



## Using PUF disk passive samplers to simultaneously measure air concentrations of persistent organic pollutants (POPs) across the Tuscany Region, Italy

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### ABSTRACT

Passive air samplers consisting of polyurethane foam (PUF) disks were deployed simultaneously over 2–4 month periods from April to July 2008 at 19 locations throughout the Tuscany Region at urban ( $n = 9$ ), rural ( $n = 7$ ) and agricultural sites ( $n = 3$ ). The purpose of the study was to assess the gas-phase air concentrations of PCBs, OCPs, PBDEs and PAHs on a local and regional scale. Derived air concentrations ( $\text{pg m}^{-3}$ ) ranged from below detection limit (BDL) to 300 for  $\Sigma_6\text{PCBs}$  and from BDL to 30 for  $\Sigma_3\text{PBDEs}$ . As expected, the highest PCB concentrations ( $\text{pg m}^{-3}$ ) were observed at urban sites, peaking in Piombino (300). PBDEs, however, exhibited a "reverse gradient" (i.e. rural>agricultural>urban) with highest air concentration at the rural site, Arcidoso (30). Levels of OCPs showed less distinct differences among the three site types. The most frequently detected OCPs were Endosulfan I,  $\gamma$ -HCH and  $\alpha$ -HCH. Endosulfan I ranged from BDL to 2 200  $\text{pg m}^{-3}$ ,  $\alpha$ -HCH from BDL to 610, and  $\gamma$ -HCH from BDL to 1 100. The high air concentrations of HCHs were surprising and possibly due to continued and illegal use – especially at agricultural and urban sites that exhibited the highest levels in air. PAHs showed highest concentrations ( $\text{pg m}^{-3}$ ) at agricultural and urban sites, ranging from 290 to 4 700 and were generally consistent with other data sets from Europe. PAHs were dominated by the 3-ring PAHs ( $76 \pm 6\%$ ), with phenanthrene alone accounting for ( $45 \pm 11\%$ ) of the total PAHs. This study demonstrates the feasibility of using PUF disks as time-integrating passive air samplers for assessing local and regional scale concentrations of a wide range of POPs in central Italy. Given their low cost and simplicity, passive air samplers are the preferred option for conducting concurrent sampling at multiple sites for monitoring and research purposes.

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### 1. Introduction

Persistent Organic Pollutants (POPs) are long-lived in the environment, bioaccumulate through the food web, and exhibit toxic effects that may threaten the health of the environment. They are transboundary pollutants and undergo long-range atmospheric transport (LRAT) from sources to remote regions (Stockholm Convention, 2011). National and International controls on the production, emission, and use of POPs have been and are being introduced with the Stockholm Convention on POPs, and with the Convention on Long range Transboundary Air Pollution (CLRTAP) POPs Protocol of the United Nations Economic Commission for Europe (UNECE). Italy is a signatory country of the Stockholm Convention since 2001, and of the UNECE POPs Protocol since 2003. Under the UNECE POP protocol, Italy has banned the production and use of some POPs (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene), while others are scheduled for elimination at a later stage (DDT, heptachlor, hexachlorobenzene, PCBs) and/or have severely restricted uses [e.g. DDT, HCH (including lindane) and PCBs] (UNECE, 2010). However, Italy is the only country in Europe (including the Russian Federation) that has not yet ratified the Stockholm Convention on POPs (Stockholm Convention, 2011).

Polychlorinated Biphenyls (PCBs) are immunotoxic and affect reproduction (Stockholm Convention, 2011). Breivik et al. (2007) estimated a PCBs global production of  $\sim 1.3$  Mt with more than 70% comprising tri-, tetra- and penta-PCBs and with almost 97% of the global historical use of PCBs occurring in the Northern

Hemisphere. In Italy, the production of PCBs began in 1958 and ended in 1983 with cumulative production of approximately 31 092 t (Breivik et al., 2007). PCBs have been reported in air in sub-alpine northern Italy (21 to 72  $\text{pg m}^{-3}$ ) (Castro-Jimenez et al., 2009), at background sites in southern Italy (23–39  $\text{pg m}^{-3}$ ) (Pozo et al., 2009), and at several locations ( $n = 8$ ) in north-central Italy (20 to 1 700  $\text{pg m}^{-3}$ ) (Jaward et al., 2004a).

Polybrominated diphenyl ethers (PBDEs) have been widely used in Europe and North America as flame retardants in various products such as furnishing foam, plastics, textiles, wire and cable insulation and electronics. They reduce the risk of fire by interfering with the combustion process (de Wit, 2002; Jaward et al., 2004a). Commercial mixtures of PBDEs have been recently listed under the Stockholm Convention on POPs (Stockholm Convention, 2011).

Polycyclic Aromatic Hydrocarbons (PAHs), are associated with a variety of combustion processes including incomplete combustion of fossil and carbon fuels, incineration, power generation, domestic heating and road traffic (Bi et al., 2003). Consequently, higher air concentrations of PAHs are typical in urban environments. The fate of PAHs is of great environmental concern due to their well known carcinogenic, toxic and mutagenic properties (WHO, 2003), in conjunction with their continual and widespread atmospheric emissions. A number of epidemiological studies have demonstrated that people living in urban areas have an increased risk of lung cancer compared to people living in rural areas due to higher levels of air pollution (WHO, 2003).

