002) was used, which considers the full uptake profile (linear phase and the plateau phase). The plateau phase may be important for the more volatile chemicals, with lower

Table 1 Concentrations (pg m^{-3}) in air for OCPs, PCBs, and PBDEs in coastal areas of Sicily during two deployment periods

	Sampling site	Criteria	α-HCH	γ-HCH	α/γ	ENDO I	*p,p′*-DDE	*p,p′*-DDT	DDE/DDT	PCBs	PBDEs
			Period 1								
East	Lipari	RU	90	BDL	–	BDL	30	BDL	–	10	0.7
	Milazzo	UR	360	230	2	BDL	60	100	1	220	0.1
	Catania	UR	ns	ns	ns	ns	ns	ns	ns	ns	ns
Northwest	Isola delle Femmine	BA	370	280	1.3	1000	40	100	0.4	70	2.5
	Sferracavallo	BA	1000	730	1.4	570	370	780	0.5	300	0.7
	Ustica	RU	50	60	1	320	30	10	2.9	10	BDL
West	Stagnone di Marsalla	RU	100	200	0.5	140	240	580	0.4	70	0.3
	Menfi	UR	360	270	1.3	100	220	190	1	40	0.9
	Menfi C.da Torrenova	RU	120	340	0.3	60	30	20	2	20	0.3
	Mean		310	270	1	370	130	260	1	90	0.8
	SD		320	220	0.5	360	130	300	0.9	100	0.8
			Period 2								
East	Lipari	RU	ns	ns	ns	ns	ns	ns	ns	ns	ns
	Milazzo	UR	300	650	0.5	BDL	80	100	0.8	70	BDL
	Catania	UR	950	970	1.0	110	30	30	1.1	120	0.5
Northwest	Isola delle Femmine	BA	350	510	0.7	120	20	30	0.7	40	1.2
	Sferracavallo	BA	740	710	1.0	200	40	20	2.2	180	2
	Ustica	RU	50	25	2.0	150	30	40	0.9	BDL	BDL
West	Stagnone di Marsalla	RU	90	100	0.9	70	200	350	0.6	BDL	BDL
	Menfi	UR	630	550	1.1	70	80	140	0.6	70	BDL
	Menfi C.da Torrenova	RU	280	170	2	80	BDL	BDL	1.1	30	BDL
	Mean		420	460	1	120	60	90	1	60	1
	SD		320	340	0.5	50	60	15	0.5	60	0.8
	MDL[a]		<5	<8	–	<15	<20	<20	–	–	–

OCPs = α- and γ-HCHs, endosulfan I, *p,p′*-DDE, *p,p′*-DDT (Ultra Scientific, North Kingstown, RI, USA). PCBs (28 congeners) (Supelco INC, USA) = 3-Cl: PCB-18, PCB-17, PCB-16 + 32, PCB-28 + 31, PCB-33; 4-Cl: PCB-52, PCB-49, PCB-44, PCB-42, PCB-70, PCB-66, PCB-56 + 60; 5-Cl: PCB-95, PCB-101, PCB-99, PCB-114, PCB-118, PCB-105; 6-Cl: PCB-149, PCB-151, PCB-153, PCB-138; 7-Cl: PCB-180, PCB-170; and 10-Cl: PCB-209. PBDEs (26 congeners) (Supelco Analytica, USA) = BDE-3, BDE-7, BDE-15, BDE-17, BDE-47, BDE-49, BDE-66, BDE-71, BDE-77, BDE-85, BDE-99, BDE-100, BDE-119, BDE-126, BDE-138, BDE-153, BDE-154, BDE-156, BDE-183, BDE-184, BDE-191, BDE-196, BDE-197, BDE-206, BDE-207, and BDE-209

BDL below detection limit, *ns* not sampled/not available, *MDL* method detection limit, *SD* standard deviation, *HCH* hexachlorocyclohexane

[a] The MDLs in pg m^{-3} were calculated based on an average estimated air volume of 380 m^3 day^{-1}

K_{oa} (<6) values that may approach equilibrium during deployment, resulting in reduced sample air volumes. However, the chemicals targeted in this study are K_{oa} of ≈7–10.

