Passive sampling of polychlorinated biphenyls (PCB) in indoor air

towards a cost-effective screening tool

Vorkamp, Katrin; Mayer, Philipp

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

PASSIVE SAMPLING OF POLYCHLORINATED BIPHENYLS (PCB) IN INDOOR AIR: TOWARDS A COST-EFFECTIVE SCREENING TOOL

Scientific Report from DCE – Danish Centre for Environment and Energy No. 128 2014

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

[Blank page]

PASSIVE SAMPLING OF POLYCHLORINATED BIPHENYLS (PCB) IN INDOOR AIR: TOWARDS A COST-EFFECTIVE SCREENING TOOL

Scientific Report from DCE – Danish Centre for Environment and Energy No. 128 2014

Katrin Vorkamp[1]
Philipp Mayer[2]

[1] Aarhus University, Department of Environmental Science
[2] Technical University of Denmark (DTU), Department of Environmental Engineering

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Series title and no.:	Scientific Report from DCE – Danish Centre for Environment and Energy No. 128
Title:	Passive sampling of polychlorinated biphenyls (PCB) in indoor air: Towards a cost-effective screening tool
Author:	Katrin Vorkamp[1] and Philipp Mayer[2]
Institutions:	[1]Aarhus University, Department of Environmental Science [2]Technical University of Denmark (DTU), Department of Environmental Engineering
Publisher:	Aarhus University, DCE – Danish Centre for Environment and Energy ©
URL:	http://dce.au.dk/en
Year of publication:	January 2015
Editing completed:	December 2014
Quality assurance, DCE:	Susanne Boutrup
Financial support:	Danish Energy Agency
Please cite as:	Vorkamp, K. & Mayer, P. 2015. Passive sampling of polychlorinated biphenyls (PCB) in indoor air: Towards a cost-effective screening tool. Aarhus University, DCE – Danish Centre for Environment and Energy, 118 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 128. http://dce2.au.dk/pub/SR128.pdf

Abstract: PCBs were widely used in construction materials in the 1906s and 1970s, a period of high building activity in Denmark. The objective of this study was therefore to use passive sampling techniques to develop a simple and cost-effective screening tool for PCBs in indoor air. The study proceeded in three phases combining a literature review, laboratory experiments and measurements in buildings potentially containing PCBs in indoor air. The laboratory experiments showed a strong influence of air velocity on the PCB partitioning between air and the passive sampler. Based on the results of the first two phases and comments from experts in the field of PCB containing construction materials, a kinetic sampler (petri dish with silicone) and a potential equilibrium sampler (silicone-coated paper) were tested in buildings. Calibration and validation were based on conventional active sampling, for both methods in their kinetic sampling phase. The methods were sensitive and precise, but tended to overestimate the concentration obtained by active sampling. More work will be needed to test the silicone-coated paper under equilibrium sampling conditions.

Keywords:	Equilibrium sampling, indoor air concentrations, kinetic sampling, partition coefficients, sampling rates,
Layout:	Graphic Group, AU-Silkeborg
Front page photo:	Rambøll
ISBN:	978-87-7156-109-8
ISSN (electronic):	2245-0203
Number of pages:	118
Internet version:	The report is available in electronic format (pdf) at http://dce2.au.dk/pub/SR128.pdf

Contents

Summary

Polychlorinated biphenyls (PCBs) are non-flammable and chemically stable substances with a large variety of former industrial and commercial applications. Their production and use peaked in the 1960s and 1970s, concurrently with a time period of high building activity in Denmark. Although ultimately banned in Denmark in 1986, PCBs are still being released from construction materials today, thus potentially causing exposure of people staying in buildings with PCB containing materials. The objective of this study was to develop a robust and inexpensive screening tool based on passive sampling, which allows an initial assessment of indoor air concentrations in relation to the cut-off values of 300 and 3000 ng PCB/m^3 air set by the National Board of Human Health.

The work proceeded in three phases combining a literature review, laboratory studies and field work. The literature review of the suitability of passive sampling formats for the purpose of this project resulted in recommendations of semipermeable membrane devices (SPMDs), silicone-coated vials and stir bar sorptive extraction (SBSE) for further work. As the use of performance reference compounds (PRCs) in an indoor setting was declined SPMDs were eventually deselected and replaced by silicone-coated petri dishes.