Passive air samplers consisting of polyurethane foam (PUF) disks are simple and cost-effective tools for monitoring POPs, especially for simultaneous monitoring across multiple sites. The samplers are easy to handle and do not require electricity. In contrast, high volume or active air samplers are relatively expensive and require a constant source of electricity which results in greater logistical and budget requirements. Passive samplers have been used successfully over a range of geographic scales including local (Harner et al., 2004), national (Zhang et al., 2008), continental (Jaward et al., 2004a; Jaward et al., 2004b; Klanova et al., 2009) and at global scale (Pozo et al., 2006; Pozo et al., 2009).

However, in Italy there are only limited data on the presence, distribution and fate of POPs in the atmosphere. The aim of this study is to demonstrate the application of PUF disk samplers in Italy and contribute new information on a wide range of POP classes in the atmosphere of the Tuscany region across a variety of site types.

## 2. Material and Methods

### 2.1. Sampler preparation and deployment

Prior to their exposure, PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm<sup>2</sup>; mass, 4.40 g; volume, 207 cm<sup>3</sup>; density, 0.0213 g cm<sup>-3</sup>) (Tisch Environmental, Village of Cleaves, Ohio), were pre-cleaned with water and then by Soxhlet extraction for 24 h using acetone and then for another 24 h using petroleum ether (Pozo et al., 2006; Pozo et al., 2009). The PUF disks were dried under vacuum. Prior to and after sample collection and during shipping, PUF disk were stored in solvent-cleaned, 1 L glass jars having Teflon-lined lids. PUF disks were deployed at sampling sites for 60–160 days (d) from April–July, 2008 (spring–summer period) (see the Supporting Material, SM, Table S1) and were housed inside stainless steel chambers consisting 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. The chambers provide protection from direct precipitation, UV sunlight, and particle deposition and also reduce the dependence of sampling rate on wind speed (see the SM, Figure S1) (Pozo et al., 2004; Tuduri et al., 2006).

PUF disk passive samplers have been calibrated previously by Shoeib and Harner (2002) for non-polar hydrophobic chemicals. Briefly the uptake by passive sampling media has been shown to be controlled by the air-side mass transfer coefficient,  $k_A$  (m h<sup>-1</sup>), which is a weak function of temperature (Shoeib and Harner, 2002; Gouin et al., 2005). The linear phase uptake sampling rate used in the present study was 3.9 m<sup>3</sup> d<sup>-1</sup>, based on calibration of the PUF disks in previous studies (Gouin et al., 2005; Pozo et al., 2006; Pozo et al., 2009). This results in sample air volumes of approximately 200 m<sup>3</sup> to 600 m<sup>3</sup>, depending on the length of deployment and the properties of the chemical.

### 2.2. Derived air sample volumes

Information on sampler performance, calibration and methods to derive air concentrations were published previously (Shoeib and Harner, 2002; Pozo et al., 2004; Bartkow et al., 2005; Chaemfa et al., 2008). Briefly air concentration for the target chemicals were derived from the amount accumulated in the PUF disk (ng sampler<sup>-1</sup>) divided by the effective air volume. For most compounds, the effective air volumes ( $V_{air}$ , m<sup>3</sup>) were between 200 to 600 m<sup>3</sup> (see the SM, Tables S2 and S3), based on a linear sampling rate ( $R$ ) of 3.9 m<sup>3</sup> d<sup>-1</sup> and a deployment time of 60 to 160 days (see the SM, Table S1). For the estimation of the effective air volume ( $V_{air}$ , m<sup>3</sup>) the Equation (2) from Shoeib and Harner (2002) was used; this equation considers the full uptake profile—linear phase and the plateau phase. For the less volatile POPs having higher octanol–air partitioning coefficient ( $K_{OA}$ ) values and

hence higher PUF–air partition coefficient ( $K_{PUF-A}$ ), the effective air volumes are maximized and essentially equivalent to the linear phase, with a  $R$  value of 3.9 m<sup>3</sup> d<sup>-1</sup> times the number of days of deployment (see the SM, Table S1). The plateau phase is relevant for chemicals with lower  $K_{OA}$  values (e.g. HCB, HCHs, PAHs) that may approach equilibrium (saturation with respect to air) during deployment time of 2–4 months, resulting in reduced sample air volumes compared to higher  $K_{OA}$  chemicals.  $V_{air}$  are given in Tables S2 and S3 (see the SM) for PAHs, PBDEs, PCBs, and OCPs, respectively and were calculated on a template provide by the GAPS Network (gaps.network@ec.gc.ca).

An important consideration for the calculation of PAH concentrations is that the PUF disk medium mainly samples the gas–phase (which are mainly the lower molecular weight PAHs) and only about 10% of ambient particles (mainly higher molecular weight PAHs). This is due to the protective chamber (Klanova et al., 2008) around the PUF disk. Considering this PAHs distribution in the atmosphere, PAHs were estimated using the  $R$ -value for entirely gas–phase PAHs of ~4 m<sup>3</sup> d<sup>-1</sup> while for PAHs that are entirely on particles (e.g 5 and 6-rings PAHs), it is about ~0.4 m<sup>3</sup> d<sup>-1</sup> (Klanova et al., 2008).

### 2.3. Sampling sites

Nineteen locations were selected in the Tuscany region in central Italy (see the SM, Figure S2). PUF disks were deployed (one sampler per site) for one sampling period of approximately 2–4 months from April to July 2008. The sampling locations were divided in three categories, urban ( $n = 9$ ), rural ( $n = 7$ ), and agricultural ( $n = 3$ ). Details of each sampling site are given in the Supporting Material (Table S1).