Collection by PUF disk samplers is dominated by diffusion. Hence, atmospheric pollutants in the gas-phase (in which the lower molecular weight compounds are mainly found) are collected efficiently, but small particles (with significantly high diffusion coefficients) (where the higher molecular weight chemicals are mainly associated) are collected, too, though to a lesser extent (Chaemfa et al. 2008; Klánová et al. 2008). Therefore, substances which are partly associated with the particulate phase, i.e., PCB-153, PCB-180, BDE-47, BDE-99, and BDE-100, are likely incompletely collected. The extent of underestimation is limited by the partitioning (i.e., <20–60 % for PCB-153, PCB-180, and BDE-47, and up to 90 % for BDE-99 and BDE-100 in the Mediterranean region (Chrysikou and Samara 2009; Besis and Samara 2012; Mulder et al. 2015) and dependent on temperature, aerosol mass concentration, and composition. In this study, EAV were calculated using an average sampling rate (R) of ~4 m^3 day^{-1} and ultimately to derive air concentrations of chemicals. R value was obtained using depuration compounds (DCs) which are chemicals that do not typically exist in the air or their concentrations are negligible, but can cover a range of volatility based on their K_{oa} values. The losses of DCs were used to assess the site-specific air sampling rate. The rate of uptake of chemicals will be the same as the rate of loss of DCs (Pozo et al. 2009; He and Balasubramanian He and Balasubramanina 2010). Obtained air volumes fluctuated in the range of approximately 50 to 600 m^3 depending on the length of deployment and the specific molecule analyzed. More detail is presented elsewhere (Estellano et al. 2012).

Air back trajectory analysis

To examine the influence of air mass movement from source regions, Lagrangian modeling was performed (HYSPLIT model using GDAS meteorological inputs; Draxler and Rolph 2003). Trajectories were released every 6 h, at 100 m of altitude, and run for 24 h back in time. In order to perform a weighted trajectory analysis, the model output for each location and sampling period were post processed using the ArcGIS software.

Results and discussion

Table 1 presents the concentrations in the air for OCPs and PCBs in coastal areas of Sicily over the two deployment periods during 2007. Figure 1 summarizes trends for OCPs and PCBs along the coast of the island. The individual PBDE concentrations are presented in Table S2. Results are discussed using minimum and maximum values (arithmetic mean ± SD).

Air mass back trajectory analysis

As is shown in the SM (see Figs. S2, S3, S4, and S5), the origin of trajectories arriving to Sicily is highly variable, covering all directions on the regional scale with a small preference for W-NW. During the last 5 days prior to arrival, most trajectories traveled west or east of the Alps. A similar statistic of the pathways of air masses in the region was observed in summer 2010 and 2012 (Mulder et al. 2015, and unpublished). Two air mass patterns were identified. First, the prevalently northerlies receiving mostly air masses traveling over northern and eastern Europe and the second pattern receiving southerly advection. Southerlies are passing over North Africa (distance to coast ~150–500 km) and mainland Southern Italy.

For the sites in the northeast, the trajectory analysis showed that most of the sampled air came from Sicily and the south of mainland Italy. The Catania site received mostly local air from inland Sicily. In contrast, the sites in western Sicily received mostly advection from the outside of Sicily and mainland Italy, and have a bigger influence from Sardinia, Corsica, southern France, and Northern Africa (see SM, Figs. S2, S3, S4, and S5). To assess the contribution of different parts of Italy, we have illustrated the percentage of air masses that have contributed to each sampling site (Fig. S6).

OCP concentrations in air

Of the 20 OCPs that were analyzed, five were routinely detected in the samples. Aldrin, dieldrin, β-HCH, and δ-HCH were not detected in any of the samples. The dominant OCPs were hexachlorocyclohexanes (α- and γ-HCHs), DDTs (p,p'-DDT and p,p'-DDE), and α-endosulfan.

