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Optimisation and application of accelerated solvent extraction and flash chromatography for quantification of PCBs in tree barks and XAD-2 passive samplers using GC–ECD with dual columns

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ABSTRACT

An analytical method for the quantification of Polychlorinated biphenyls (PCBs) concentrations in XAD-2 passive air samplers (PAS) and tree barks collected close to the Rhine River between France and Germany was developed. This method used Accelerated Solvent Extraction (ASE) followed by a purification step by flash chromatography using a 4gr cartridge (3 g of silica gel and 1 g of 44% acidified silica) and analysis by GC–ECD with dual columns.

Quantification (QL) and detection (DL) limits varied 0.5 from and 5.7 ng PAS^{-1} and from 0.5 and 3.0 ng PAS^{-1} respectively. For tree barks, quantification and detection limits were calculated for each congener on washed tree bark sample with a signal to noise ratio of 3:1 and 10:1 (corresponding to a LQ in the range of 1–4 ng per bark sample by congeners).

Uncertainties on each congener concentration were calculated to be in the range of 3–20% XAD-2 passive samplers were field calibrated by using Hi-vol. Samplers. Sampling rates of 4.2, 11.5, 1.6, and 7.9 m^3 PAS^{-1} d^{-1} for tri-, tetra-, penta- hexa-PCBs, respectively were obtained and are comparable to those already obtained with PUF-PAS for gas phase only (gas/particle distribution was 90/10).

Method was applied to real atmospheric samples collected by XAD-2 passive samplers and tree barks in the east of France.

1. Introduction

Among the Stockholm convention classified list of persistent organic pollutants (POPs), Polychlorinated Biphenyls (PCBs) are a significant class of semi volatile organic pollutants (SOCs). Due to their thermal and chemical stability and their electrical insulation properties, they were widely used for transformers, dielectric fluids, capacitors, printing ink,… The Bayer AG (Germany) and Prodelec (France) have been the most important PCB producers (chlophen and pyralene, respectively) during the past [32]. However, their interesting industrial properties induce adverse environmental problems in relation to their toxicity due to the presence of chlorine atoms, their long environmental life time in favour of long range transport capacities, their capability of bioaccumulation through the food chain and their mutagenic/carcinogenic human health effects. Consequently, they are increasingly enriched in the biosphere since the beginning of the last century due to human activities and they became 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 [2,4,9]. 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.

Atmospheric measurements of POPs in Europe point to high levels of PCBs around industrial areas, even in remote areas such as the Vosges Mountains and Black Forests (Western and eastern) [12].

Indeed, the atmosphere is well known to be a good pathway for the worldwide dissemination of POPs and PCBs may enter to the atmosphere directly from industrial emissions but also from contaminated soils and water through air–soil and air–water exchanges processes [15,19] and will be partitioned between

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the gas and particle phases in function of many parameters like their concentrations, their vapour pressure, the concentration of particles in the atmosphere [31].

The atmospheric concentration levels of PCBs can be high and range for instance from 0.42 ng m^{-3} to 8.31 ng m^{-3} in Chicago [31], 0.15 ng m^{-3} to 1.17 ng m^{-3} in Paris [3] and 0.16 ng m^{-3} to 2.72 ng m^{-3} in south China [7].

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.

Analysis of PCBs in environmental matrices is done by gas chromatography coupled to electron capture detectors for their sensitivity and selectivity [25] or mass spectrometer in electronic impact or negative chemical ionisation modes [33,8]. Prior to analysis, a fractionation step is required due to very low level of PCBs and the complexity of matrices [38,18].

The conventional and classical method for extraction of PCBs and PBDEs (Poly Bromo Diphenyls Ethers) from environmental samples is Soxhlet extraction. However, this method is time consuming and requires large amounts of solvent. Accelerated Solvent Extraction (ASE) is a relatively recent method permitting the reduction of the time of extraction and the consumption of solvents and consequently the dilution of the extract with very efficient extraction properties. In addition, using extraction cell permits the addition of adsorbents (i.e. silica gel) in order to perform a first purification of the sample [10].

In the present study, an analytical methodology coupling Accelerated Solvent Extraction (ASE), flash chromatography and analysis by gas chromatography–electron capture detection with dual columns for the quantification of trace levels of PCBs in tree barks and XAD-2 passive samplers have been developed. The field calibration of these XAD-2 samplers has been also performed by coupling high volume sampling and XAD-2 passive samplers exposure.