### 2.4. Analysis

Details on extraction procedures have been reported elsewhere (Pozo et al., 2009). Briefly, prior to extraction PUFs disks were spiked with recovery standards consisting of <sup>13</sup>C PCB–105 (99%, Cambridge Isotope Laboratories) and Phenanthrene–d<sub>10</sub> (99%, Supelco Analytical). PUF disk samples were extracted in a Soxhlet for 24 h using petroleum ether (300 mL) and extracts were concentrated by rotary evaporation followed by blow down under a gentle stream of nitrogen to 0.5 mL and solvent exchanged to isoctane. Mirex (100 ng) was added as internal standard for volume correction.

PUF disk samples were analyzed for a suite of target compounds that included 19 OCPs, 21 PCBs, 26 PBDEs, and 15 PAHs. Analysis of PUF disk extracts for OCPs, PCBs and PAHs were carried out by gas chromatography–mass spectrometry (GC–MS) on a GC–Trace™ GC 2000 (equipped with auto sampler AS3000), and ion-trap MS *PolarisQ* (ThermoFinnigan), using positive electron impact–selected ion monitoring (EI–SIM). PBDEs were analyzed on a GC Trace 2000 (auto sampler AS2000), coupled to an ion trap MS GCQ–Plus (ThermoFinnigan), using negative chemical ionization (NCI) in SIM mode with methane as the reagent gas. The details about the oven conditions are presented in the supporting information text (see the SM, Text S1). Details on the target chemicals and their target/qualified ions are described in the supporting information text (see the SM, Text S2).

### 2.5. Quality assurance/quality control (QA/QC)

The instrumental detection limits were determined by assessing the injection amount that corresponded to a signal–to–noise value  $\geq 3$ . Method detection limits (MDL) in air samples were defined as the average solvent blank ( $n = 9$ ) plus three standard deviations (SD). When target compounds were not detected in blanks, 1/2 of the instrumental detection limits (IDL) value was substituted for the MDL. Field blanks ( $n = 4$ ) were below the detection limit or showed signal to noise ratios  $< 3$ , for all screened

compounds consequently, no blank correction was required. Peaks were only integrated when the signal to noise ratio was  $\geq 3$ ; otherwise, they were considered not detected. The values of IDL and MDL for each group of compounds are reported in the Supporting Material (Table S2, Table S3).

Average method recoveries were satisfactory ( $70 \pm 5\%$ ) for  $^{13}\text{C}$ -PCB-105 and ( $75 \pm 10\%$ ) for phenanthrene-d10, and no recovery correction was applied to the samples.

### 3. Results and Discussion

Passive sampler derived air concentrations for OCPs, PCBs, PBDEs and PAHs are summarized in Table 1. Of the 19 OCPs analyzed only five were routinely detected including:  $\alpha$ - and  $\gamma$ -HCH, HCB, Endosulfan I and *p,p'*-DDT. Results for these compounds are discussed below. Target compounds that were not detected in any of the samples included:  $\beta$ -,  $\delta$ -HCHs, aldrin, heptachlor, *cis*- and *trans*-heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, *o,p'*-DDE, *p,p'*-DDE, *o,p'* DDD, *p,p'*-DDD and *o,p'*-DDT.

#### 3.1. OCPs

**HCHs.** Hexachlorocyclohexane (HCH) was used as a commercial insecticide in two formulations: (i) technical HCH, which includes multiple stereoisomers but dominated by  $\alpha$ -HCH ( $\sim 80\%$ ) and  $\gamma$ -HCH ( $\sim 15\%$ ); and lindane which consists almost entirely of  $\gamma$ -HCH (Shen et al., 2004). Currently, both the technical mixture of HCH and lindane formulation are included in the POPs list under the Stockholm Convention of POPs and the use of these compounds in agriculture is banned (Stockholm Convention, 2011). Despite the fact that Italy is not a Party to the Stockholm Convention, the use of HCHs is severely restricted (e.g. use for agriculture, import and export) due to other regulatory mechanisms such as a European Directive in 2000, the UNECE POPs Protocol and the Rotterdam Convention.

Concentrations of  $\alpha$ -HCH in air ( $\text{pg m}^{-3}$ ) ranged from BDL to 610 ( $150 \pm 230$ ) (see the SM, Table S3, Figure 1, green bars) with highest concentrations at urban sites ( $230 \pm 230 \text{ pg m}^{-3}$ ) followed by agricultural sites ( $210 \pm 350 \text{ pg m}^{-3}$ ) (Table 1). The highest value was at the agricultural site of Siena Nord ( $610 \text{ pg m}^{-3}$ ). At all of the rural sites,  $\alpha$ -HCH was BDL, indicating that the elevated concentrations in urban and agricultural sites were due to local activities. These results are much higher than those previously reported by Jaward et al. (2004a) in several sites ( $n=8$ ) in northern and central Italy ( $<1.72$ – $2.29 \text{ ng sample}^{-1}$ ;  $\sim 10$ – $20 \text{ pg m}^{-3}$ ). Air concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH showed a positive correlation ( $\rho_{x,y} = 0.66$ ) indicating a similar source. This pattern agrees with data reported

by Shunthirasingham et al. (2010), suggesting that lindane use may contribute to  $\alpha$ -HCH air burdens, presumably because of the presence of  $\alpha$ -HCH as an impurity in the lindane formulation (WHO, 2009). This is considered further below.

