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RESEARCH ARTICLE

Concomitant evaluation of atmospheric levels of polychlorinated biphenyls, organochlorine pesticides, and polycyclic aromatic hydrocarbons in Strasbourg (France) using pine needle passive samplers

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Abstract In this study, pine needles were used as cost-effective and reliable passive bio-monitors to concomitantly evaluate atmospheric concentrations of three classes of persistent organic pollutants, polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs). The extraction of persistent organic pollutants (POPs) from needle samples was performed. Eleven PCBs, 11 OCPs, and 15 PAHs were detected and followed through time in needle samples from three sites in the Strasbourg region. The urban and rural sites were more exposed to PCBs than the suburban site. The highest concentration of PCBs was found at the urban site, but the largest number of congeners (10) was detected at the rural site. PCB 189 and 156 were the predominant congeners in the rural site and PCB 70 in the urban site. For OCPs, the rural site displayed the highest concentrations (up to 22.9 ng g^{-1}) and number of compounds investigated (9). The high concentration of γ- and β-hexachlorocyclohexane (HCH) at that time in the urban site was the reason for this result. γ- and β-HCH were the two predominant compounds in all samples. The suburban and urban sites were the most exposed with PAHs with pyrene, phenanthrene, and acenaphthene being the three predominant compounds in these sites. No specific trend in terms of time was apparent for PCBs and OCPs. However, higher concentrations were detected for some compounds in the first sampling, especially for PAHs, and this is attributed to variations in meteorological conditions (e.g., temperature, wind, rain) and variable inputs from both identified and unidentified sources.

Keywords Atmospheric pollution · Urban air · Pine needles · OCP · PCB · PAH · SPE · SPME · GC-ECD · HPLC-FL

Responsible editor: Constantini Samara

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Introduction

Air pollution is a dynamic and highly complex process (Hinds 1999). Emissions sources, discharge conditions, and atmospheric climatic conditions all influence transport and chemical transformation of pollutants, thereby defining the diversity and concentration levels of pollutants in the atmosphere and their potential toxic effects.

Among the large variety of atmospheric pollutants, persistent organic pollutants (POPs) represent a class of highly hazardous chemical contaminants, including

polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polycyclic aromatic hydrocarbons (PAHs), and share similar characteristics of persistence and bioaccumulation in fatty tissues of living organisms (Jones and de Voogt 1999). Given available evidence for long-range transport of these substances to regions in which they were never used or produced (Kallenborn et al. 1998), POPs were recognized as a serious global threat to human health and ecosystems. The objective of reducing the release of these chemicals into the environment was formalized by the Stockholm Convention on POPs, which was adopted in May 2001 and came into force in May 2004 (Weinberg 2008).

In this context, regular monitoring of air quality in the vicinity of point sources is of great importance. Currently, the majority of atmospheric monitoring programs rely on the use of active (AAS) and passive air samplers (PAS) (Hayward et al. 2010), which allow accumulation of chemical compounds on an adsorbent material with or without the use of pumps, respectively. AAS and PAS provide reliable quantitative concentration data, but the high costs and time effort associated with their operation, especially in the case of AAS, have prompted the exploration of alternative solutions for routine monitoring of air quality. In particular, the use of plants as simple and inexpensive passive monitors of atmospheric concentrations of POPs has received significant attention (e. g., Simonich and Hites 1995; Romanić and Klinčić 2012).

Needles from evergreen and ubiquitous pine species are well-suited for such analyses and represent one of the most common plant matrices used for monitoring semi-volatile organic compounds (SVOCs) (Tremolada et al. 1996; Wenzel et al. 1998). Contaminants present in the vapor phase of air can be adsorbed to or absorbed into needles via stomata (Strachan et al. 1994), and the high lipid content of epicuticular wax leads to accumulation of lipophilic compounds in needles (Reischl et al. 1989). Pine needles have been used for passive monitoring of several classes of pollutants such as pesticides (Ratola et al. 2014), PAHs (Lehndorff and Schwark 2004; Amigo et al. 2011), PCBs (Wyrzykowska et al. 2007), polybrominated diphenyl ethers (Ratola et al. 2011), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Ok et al. 2002). However, only a single class of pollutants was analyzed in these studies.

The aim of this work was thus to demonstrate the possibility of integrative concomitant assessment of the spatial and temporal distribution of pesticides from three widespread classes of POPs, including 12 PCBs, 19 OCPs, and 17 PAHs, using pine needles collected from three sites representative of urban, suburban, and rural areas in and around Strasbourg (France).

