

Persistent organic pollutants in the atmosphere from urban and industrial environments in the Rhine Valley: PCBs, PCDD/Fs

Florence Guéguen · Peter Stille · Maurice Millet

Received: 2 August 2012 / Accepted: 12 November 2012 / Published online: 24 November 2012
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Abstract Polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxin and furan (PCDD/F) concentrations in the atmosphere were analysed using passive air samplers (PAS) close to the Rhine River between France and Germany. Collectors were placed in industrial, urban, rural and remote areas (Vosges Mountains) between March 2009 and August 2010, and the mean PCB concentrations (sum of 22 congeners) were 3.3, 3.9, 4.1 and 1.4 ngPAS⁻¹ day⁻¹, respectively. Two events during the sampling period were observed in April 2009 and February–March 2010 with the highest PCB concentrations found in the industrial area (19.6 ngPAS⁻¹ day⁻¹). PCDD/F level were measured during these periods, and the maximum concentration observed was from 37.5 fgWHOPAS⁻¹ day⁻¹

Keywords PCBs · PCDD/Fs · Passive air samplers · Industrial emissions

Introduction

The Stockholm convention classified polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins and

furans (PCDD/Fs) as persistent organic pollutants (POPs). They are dispersed in the atmosphere and increasingly enriched in the biosphere since the beginning of the last century due to human activities. The northern hemisphere was more contaminated than other regions of the world (Wagrowski and Hites 2000). POPs have been observed in trace concentrations even in polar areas (Stern et al. 1997). The atmospheric concentration levels of PCBs can be high and range for instance from 0.42 to 8.31 ngm⁻³ in Chicago (Tasdemir et al. 2004), 0.15 to 1.17 ngm⁻³ in Paris (Blanchard et al. 2006) and 0.16 to 2.72 ngm⁻³ in south China (Chen et al. 2009). The Bayer AG (Germany) and Prodelec (France) have been the most important PCB producers (chlophen and pyralene, respectively) during the past (de Voogt and Brinkman 1989). PCBs in dated lake sediments are witnesses of these activities (Zennegg et al. 2007). Thus, PCBs are ubiquitous contaminants of the biosphere due to their significant production until they became banned at the end of 1980, and important quantities of these products can still be found in old electrical equipment (transformers....). Otherwise, POPs can still be emitted by industries and other human activities with especially PCB and PAH emissions from vehicles and residential heating facilities (Cooper et al. 1996; Lohmann et al. 2000; Biterna and Voutsas 2005). Thus, although these compounds have been banned or restricted, they are still largely present in particular in urban and industrial environments and, therefore, generate still a considerable concern for the potential risks associated with these emissions. Consequently, the survey of such environments with respect to such emissions is of importance and allows assessing the human exposure to these hazardous pollutants and the health risks of the population.

The urban and industrial environments of the neighboured cities of Strasbourg (France) and Kehl (Germany) situated on both sites of the Rhine river have been chosen in

Responsible editor: Philippe Garrigues

F. Guéguen · M. Millet (✉)
Equipe de Physico-Chimie de l'Atmosphère—Laboratoire Matériaux,
Surfaces et Procédés pour la Catalyse—(UMR 7515
CNRS—Université de Strasbourg)—1, Rue Blessig,
67084 Strasbourg Cedex, France
e-mail: mmillet@unistra.fr

F. Guéguen · P. Stille
Laboratoire D'Hydrologie et de Géochimie de Strasbourg
(LHyGeS), (UMR 7517 CNRS-Université de Strasbourg)—1,
Rue Blessig,
67084 Strasbourg Cedex, France

order to measure PCB and PCDD/F concentrations in the atmosphere over the period of 1 year. This region suffers from substantial air pollution due to road and river transport and due to the presence of different industrial activities along the Rhine River including steel and thermal power plants, chemical and domestic waste incinerators and other chemical industries. All of them are potential PCB and PCDD/F emitters (Wang et al. 2003; Choi et al. 2008; Onofrio et al. 2010). Moreover, the topography of the Rhine Valley between Vosges Mountains and Black Forest provides a particularly unfavourable situation in respect of ventilation and dispersion of the pollutants. Predominant wind directions are SW-NE. Recent studies using tree barks as biomonitors and Pb, Sr and Nd isotope ratios, trace element distribution patterns and PCB-PCDD/F concentration data allowed to identify sources and to trace plumes of pollutant emissions in the field (Lahd Geagea et al. 2007, 2008a; Guéguen et al. 2012a). Atmospheric measurements of POPs in Europe point to high levels of PCBs around the selected studied area, even in remote areas such as the Vosges Mountains and Black Forests (western and eastern) (Halse et al. 2011).

Passive air samplers (PAS) which have been developed to ease the monitoring of atmospheric pollutants were used in the present study. As they do not need electrical equipment and allow to collect during several weeks, PAS are particularly helpful for easily survey field work for a long period. Several adsorbents and methods were used to collect passively air samples: XAD-2 resin, polyurethane foam (PUF) and semipermeable membrane devices SPMD (Mari et al. 2008a; Schuster et al. 2010; Halse et al. 2011). The XAD-2 resin, a styrene-divinylbenzene copolymer which has lipophilic properties and accumulates PCBs and PCDD/Fs with time (Klánová et al. 2006), has been chosen in this study.