$\gamma$ -HCH is the main component of lindane and in Italy it was produced during the 1950s to 1970s in Colferro, in the Lazio Region (central Italy), approximately 200 km from Tuscany. In 1975, the use and production of lindane was banned and its current-use is limited to pharmaceutical purposes for the control of head lice and scabies (UNECE, 2010).

Air concentrations of  $\gamma$ -HCH ranged from BDL to  $1\,100 \text{ pg m}^{-3}$  ( $270 \pm 340$ ) (see the SM, Table S3, Figure 1, red bars). Similar to  $\alpha$ -HCH, the highest concentrations of lindane were at urban sites ( $380 \pm 390$ ), followed by the agricultural sites ( $240 \pm 410$ ) (Table 1, Figure 1, red bars). These results are consistent with those air concentrations reported by Jaward et al. (2004a) across European countries ( $9$ – $390 \text{ pg m}^{-3}$ ), however, these results are higher than those previously reported for other Italian sites ranging from 2 to  $11 \text{ ng sample}^{-1}$  ( $\sim 10$  to  $80 \text{ pg m}^{-3}$ ) (Jaward et al., 2004a). These data suggest a fresh but unknown input of lindane, particularly in urban and agricultural locations. Interestingly, Yao et al. (2010) also reported elevated  $\gamma$ -HCH concentrations in Toronto (peaking at  $3\,000 \text{ pg m}^{-3}$ ) during a 3-day episode in 2005, following a lindane ban in Canada. In the Toronto study, the illegal source of lindane was not discovered but seemed to be originating in the city as air monitoring stations upwind of the city did not experience the episode.

The relative abundance of the two main HCH isomers is often expressed by the  $\alpha/\gamma$ -HCH ratio. The  $\alpha/\gamma$ -HCH ratio in the technical HCH mixture is in the range 4–7 (Shen et al., 2004). In air samples from this study, the ratio ranged from 0.66 to 0.94 reflecting the use of lindane ( $\gamma$ -HCH). These results are in agreement with the data reported by Jaward et al. (2004a) throughout Europe ( $0.77 \pm 0.8$ ). The proportion of  $\alpha$ -HCH in the air samples is much larger than expected based on its occurrence as a minor impurity in the formulation of lindane as discussed previously. It seems that illegal use of  $\alpha$ -HCH may be occurring in agriculture and at urban sites in Tuscany, probably linked to old stocks of this pollutant.

**HCB.** Hexachlorobenzene (HCB) was first introduced in 1933 as a fungicide for use on the seeds of onions, sorghum and crops such as wheat, barley, oats and rye. It is believed that agricultural use of HCB dominated its emissions during the 1950s and 1960s. Estimates of global HCB production exceeded 100 000 tons and primary emissions to the atmosphere likely peaked in the 1970s (Barber et al., 2005). Although the use of HCB as a fungicide was

**Table 1.** Air concentrations ( $\text{pg m}^{-3}$ ) of target compounds for urban, rural and agricultural sites in the Tuscany region of central Italy

	Urban (n = 9)		Rural (n = 7)		Agricultural (n = 3)	
	Range	Avg (GM) $\pm$ SD	Range	Avg (GM) $\pm$ SD	Range	Avg (GM) $\pm$ SD
$\alpha$ -HCH	BDL – 570	230 (90) $\pm$ 230	BDL	BDL	BDL – 610	210 (30) $\pm$ 350
$\gamma$ -HCH	BDL – 1 100	380 (140) $\pm$ 390	BDL – 340	90 (30) $\pm$ 130	BDL – 720	240 (40) $\pm$ 410
HCB	BDL – 30	4 (3) $\pm$ 12	BDL – 170	60 (20) $\pm$ 70	8 – 150	20 (15) $\pm$ 20
Endo 1	BDL – 2 000	560 (60) $\pm$ 780	BDL – 2 000	300 (30) $\pm$ 750	BDL – 2 200	740 (70) $\pm$ 1 200
$\Sigma_5$ PCBs	BDL – 300	80 (70) $\pm$ 120	BDL – 45	18 (19) $\pm$ 19	BDL	BDL
$\Sigma_7$ PBDEs	BDL	BDL	BDL – 30	9 (0.5) $\pm$ 12	BDL – 4	2 (1) $\pm$ 2
<i>p,p'</i> -DDT	BDL – 180	50 (40) $\pm$ 60	BDL – 180	80 (40) $\pm$ 100	BDL – 730	260 (70) $\pm$ 410
3ring-PAHs	750 – 2 700	1 700 (1 500) $\pm$ 810	130 – 1 800	920 (730) $\pm$ 560	1 200 – 4 000	2 400 (2 100) $\pm$ 1 500
4ring-PAHs	140 – 960	600 (510) $\pm$ 280	80 – 500	270 (220) $\pm$ 180	870 – 900	800 (800) $\pm$ 150
5ring-PAHs	BDL – 10	1 (1) $\pm$ 3	BDL – 10	4 (2) $\pm$ 5	BDL – 16	9 (5) $\pm$ 8
$\Sigma_9$ PAHs	890 – 3 500	2 300 (2 000) $\pm$ 1 100	300 – 2 300	1 200 (970) $\pm$ 730	2 110 – 4 700	3 200 (3 000) $\pm$ 1 300

Avg. = arithmetical mean; GM = geometrical mean.