Materials and methods

Chemical reagents and standard solutions

HPLC-grade acetonitrile (ACN), methanol (MeOH), ethyl acetate (EA), and toluene (TOL) (Biosolve, Dieuze, France), dimethyl formamide (DMF), silica gel and "Fontainebleau" sand (Prolabo, France), and ultrapure water (Milli-Q water system, Millipore, France) were used. Internal standards octachloronaphtalene (OCN) (97 % purity) and triphenylbenzene (TPB) (97 % purity) were obtained from Sigma Aldrich (L'Isle d'Abeau, France). Certified mixtures of PCBs (18, 28, 31, 44, 52, 70, 81, 101, 105, 114, 118, 123, 126, 138, 149, 153, 156, 157, 180, 167, 169, 189) and OCPs (hexachlorobenzene (HCB), α-hexachlorocyclohexane (HCH), lindane (γ-HCH), heptachlor, aldrin, β-HCH, δ-HCH, heptachlor epoxide A, heptachlor epoxide B, 2,4′-DDE, α-endosulfan, trans-chlordane, cis-chlordane, dieldrin 2,4′-DDT, 2,4′-DDD, β-endosulfan, and 4,4′-DDT) (>99 % purity) were obtained from Cluzeau Info Labo (St. Quentin Fallavier, France). Individual PAH standards were supplied by Sigma-Aldrich (L'Isle d'Abeau, France). Purity was >99 % for pyrene (PYR), benz[a]anthracene (BaA), benzo[e]pyrene (BeP), benzo[k]fluoranthene (BkF), indeno[1,2,3-cd]pyrene (IcdP), and coronene (COR); >98 % for fluoranthene (FLA), chrysene (CHR), benzo[g,h,i]perylene (BghiP), and benzo[b]fluoranthene (BbF); and >96 % for benzo[a]pyrene (BaP) and dibenz[a,h]anthracene (DBaA).

Sample collection

Samples were collected at three sites in Strasbourg (Fig. 1): urban (U, in the botanical garden of central Strasbourg, and on the Strasbourg University campus), suburban (S, Robertsau forest nearby an industrial harbor), and rural (R, Wantzenau recreational forest area surrounded by agricultural fields).

Sampling was performed over a period of 5 weeks in April and May 2013, on April 14, 22, and 29 and May 13 and 21, yielding a total of 15 samples. Six-month- to 1-year-old needles were collected by cutting only the terminal part of pine branches. Samples were transported to the laboratory and stored frozen in plastic bags (−18 °C) until further processing. Needles were cut into small pieces (<0.2 cm) after discarding the twigs, placed into glass vials, and then kept frozen until extraction.

Cleanup of ASE extracts

Finely cut needles (10 g) were mixed with sand and placed in layers into the accelerated solvent extraction (ASE) cells (33 mL) with filters fitted at the bottom to prevent the passage
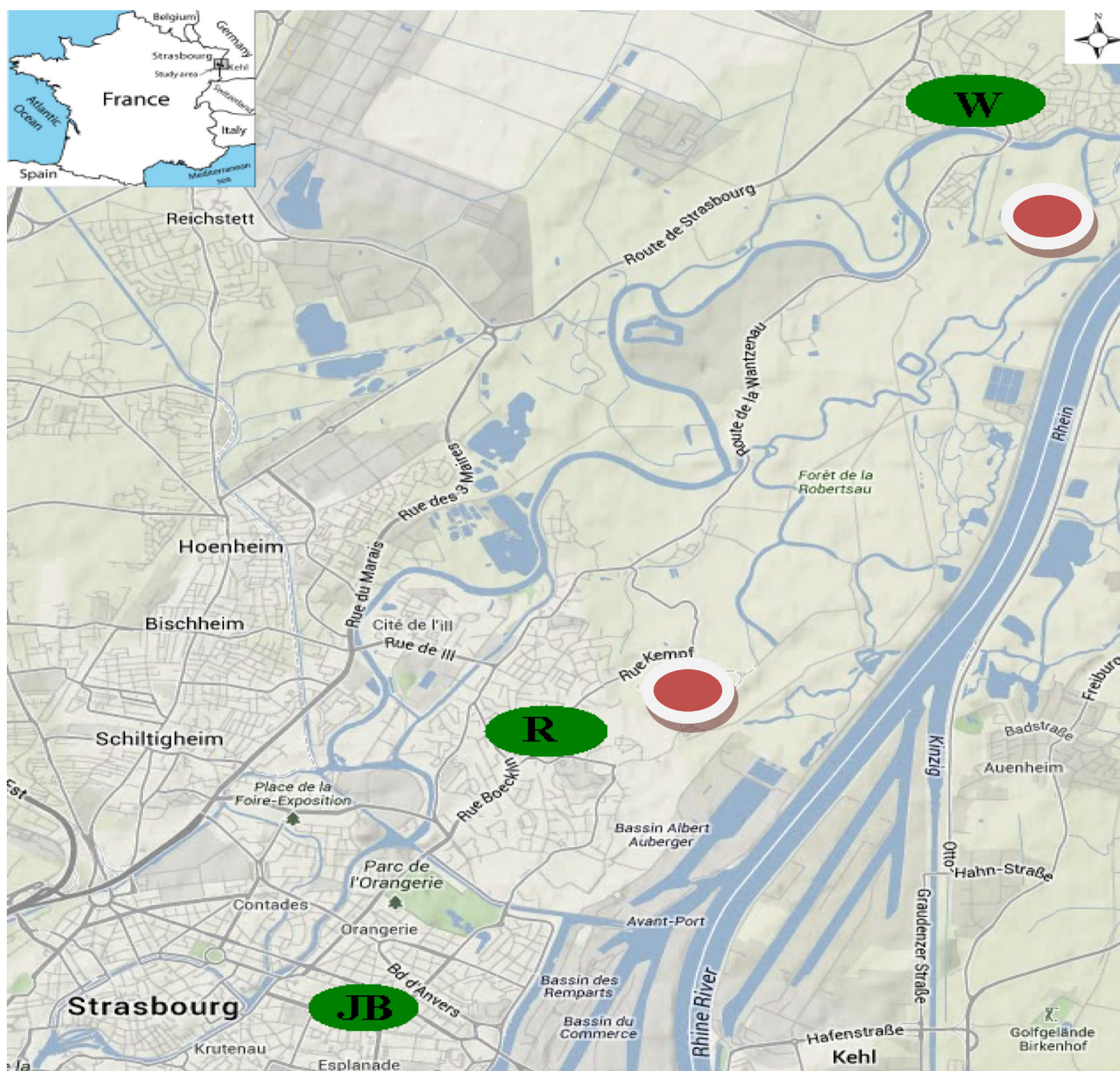
Fig. 1 Localization of the sampling sites