2. Materials and methods

2.1. Chemicals and solutions

Methanol, 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 octachloronaphtalene (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 g L^{-1}) was prepared for each PCB with *n*-hexane and mixture solutions at different concentrations were prepared from stock solutions in *n*-hexane for analysis. The stock solution of octachloronaphtalene was prepared in *n*-hexane.

2.2. Sampling site and strategy

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 order to monitor PCB concentrations in the atmosphere over through tree barks and XAD-2 passive samplers. This region suffers from substantial air pollution due to road and river transport and due to the presence of different industrial sites 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 emitters [35,8,26]. 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.

Tree bark samples have been collected during the years 2008 to 2010 and most samples were taken from *Tili*, (one from *Fagus sylvatica*) from trunks with a diameter of 30 to 50 cm in order to have the same integration time of pollution. For this purpose, 5–30 g of tree barks were collected with a patented drill machine as described previously [22]. It allowed obtaining regular and representative bark samples of 1 mm thickness corresponding to about 2–8 years exposure [17]. 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.

Air samples used for calibration of XAD-2 passive samplers were collected in the meteorological station located in the botanical garden of the University of Strasbourg. This station is situated close to the centre of Strasbourg, a big industrialised city of about 400,000 inhabitants situated in the east of France, and not so far from industrial direct emissions (about 3 km), principally steel production, thermal power, waste and chemical incinerators, and petrol harbour.

Five sampling campaigns were performed: between 05 and 19 December 2009, between 09 and 23 April 2010, between 23 April and 07 May 2010, between 07 and 21 May 2010 and between 21 May and 06 June 2010.

2.3. Cleaning of traps before use

Before use, XAD-2 based passive samplers (PAS) and XAD-2 resin used for High Volume sampling were successively washed using an Accelerated Solvent Extraction (ASE®, Dionex) with methanol, methylene chloride and *n*-hexane (2 cycles, $T=150$ °C), carefully wrapped in aluminium (for PAS) of stored in clean capped bottles until used. The cleaning was performed no later than 2 days before use in order to avoid potential contamination of XAD-2 which is known to be very efficient for adsorbing atmospheric contaminants.

Glass fibre filters were first washed with methanol (1 day) and then washed by methylene chloride/*n*-hexane (50:50 v/v) (1 day) in a Soxhlet apparatus, dried and wrapped in an aluminium foil until use.

2.4. Calibration of XAD-2 passive samplers

The passive samplers used in this study were stainless steel, meshed cylinders filled with XAD-2® resin, based on the design presented by Wania et al. [36]. Though, in order to simplify the extraction of the resin cartridges it was decided to adapt the dimensions of the tubes of adsorb to 100 mL ASE (accelerated solvent extraction) extraction cells. A plastic shelter was produced in order to protect the samplers towards climatic hazards (wind, rain, …) when exposed in the field.

For calibration, two PAS were exposed simultaneously during 2 weeks in order to determine the repeatability.

Calibration was carried out by comparison of the results obtained with active air and passive air samplers.

Particle and gas phases were collected by using a High Volume sampler (Hi.-Vol. sampler) on a glass filter and on XAD-2 resin, respectively, at a flow rate of 6.5–7 m^3 h^{-1} during the same time as the exposure of PAS. In order to avoid potential losses of PCBs on the traps (Filter and resin) due to long pumping period, filter and XAD-2 resin were changed all 3 days.

2.5. Extraction and purification of PCB extracts

Extraction was performed by using ASE 300 system with methylene chloride/*n*-hexane 50:50 (oven: 150 °C, 3 cycles, static time: 15 min, flush 60%, purge time: 150 s). After evaporation, a purification step with a 4 gr Redi*Sep*® cartridge (3 g of silica gel and 1 g of 44% acidified silica gel) on an Isco Combi*Flash*® system was performed at a flow rate of 20 mL min^{-1}. The gel was conditioned with 25 mL of *n*-hexane and then the extract was deposed in the head of the cartridge. The first fraction containing PCBs was eluted with 25 mL of *n*-hexane. A last evaporation to concentrate the substrate to less than 1 mL was performed. Octachloronaphtalene was added as internal standard to the final extract.