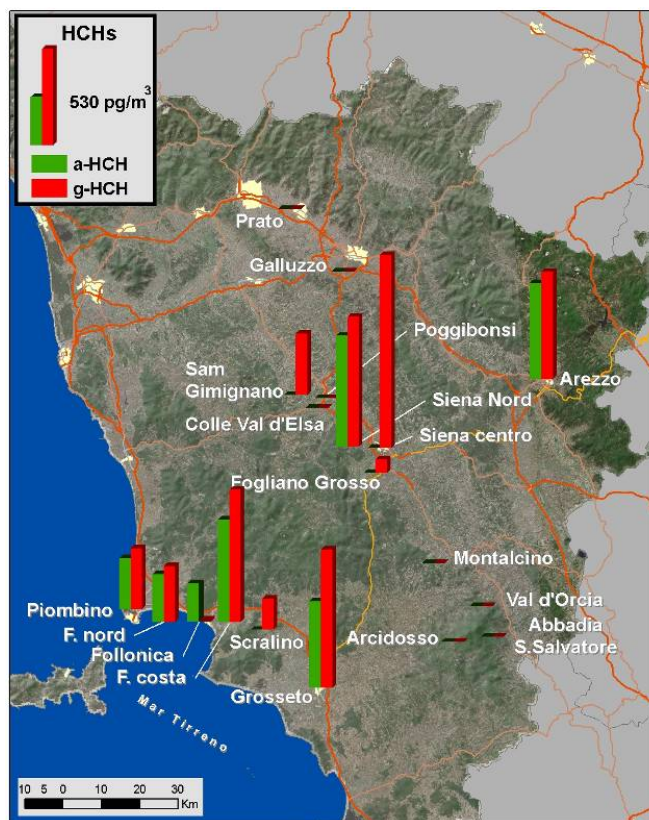


Figure 1. Air concentrations ( $\text{pg m}^{-3}$ ) of HCHs ( $\alpha$ - and  $\gamma$ -) in the Tuscany region of central Italy.

banned in most countries, it is still present as a by-product and/or impurity in the manufacture of chlorinated solvents, chlorinated aromatics and pesticides and produced during combustion processes (Barber et al., 2005).

Air concentrations ( $\text{pg m}^{-3}$ ) of HCB ranged from BDL to 170 ( $30 \pm 50$ ) (Tables 1, and Table S3). These values ( $\text{pg m}^{-3}$ ) were higher at the rural sites ( $60 \pm 70$ ), followed by the agricultural sites ( $20 \pm 20$ ), and were slightly lower at the urban sites ( $4 \pm 12$ ). These levels are consistent with those reported by Dvorska et al. (2008) for ten years (1996–2005) of continuous sampling at a rural site in Kosetice (Czech Republic) ( $83$ – $236 \text{ pg m}^{-3}$ ), and by Jaward et al. (2004a) across Europe ( $11$ – $50 \text{ pg m}^{-3}$ ). In addition, our results are similar to the estimated average concentration for the Northern Hemisphere (based on background air concentrations from recent studies) of  $55 \text{ pg m}^{-3}$  (Barber et al., 2005). HCB air concentrations in central Italy showed a fairly uniform distribution indicating that air concentrations are associated mainly with diffuse continental sources rather than local/regional hot spots.

**Endosulfan.** Endosulfan is a modern OCP that is used globally. It consists of two isomers,  $\alpha$  and  $\beta$ , in the ratio of about 7:3 (technical mixture) that breakdown in the environment to produce endosulfan sulfate ( $\text{SO}_4$ ). Endosulfan is used on a wide variety of crops and also for the control of disease vectors (Li and Macdonald, 2005). Cumulative global use of endosulfan for crops is estimated to be 338 kt. The estimated annual endosulfan consumption on a global basis is  $10.5 \text{ kt yr}^{-1}$  from 1980 to 1989 and  $12.8 \text{ kt yr}^{-1}$  from 1990 to 1999 (Li and Macdonald, 2005). In 2011, it was included in the list of POPs, becoming the 22<sup>nd</sup> POP compound listed under the Stockholm Convention on POPs (Stockholm Convention, 2011).

Of the three isomers of endosulfan that were screened (Endo I, Endo II and Endo  $\text{SO}_4$ ) only Endo I was detected due partly to analytical problems (low sensitivity) for the minor isomer (Endosulfan II) and the degradation product (Endo  $\text{SO}_4$ ). With the

exception of Siena Nord (Ag), Fogliano Grosso (Ru), and Piombino (Ur), air concentrations ( $\text{pg m}^{-3}$ ) of the Endosulfan I ranged from BDL to 64 (see the SM, Table S3). These concentrations are in the middle-to-high range of endosulfan concentrations in air reported across a range of GAPS Network site types during 2005 (Pozo et al., 2009). The highest values observed at Siena Nord ( $2\,200 \text{ pg m}^{-3}$ ), Fogliano Grosso (1990), and Piombino (2000), are likely associated with the wide variety of agricultural activities (e.g., olives, vineyards, sunflower) in the surrounding areas. Furthermore, this high level of Endo I at Siena Nord is similar to results from mainly agricultural sites in India ( $n = 9$ ) where mean values of Endosulfan I ( $\text{pg m}^{-3}$ ), during 2006 and 2007, were 4 870 and 1 600, respectively (Pozo et al., 2011) and also to some of the agricultural sites reported under the GAPS Network (Pozo et al., 2009).