Hexachlorocyclohexanes (α- and γ-HCH) The concentrations in the air (pg m^{-3}) of α-HCH were relatively high and ranged from 50 to 1000 (310 ± 320) during period 1, and similar values were detected for period 2, i.e., 50–950 (290 ± 380) (Table 1) (Fig. 1). These results are approximately five times higher than typical global background concentrations of α-HCH (50 pg m^{-3}) (Pozo et al. 2009). Elevated concentrations (pg m^{-3}) were observed at the background site Sferracavallo (1000 pg m^{-3} by average) during period one and at the urban site Catania (950 pg m^{-3} by average) during period 2. As expected, the lowest concentrations were detected at background sites, Ustica (50) and Lipari (90). Comparing our results with other studies, we observe that levels of α-HCH are higher than those reported in central and eastern Mediterranean region (Lammel et al. 2015) (Table S2). To explain this result, we suggest two plausible explanations: first, although α-HCH is banned in Italy, some usage may still be occurring in neighboring regions. For instance, Klánová et al. (2009) found extremely high concentrations of α-HCHs (up to 17,000 ng $sampler^{-1}$) (~70 ng m^{-3}) in Tunis, Tunisia (which is located about 200 km from Sicily). Therefore, these results might be partially associated with long-range transport (LRT). To assess LRT, we conducted the air back trajectory analysis, which shows some influence of the air masses from Southern Italy (accounting for 30 %), inland Sicily (25 %), and North Africa (10 %) but did not provide a convincing answer for the differences of HCHs between the different sampling locations (Fig. S6). Accordingly, the high concentrations detected at Sferracavallo (BA) and Catania (UR) are probably more influenced by local sources. Second, we suspect that air-water exchange may have significantly contributed to the high HCH concentrations in the air, since the Mediterranean area is characterized by high levels of POPs, in particular during the summer, due to high temperatures which may enhance the volatilization of chemicals from surface water. Revolatilization of HCHs (Lammel et al. 2015), HCB from surface seawater had been observed in the Mediterranean, while PCBs are reported to be close to equilibrium nowadays (Berrojalbiz et al. 2014; Lammel et al. 2016).

γ-HCH is the main component of lindane (90–99 %); however, a substantial fraction of the other HCH isomers (85 % of the raw product) are produced as a by-product of lindane and became hazardous waste (Vijgen et al. 2011). In Italy, lindane was used as seed dressing in crops and phased out for agricultural usage in 2002 (UNEP 2011). In this study, the concentrations in the air of γ-HCH fluctuated from 1 to 730 pg m^{-3} (270 ± 220), for period 1, and from 25 to 970 pg m^{-3} (410 ± 350), during period 2. The highest values were recorded at Catania (UR) (~970 pg m^{-3}) and at Sferracavallo (IN)