of very small needle particles into the tubing. Initial purification was done directly in the extraction cell by addition of acidic silica gel (5 g) at the cell bottom. Extraction was carried out (total extraction time 25 min) with ACN (100 %) by a protocol consisting of heating the cell to 150 °C for 5 min, three static cycles of 5 min each (50 °C, 1500 psi), flushing 60 %, and purging for 300 s. The final light green-colored extracts (volume) were collected in the ASE bottle.

Solid phase extraction (SPE) was then used to purify the crude ASE extracts, which were diluted to 1000 mL with acidified Milli-Q water and transferred to clean amber bottles.

CHROMABOND® EASY cartridges (Macherey-Nagel, France), consisting of a polar modified polystyrene-divinyl benzene copolymer, were used as adsorbents (mean pore diameter 60 Å, surface area 623 m^2/g, and mean particle size 91 μm). The SPE procedure was optimized as follows: conditioning of the cartridge with 5 mL of MeOH followed by 10 mL of Milli-Q water, flushing of the sample into the cartridge at 10 mL min^{-1} and then drying by N_2 flushing for 15 min, and sequential elution with 2 mL of EA, TOL, and ACN. DMF (100 μL) was added to the extract as a keeper to avoid analyte loss during the final evaporation with a gentle

stream of nitrogen gas. After dryness, 5 mL of ACN was added to yield the final extract.

Analysis of SPE extracts

PCB and OCP concentrations were determined by gas chromatography (GC) using electron capture detectors (ECD) with a Combi Pal autosampler mounted on a TRACE GC (Thermo Fisher Scientific, Les Ulis, France) equipped with two split/splitless injectors and two electron capture detectors. Introduction of the sample into the columns was done by using a 100-µm PDMS SPME fiber. Twenty-milliliter SPME vials were prepared that contained 2 mL of the needle extract, 10 µl OCN (9.8 mg L^{-1}), and Milli-Q water (1.5 % NaCl). SPME fiber was inserted into the solution at a temperature of 80 °C for 40 min. Extraction was done two times for each sample in order to permit the successive injection into the two split/splitless injectors maintained at 250 °C in the splitless mode (5 min) and connected to two capillary columns (each 30 m × 0.25 mm, 0.25-µm film thickness). Quantification was done on a Varian VF-1701 (14 % cyanopropyl/phenyl—86 % poly dimethyl siloxane (PDMS)) while the second column (Macherey-Nagel OPTIMA-5 (5 % phenyl—95 % dimethyl-polysiloxane)) was used for qualification by comparison of the retention time between the two columns for quantification. The ECDs were maintained at 350 °C, with Ar/CH$_4$ at 30 mL min^{-1} as make-up gas. Hydrogen was used as carrier gas at a flow rate of 1 mL min^{-1}, and separation was performed with the following temperature gradient: 50 °C (5 min), 12 °C/min to 170 °C, 0.5 °C/min to 180 °C (2 min), 1 °C/min to 200 °C (8 min), and 10 °C/min to 280 °C (5 min). Separation of PCBs and OCP was achieved in 76 min.

For PAHs, vials of 2 mL volume were prepared as follows: 400 µL ACN, 100 µL triphenylbenzene (TBP) at 10.7 mg L^{-1}, and 500 µL of needles extract. The analytical column oven temperature was set to 25 °C, the injection volume was 50 µL, and the separation of PAHs was performed by using a methanol/water mobile phase at a flow rate of 1 mL min^{-1} by using a Macherey-Nagel (MN, Hoerth, France) reversed phase column (EC 250/8/4 Nucleosil 100-5 C$_{18}$ PAH, 250×4 mm i.d.; particles 5 µm, 100 Å pores) equipped with a MN guard column (CC 8/4 Nucleosil 100-5 C$_{18}$ PAH). The HPLC system consisted of two Kontron 420 pumps, a M 491 Kontron mixing chamber, a 482 Kontron controller, a Kontron 465 automatic injector, a Jasco FP-1520 scanning fluorescence detector, a 402 Kontron thermostat controller maintained at 25 °C, a 3493 Kontron degassing system, and a Kromasystem 2000 chromatography software. Detailed chromatographic conditions, excitation/emission wavelengths, and detection limits of the method were reported previously (Morville et al. 2004).