Experimental

Chemical reagents and standard solutions

Methylene chloride and *n*-hexane of HPLC grade (Prolabo; France) and ultrapure water (Milli-Q water system, Millipore, France) have been used for analysis. Standards of individual octachloronaphthalene (internal standard) and PCBs (18, 28, 31, 44, 52, 70, 81, 101, 105, 114, 118, 123, 126, 138, 149, 153, 156, 157, 180, 167, 169, 189) (>99 % purity) were supplied from Sigma-Aldrich (L'Isle d'Abeau, France) and Cluzeau Info Labo (France), respectively.

A stock solution (1 gL⁻¹) was prepared for each PCB with *n*-hexane and a mixture solution of each congener was prepared in *n*-hexane for analysis. The stock solution of octachloronaphthalene was prepared in acetonitrile.

Sampling sites and method

Atmospheric samples ($n=80$) were collected between March 2009 and June 2010 in Strasbourg (France) and Kehl (Germany) in order to determine the PCB baseline concentration in the atmosphere of this urban environment and to detect concentration peaks due to unwanted industrial emissions, great fires etc.

Collectors used during this study were similar to those designed and described by Wania et al. (2003) with a PVC shelter and a stainless steel cylinder as XAD-2 resin container (Schummer et al. 2010). All samplers were exposed for 1 month. Dimensions were modified in order to easily permit their introduction in Dionex Accelerated Solvent Extraction (ASE)[®] cells.

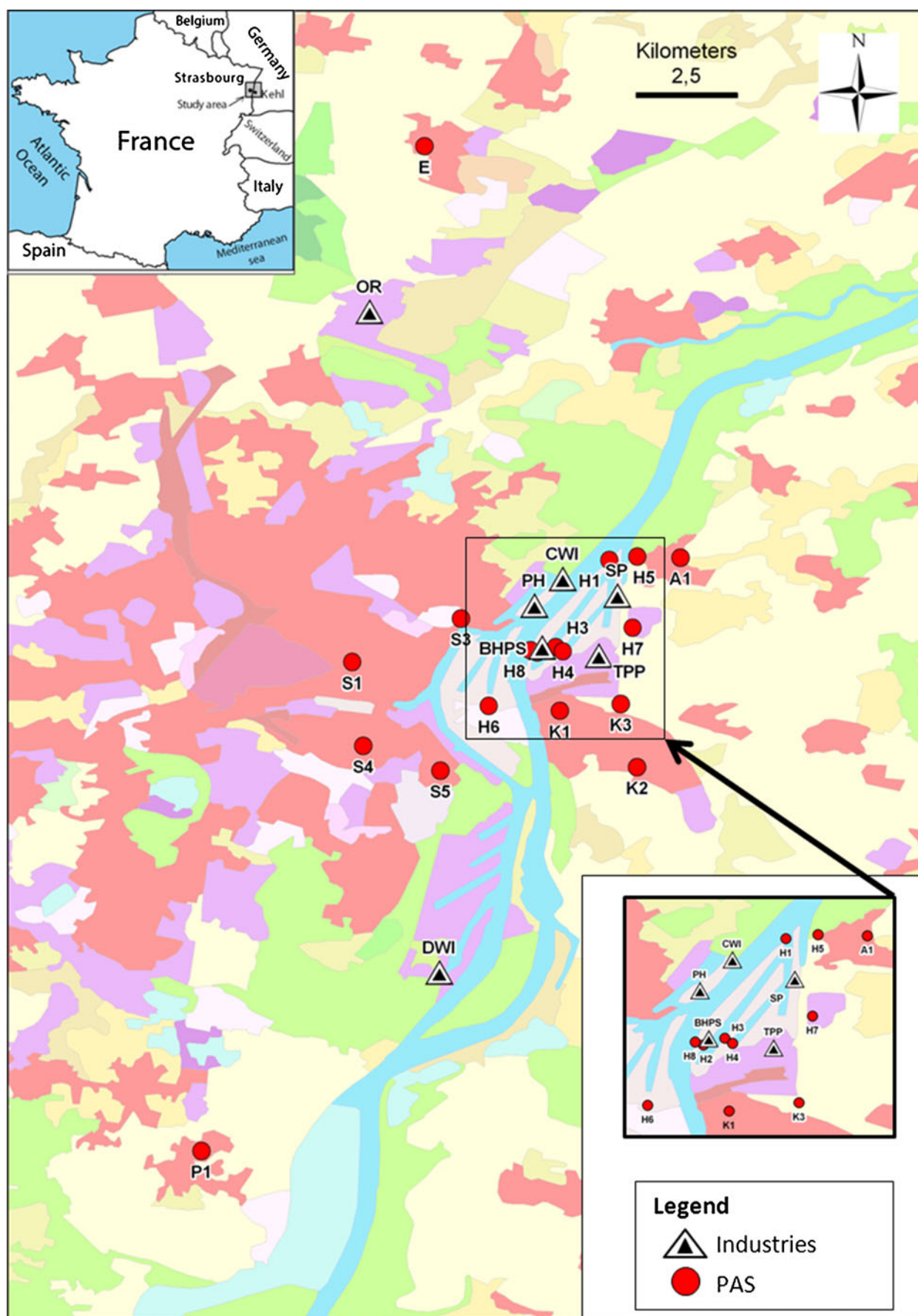
This sampling area on both part of the river Rhine is situated in the Rhine valley and corresponds to an agglomeration of 450,000 inhabitants. Potential sources of PCBs in the industrial harbour and the petrol harbour are steel plant (production of steel of 1.9 Mtyear⁻¹), thermal power plant, bio-mass heating power station (burning of wood pellets/dust 12 th⁻¹), chemical waste incinerator and domestic waste incinerator (350,000 tyear⁻¹). PCBs were collected in the cities of Strasbourg and Kehl and in the industrial harbour. Sampling sites are shown in Fig. 1. Sampling sites K1, A1 and S1 were operating during 10 months. These sites are located around the industrial Rhine harbour, in the centre of the city of Strasbourg (40 m above ground; Institute) (S1), Kehl city centre (K1) and in a garden of a rural site (village of Auenheim) at the northeast of the industrial area (A1). On all other sites of the urban environment, the collection time was shorter (1 to 3 months). The distance between the city centres of Strasbourg and Kehl and the industrial harbour is <4 km. These sites were chosen in order to assess background/transfer contamination (urban and rural sites) and potential emissions sites (harbour, industrial sites).