2.6. Extraction and purification of tree barks

Tree barks were extracted following the method described in Müller et al., 2001. 10 g of barks were introduced, between two glass fibre filters, in the ASE cell containing 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.

2.7. Analytical of PCBs in PAS and tree barks extracts

The separation of 22 PCBs (18, 28, 31, 52, 44, 70, 101, 81, 149, 123, 118, 114, 153, 105, 138, 126, 167, 156, 157, 180, 169 and 189) was performed by simultaneous injections on two columns; an OPTIMA-5 (30 m × 0.25 mm × 0.25 μm thickness) capillary columns provided from Macherey-Nagel (Hoerdt, France) and a Varian FactorFour VF-1701 pesticides FS (30 m × 0.25 mm × 0.25 μm thickness) connected each to an ECD detector. The simultaneous injection was possible by automated dual injection with the use of a Combi-Pal® autosampler.

The operating conditions were as follows: oven temperature programme 50 °C (3 min), 15 °C/min to 200 °C, 10 min at 200 °C, 1 °C min^{-1} to 205 °C, 3 min at 205 °C, 1 °C min^{-1} to 210 °C, 5 min at 210 °C, 2 °C min^{-1} to 240 °C, 100 °C min^{-1} to 280 °C, 15 min at 280 °C. Separation of PCBs was achieved for 70 min.

The quantification was done on the Varian Factor four VF-1701 while confirmation was done on the Macherey-Nagel OPTIMA-5 column by comparison of the retention time between the two columns.

Whatever the column used, it was not possible to separate PCB 28 and PCB 31 and PCB 157 and 180. Quantification of these PCBs was done on the sum of the two co-eluted PCBs.

Uncertainties on each congener concentration were calculated to be in the range of 3–20%.

LD and LQ were calculated to be (0.5–3.0 ng PAS^{-1}) and (0.5–5.7 ng PAS^{-1}) for XAD-2 passive sampler respectively. For washed tree barks, LD and LQ were calculated for each congener to be (0.05–0.35 ng g^{-1}) and (0.1–0.4 ng g^{-1}) for 10 grs of bark respectively.

3. Results and discussion

3.1. Extraction of XAD-passive samplers, Hi-Vol traps (filter and resin) and tree barks

Dimensions of XAD-2 passive samplers were chosen in order to permit a direct introduction of the sampler (without removing XAD-2 from the mesh cylinder) onto a 100 mL ASE-300 cell. By this procedure, a contamination and an easiest carrying of the sampler was possible. Optimisation of the extraction was performed on spiked XAD-2 resin at different concentrations. Since PCBs are low polar compounds, extraction was done with a mixture of 50:50 *n*-hexane (*n*-hex)-methylene-chloride (CH_2Cl_2).

Parameters of the ASE were optimised in particular, extraction temperature (100 and 150 °C), number and duration of static cycles (2–3 and 10–15 min. respectively). Final optimum ASE parameters were as follows: 3 static cycles of 15 min at 150 °C (1500 PSI) with *n*-hex-CH_2Cl_2 (50:50), a flush for 60 s and a purge of the cell for 100 s.

Traps resulting from high volume sampling were also extracted following the same procedure except the addition of glass beads onto the cell in order to minimise the "death volume" of the cell and consequently the use large amount of solvents.

Due to the nature of tree barks, the extraction procedure developed for XAD-2 resin needs to be modified. Indeed, a static cycle at 150 °C will induce the extraction of large amount of lignin and sap and consequently generate a very difficult flash chromatography purification step. For this reason, the temperature of the static cycle was reduced too 50 °C and a first purification step directly onto the cell was performed following the procedure proposed by Müller et al., (2001) as follows: two filters were introduced onto the 100 mL ASE cell followed by 5 g of acidified silica gel, two filters, 10 g of tree barks, two filters, glass beads and finally two filters. Other ASE parameters were identical as those defined for XAD-2 resin extraction.

Evaporation of extracts coming from XAD-2 or tree barks was done by using a rotary evaporator connected to a vacuum device permitting the selection of pressure. In order to reduce losses of PCBs during the evaporation, two pressures were selected: 400 mbar (CH_2Cl_2) followed by 250 mbar (*n*-hex). Three bath temperatures were tested (35 °C, 40 °C and 50 °C) and it appears that 35 °C gives the better recoveries in comparison with the two other temperatures (Fig. 1).