Quality assurance/quality control

Analytical quality of the data was determined using linearity, extraction recoveries, and determination of limits of detection (LOD) and quantification (LOQ).

Good linearity was observed for most of the PCBs and OCPs, with correlation coefficients ranging between 0.932 (PCB 157) and 0.997 (PCB 28+PCB 31). Five compounds showed poor linearity (δ-HCH, β-endosulfan, and PCB 101, 126, and 169), and two compounds could not be quantified (2, 4′-DDT and 4,4′-DDT). For PAHs, good linearity was observed with correlation coefficients ranging between 0.991 (COR) and 0.999 (FLU, ANT).

Limits of detection (LOD) and limits of quantification (LOQ) were determined from calibration curves. LOD=3.3 (S$_b$/a) and LOQ=10 (S$_b$/a) where "S$_b$" is the standard deviation of y-intercepts and "a" is the slope of the curve. LOD were determined as the lowest concentration where all peaks selected for a compound were observed at three times the signal/noise ratio and LOQ as ten times the signal/noise ratio. For PCB and OCP, LODs were between 3.5 and 21 pg g^{-1}, and LOQs between 10.5 and 62 pg g^{-1}. For PAH, LODs were between 150 and 3000 pg g^{-1} dw and LOQs between 10,000 and 62 pg g^{-1}. Where indicated, zero (0) values indicate below detection.

Recovery efficiency of SPE extraction (including the potential influence of acidic silica) was determined by spiking sand of the mixture of compounds and application of the entire analytical procedure. Recoveries varied between 76 % (HCB) and 107 % (PCB 157) for PCBs and OCPs and between 75 % (NAP) and 103 % (ACE) for PAHs.

Extraction reproducibility was evaluated by three consecutive ASE extractions of 10 g of the same pine needle sample and varied between 15 % for PAHs and 20 % for PCBs and OCPs.

Potential contamination was evaluated by application of the entire extraction and analysis method to clean sand. All investigated POPs were below the detection limits of the method. Finally, the absence of a potential "memory effect" from the SPME fiber was regularly checked by extraction of pure water.

Results and discussion

The aim of this study was to demonstrate the feasibility of concomitant integrative passive monitoring of POPs in the air of a typical urban environment using pine needles, taking Strasbourg, a typical middle-sized European city, as a case example.

The spatial distribution and temporal variation of PCBs, OCPs, and PAHs was analyzed from data obtained from 15

Table 1 Concentration range, total, and mean concentrations of PCBs (ng g^{-1})

	Urban	Suburban	Rural
PCB 18	1.2	0.2	0.25
PCB 70	1–2	<LD	<LD
PCB 114	<LD	<LD	0.323
PCB 118	<LD	<LD	0.2
PCB 123	<LD	<LD	0.1–0.35
PCB 149	<LD	<LD	0.3
PCB 156	0.2	0.3-0.7	0.2–0.8
PCB 157	0.6	0.1	0.5
PCB 167	–	0	<LD–0.24
PCB 180	–	–	<LD–0.79
PCB 189	0.5–1	0.2–0.4	0.340–1
	Range		
ΣPCB	1.–2.7	0–1.1	0.2–2.7
	Median		
ΣPCB	1.85	0.6	1.7

Table 2 Concentration range, total and, mean concentrations of OCPs (ng g^{-1})

	Urban	Suburban	Rural
HCB	<LD	<LD–0.1	<LD–0.1
α-HCH	<LD	0.5–0.6	0.4–1.1
Lindane (γ-HCH)	3.2–22.2	2–4.1	2.7
Heptachlor	<LD	0.3–0.4	<LD
Aldrin	<LD	<LD	0.154
β-HCH	2–18	<LD–6.8	<LD 22.9
heptachlor epoxide B	<LD	0.15-0.3	<LD
α-Endosulfan	<LD	<LD–0.7	0.3–4.5
cis-Chlordane	0.2–1.6	0.2–0.4	0.2
4,4′-DDE	<LD	0.1–0.2	0.1
2,4′-DDD	<LD	<LD	0.2
	Range		
ΣOCP	3.8–41.9	5.8–8.3	1.1–26.9
	Median		
ΣOCP	13.9	6.6	12.1

samples, taken at five successive time points over a period of 5 weeks, at three different sites (Fig. 1) representative of urban (U), suburban (S), and rural (R) zones in and around Strasbourg (France). Analytical samples were obtained from needles by pressurized liquid extraction (ASE) and purified by solid phase extraction (SPE), and a total of 48 POPs (12 PCBs, 19 OCPs, and 17 PAHs) were quantified by gas chromatography coupled to electron capture detection (GC/ECD) or high-performance liquid chromatography coupled to fluorescence detection (HPLC-FLD).

PCBs

Total and median PCB concentrations were similar and showed the same temporal trend at the three sites investigated (Table 1). In total, 11 PCB congeners could be detected among the 12 investigated. A related study of pine needles (*Pinus sylvestris* L.) collected from urban and rural sites in Sweden also showed a higher total PCB concentration at the urban site (0.23–0.47 ng g^{-1}) than at the rural site (0.12–0.21 ng g^{-1}) for the 13 PCB congeners investigated (Getachew 2012).