The baseline concentration of PCBs in the atmosphere of a remote environment was quantified during 1 year with samplers installed in the Vosges Mountains (Strengbach forested catchment: alt. 1,000 m) (Lahd Geagea et al. 2008b) not shown on the map. At this site, samples (BKG) were taken during 14 months. The exposure time for one sample was fixed to 1 month in order to obtain enough accumulation on the PAS.

Extraction and purification of PCB and PCDD/Fs extracts

Before use, XAD-2 based passive samplers were successively washed using an accelerated solvent extraction

Fig. 1 Map showing sampling site of PAS (circles) and industrial sites (triangles). CWI chemical waste incinerator, DWI domestic waste incinerator, TPP thermal power plant, SP steel plant, BHPS bio-mass heating power station, OR oil refinery. Map: European Union SOEs, Corine Land Cover 2006



(ASE®, Dionex) with methanol, methylene chloride and *n*-hexane (two cycles, $T=150\text{ }^{\circ}\text{C}$) following the procedure used for Hi-Vol. samplers traps. After sampling, the resin container was wrapped with an aluminium foil and stored at $-22\text{ }^{\circ}\text{C}$ before extraction.

Extraction was performed with methylene chloride/hexane 50:50 (oven: $150\text{ }^{\circ}\text{C}$, three cycles, static time 5 min, flush 60 %, purge time 150 s). After evaporation, a purification step with a 3 g of silica gel and 1 g of acidified silica gel in a cartridge on a CombiFlash® system was performed. The gel was washed with 25 mL of eluant (*n*-hexane), and then the fraction containing PCBs and PCDD/Fs was eluted with 25 mL of *n*-hexane. A last evaporation to concentrate the substrate to less than 1 mL was performed. Octachloronaphthalene was added as internal standard to the final extract.

Collection, extraction and purification of tree barks

Five to 30 g of tree barks was collected with a patented drill machine as described previously (Lahd Geagea et al. 2007). It allowed to obtain regular and representative bark samples of 1 mm thickness corresponding to about 2 to 8 years exposure (Hofmann et al. 2001). Bark samples were collected all around the trunk, avoiding the lichens if they were present, at about 150–200 cm above ground. By this way, no wind direction was favoured.

Most bark samples were taken from *Tili*, one from *Fagus sylvatica*. Barks from trunks with a diameter of 30 to 50 cm were only collected in order to have the same integration time of pollution.

Tree barks were extracted following the method described in Müller et al. 2001. Ten grams of barks was introduced in the ASE cell, with 5 g of acidified silica gel. Then the extract was purified with 4 g of silica gel cartridge on a CombiFlash® and elution with 25 mL of *n*-hexane before addition of the internal standard.

Analytical method

PCB concentrations were determined by using a gas chromatograph (TRACE GC, Thermo Fisher Scientific, Les Ulis, France) equipped with two split/splitless injectors and two electron capture detectors. Temperature of injectors and detectors was 250 and 350 $^{\circ}\text{C}$, respectively. Hydrogen (1 mL min^{-1}) and 5 % Ar/CH₄ (30 mL min^{-1}) were used as carrier and make-up gas, respectively. All gases flow rate were electronically controlled. Injections (1 μL) were automatically performed in the splitless mode (1 min) by using a combiPAL® autosampler.

Separation of PCBs was performed by using an OPTIMA-5 ($30\text{ m}\times 0.25\text{ mm}\times 0.25\text{ }\mu\text{m}$ thickness) capillary

columns provided from Macherey-Nagel (Hoerd, France) and a Varian FactorFour VF-1701 pesticides FS ($30\text{ m}\times 0.25\text{ mm}\times 0.25\text{ }\mu\text{m}$ thickness). The operating conditions were as follows: oven temperature program $50\text{ }^{\circ}\text{C}$ (3 min), $15\text{ }^{\circ}\text{C min}^{-1}$ to $200\text{ }^{\circ}\text{C}$, 10 min at $200\text{ }^{\circ}\text{C}$, $1\text{ }^{\circ}\text{C min}^{-1}$ to $205\text{ }^{\circ}\text{C}$, 3 min at $205\text{ }^{\circ}\text{C}$, $1\text{ }^{\circ}\text{C min}^{-1}$ to $210\text{ }^{\circ}\text{C}$, 5 min at $210\text{ }^{\circ}\text{C}$, $2\text{ }^{\circ}\text{C min}^{-1}$ to $240\text{ }^{\circ}\text{C}$, $100\text{ }^{\circ}\text{C min}^{-1}$ to $280\text{ }^{\circ}\text{C}$ and 15 min at $280\text{ }^{\circ}\text{C}$. Separation of PCBs was achieved for 70 min.