The second project phase focused on the effect of non-standardized uptake conditions in terms of variable air velocities on the partition kinetics of PCBs between air and the sampler, on detection limits, precision and questions of practical handling. Elimination experiments showed a substantial dependency of elimination rates on air velocity: Variations from 0.1 to 0.3 m/s or 0.3 to 1 m/s led to changes in elimination rates by up to a factor of 3, with implications for accuracy. Detection limits and precision were considered satisfactory, i.e. detection limits were generally < 1 ng/m^3 or even < 0.1 ng/m^3 based on uptake rates from the literature and an injection volume of 0.1 % of the final extract. Relative standard deviations between duplicates were generally < 10 %, with few exceptions.

Results of the first two project phases were presented to experts in the field of PCB containing construction materials, e.g. consulting engineers, laboratories, researchers and other interested parties, who were supportive of a third project phase with focus on measurements in buildings with potential PCB sources. There was consensus to test the silicone-coated petri dishes as a kinetic sampler as well as silicone-coated paper sheets with a view to equilibrium sampling.

These two formats, i.e. petri dishes with a thin layer of silicone and silicone-coated paper, were tested in the third project phase, in terms of two time series and ten 24-hour-measurements in buildings alongside conventional active measurements taken by the companies Rambøll and Grontmij A/S. The sampling experiments were run with several replicates which confirmed the high precision observed in project phase 2. The time series showed linear uptake of lower chlorinated PCB congeners on the silicone in petri dishes. The micrometer thin silicone layer on paper reached equilibrium between 1-10 days, depending on the PCB congener. This means that the 24-hour-measurements still covered the kinetic phase and sampling periods of 1-2 weeks will be required for equilibrium sampling. The samplers were calibrated by comparison with

results from five active measurements, resulting in sampling rates for CB-28, CB-52, CB-101, CB-118 and CB-153. Using these sampling rates, concentrations were calculated for the remaining five locations and compared with the results of the active measurements (validation). The kinetic sampling showed a tendency of overestimating the concentrations obtained by active sampling, by up to roughly a factor of 3. For two of the petri dishes, the concentrations of the active measurements were exceeded by a factor of 10. It was possible to calculate low concentrations of CB-118 and CB-153, which were below detection limits in the active measurements.

The results of the third project phase were presented to a group of experts again, with the main conclusions that both methods were precise and the silicone-coated paper in particular showed high sensitivity, but more work would be needed to evaluate the paper under equilibrium conditions. Both passive samplers are generally robust and easy to handle. Accuracy remains the main challenge, but might be considered acceptable for the purpose of an initial screening.

Sammenfatning

Polychlorerede biphenyler (PCB'er) er ikke brændbare og kemisk stabile stoffer med en tidligere bred industriel og kommerciel anvendelse. Deres maksimale produktion og anvendelse lå i 1960'erne og 1970'erne, en periode med høj byggeaktivitet i Danmark. Selvom de sidste PCB-anvendelser blev forbudt i 1986, udgør PCB'er i byggematerialer i dag stadig en emissionskilde og kan føre til eksponering af de mennesker, der opholder sig i bygninger med PCB-holdige materialer. Formålet med denne undersøgelse var derfor at udvikle et robust og billigt screeningsværktøj baseret på passiv opsamling. Med screeningsværktøjet skal det være muligt at foretage en første vurdering af indeluftkoncentrationen i forhold til Sundhedsstyrelsens aktionsværdier på 300 og 3000 ng PCB/m^3.

Projektet blev udført i tre faser omfattende en litteraturgennemgang, laboratorieforsøg og undersøgelser i bygninger. I litteraturgennemgangen blev det undersøgt, hvilke formater af passive opsamlere, der ville være egnede til projektets formål. På baggrund af litteraturgennemgangen blev semipermeable membraner (semipermeable membrane devices, SPMD), glas med silikone-støbning (silicone-coated vials) og stir bar sorptive extraction (SBSE) anbefalet til det videre arbejde. Da anvendelsen af såkaldte performance reference compounds (PRC) til kalibreringen af den passive opsamler blev fravalgt i en indendørsmåling, blev SPMD efterfølgende erstattet med petriskåle med et tyndt silikone-lag i den videre undersøgelse.