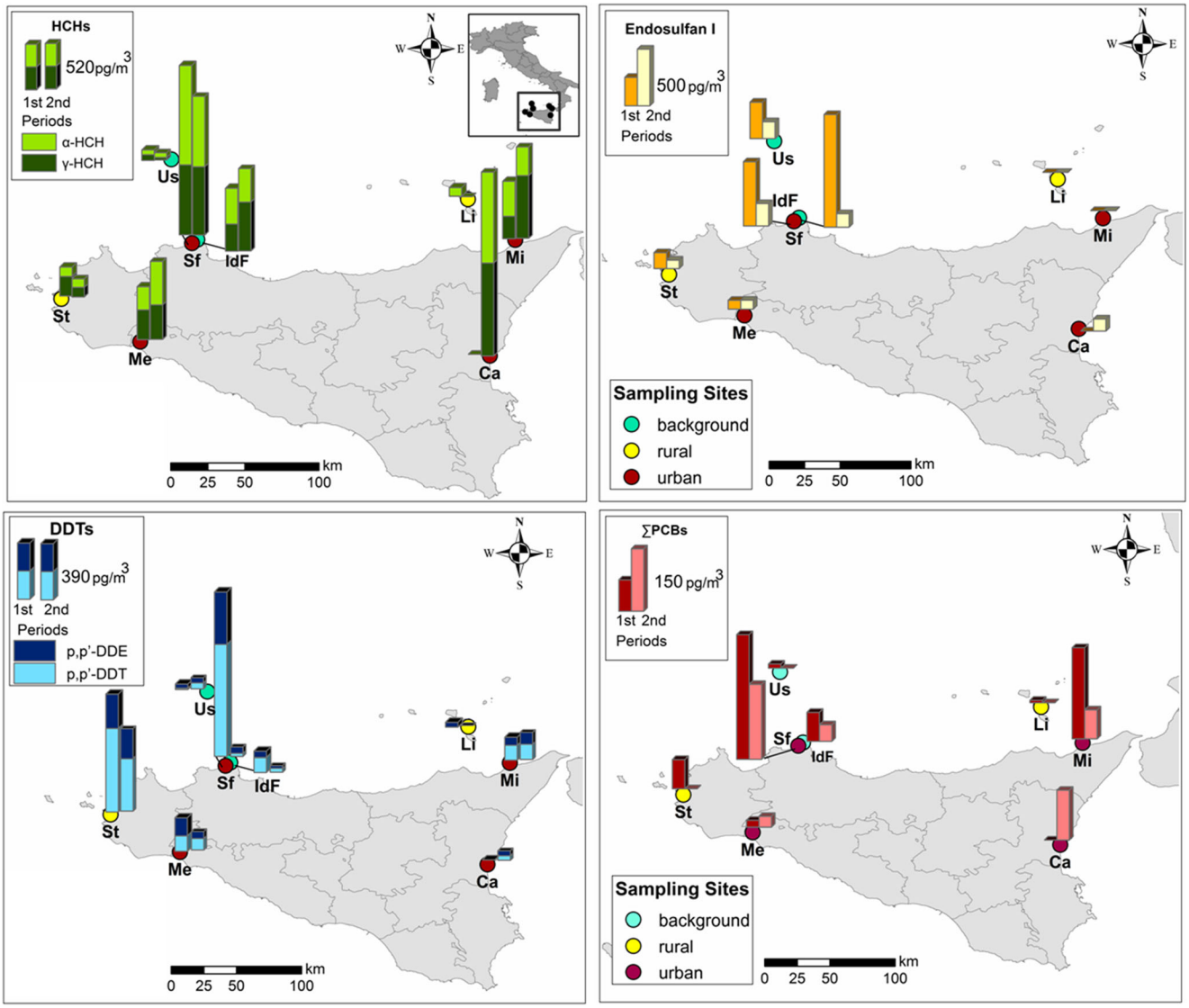

Fig. 1 The concentrations (pg m^{-3}) in air of α- and γ-HCH, *p,p′*-DDT and *p,p′*-DDE, endosulfan I, and PCBs in coastal areas of Sicily during two periods from July to December 2007. *Us* Ustica, *St* Stagnone di Marsalla, *Me* Menfi, *Sf* Sferracavallo, *IdF* Isola delle Femmine, *Li* Lipari, *Mi* Milazzo, *Ca* Catania

(~700 pg m^{-3}) (Table 1 and Fig. 1). These results are in the same range of values of those detected in Tuscany, where 1100 pg m^{-3} was found at urban sites (Estellano et al. 2012). Figure S6 shows that the main contribution of air masses was from inland Sicily (~30 % contribution of air masses) and southern Italy (20 %).

The relative abundance of the two HCH isomers is often expressed by the α/γ ratio. The α/γ-HCH ratio in the technical mixture is around 4–7 (Li et al. 2007). The average α/γ ratio of the Sicilian sites was 1 ± 0.5 particularly during period 1 (July–October), reflecting the transition from technical HCHs to lindane. The Pearson correlation (r) analysis indicates significant ($p > 0.05$) correlation agreement between both compounds during both periods with r values of 0.90 for period 1 and 0.7 for period 2. These results might be linked to the use of pesticides in agricultural areas near the sampling sites.