PCDD/Fs were analysed by Wessling Laboratorien GmbH Umweltanalytik (48341 Altenberge, Germany) following the US EPA method 1613a, after extraction and purification in our laboratory. Extracts were first analysed for PCBs and shipped to Wessling Laboratorien for PCDD/Fs quantification.

Quality assurance/quality control

For calibration, a resin was doped with a standard mix. The total procedure (including extraction, purification and concentration) has been performed five times for different concentrations ($5\text{--}50\text{ }\mu\text{g L}^{-1}$). Quality assurance/quality control was also checked and recoveries ranged between 50 and 130 % for the 22 congeners, which is in agreement with the US EPA 1668a norm. Limits of detection ($0.5\text{--}3.0\text{ ng PAS}^{-1}$) and limits of quantification ($0.5\text{--}5.7\text{ ng PAS}^{-1}$) were calculated for each congener on a signal-to-noise ratio of 3:1 and 10:1 basis, respectively. Uncertainties on each congener concentration were calculated to be in the range of 3–20 %.

Results and discussion

PCBs in the atmosphere

The long sampling period for K1, A1, S1 and BKG allows to derive baseline concentrations for these different environments. The $\Sigma_{22}\text{PCB}$ mean values for all sampling sites are given in Table 1, and the spatial and temporal variations derived from the long-term observations are shown in Fig. 2. From the long-term observations, one derives that the most enriched site was K1 ($4.6\text{ ng PAS}^{-1}\text{ day}^{-1}$) followed by A1 ($4.1\text{ ng PAS}^{-1}\text{ day}^{-1}$) and S1 ($3.1\text{ ng PAS}^{-1}\text{ day}^{-1}$). BKG showed the lowest concentrations with an average value of $1.3\text{ ng PAS}^{-1}\text{ day}^{-1}$.

Spatial and temporal variations

The PCB concentration profiles of K1, A1 and S1 are rather similar for the period between September 2009 and April 2010, rather low between April and September ($0.6\text{--}2.2\text{ ng PAS}^{-1}\text{ day}^{-1}$) and high in winter between October and

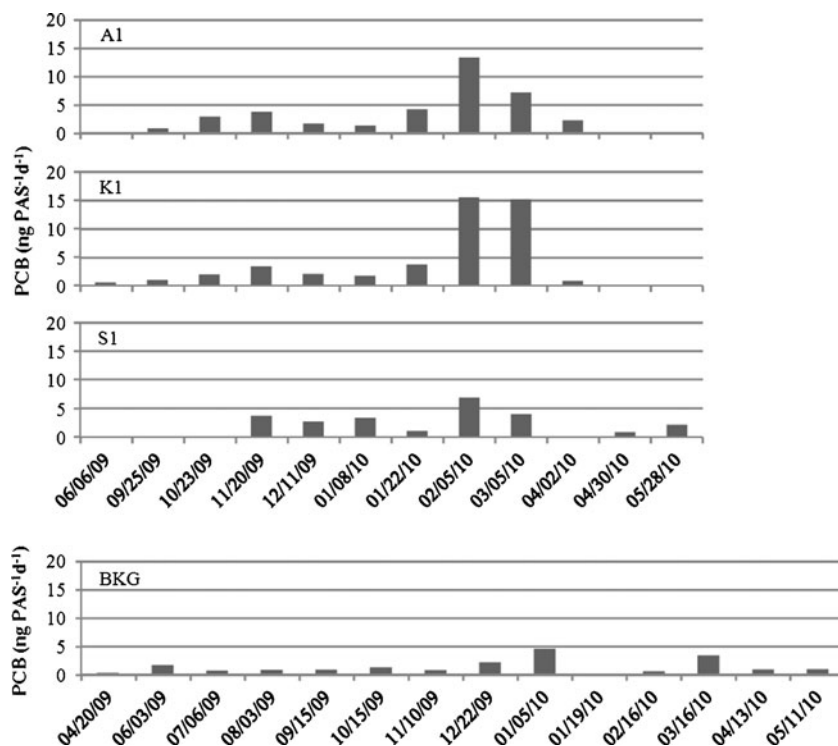
Table 1 Range of PCB concentrations (mean concentration in brackets) and PCB WHO-TEQ concentrations measured in different sites

Sites	Type	Number of samples	Range of concentration $\Sigma_{22}\text{PCB}$ (ngPAS ⁻¹ day ⁻¹)	Mean $\Sigma_{22}\text{PCB}$ WHO-TEQ 2005 (ngPAS ⁻¹ day ⁻¹)
BKG	Rural (forest)	14	0.1–3.4 (1.3)	7.8×10^4
S1	Urban	8	0.9–6.8 (3.1)	5.4×10^3
A1	Rural (NE of harbour)	9	0.8–13.2 (4.1)	4.0×10^3
K1	Urban	10	0.6–15.5 (4.6)	3.8×10^3
H1	Harbour	4	1.2–1.8 (1.5)	2.6×10^4
H3	Harbour	2	1.2–1.9 (1.6)	1.0×10^3
H2	Harbour	2	1.8–8.7 (5.2)	5.6×10^4
H4	Harbour	7	1.0–19.6 (5.4) ^a	5.6×10^{3a}
H7	Harbour	5	1.3–9.5 (3.9) ^a	9.2×10^{3a}
H8	Harbour	3	1.3–2.1 (1.6)	$1.7\text{E}-06$
H6	Harbour	1	0.5	$5.9\text{E}-06$
H5	Harbour	1	1.2	$2.7\text{E}-05$
S3	Harbour	3	1.7–8.2 (3.9) ^a	2.1×10^{3a}
K3	Urban	2	0.7 (0.7)	$1.5\text{E}-05$
S4	Urban	1	1.1	0.01
S5	Urban	1	1.1	9.5×10^3
K2	Urban/rural	3	0.5–9.3 (3.6) ^a	4.6×10^{4a}
E	Rural	1	0.5	$7.0\text{E}-06$
P1	Rural	2	1–1.5 (1.3)	$3.9\text{E}-06$