**DDTs.** Widely applied as an insecticide in the past, DDT continues to be the most produced and used POP listed in the Stockholm Convention, mainly for control of insects such as mosquitoes that are vectors for malaria and other diseases (Pacyna et al., 2003; Stockholm Convention, 2011). Most European usage of  $p,p'$ -DDT occurred in Eastern Europe, Spain, Italy, and France. Through the period 1970–80s various countries introduced bans and restrictions on DDT. In Italy the use of DDT was severely restricted in 1988 and banned as an agricultural chemical (Pacyna et al., 2003).

Air concentrations ( $\text{pg m}^{-3}$ ) of DDT isomers were dominated by  $p,p'$ -DDT ranging from BDL to 730 ( $80 \pm 180$ ) (see the SM, Table S3) and followed the gradient agricultural>rural>urban sites which is indicative of agricultural sources (Table 1). The principal metabolite  $p,p'$ -DDE was not detected at any of the sampling sites. These results suggest that DDT air concentrations during the first period are probably associated with fresh inputs. Although DDT is banned in Italy, the main isomer was previously reported across Europe by Jaward et al. (2004a) showing a very wide range of concentrations in air, peaking in Russia ( $32 \text{ ng sample}^{-1}$ ) and Italy ( $25 \text{ ng sample}^{-1}$ ).

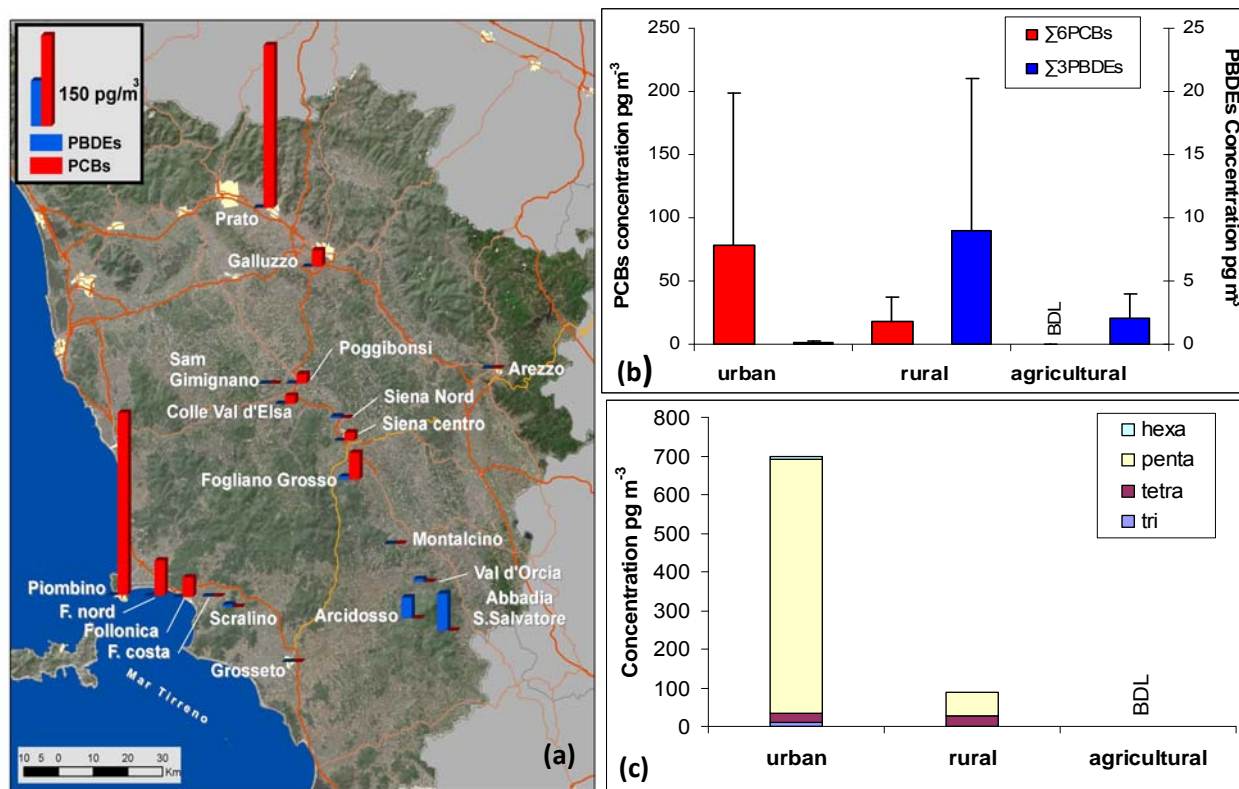
### 3.2. PCBs

PCBs are a class of synthetic organic chemicals. Since ~1930, PCBs were used for a variety of industrial uses (mainly as dielectric fluids in capacitors and transformers but also as flame retardants, ink solvents, plasticizers) because of their chemical stability (Breivik et al., 2007).

PCB air concentrations and spatial distributions are shown in (Figure 2a, red bars). Of the 21 PCB congeners that were analyzed only 6 (28/31, 52, 99, 149, 118 and 105) were detected (see the SM, Table S3).  $\sum_6\text{PCB}$  air concentrations ( $\text{pg m}^{-3}$ ) ranged from BDL to 300 ( $50 \pm 100$ ) (Table 1, see the SM, Table S3). As expected the highest PCB concentrations ( $\text{pg m}^{-3}$ ) were detected in urban sites ( $80 \pm 120$ ) peaking in Piombino (310) and Prato (270) (see the SM, Table S3), and then followed by the rural sites ( $18 \pm 19$ ). Levels at the agricultural sites were BDL (Figure 2b, Table 1). Although the urban–rural–agricultural gradient in PCB air concentrations is similar to other studies (e.g. Jaward et al., 2004a), the air concentrations at the urban sites in Tuscany are lower compared to other urban sites investigated under the GAPS Network (Pozo et al., 2009). Examples of PCB air concentrations at urban sites include  $1\,700 \text{ pg m}^{-3}$  in Moscow, Russia (Jaward et al., 2004a) and  $1\,077 \text{ pg m}^{-3}$  in Bangalore, India (Zhang et al., 2008). These differences are likely due to the smaller scale of urban sampling sites in Tuscany (lower industrial activity, few emission sources). For instance, the largest urban center was Grosseto with approximately 80 000 inhabitants.