Fig. 2 PCB concentrations (ng g^{-1} dw) in rural, suburban, and urban sites, respectively (up to down), as function of sampling period
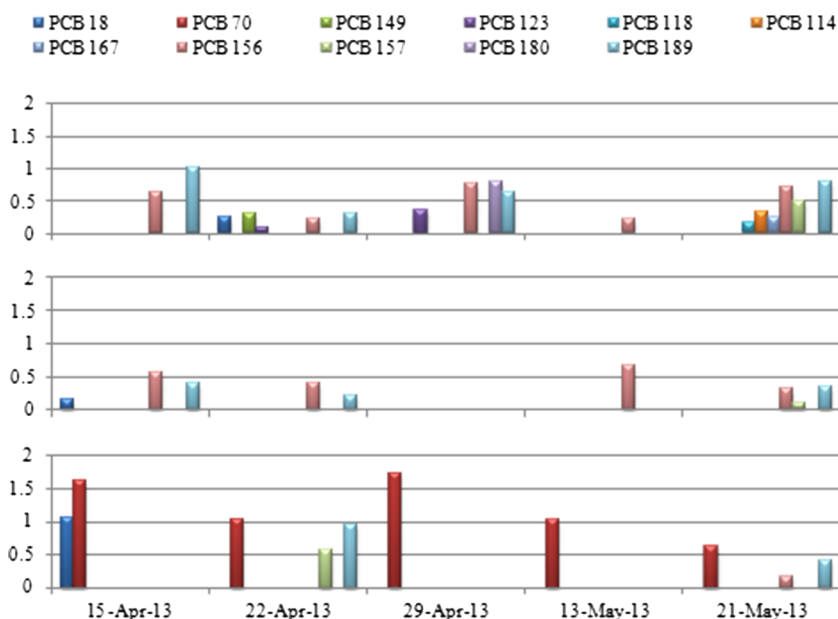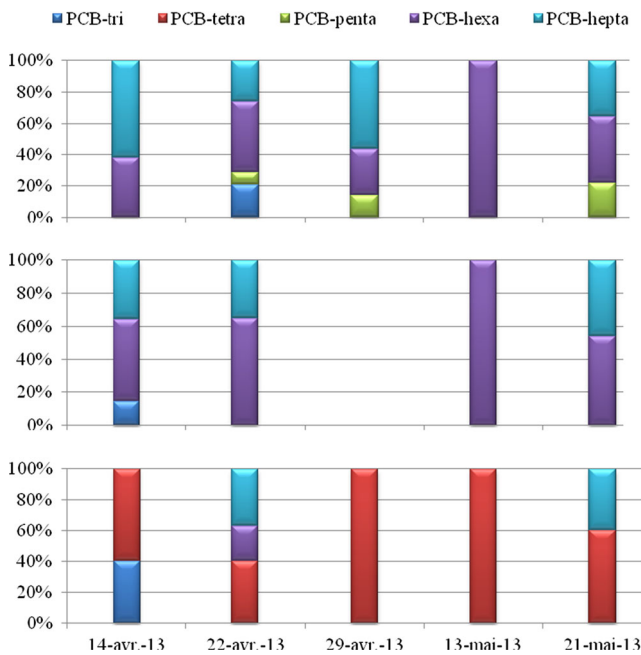
Fig. 3 PCB homologues distribution at rural, suburban, and urban sites, respectively

The concentration range of individual PCBs was 0–1.74 ng g^{-1} at the urban site, 0–1.02 ng g^{-1} at the rural site, and 0–0.66 ng g^{-1} at the suburban site (Table 1). In addition, a clear difference in the distribution of PCB congeners in the three sites was apparent, with the rural site displaying the highest number of different PCB congeners (PCB 18, 114, 118, 123, 149, 156, 157, 167, 180, and 189), with PCB 189 showing the widest variation in concentrations (0.30–1.02 ng g^{-1} dw). However, the highest concentrations of PCB congeners PCB 18, 70, 156, 157, and 180 were detected at the urban site as noted previously (Cindoruk and Tasdemir 2007), with PCB 70 displaying the highest concentration of all PCB congeners detected on all three sites (0.63–1.74 ng g^{-1}). Notably, concentrations of congeners PCB 156 and 189 (0.66 and 0.39 ng g^{-1}, respectively) were only marginally lower at the suburban site than at the rural site, despite the lowest total levels of PCBs at the suburban site. Generally and somewhat surprisingly, however, PCB concentrations measured in our study were lower than those of the 17 PCB congeners analyzed in different species of pine needles (*P. sylvestris* and *Pinus nigra*) collected at eight sites along the eastern Adriatic

coast (Croatia), in which concentrations of up to 7.05 ng g^{-1} were measured (Romanić and Klinčić 2012).