^aSamples which were collected during particular events

March (0.8–15.5 ng PAS⁻¹ day⁻¹). Two significant PCB peaks with concentrations of up to 15.5 ngPAS⁻¹ day⁻¹ (K1; February 5, 2010–March 5, 2010) are observable for all three samples. Statistical tests (Wilcoxon rank sum test) are used to determine significant differences among months

for each site *P* values determined for all sites are inferior to 0.015; this confirms that the PCB concentration variations observed for a few months are related to particular events which shall be discussed below. Of course, these data should be excluded from baseline estimations. The following

Fig. 2 PCB concentrations during particular events: **a** April 2009, **b** February 2010, **c** March 2010

baseline concentrations can be derived for K1, A1 and S1: $1.9 \text{ ngPAS}^{-1}\text{day}^{-1}$ ($n=8$), $2.4 \text{ ngPAS}^{-1}\text{day}^{-1}$ ($n=7$) and $2.3 \text{ ngPAS}^{-1}\text{day}^{-1}$ ($n=6$), respectively. These values are slightly higher than those found in other samples from the urban environments of Strasbourg and Kehl (K2, K3, S4, S5) and collected outside the particular events ($0.3\text{--}1.0 \text{ ngPAS}^{-1}\text{day}^{-1}$). Sampling site S1 has about the same distance to the industrial sources like S4 and S5; however, site S1 is situated 40 m above ground and, therefore, much more exposed to chimney emissions. The different sites H4, A1, K1 and S1 compared each other by pair are similar in view of variation of PCB concentrations ($P>0.4$).

The samples from the urban environment show generally slightly higher PCB concentrations than BKG. Statistical test yields P values inferior to 0.05 by comparing urban and industrial with BKG samples. In both environments, PCB concentrations are higher during winter than summer. The PCB concentrations of BKG are during April–September period about $0.9 \text{ ngPAS}^{-1}\text{day}^{-1}$ ($n=7$) and $1.8 \text{ ngPAS}^{-1}\text{day}^{-1}$ ($n=7$) in October–March. This is in contrast to earlier studies observing lower PCB concentrations in the atmosphere in winter than in summer due to temperature and volatilization rise in summer (Hermanson and Hites 1989; Coleman et al. 1997). Usually, the low temperature in winter involves higher PCB mass deposition rates which are remobilized by degassing at warmer temperatures. However, due to the geographical situation of the here studied area situated in the valley between the Black Forests and Vosges Mountains, often occurring temperature inversions in winter keep the pollutants in the valley.

Similarly, high concentrations of particle phase PCBs have been found during cold periods due to the lower temperature as well as due to increasing amounts of atmospheric particulate matter (PM) (Granier and Chevreuil 1991; Brunciak et al. 2001; Yeo et al. 2003; Biterna and Voutsas 2005). PM has also been trapped by PAS, as observed during this study and before (Jaward et al. 2004; Mari et al. 2008a). The influence of wood heating combustion is one possible source of PCBs (Lee et al. 1996) which also explains the high PCB concentrations found in a remote area of the Vosges Mountains. Emissions from residential wood combustion close to the sampling site might have caused the high PCBs level in the December, January and March samples. The higher PCB concentrations in the studied urban environment of the cities of Strasbourg and Kehl were more important in this period, and an increase of emissions of industrial activities caused probably the higher PCB concentrations. Indeed, the industrial PCB concentration baseline should be higher in cold period as no dilution effect due to long-range transport occurred.

PCB enrichments in the atmosphere (events)

Two particular emission events have been observed between March 2009 and May 2010: The first one occurred in April 2009, the second one in February–March 2010 (Fig. 3). The highest concentrations have been found in the industrial harbour with $8.7 \text{ ngPAS}^{-1}\text{day}^{-1}$ at site H2 in April 2009 (Fig. 3a) and $19.6 \text{ ngPAS}^{-1}\text{day}^{-1}$ at site H4 in February 2010 (Fig. 3b). The H2 event is also visible in H1 with $1.8 \text{ ngPAS}^{-1}\text{day}^{-1}$ and H3 with $1.9 \text{ ngPAS}^{-1}\text{day}^{-1}$. At site K3, the concentration was $0.7 \text{ ngPAS}^{-1}\text{day}^{-1}$ and, therefore, close or identical to that of the baseline. The source of this event is not identifiable. The principal wind direction in the Rhine valley is NNE-SSW (©REKLIP, <http://www.reklip.org>). The fact that the PCB concentrations decrease in NE direction might suggest that the source of this emission is situated to the SW of site H2 somewhere in the southern part of the French harbour on the left side of the river Rhine.