The PCB congener composition in Tuscany air was dominated by 4-Cl (28/31, and 52; 7%) and 5-Cl congeners (congeners 99, 105, and 118; 91%) (Figure 2c). Dominance by the middle-range molecular weight PCBs was also observed across Europe by Jaward et al. (2004a).





**Figure 2.** Air concentrations ( $\text{pg m}^{-3}$ ) of (a) total PBDEs (blue bars) and PCBs (red bars), (b) comparison of urban, rural and agricultural sites, (c) PCB congeners composition. BDL = Below detection limit.

### 3.3. PBDEs

PBDEs are a relatively new class of persistent organic pollutants with their production and use occurring over the last few decades and emissions peaking much later than for the organochlorine pesticides (Jaward et al., 2004a). Of the 26 PBDEs that were analyzed, only 3 were frequently detected: -47, -100, and -99 (see the SM, Table S3). Air concentrations ( $\text{pg m}^{-3}$ ) for  $\Sigma_3$ PBDE are reported in Table 1 and Table S3. Air concentrations at the study sites ranged from BDL to 5 ( $3 \pm 8$ ) (see the SM, Table S3, Figure 2a, blue bars), with the exception of the rural sites of Arcidosso (30) and Abbadia San Salvatore (20) which showed the highest values. PBDE air concentrations ( $\text{pg m}^{-3}$ ) were generally higher at the rural sites ( $9 \pm 12$ ), and lower at the urban sites (BDL), resulting in an unexpected "reverse gradient" i.e. rural>agricultural>urban, during the spring–summer season. These results are similar to those reported by Gouin et al. (2002) and Harner et al. (2006), in a rural–urban transect in Toronto, where a PBDEs "reverse gradient" was likely related to a "spring pulse".

The reasons for the PBDEs reverse–gradient, observed in this study are unknown. Nevertheless, compared to other compound classes, PBDEs are likely released differently to the environment and/or once released they undergo different partitioning because of their physical chemical properties (Harner et al., 2006). PBDEs have much higher  $K_{oa}$  values than PCBs and PAHs (Harner and Shoeib, 2002). This results in enhanced partitioning to aerosols, soil and other environmental organic phases. These factors may partly contribute to the differences observed for PBDEs. It is also possible that the PBDEs air burden in this study could be mainly related to advection from more distant regional sources that had a greater influence on the rural sites. It is also possible that analytical interferences in the urban samples played some role. This study presents the first period of a longer term monitoring program of POPs conducted in Tuscany. Results from additional sampling periods will provide additional information for evaluating this result.

In general, the magnitude of air concentrations of PBDEs in the Tuscany region are lower than those reported by Mariani et al. (2008) in, a suburban location at 70 km from the center of Milan, Northern Italy ( $106 \text{ pg m}^{-3}$ ) and by Jaward et al. (2004a) throughout Europe where  $\Sigma$ PBDEs in air were in the range  $0.5\text{--}250 \text{ pg m}^{-3}$  with the highest concentrations ( $\text{ng sample}^{-1}$ ) at the urban sites of London (11), Manchester (43), Milan (12), Athens (13), and Seville (22). Similar to PCBs, the low PBDE air concentrations at urban Tuscany sites compared to other urban sites is likely associated with the smaller scale of the urban sites in Tuscany.

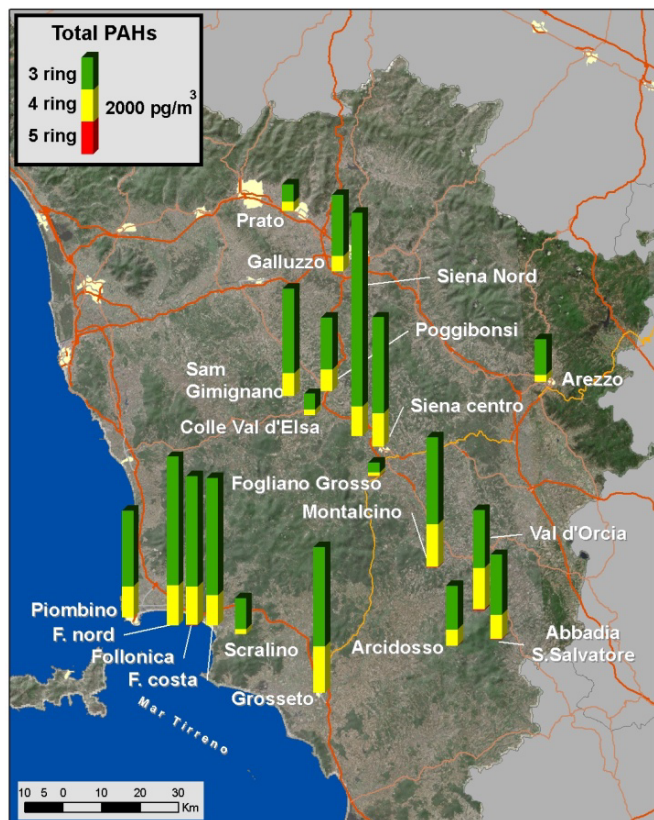
### 3.4. PAHs

Polycyclic aromatic hydrocarbons (PAHs) are by–products of incomplete combustion. The key emission sources of PAHs to air include motor vehicles, domestic burning of coal and wood for space heating, power generation via combustion of coal and oil, incineration, wood burning, cooking, smoking, and burning of natural gas (Jaward et al., 2004b).