Industrial activities are usually held responsible for PCB emissions, but road traffic (Guéguen 2011) and residential firewood combustion (Hedman et al. 2006) may also contribute. PCBs reach the atmosphere through air-water/soil exchange, vaporization from waste disposal areas, sludge dewatering beds, electronic devices containing PCBs, and incineration of PCB-containing materials (Biterna and Voutsa 2005). Accordingly, the largest diversity of PCB congeners observed at the rural site may tentatively be assigned to emissions from a chemical waste incinerator industry near this site (Guéguen 2011) and to wood combustion for heating purposes. The lower number and concentration range of these congeners at the suburban site may reflect the larger distance of this site from the corresponding emission source and by prevailing dominant winds (SW to NE) tending to direct air masses at the rural site away from the suburban site. In contrast, the exclusive detection of PCB 70 at the urban site could be caused by emissions from an unknown nearby point source.

No marked overall temporal trend in PCB concentrations were observed between the first to the final sampling, with some congeners found in the initial campaigns, absent in the next two, and then detected again (e.g., PCB 189 at urban and suburban sites). This suggests that the concentration of airborne PCBs is strongly multifactorial and affected by many parameters such as temperature, rain, and wind. Nevertheless, the temporal profile of PCBs at the three sites, overall, featured higher PCB concentrations in April than in May (Fig. 2). The needle/air partition coefficient is strongly affected by temperature and increases with temperature decrease (Komp and McLachlan 2000). Thus, lower temperatures associated with larger emissions from wood combustion for heating purposes may contribute to explain the slightly greater accumulation of PCBs on needle surfaces that were observed in April.

OCPs

Eleven OCPs out of 19 considered in this study were detected in needle samples, i.e., HCH isomers (α-, β-, and γ-HCH), 4,4′-DDE, 2,4′-DDD, heptachlor, HCB, aldrin, α-endosulfan, *cis*-chlordane, and heptachlor epoxide B. The concentration

Table 3 Comparison of OCP concentrations in this study with published data

Authors	Country	Pine species	Concentration range (ng g^{-1} dw)	ΣOCPs	Predominant compounds
Romanić and Klinčić 2012	Croatia	*Pinus strobus* *Pinus nigra*	<LD–15.6	7	β-HCH and γ-HCH
Lei et al. 2013	Northern Xinjiang	–	2.9–186	17	HCHs and DDTs
This study	France	*Abies alba*	<LD–22.9	11	β-HCH and γ-HCH

Table 4 Concentration range, total and mean concentrations of PAHs (ng g^{-1})

	Urban	Suburban	Rural
Naphthalene	28.5	<LD	<LD
Acenaphthene	27.4–43.8	38.1–56.9	33.9–54.6
Fluorene	4.0–12.9	2.7	<LD
Fluoranthene	<LD	4.8–7.4	5.0
Pyrene	16.0–134.3	10.1–140.4	6.3–92.7
Benzo[a]anthracene	4.3–27.1	3.6–45.2	1.3–24.6
Chrysene	35.3	30.3–30.8	<LD
Benzo[b]fluoranthene	3.1–13.8	4.1–15.0	3–9.1
Benzo[k]fluoranthene	2.3–10.4	0.7–11.2	0.6–6.7
Benzo[a]pyrene	4.4–23.6	8.4–40.7	2.3–17.1
Benzo[gih]perylene	<LD–4.1	0.1–81.9	<LD–2.3
Dibenzo[a,h]anthracene		7.1	
Phenanthrene	26–112.3	12.0–88.1	11.9–70
Anthracene	1.4–3.6	0.6–4.9	0.7–5.0
Benzo[e]pyrene	<LD	<LD	3.2
	Range		
ΣPAH	78.4–373	92.3–418	71.5–253
	Median		
ΣPAH	199	254	157

range of these compounds at the three sites is summarized in Table 2, and their spatial and temporal distribution can be visualized in Fig. 3.

The suburban site was the most exposed to OCPs overall, although concentrations were generally similarly low at the three sites. Only four compounds were found at the urban site, but high concentrations of γ-HCH and β-HCH nevertheless

resulted in a high total maximal concentration of OCPs (41.8 ng g^{-1}). Worthy of note, α-endosulfan was found mostly at the rural site. All other OCPs were consistently detected at concentrations below 2 ng g^{-1} (Table 2).

OCPs β- and γ-HCH predominantly detected in this study were also the most prominent in several other studies from different countries that have focused on OCPs on pine needles (Table 3). Commercial HCHs were produced and used mainly in two forms, as technical HCH containing about 55–70 % α-HCH, 5–14 % β-HCH, 10–18 % γ-HCH, 6–10 % δ-HCH, and minor fractions of other isomers or as the purified γ-isomer of lindane (γ-HCH>99 %) (Li et al. 1998). In contrast to the original technical formulation, β-HCH was the most abundant isomer detected in this study (Fig. 3), confirming the absence of recent technical HCH input (Li et al. 1998). It is suggested that HCHs detected in high concentrations today are mainly weathered HCHs preserved in the agricultural soils. A similar explanation can be put forward for endosulfan, also often detected in the present study. Technical endosulfan is a 7:3 mixture of stereoisomers designated α and β. β-Endosulfan progressively converts to the stabler α-form, although the conversion is slow. This is in good agreement with the non-detection of the β-form in this study and with the detection of the α-form at higher levels at the rural site, with spreading by wind the likely factor for its detection at the suburban site.