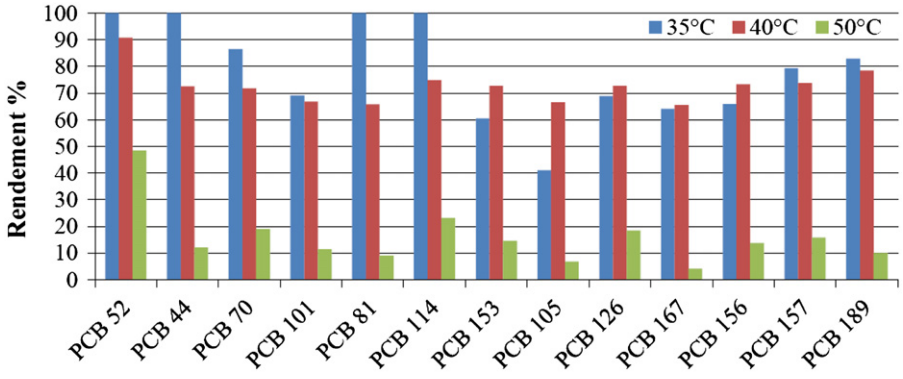

Fig. 1. Recoveries of PCBs after some bath temperature.

3.2. Fractionation by flash chromatography

First analysis by GC–ECD of concentrated extracts have shown the evidence that a fractionation was necessary to remove interfering compounds on the chromatograms.

Fractionation was done by using a Combi-flash® companion flash chromatography system (Isco, USA).

For samples containing PCBs fractionation, different silica mixtures can be used; SiOH [29], SiOH-H^+/Alox-N [6], SiOH/Florisil/$AgNO_3^-$ SiOH/AlOx-N [37], SA/SiOH, SiOH-H^+/SA. In this study, different tests have been performed in order to determinate the better fractionation conditions for the PCB fraction: (a) SiOH, (b) SiOH/SiOH-H^+, (c) SiOH/ SiOH-H^+/SA, (d) SiOH/Florisil, (e) SiOH/Alox-N, (f) SiOH-H^+/SA/Alox-N and (g) SiOH/SiOH-H^+/Alox-N.

Acidified silica was shown as very efficient for lipophilic compounds like PCBs fractionation. Tests (c) and (g) combining SiOH/SiOH-H^+ with SA and Alox-N respectively have shown an equivalent fractionation potential than the simple mixture SiOH/SiOH-H^+ in proportion 3:1. Then, this mixture was selected for sample fractionation.

As for adsorbents, some solvents configurations have been tested: *n*-hexane, methylene-chloride and mixture of *n*-hexane/methylene-chloride in 50:50, 30:70 and 20:80 ratios with different elution volumes (5, 10, 15, 20 and 25 mL). It will be observed that all PCBs are eluted from the adsorbent below to 10 mL of *n*-hexane. Then, a final volume of elution of 20 mL was selected, as there is no interference with elution volume greater than 10 mL, in order to guarantee that all PCBs are eluted from the column.

Each cartridge was used for three purifications. A washing with 50 mL of *n*-hexane was done between each fractionation.

After the fractionation, solvent was evaporated until 1 mL and octachloronaphtalene was added (100 $\mu g\,L^{-1}$) as internal standard [1].

3.3. Calibration, recoveries of extraction and uncertainties

For calibration of XAD-2 passive samplers, resin was spiked with a standard mix at different amounts (1.0 to 50.0 ng PAS^{-1}) and the total procedure including extraction, purification and concentration have been applied on each concentration. This procedure was repeated 5 times. Six point calibration curves have been plotted as the ratio between the peak area and the area of the internal standard versus the ratio of the concentration of the congener with the concentration of the internal standard. These curves were linear between 1.0 and 50.0 ng PAS^{-1}.

Uncertainty of the entire method, including inter-and intraday variations was between 3 and 20% (Table 1). Limit of detection (LoD) and quantification (LoQ) were calculated for each congener on a signal to noise ratio of 3:1 and 10:1 basis.