The second event is more important and has been observed during February and March 2010 (Fig. 3b, c). In February, not only the H4 site but also other sites show a strong increase in PCB concentrations: K1 (centre of Kehl, 2 km SE of the industrial harbour— $15.5 \text{ ngPAS}^{-1}\text{day}^{-1}$); A1 (Auenheim village, 2 km NE of the industrial harbour— $13.2 \text{ ngPAS}^{-1}\text{day}^{-1}$); H7 (Kehl-Auenheim village, 1 km E of the industrial harbour— $9.5 \text{ ngPAS}^{-1}\text{day}^{-1}$); S1 (centre of Strasbourg on the roof of the institute, 4 km W of the industrial harbour— $6.8 \text{ ngPAS}^{-1}\text{day}^{-1}$). P value determined for these sites is 0.06 (1.2 without the S1 PCB concentration value).

Also for this event, it is difficult to evaluate the source of emission because high concentrations have been found SE (K1) and NE (A1) of the harbour. In E direction, PCB concentrations decrease over a distance of 1 km rather quickly probably due to the closeness and protection of a building (H7— $6.8 \text{ ngPAS}^{-1}\text{day}^{-1}$) whereas at site S1, 4 km W of the centre of the harbour, the concentrations remain comparatively high ($6.8 \text{ ngPAS}^{-1}\text{day}^{-1}$). This might indicate that the source is situated in the centre of the harbour and that changing wind directions (S and NNE) dispersed the PCBs in these directions.

In March, the highest concentrations have been observed in the centre of Kehl (K1— $15.1 \text{ ngPAS}^{-1}\text{day}^{-1}$); thus, the concentration remained as high as in February. South of the city of Kehl at the K2 site the concentration decreases significantly to $9.3 \text{ ngPAS}^{-1}\text{day}^{-1}$. To the NE of the harbour at site A1, the concentration is $7.1 \text{ ngPAS}^{-1}\text{day}^{-1}$ and therefore slightly lower than at the more distant K2 site. Site S3 situated NE of Strasbourg and E of the harbour shows similar to A1 a concentration of $8.2 \text{ ngPAS}^{-1}\text{day}^{-1}$. The concentrations of S1 in the centre of Strasbourg are $4 \text{ ngPAS}^{-1}\text{day}^{-1}$ and therefore slightly lower than in February ($6.8 \text{ ngPAS}^{-1}\text{day}^{-1}$). Again, these data do not allow to identify the source but probably it is situated in

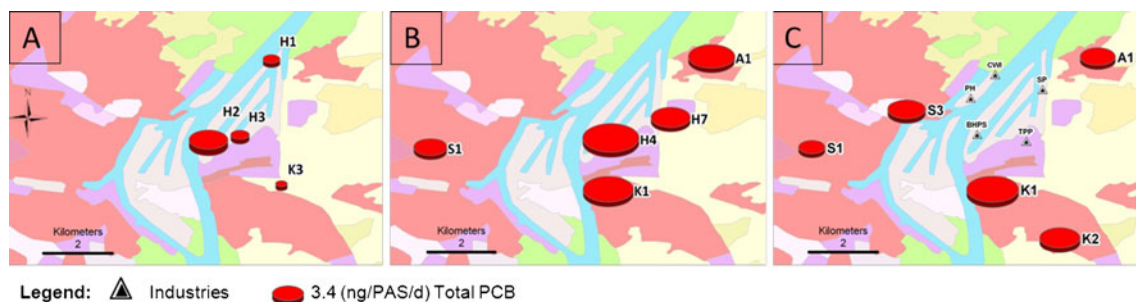


Fig. 3 Spatial and temporal trend. PCBs concentrations in urban (K1 and S1), rural area close to the industrial area (A1) and in a remote area in the Vosges Mountains (BKG)

the industrial harbour of the city of Kehl and emitted PCB under similar wind conditions like in February. Potential PCB emitters are among others wood burning industries (e.g. thermal power plants) (Hedman et al. 2006; Lahd Geagea et al. 2007, 2008a) or steel plants (Liu et al. 2009). During a period where steel production stopped, the PCB concentration at site H4 was $1.6 \text{ ngPAS}^{-1} \text{ day}^{-1}$ and after its restart $1.0 \text{ ngPAS}^{-1} \text{ day}^{-1}$. Thus, these observations do not allow any conclusion about the steel plants PCB emissions, but it seems that steel plant is not the main polluting source. Pb, Sr and Nd isotope measurements of particulate matter collected at the time of PCB sampling might help to elucidate the sources of PCB emissions (Lahd Geagea et al. 2008a).

Characterization of the PCB homologues and their relative abundances in function of the sampling sites

The distribution of PCB homologues observed at sites A1, K1 and S1 are presented in Fig. 4, where the different classes tri-, tetra-, penta-, hexa- and hepta-PCB are identified. The contribution of each class to the total PCB concentration in nanograms per cubic meter is evaluated. Indeed, the volatilization of tri-PCBs (the most volatile) occurred during the sampling time. So, the sampling rate determined for tri-PCBs during the calibration of PAS allow to correct this loss. LQ of tri-PCB (18, 28+31) are the highest with respect to the other elements that might explain that they were not observed when PCB concentrations were very low. The most present homologues are usually tri-PCB and penta-PCB > hexa-PCB > tetra-PCB. The contribution of tri-, tetra-, penta- and hexa- were about 30, 15, 30 and 20 %, respectively. Thus, the PCB homologue distribution during one period at different sites is similar which means that PCB emissions came from the same source. Tri- and tetra-PCB homologues were usually the most concentrated in the atmosphere (Mandalakis et al. 2002; Han et al. 2010) especially in the vapour phase, but tri and penta-PCBs could also be found as the most preponderant (Halsall et al. 1995; Sun et al. 2006). The high level of penta-PCB concentration, often associated with the particulate phase, is certainly characteristic of

industrial PCB emissions. PCB 118, 138 were always analysed as they are markers of vehicles, refuse wood and central heating (Biterna and Voutsas 2005) whereas PCB 180, which has not often been detected, might result from bio-mass heating. The important contribution of tetra-PCBs, especially during the particular event (more than 40 % in A1 and K1 sites), was probably the signature of the polluting source.