With regard to the temporal variation of OCPs, it was noteworthy that the highest concentrations (above 10 ng g^{-1}) were observed in the first sampling campaign at rural and urban sites (Fig. 3). However and as for PCBs, no consistent trends in concentrations could be observed, and the same reasoning as presented above for PCBs can be advanced.

Fig. 4 OCP concentrations (ng g^{-1} dw) in rural, suburban, and urban sites, respectively (up to down), as function of sampling period
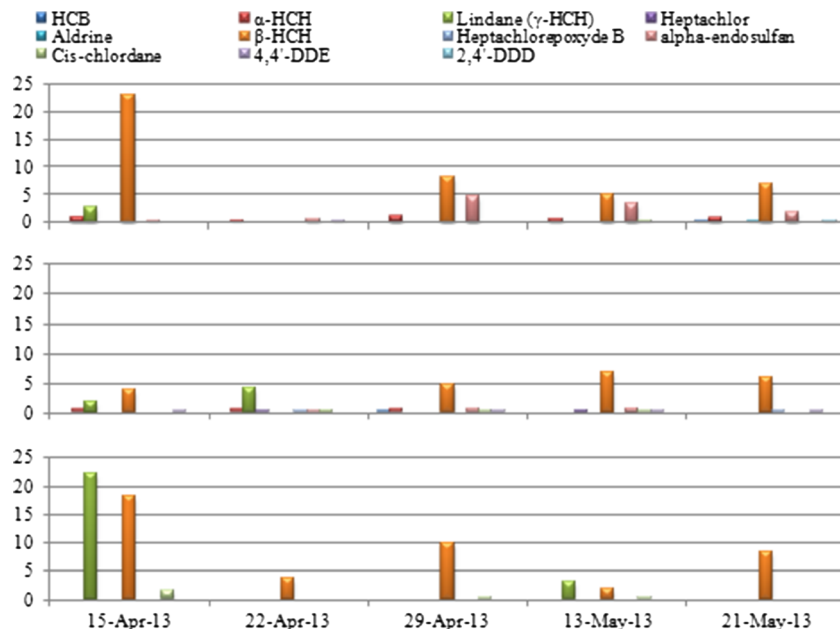
**Table 5** Comparison of PAH data in this study with published data

Authors	Country	Location	Tree species	Total concentration range (ng g^{-1})		ΣPAHs
Ratola et al. 2010	Portugal	Urban	*P. pinaster*	473–1944		16
			P. pinea	232–751		
		Rural	*P. pinaster*	340–1184		
			P. pinea	114–472		
Tomashuk et al. 2012	USA		*Pinus nigra*	2543–6111		16
			Pinus strobus	127–589		
Oishi 2013	Japan		*Pinus thunbergii* Parl.	122.65		16
This study	France		*Abies alba*	Suburban	92.3–418.0	15
				Urban	78.4–372.9	
				Rural	71–5-253.3	

PAHs

In total, 17 PAHs were considered in this study, and 15 were detected. Indeno[1,2,3-cd]pyrene and coronene were not found in any sample. Some compounds, such as phenanthrene and benzo[a]pyrene, were measured in all samples, whereas others, such as naphthalene, were found only once (Table 4, Fig. 4). Notably, three PAHs were generally present and at significantly higher concentrations than all others, i.e., pyrene (6.3−140.4 ng g^{-1}) followed by phenanthrene (11.9–112.4 ng g^{-1}) and acenaphthene (27.4−56.9 ng g^{-1}). The high levels of phenanthrene are in agreement with a recent study of an US American metropolitan area in which phenanthrene was found to be highest during the summer season (Tomashuk et al. 2012).

However, comparison of the data obtained with the literature suggests that PAH concentrations around and in Strasbourg were generally lower than those measured in others urban settings so far (Table 5; see e.g., Tomashuk et al. 2012). Here, total concentration of PAHs was found to be higher at the suburban site (92.3–418.0 ng g^{-1}) than at the urban site (78.4–372.9 ng g^{-1}) and lowest at the rural site (71.5–253.3 ng g^{-1}), as also found previously (Ratola et al. 2010) and as expected for sites where vehicle emissions are dominant and where the main source of PAHs is likely motor vehicle exhaust (Lim et al. 1999). Nevertheless, other industrial activities listed by Guéguen (2011), such as incinerators of chemical and domestic waste, thermal power plants, steel plants, biomass heating power stations, oil refineries, and paper producers, contribute to increase the concentration of