Recoveries were checked and ranged between 50% and 130% for the 22 congeners, which is in agreement with the US EPA 1668a norm.

For calibration of tree barks, a tree bark sample has first been cleaned until all PCBs have been extracted. This has been checked by the absence of the PCB signal. In order to cover the expected calibration range of concentrations in tree bark, six standard mixtures with different amounts (1.0, 5.0, 10.0, 20.0, 50.0 and 100.0 ng g^{-1}) have been produced and analysed.

As for XAD-2 passive samplers, this procedure was repeated 5 times in order to determine the reproducibility.

Validations parameters are presented on Table 2. Uncertainty of the entire method, including inter- and intraday variations was between 3 and 67% (67% for PCB 169 congener) which is commonly observed for this kind of matrix [37].

Recoveries of the entire procedure ranged between 57% and 69% for the 22 components which is accepted by the US EPA 1668a norm.

Table 1
Validation parameters for the extraction and purification and analysis of PCBs in XAD-2 passive samplers.

Congeners	*Tr* (min)	R^2	Uncertainty (%)	LD (ng/PAS)	LQ (ng/PAS)	Recovery total procedure (%)
PCB 18	15.17	0.994	4	3.0	5.8	119
PCB 28+31	16.57	0.996	10	2.1	3.6	95
PCB 52	17.77	0.996	14	1.1	1.9	104
PCB 44	18.92	0.999	8	1.1	5.5	121
PCB 70	21.07	0.992	5	2.7	2.7	104
PCB 101	22.33	0.999	14	0.0	0.0	96
PCB 81	25.43	0.996	11	1.3	1.4	100
PCB 149	27.22	0.997	12	0.6	0.7	93
PCB 123	27.7	0.997	15	1.1	1.1	83
PCB 118	28.28	0.986	10	2.5	2.6	104
PCB 114	28.83	0.996	13	0.5	0.6	91
PCB 153	29.53	0.997	20	0.0	0.0	98
PCB 105	31.47	0.997	10	1.1	1.1	91
PCB 138	33.13	0.996	13	0.9	0.9	89
PCB 126	37.32	0.996	7	1.9	1.9	97
PCB 167	37.88	0.996	12	0.9	0.9	82
PCB 156	41.08	0.996	7	1.2	1.3	87
PCB 157+180	42.7	0.998	8	0.5	0.5	87
PCB 169	48.33	0.999	3	0.8	0.8	93
PCB 189	51.85	0.997	4	1.4	1.4	86

Table 2
Validation parameters for the extraction, purification and analysis of PCBs in tree-barks.

Congeners	*Tr* (min)	R^2	Uncertainty (%)	LD (ng/g)	LQ (ng/g)	Recovery total procedure (%)
PCB 18	15.12	0.95	3	3.4	11.4	57
PCB 28+31	16.5	0.96	20	1.2	3.9	56
PCB 52	17.7	0.97	5	0.4	1.4	60
PCB 44	18.83	0.96	9	3.9	13.0	58
PCB 70	21.2	0.97	9	0.9	3.1	55
PCB 101	22.22	0.94	12	0.0	0.0	61
PCB 81	25.77	0.95	14	0.8	2.7	60
PCB 149	27.07	0.94	14	0.4	1.4	61
PCB 123	27.55	0.94	22	0.5	1.7	57
PCB 118	28.08	0.94	19	0.8	2.7	66
PCB 114	28.93	0.94	27	0.7	2.2	61
PCB 153	29.37	0.94	30	1.0	3.2	63
PCB 105	31.68	0.95	22	0.8	2.8	62
PCB 138	33.28	0.95	20	0.5	1.6	63
PCB 126	35.6	0.96	20	1.0	3.4	66
PCB 167	37.08	0.95	35	0.3	1.2	62
PCB 156	40.97	0.95	31	0.9	3.1	61
PCB 157+180	42.08	0.95	51	0.4	1.4	64
PCB 169	47.85	0.96	67	0.3	0.9	69
PCB 189	51.85	0.96	28	0.4	1.5	67

Globally, method parameters obtained with tree barks are lower than those observed for XAD-2 passive samplers and are correlated with the complexity of the matrix (Tables 1 and 2). Indeed, the bark contains presents an strong level of organic matter in comparison the XAD-2 which can be co-extracted with the ASE procedure and then inducing an important matrix effect even if a very specific detection method is used.