PCDD/Fs in urban and industrial area

Dioxins and furans were analysed on samples collected during the particular events in April 2009 and February–March 2010



Fig. 4 PCB homologues distribution at sites A1, K1 and S1. The date indicates the start of sampling period (4 weeks except in January 2 weeks) In blue are PCB-tri, red PCB-tetra, green PCB-penta, purple PCB-hexa

(Table 2). Due to matrix effects, samples H2, S1 and BKG have high detection limits. In the samples H4, A1, S3 and K1, the following enrichment trend in heavy PCDD/F congeners have been observed: OCDD>1234678-HpCDD>OCDF>OCDD>1234678-HpCDF. OCDD contribute to about 33–76 % of the sum of concentrations and range between 128 and 5,924 fgPAS⁻¹ day⁻¹. High dioxin concentrations were only found northeast of the steel plant (A1). The OCDD concentration measured in A1 was 20 to 40 times higher than in S3 and K1. With the exception of the sample from site A1 in the samples from the other sites, the OCDDs do not contribute to their toxicity. The most toxic contributors are usually 12378-PeCDD (30 %), 23478-PeCDF (15 %) and 123678-HxCDD (10 %) which are generally low in all samples. 123678-HxCDD is only enriched in A1 (48 fgWHO-TEQPAS⁻¹ day⁻¹). Therefore, A1 is the most toxic with 37.5 fgWHO-TEQPAS⁻¹ day⁻¹ (Van den Berg 2006). The toxicities of samples collected at sites H4, S3 and K1 are similar: 11.9, 9.9 and 12.5 fgWHO-TEQPAS⁻¹ day⁻¹. These PCDD/F concentrations are similar to those found in Barcelona industrial area collected with PUF PAS (Mari et al. 2008b). Dioxin and furan emissions were not important for the urban areas of Strasbourg and Kehl, and the PCB event appears not to be correlated with the PCDD/Fs. The PCDD/F ratios are higher than 1 and, therefore, point to industrial sources (Lohmann and Jones 1998). The not detectable dioxins and furans in samples

from sites H2, S1 and BKG confirm their weak presence during the PCB events.

However, sample A1 located in rural area was strongly enriched in dioxins with a PCDD/Fs ratio of 24. This might be due to wood heating combustion (Lohmann and Jones 1998).

PCB concentration determined after calibration of PAS

Following calibration experiments performed (Guéguen et al. 2012b), it was possible to determine PCBs concentrations. By this way, PAS-derived PCB concentrations were converted in total PCB concentrations (gas and particulate phase) and, therefore, allow the comparison with published data. Total PCB concentrations were in the range of 0.16–2.0 ngm⁻³ in the industrial area and 0.06–1.71 ngm⁻³ in the urban area (K1 and S1). The background level measured in a remote area of the Vosges Mountains was in the range of 0.005–0.55 ngm⁻³. Table 3 presents published air PCB concentrations from urban/rural areas. Our PCB concentrations found in remote area are similar to those found in rural areas for instance in the east of Germany (PCB concentration in the range of 0.048–0.37 ngm⁻³) (Mandalakis and Stephanou 2007). Hiester et al. (1997) have analysed PCBs in industrial cities of Germany and reported Σ_6 PCB concentration between 273 and 480 pgm⁻³. Some studies giving an overview of PCB distribution in Europe showed high

Table 2 PCDD/Fs concentration of PAS in femtograms per PAS per day

	H2 April 9, 2009 May 5, 2009	H4 February 5, 2010 March 5, 2010	A1 March 5, 2010 April 2, 2010	S3 March 12, 2010 April 14, 2010	K1 March 5, 2010 April 2, 2010	S1 March 5, 2010 April 2, 2010	BKG February 16, 2010 March 16, 2010	BKG March 16, 2010 April 13, 2010
2378-TCDD	<7	<3	<3	<3	<3	<3	<4	<5
12378-PeCDD	<14	<7	<7	<6	<7	<6	<9	<9
123478-HxCDD	<21	<10	11	<9	<10	<9	<13	<14
123678-HxCDD	<21	18	48	15	13	10	<13	<14
123789-HxCDD	<21	<10	21	<9	<10	<9	<13	<14
1234678-HpCDD	<103	118	1455	68	66	<46	<66	<70
OCDD	<343	279	5924	128	198	<154	242	<232
2378-TCDF	<14	12	12	16	12	<11	<9	<9
12378-PeCDF	<14	<7	<7	10	8	<6	<9	<9
23478-PeCDF	<14	12	19	7	17	<6	<9	<9
123478-HxCDF	<21	12	14	12	12	<9	<13	<14
123678-HxCDF	<21	16	20	15	17	<9	<13	<14
234678-HxCDF	<21	14	20	11	11	<9	<13	<14
123789-HxCDF	<21	<10	<10	<9	<10	<9	<13	<14
1234678-HpCDF	<103	<24	85	<20	<24	<46	<66	<70
1234789-HpCDF	<103	<24	<24	<20	<24	<46	<66	<70
OCDF	<34	<34	98	<29	<35	<15	<22	<23
PCDD/PCDF ratio	—/—	3	24	2	2	—/—	—/—	—/—
WHO-TEQ 2005	—/—	11.9	37.5	9.9	12.5	1.0	—/—	—/—