Fig. 5 PAH concentrations (ng g^{-1} dw) in rural, suburban, and urban sites, respectively (up to down), as function of sampling period
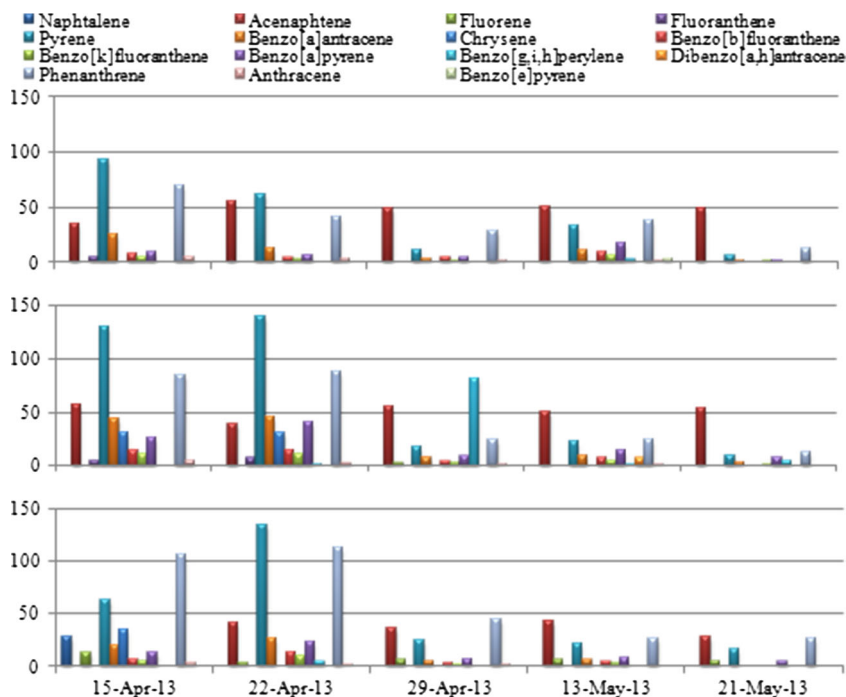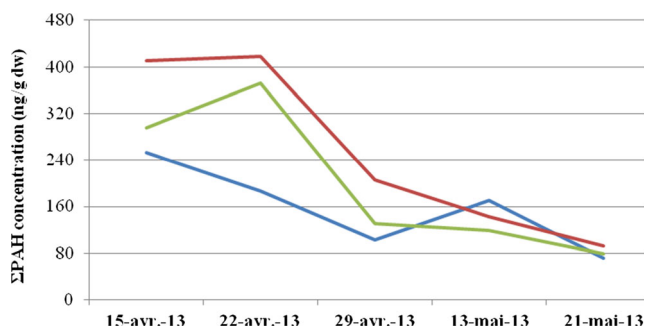
Fig. 6 Temporal trend of PAH in rural (*blue*), suburban (*red*), and urban (*green*)

PAHs in the environment by dispersing them during combustion processes.

An attempt was made to rationalize observed temporal trends of PAHs at the urban, suburban, and rural sites (Figs. 5 and 6). The total concentration of PAHs tended to decrease throughout the sampling period (i.e., 410 to 92 ng g^{-1} at the suburban site, from 296 to 78 ng g^{-1} at the urban site, and from 253 to 72 ng g^{-1} at the rural site). This clear decreasing trend could be correlated with the increase in temperature in May, by lesser winds, and possibly by heavier rainfall, as spring progressed. In contrast to analytical direct measurements of pollutant concentrations in air, however, the data presented in this study are integrative, and it seems difficult to attempt to reconcile them with meteorological data which may change often and drastically over the investigated time period.

Conclusion and perspectives

In this study, pine needles were used as cost-effective and reliable passive biomonitors to simultaneously evaluate atmospheric concentrations of three classes of persistent organic pollutants, i.e., PCBs, OCPs, and PAHs.

The extraction of POPs from needle samples was performed using ASE, cleanup using SPE, and quantitative analysis on GC-ECD for PCBs and OCPs and on HPLC-FLD for PAHs. SPME, another purification method, was additionally used for PCBs and OCPs after SPE. This method was found to be efficient for comprehensive monitoring of three classes of organic pollutants with the same sample. In this study, 11 PCBs, 11 OCPs, and 15 PAHs were detected in the samples. The urban and rural sites were more exposed to PCBs than the suburban site. The highest concentration of PCBs was found at the urban site (0–1.74 ng g^{-1}) and the highest number of congeners at the rural site (10 congeners). PCB 189 and 156 were the predominant congeners in the rural site and PCB 70 in the urban site.

For OCPs, the rural site displayed the highest concentrations (up to 22.90 ng g^{-1}) and number of compounds investigated (9). The high concentration of γ- and β-HCH at that time in the urban site was the reason for this result. γ- and β-HCH were the two predominant compounds in all the samples. The suburban and urban sites were the most exposed with PAHs with a median concentration of 253.6 and 199.3 ng g^{-1}, respectively, with pyrene, phenanthrene, and acenaphthene being the three predominant compounds in these sites.

No specific trend in terms of time was apparent for PCBs and OCPs. However, higher concentrations were detected for some compounds in the first sampling, especially for PAHs, and this is attributed to changes in climatic conditions (e.g., temperature, wind, rain) or inputs from both identified and unidentified sources with a pronounced stochastic component.

The results obtained in this study strongly suggest that pine needles may represent cost-effective and informative integrative passive samples of air quality in an urban environment. Increasing the number of monitored sites will be of great interest, both to evaluate more precisely emission sources of POPs and to establish a spatial and temporal map of air quality in the Strasbourg metropolitan area. The developed method suggests a cost-effective and flexible strategy to implement a substantial increase of sites for long-term monitoring of air quality in urban and rural environments without the need for potentially prohibitive financial and time investment.

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