3.4. Calibration of XAD-2 passive samplers

Passive air samplers (PAS) were developed to ease the monitoring of atmospheric pollutants. As they do not need electrical equipment and allow collecting during several weeks, PAS are particularly helpful for survey field work. Several techniques were

used to collect air samples: XAD-2 resin, polyurethane foam PUF and semi-permeable membrane devices SPMD (Mari et al., 2008a; [30,12]). The XAD-2 resin, a styrene–divinylbenzene copolymer which has lipophilic properties and accumulates PCBs and PCDD/Fs with time [21] has been chosen in this study.

Several campaigns of calibration were necessary in order to determine the sampling rate of the passive air sampler. Calibration was carried out by comparison of the results obtained with active air and passive air samplers located in the same area (Botanical garden of the University of Strasbourg) far from direct emissions. Samplings have been performed in December 2009 and between April and June 2010.

Sampling rates were calculated using the equation described by Persoon and Hornbuckle [27].

Results are presented in Table 3. This calibration yield a gas/particle concentration distribution for the studied area in the range of 50/50 in December and April (C1–C2) at low temperatures (<0 °C) and 90/10 in May and June (C3–C4) under warmer conditions (>25 °C) as shown in Fig. 2. In Fig. 3 are presented data for each group of congener with respect with the period of air sampling. It can be seen that all congener presents the same trends as an increase of the gas phase partition with the increase of the ambient air temperature. This observation involves sampling rates determined with help of both particle and gas phases (brackets in the Table 3). Comparison with data from Persoon and Hornbuckle [27] indicate that these experiments allowed to deduce similar sampling rates of 4.2, 11.5, 1.6, and 7.9 m^3 PAS^{-1} d^{-1} for tri-, tetra-, penta- hexa-PCBs (Table 3), respectively with help of PUF-PAS for gas phase only (gas/particle distribution was 90/10).

Table 3
Sampling rate determined with active air sampler. *R* is given for gas phase and gas+particle phases in brackets.

R (m^3 PAS^{-1} d^{-1})	C1	C2	C3	C4	Mean
PCB tri	12 (9)	8 (6)	3 (3)	5 (4)	**5.6**
PCB tetra	54 (23)	43 (16)	16 (13)	16 (13)	**16.1**
PCB penta	23 (7)	20 (6)	11 (9)	3 (3)	**6.0**
PCB hexa	24 (6)	15 (5)	7 (6)	4 (3)	**4.8**
PCB hepta	–	–	–	–	–

3.5. Application to atmospheric samples

Recent studies have shown that tree bark biomonitoring is efficient to evaluate past organic [5,13,14,37] pollution.

In first studies on PCB pollution, tree barks are suggested to behave such as a lipophilic absorbent of organic compounds [24]. Only recently, it has been demonstrated that tree barks record the atmospheric vapour phase with a very good correlation in PCB, polybrominated diphenyl ether (PBDE) and pesticides [28].

PCB concentrations in tree barks are given in sum of indicators (Σ_7 PCB_{ind}) corresponding to 28+31 (because they were co-eluted), 52, 101, 138, 153, 180. The toxicity equivalent (TEQ) is calculated for the dioxin-like PCB (ΣDL-PCB): 81, 105, 114, 118, 123, 126, 167, 169, 189. Especially the congener 126 has low concentrations in tree barks ranging between 0.1 ng g^{-1} and 0.8 ng g^{-1}. Therefore, only for samples #51, #52, #53, #54, #55 and #59 (Table 1) the dioxin-like PCB 126 has been measured. For all other samples the WHO-$TEQ_{DL\ PCB}$ concentration value might be largely underestimated because the factor of toxicity equivalent (TEF) is high (0.1) compared to the other dioxin-like PCBs.