Endosulfan and derivative Concentrations of endosulfan in air were detected at most of the sampling sites. Technical endosulfan is used on a wide range of crops and also for the control of disease vectors. It comprises two isomers (α and β, with $\alpha/\beta \sim 2.3$). In the environment, it is broken down, with endosulfan sulfate ($endoSO_4$) being the main product (Weber et al. 2010). In this study, α-endosulfan was the only isomer detected. This is related to higher MDLs for the β isomer and $endoSO_4$. With the exception of the sites of Isola delle Femmine (1000 pg m^{-3}) and Sferracavallo (570 pg m^{-3}), the concentrations in the air, during period 1, ranged from 60 to 300 (160 ± 120) pg m^{-3}; during period 2, the values were

much more homogeneous ranging from 70 to 200 (120 ± 50) pg m^{-3} throughout all the sampling sites (Table 1). Figure 1 shows the distribution of α-endosulfan at different sampling sites. High levels were detected at Isola delle Femmine (~1000 pg m^{-3}) and Sferracavallo (~570 pg m^{-3}) (these sites are located on the Northwestern side of Sicily) and are very close to each other (see SM Fig. S1). The trajectory analysis shows, for western Sicily, that air masses are advected from overseas, with possibly influence from Sardinia, Corsica, and southern Italy (see SM Fig. S3, S4, and S5). These results were lower than those reported by Estellano et al. (2012) in Tuscany (10–2200 pg m^{-3}) and in other parts of the world (Pozo et al. 2009; Tombesi et al. 2014).

DDT isomers Despite the environmental threats posed by DDT, it has been the most cost-effective and efficient way of controlling malaria. In Italy, DDT-based pesticides were banned in the 1970s (Pacyna et al. 2003).

From all DDT isomers analyzed, only *p*,*p*′-DDT and *p*,*p*′-DDE were frequently detected. Other related substances, *p*,*p*′-DDD, *o*,*p*′-DDE, *o*,*p*′-DDD, and *o*,*p*′-DDT, were <DL in all samples. Concentrations of *p*,*p*′-DDT in air ranged <10–780 pg m^{-3} (260 ± 300) for period 1 and from 10 to 350 pg m^{-3} (90 ± 15) during period 2 (Table 1) while for *p*,*p*′-DDE concentration ranged 30–370 pg m^{-3} (130 ± 130) during period 1 and 20–200 pg m^{-3} (60 ± 60) for period 2. These levels are at least double of the highest values reported from other parts of the world (Klánová et al. 2009; Pozo et al. 2009; Tombesi et al. 2014).

Figure 1 depicts DDT distribution at all sampling sites. Results show that *p*,*p*′-DDT is significantly ($p > 0.05$, Pearson test, $r = 0.9$ and 0.8 during periods 1 and 2, respectively) correlated with its derivative *p*,*p*′-DDE. Although *p*,*p*′-DDE was detected at most of the sites, its concentrations in the air were slightly lower than *p*,*p*′-DDT during both periods. A DDT/DDE ratio was also calculated in order to identify their recent use (Table 1). DDT/DDE <1 indicates previous use and atmospheric release from environmental matrices, while DDT/DDE >1 indicates new input of DDT (Harner et al. 2004). In this study, DDT/DDE = 0.4–3.0 (1.0 ± 0.7 for both periods) suggesting past and fresh inputs of DDT at the sampling sites. For example, high DDT/DDE = 2–3 was found at Ustica, Menfi (period 1), and at Sferracavallo (period 2), which indicate fresh DDT use. Recently, high concentrations of DDT were detected at polluted sites in Africa, peaking at Kitengela, Kenia, with concentrations up to 8970 ng $sample^{-1}$ (890 ng m^{-3}) for the sum of DDTs (Klánová et al. 2008).

The potential influence of emissions in neighboring countries from northern Africa continent to the Sicilian atmosphere was tested calculating the air masses contribution as shown in Fig. S6. This analysis illustrated that during the sampling period North Africa only accounted with 10 % of air masses and suggest that the main sources are related to inland and Southern Sicily (Fig. S6).