Table 3 Comparison of PCB air concentration with published data

Authors	City	Environment	Range concentration (ngm ⁻³)	PCB congeners
Halsall et al. 1995	London, Cardiff, Manchester... (UK)	Urban	0.1–3.85	8
Chevreuil et al. 1996	Near Paris (France)	Rural	0.3–4.9	15
Blanchard et al. 2006	Paris	Urban	0.15–1.17	7
Stern et al. 1997	Canadian arctic		0.001–0.148	100
Yeo et al. 2003	Kyonggi-do (South Korea)	Rural	0.065	24
Tasdemir et al. 2004	Chicago (USA)	Campus (land space area)	0.42–8.31	50
Motelay-Massei et al. 2005	Toronto (Canada)	Urban	0.1–1.3	13
Mandalakis and Stephanou 2007	Melpitz (Germany)	Rural	0.048–0.374	54
Mari et al. 2008a	Barcelona (Spain)	Industrial area (waste incinerator)	0.076–0.297	7
Mari et al. 2008b	Barcelona (Spain)	Urban/industrial	0.162–0.178	7
Hu et al. 2010	Chicago (USA)	Urban	0.075–5.5	169
	Aubure	Rural (forest)	0.005–0.55	
This study	Kehl	Industrial	0.16–1.99	22
	Strasbourg/Kehl	Urban	0.06–1.71	

level in France (Halsall et al. 1995; Jaward et al. 2004). By comparison with other data of Europe, North America and Asia (Chen et al. 2009), concentrations measured in the study area are rather low. The concentrations observed during the particular events which occurred during the collection time are comparable with other high values also observed in other urban environments, especially under wind conditions from industrial sites (Chevreuil et al. 1996; Tasdemir et al. 2004).

Air/bark comparison

Barks have successfully been used to derive past air qualities (Hermanson and Hites 1990; Hermanson and Johnson 2007). A previous work performed in the here studied area (Guéguen et al. 2011) yields PCB concentrations from tree bark monitoring. The bark/air PCB ratios given in Table 4 allow to distinguish between past and present contaminations (Hermanson and Hites 1990). High bark/air ratios reflect unpolluted or past pollution and low bark/air ratios reflect present-day pollution. For the following consideration, we only use ratios from sites where air and bark samples are available and where the baseline PCB concentrations have been determined during several months. This

is true for the BKG site in the remote area of the Vosges mountains, A1 site in Auenheim village (NE of industrial harbour), K1 site in the centre of Kehl and H site for the harbour (mean of eight sites). Due to the low PCB concentration in air and the low bark concentration at the sampling site in the Vosges Mountains (BKG), its ratio is the highest (72) compared to those from the other sites. Therefore, this ratio is considered to be the baseline ratio of an unpolluted environment. However, at site A1 (NE and close to the harbour) and in the industrial harbour (site H), similar ratios of 10 and 8, respectively, have been observed. This is to expect since mean PCB air concentrations were also on the same concentration level and consequently since barks accumulated the PCBs under identical conditions. The bark air ratio suggests actual pollution and confirms the presence of PCB emitters in the industrial harbour. A different phenomenon can be observed at site K1 in the city of Kehl. Tree bark from this site has high trace metal and PCB concentrations. However, the bark air ratio is high (38) compared to A1 and H and, therefore, points to an important past pollution at K1. Possibly are the high tree bark concentrations the result of emissions from an old and meanwhile disappeared waste landfill and a great fire close to the site; therefore, no traces of actual PCB degassing have been observed and tree barks collected near K1 carry deposition of only past pollutions. Thus, analysis of bark–air ratios is powerful tool to distinguish between past and actual pollution.

Table 4 Air–bark ratio

	Air (ngm ⁻³)	Bark (ngg ⁻¹)	Bark/air ratio
BKG	0.2	14.4	72
A1	4.1	41.7	10
K1	4.6	173	38
H	3.8	31.3	8

Conclusion

Some XAD-2 passive samplers have been placed in different places for 1 year, between 2009 and 2010 in the

industrial area of Strasbourg–Kehl, between France and Germany. Sites have been chosen to be representative of urban, sub-urban, industrial and rural areas in order to evaluate influence of industrial activities on the PCBs and PCDD/Fs contamination. Data obtained are important since few data on atmospheric contamination by PCBs in France are available.

The monitoring of PCBs and PCDD/Fs during several months has permit to calculate mean concentrations, and values obtained in urban and rural areas are very close but higher than those reported in the background remote site. Some peaks of concentrations and spatial and temporal variations were observed, but it was not possible to correlate PCB concentrations with one specific plant but neighbouring with industries and heavy roads are in favour to PCBs emissions.

Acknowledgments This study has been financially supported by a thesis grant from the “Conseil Régional d’Alsace (France)” to F.G., by Projets Exploratoires Pluridisciplinaires; Département Environnement et Développement Durable, by the city of Kehl (Germany) and by Réseau Alsace de Laboratoires en Ingénierie et Sciences pour l’Environnement (France). This is EOST contribution no.....UMR7517.

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