PCB concentrations of tree bark from industrial, urban and rural areas were determined and are presented in Table 4 [11]. Different groups can be distinguished depending on the sum of PCBs. Lowest Σ_7PCB_{ind} concentrations of 7 ± 2 ng g^{-1} were found in a rural area (sample #84), in forest (samples #65, #68, #74) and park-like environments of the city of Strasbourg and Kehl (samples #71, #78, #79, #51). A second group could be detected for samples with Σ_7PCB_{ind} concentrations ranging between 10–25 ng g^{-1}. These samples were collected close to the Rhine River (#53: 17 ± 5 ng g^{-1}, #54: 16 ± 5 ng g^{-1}, #77: 12 ± 2 ng g^{-1} and #83: 21 ± 5 ng g^{-1} respectively). The third group is represented by samples collected near a freeway, with concentrations ranging between 29 ± 7 ng g^{-1} (#80) and 37 ± 11 ng g^{-1} (#56). Finally, samples #52-#59-#82 from the city of Kehl constitutes the fourth group: these samples are highly contaminated and

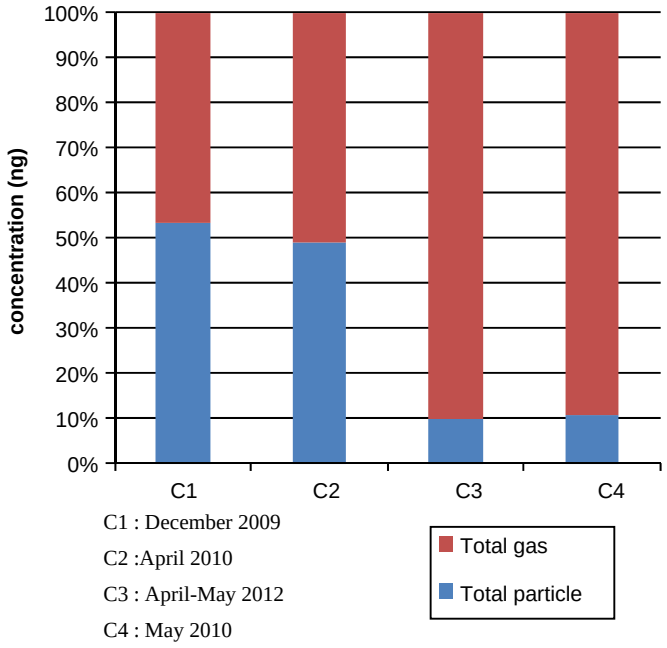

Fig. 2. Gas/particle distribution of the sum of all analysed PCBs during the four campaigns. C1: December 2009, C2: April 2010, C3: April–May 2012, C4: May 2010.