Of the 15 PAHs analyzed only 10 congeners were routinely detected in samples (see the SM, Table S2). PAH with 3–5 benzene rings are ubiquitous in the environment and typically derived from natural and anthropogenic combustion sources (Jaward et al., 2004b). However, higher molecular weight (5– and 6– ring) PAHs are much less abundant in the gas phase due to their low volatility (Bi et al., 2003).

With the exception of Siena Nord, the air concentrations ( $\text{pg m}^{-3}$ ) of PAHs ranged from 290 to 3 500 ( $1 900 \pm 1 000$ ) (Table 1 and Table S2, see the SM). The highest value was reported at the agricultural site of Siena Nord (4 700) (Figure 3, Table S2, see the SM). This is likely due to close proximity of the sampling site ( $\sim 700 \text{ m}$ ) to the Siena–Florence highway, and additional influences from local wood combustion. The lowest air concentration of PAHs was detected at the rural site of Fogliano Grosso (290) (see the SM, Table S2). Overall, PAH air concentrations were comparable at the

agricultural sites ( $3\,200 \pm 1\,300$ ) and urban sites ( $2\,300 \pm 1\,100$ ) (Table 1, Figure 3). These results are consistent with data from Kosetice (Czech Republic) with an average value of  $10\,000\text{ pg m}^{-3}$  ( $10\text{ ng m}^{-3}$ ) over ten years of monitoring (Dvorska et al., 2008), and with a European survey where PAHs were typically  $<10\,000\text{ pg m}^{-3}$  ( $10\text{ ng m}^{-3}$ ) [ranging of  $500$  to  $60\,000\text{ pg m}^{-3}$  ( $0.5$  to  $60\text{ ng m}^{-3}$ )] (Jaward et al., 2004b).



**Figure 3.** Air concentrations ( $\text{pg m}^{-3}$ ) of total PAHs in the Tuscany region of central Italy.

The average composition of PAHs across all sites was as follows: 3-ring PAHs, ( $76 \pm 6\%$ ); 4-ring, ( $24 \pm 6\%$ ); and 5-ring, ( $0.1 \pm 0.3\%$ ) (Table 1). Phenanthrene alone accounted for the ( $45 \pm 11\%$ ) of the total PAHs (see the SM, Table S2). This composition pattern is consistent with other studies. For instance, Santiago and Cayetano (2007) reported ( $68 \pm 5\%$ ) for 3-ring PAHs, and ( $30 \pm 4\%$ ) for 4-ring PAHs, in Philippines, Gouin et al. (2010) showed that more than 90% of the air concentration was dominated by 2-, and 3-ring PAHs, in Fairbanks, Alaska. Furthermore, Jaward et al. (2004b) reported a PAH composition of 60% to 85% for 3-ring PAHs and 15% to 35% for 4-ring PAHs, across Europe.

#### 4. Conclusions

This study demonstrates the feasibility of using PUF disks as time-integrating passive samplers, to assess local and regional air concentrations of POPs and PAHs at different land use sampling sites throughout Tuscany region. Some interesting trends and results were observed.

In the case of PCBs, air concentrations were generally low compared to other developed regions of the world. PBDE levels showed a "reverse-gradient" with highest concentrations at rural sites, atypical to what is usually observed. This may indicate that the small scale urban sites investigated in this study were not important emissions sources of PBDEs to the regional atmosphere. Of all the OCPs analyzed, Endosulfan I,  $\gamma$ -HCH and  $\alpha$ -HCH had the highest air concentrations with Endo I exhibiting high concen-

trations across all site categories in the region. The HCH isomers were abundant in air at agricultural sites but more surprisingly, they were also abundant at urban sites indicating some ongoing and illegal use of these banned pesticides, perhaps from old stocks. PAH levels in air were similar to those reported throughout Europe and were dominated by Phenanthrene.

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#### Supporting Material Available

Text S1 reported the oven conditions. Text S2 reported the: OCPs, PCBs, PBDEs and PAHs screened and the target/qualified ions. Figure S1 is a schematic representation of the PUF disk sampler and photo showing its deployment at one site in this study. Figure S2 is a map showing location of urban, rural and agricultural air sampling sites in the Tuscany region of central Italy. Table S1 provides sampling sites information, temperature ( $^{\circ}\text{C}$ ) and deployment time. Table S2 provides air concentrations ( $\text{pg m}^{-3}$ ) of individual PAH isomers, MDL, IDL and sample air volumes. Table S3 summarizes air concentrations ( $\text{pg m}^{-3}$ ) of the OCPs, PCBs and PBDEs, MDL, IDL and sample air volumes. This information is available free of charge via the Internet at <http://www.atmospolres.com>. A template for determining effective air sample volumes for PUF disks for a range of analytes is available by email request from [gaps.network@ec.gc.ca](mailto:gaps.network@ec.gc.ca).

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