PCB Results for ∑PCBs are summarized in Table 1 and Fig. 1. PCBs were detected at all sampling sites with concentrations ranging 10–300 pg m^{-3} (90 ± 100) (period 1) and from 30 to 180 pg m^{-3} (60 ± 60) (period 2). As expected, the highest concentrations were detected at urban sites, Sferracavallo (300 pg m^{-3}) and Milazzo (220 pg m^{-3}) and the lowest at background sites, Ustica (10 pg m^{-3}) and Lipari (10 pg m^{-3}). These concentrations are similar, more to the upper end of the range to levels reported from other urban sites in Europe (Table S2). For example, Jaward et al. (2004) reported levels across Europe for the $\sum_{29}$PCBs from 20 to 1700 pg m^{-3} (with an average of 300), being higher in the urban sites than in the rural sites for at least two orders of magnitude. Similar values were found by Klánová et al. (2008) throughout Africa with a range of ~1 to ~130 ng $sample^{-1}$, Izmir, Turkey, winter/summer 2005 (644/287 pg m^{-3}). Nevertheless, these results are higher than those PCBs (seven congeners) reported in Eastern Mediterranean areas (Table S2).

PCB congener's composition was dominated by lower-middle molecular weight PCBs with the following composition: 43 % for 3-Cl, 30 % for 4-Cl, and 1 % for 5-Cl during period 1 and 23 % for 3-Cl, 50 % for 4-Cl, and 15 % for 5-Cl for period 2 (Table S3). The PCB homolog composition was different in relation to the sampling site type. The highly chlorinated PCBs (6- and 7-Cl) were predominant at urban/industrial centers (Sferracavallo, Isola delle Femmine, Menfi and Milazzo) during period 1 and accounted for 16 % 6-Cl and 5 % 7-Cl (see SM, Table S3). While less chlorinated PCBs (3- to 5-Cl) were more abundant at background sites (Lipari, Ustica, and Stagnone) (Table S3), previous studies have shown that urban/industrial areas are the main sources of PCBs. Subsequently, the distance from cities is associated with a sharp reduction in PCB concentrations and homolog composition (Harner et al. 2004). This effect was observed particularly at Sferracavallo and Milazzo (urban/industrial centers), as most PCB patterns were dominated by moderately to highly chlorinated PCBs.

From all individual PCB congeners analyzed, PCB-28 was the most predominant detected during the period 1 and accounted for 42 % of total PCB composition, followed by PCB-52 (16 %). During period 2, the individual PCB profile was dominated by PCB-56 and PCB-44 and accounted for 25 % of both congeners (see Table S3).

PBDEs Table 1 presents the concentrations in air of PBDEs in Sicily. Only three PBDE congeners were routinely detected, i.e., BDE-47, BDE-99, and BDE-100. Σ_3PBDE concentrations range from ~0.2 to 2.5 pg m^{-3} for the periods 1 and 2. The highest levels were detected at Isola delle Femmine

(2.5 pg m^{-3}) (Table S4). These levels are lower than PBDE concentrations reported at many European locations by Jaward et al. (2004) (0.5–250 pg m^{-3}) peaking at the urban centers in mainland Europe: Milan, Bilthoven (Netherlands), Geneva, Athens, and Seville. PBDE levels detected in this study are similar to those reported in remote/background sites in Europe with values around ~0.5–10 pg m^{-3} (Iceland, Ireland, Norway, and Sweden) (Halse et al. 2011). Recently, Estellano et al. (2012) also detected lower values of PBDEs (0.3–5 pg m^{-3} (3 ± 8)) in Tuscany. These results are also in agreement with PBDE measurements detected in air of Mediterranean areas (Table S2).

Conclusions

In this study, seasonal variations for POPs were observed during two sampling periods in 2007. High levels were found for HCHs and DDTs (with DDE/DDT ratio indicating past and fresh inputs of DDT at the sampling sites). This should be addressed in more detail in the area. On the other hand, endosulfan, a recently banned POPs, showed lower levels compared with other studies in Europe. A distinct PCB pattern was observed with a prevalence of higher molecular weight PCB at urban and industrial sites. PBDEs were lower than those detected in other areas of Europe. Analysis of atmospheric transports emphasized the influence of Sicily, southern Italy, and Sardinia as sources (primary and secondary) of POP in this study. The long-term trend of air-sea exchange of these and other persistent substances which are no longer primarily emitted is such that the surface seawater is increasingly turning into a continuous secondary source of these chemicals to the atmosphere. This investigation contributes valuable data to the knowledge of POPs in the atmosphere over Italy, an understudied country, and in the Mediterranean region.

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