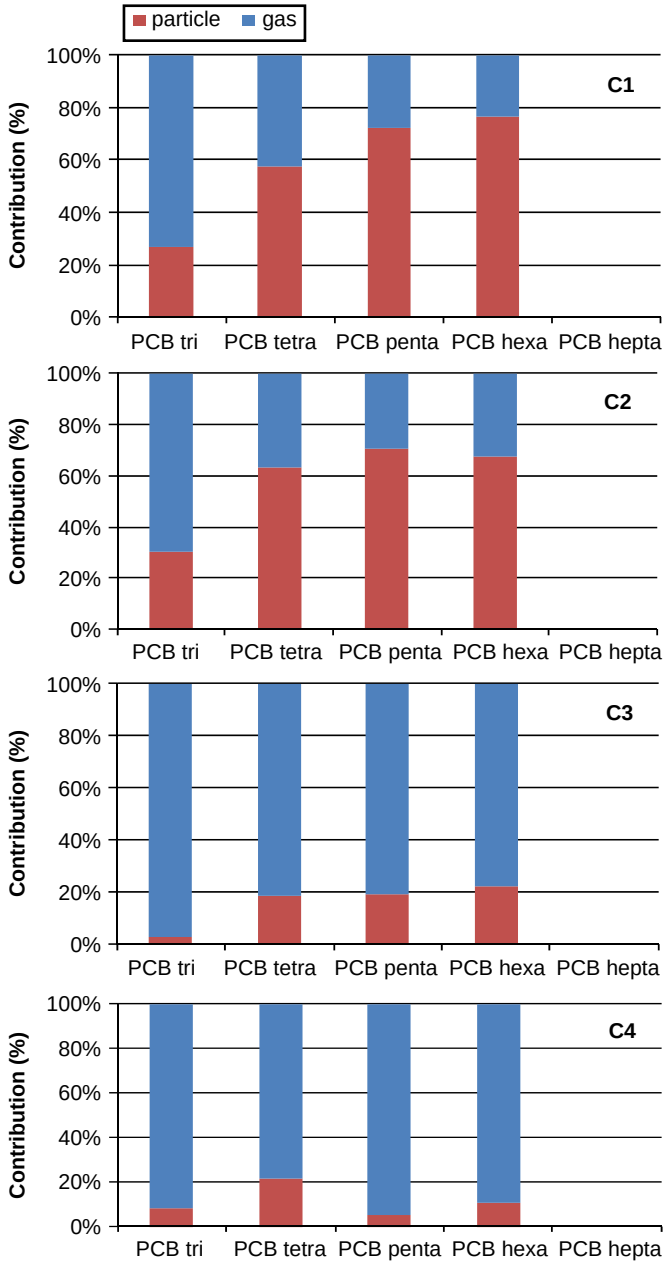

Fig. 3. Gas/particle partitioning of PCBs congeners in function of the sampling period.

show concentrations of 62 ± 16 ng g^{-1}, 134 ± 35 ng g^{-1} and 128 ± 34 ng g^{-1}, respectively.

4. Conclusion

An analytical method was developed for the quantification of PCBs in atmosphere through passive sampling and biomonitoring. This method permits to quantify 22 PCBs in XAD-2 passive samplers and tree barks with good accuracy and sensitivity. A purification step was then required for isolate PCBs from the matrix.

The extraction procedure using ASE was also accurate and a silica purification step onto the cell was required before the flash chromatography fractionation.

The fractionation step allows the use of electron capture detection with good sensitivity and the use of two columns permits to quantify and identify PCBs in XAD-2 passive samplers and tree barks.

This method permits the calibration of XAD-2 passive samplers and allows their use in long term sampling campaigns in many sites.

Tree bark biomonitoring using PCB concentrations allowed to identify former landfill activities within an urban environment but also the impact of great fires in the past.

Table 4
PCB concentrations in tree bark in ng g^{-1}, analysed by GC–2ECD [11].

Sample number		R_7PCB_{ind} (ng g^{-1})	WHO–TEQDL PCBs (ng g^{-1})
51	Urban	7 ± 1	$(45 \pm 9) \times 10^{-3}$
52	Urban	62 ± 16	$(86 \pm 17) \times 10^{-3}$
53	Urban	17 ± 5	$(52 \pm 10) \times 10^{-3}$
54	Harbour	16 ± 5	$(71 \pm 18) \times 10^{-3}$
55	Rural	14 ± 4	$(58 \pm 16) \times 10^{-3}$
56	Harbour	37 ± 11	$(8 \pm 5) \times 10^{-3}$
57	Urban (park)	12 ± 2	$(1.3 \pm 0.2) \times 10^{-3}$
59	Urban	134 ± 35	$(110 \pm 22) \times 10^{-3}$
65	Rural (forest)	4 ± 1	$(0.36 \pm 0.06) \times 10^{-3}$
68	Rural (forest)	6 ± 1	$(4 \pm 2) \times 10^{-3}$
71	Urban	6 ± 2	$(0.28 \pm 0.05) \times 10^{-3}$
72	Rural (forest)	11 ± 3	$(7 \pm 4) \times 10^{-3}$
73	Rural	9 ± 2	$(0.8 \pm 0.1) \times 10^{-3}$
74	Urban (forest)	8 ± 2	$(21 \pm 13) \times 10^{-3}$
77	Rural	12 ± 2	$(0.9 \pm 0.1) \times 10^{-3}$
78	Urban	7 ± 1	$(0.09 \pm 0.02) \times 10^{-3}$
79	Urban	6 ± 1	$(0.15 \pm 0.04) \times 10^{-3}$
80	Urban	29 ± 7	$(0.20 \pm 0.04) \times 10^{-3}$
81	Urban	8 ± 2	$(0.11 \pm 0.02) \times 10^{-3}$
82	Urban	128 ± 34	$(8 \pm 5) \times 10^{-3}$
82-1	Urban	140 ± 36	$(1.3 \pm 0.3) \times 10^{-3}$
83	Rural	21 ± 5	$(0.15 \pm 0.03) \times 10^{-3}$
84	Rural	7 ± 2	$(0.24 \pm 0.05) \times 10^{-3}$

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