Undersøgelsens anden fase fokuserede på effekten af ikke-standardiserede optagelsesbetingelser i form af varierende lufthastigheden på PCB'ernes optagelsesrater på opsamleren. Derudover blev detektionsgrænser, præcison og den praktiske håndtering af de forskellige opsamlere undersøgt og vurderet. Undersøgelser af eliminering fra opsamlerne, dvs. frigivelse af tilsatte PCB'er, viste, at elimineringsraterne afhang betydeligt af lufthastigheden på opsamlerens overflade: En ændring fra 0,1 til 0,3 m/s eller fra 0,3 til 1 m/s førte til ændringer i elimineringsrater på op til en faktor 3, med konsekvenser for opsamlerens nøjagtighed. Detektionsgrænser og præcisionen blev anset for tilfredsstillende, idet detektionsgrænsen generelt var < 1 ng/m^3 eller endda < 0,1 ng/m^3 , baseret på optagelsesrater fra litteraturen og et injektionsvolumen på 0,1 % af prøveekstraktet. Relative standardafvigelser mellem dobbeltbestemmelser var generelt < 10 %, med få undtagelser.

Resultaterne for projektfaserne 1 og 2 blev præsenteret for repræsentanter fra branchen, bl.a. rådgivende ingeniører, laboratorier og forskere, som var positive overfor en tredje projektfase med fokus på målinger i bygninger med potentielle PCB-kilder. Der var enighed om at teste petriskåle med et tyndt silikone-lag (til kinetisk opsamling) og at undersøge ligevægtsopsamling vha. silikone-belagt papir.

De to opsamlingsmetoder, henholdsvis silokonelag i petriskåle og silikonedækket papir, blev testet i undersøgelsens tredje fase, i form af to tidsserier og ti døgnmålinger i bygninger, parallelt til konventionelle aktive målinger foretaget af Rambøll og Grontmij A/S. Forsøgene blev generelt sat op som dobbeltbestemmelser, som bekræftede den gode præcision fra projektfase 2. Tidsserierne viste en lineær optagelse af de lavtklorerede PCB'er i petriskålenes silikone. Det mikrometertynde silikonelag på papiret kom i ligevægt

indenfor ca. 1-10 dage afhængig af PCB congener, dvs. at de gennemførte døgnmålingerne lå indenfor den kinetiske fase, mens ligevægt ville kunne opnås ved opsamlingstider på 1-2 uger. De to opsamlere blev kalibreret overfor resultaterne for de første fem aktive målinger. Optagelsesrater blev beregnet for CB-28, CB-52, CB-101, CB-118 og CB-153. Ud fra disse optagelsesrater blev der beregnet luftkoncentrationer for de øvrige fem lokaliteter. Sammenligningen med resultaterne for de aktive målinger (valideringen) viste, at den kinetiske opsamling havde en tendens til at overestimere koncentrationen fra den aktive måling, med op til en faktor 3. For to af petriskålene var PCB-koncentrationerne ca. 10 gange højere end for den aktive måling. Det var dog muligt at bestemme lave koncentrationer af CB-118 og CB-153, som lå under detektionsgrænsen i den aktive måling.

Resultaterne for den tredje projektfase blev igen præsenteret for en ekspertgruppe. Hovedkonklusionerne var, at begge metoder var præcise og specielt det silikone-dækkede papir var ekstremt følsomt, mens yderligere erfaringer vil være nødvendige for at vurdere papiret under ligevægtsbetingelser. Begge passive opsamlere er robuste og nemme at håndtere. Nøjagtighed ved passiv opsamling vil fortsat være den største udfordring, men kan muligvis anses for tilstrækkelig til en indledende screening.

List of abbreviations

A/V-ratio	Ratio between surface area and volume
ECD	Electron capture detector
EVA	Ethylene vinyl acetate
GC	Gas chromatography
GPC	Gel permeation chromatography
HCB	Hexachlorobenzene
ILE	Immobilised liquid extraction
LDPE	Low density polyethylene
NIOSH	US National Institute of Safety and Health
PAH	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
POG	Polymer-coated glass
PRC	Performance reference compounds
PUF	Polyurethane foam
SBSE	Stir bar sorptive extraction
SPMD	Semipermeable membrane devices
SPME	Solid-phase micro extraction

1 Literature review of suitable methods for passive sampling of PCBs in indoor air (project phase 1)

1.1 Introduction

1.1.1 Background

Due to their inertness and heat stability, polychlorinated biphenyls (PCB) had a broad range of industrial applications, among these the use as additives in construction materials, e.g. sealants. The highest use of PCB was between the 1950s and 1970s and coincided with a period of high construction activity in Denmark, leading to the extensive use of PCB containing construction materials. With time, the compounds have been released from the material into indoor air, which thus becomes a potential source of PCB exposure for people staying in these rooms. The National Board of Human Health (Sundhedsstyrelsen) operates with two cut-off values of 300 and 3000 ng PCB/m^3 air, identifying a requirement of renovation on intermediate and short term scales, respectively. More background information on this issue is summarised in Annex 1.

Given the relatively large number of buildings potentially containing PCB sources, the Danish Energy Agency (Energistyrelsen) is interested in cost-effective screening tools for PCBs in indoor air. They have therefore asked the project participants (Katrin Vorkamp and Philipp Mayer) to study possibilities of quick and cost-effective measurements of PCB concentrations in indoor air, on the basis of passive sampling methods. While the compliance check with the cut-off values should still be based on common active sampling techniques, passive sampling can possibly be applied in a larger initial screening of buildings and rooms suspected of PCB contamination.

1.1.2 Objectives

The objective of this project was to study, develop and use passive sampling for screening analyses of PCB concentrations in indoor air. This chapter describes the findings of the first phase of the project, which had the objective to select and recommend suitable passive sampling formats for a screening analysis of PCBs in indoor air. These methods were to be further developed, optimized and tested during the second phase of the project and eventually applied to a limited number of buildings in the third phase.

1.1.3 Introduction to selection criteria

The first step, the selection of passive samplers potentially suitable for indoor air analysis of PCBs (Table 1), was based on literature reports, information from manufacturers of specific passive sampling formats and the authors' own experience. Based on previous communication with the Danish Energy Agency, the following criteria were defined, which the passive sampler should meet to be functional as a screening tool for PCB analysis in indoor air. These criteria are assessed separately in section 1.2 of this report.

- Cost-effectiveness (see section 1.2.1).
  Low costs are an important prerequisite for the applicability of the passive sampler. The target was approximately half of the costs of a typical PCB analysis based on active sampling, or less.

- Robustness and easy handling (see section 1.2.2).
  The sampler should be physically robust, i.e. not susceptible to damage. Easy handling includes that the risk of errors during the sampling process as well as the risk of contamination should be low, the sampling process should not require special training and the subsequent analysis in the laboratory should follow standard procedures.

- Robustness and easy interpretation (see section 1.2.3).
  Robustness will also include that the passive sampler should not be sensitive to small changes in environmental conditions, e.g. temperature variations or boundary layer effects. Furthermore, interpretation of the data should be easy. This means that it should be clear for all compounds whether the sampling proceeds in the linear uptake phase or at equilibrium (Figure 1). Sampling rates which describe the uptake of the compounds over time in the linear uptake phase should be constant over the measurement period.

- Sensitivity (see section 1.2.4).
  The sampler will primarily be used to determine whether PCB air concentrations in a room are well below the cut-off values or whether air concentrations are close to these values or even exceed them. Quantification limits for individual PCB congeners of 0.1 ng/m^3 have been stated as adequate for the determination of elevated concentrations of PCB in indoor air (Balfanz et al., 1993). Such quantification limits should be reached within a 24 hour deployment, whereas higher quantification limits for shorter deployment might be acceptable.

- Accuracy and precision (see section 1.2.5).
  Conventional analytical methods, based on gas chromatography and PCB-specific detection, will allow the accurate and precise determination of the PCB amount collected on a passive sampler. This collected amount has to be related to a PCB concentration in air. During the linear uptake phase (Figure 1) this requires knowledge of the compounds' uptake rates or a standardisation of these rates.

1.1.4 Linear uptake vs. equilibrium partitioning

It is important to establish prior to the measurements whether a passive sampler is operated in the kinetic regime or at equilibrium. The typical uptake profile of passive sampling devices is shown in Figure 1. Depending on the design of the sampler and the sampling time, the device can function in the kinetic (linear) region, at equilibrium or in between the two. This aspect will be further discussed in section 1.2.3, under "Robustness and easy interpretation".

During the kinetic phase, the concentration in air can be deduced from the measured concentration in the passive sampler and the sampling rate (Mayer et al., 2003), which leads to measurements of average air concentrations integrated over the entire deployment period. An optimal linear uptake sampler has a large uptake capacity and a high uptake rate (Wania et al., 2003).

At equilibrium, an equilibrium partition coefficient can be used to deduce the concentration in air from the concentration in the passive sampler (Mayer et al., 2003). The concentration is a function of the present concentration and the concentration history during the deployment period. An optimal equilibrium sampler combines low detection limits with sufficiently short equilibration times (Wania et al., 2003; Mayer et al, 2003). Such equilibrium sampling devices are normally characterized by (1) a high surface to volume ratio (A/V ratio), (2) an absorptive rather than adsorptive sorbent and (3) a capacity of the sorbent which is not too high for the specific target compounds, so depletion of the sampling medium is avoided.

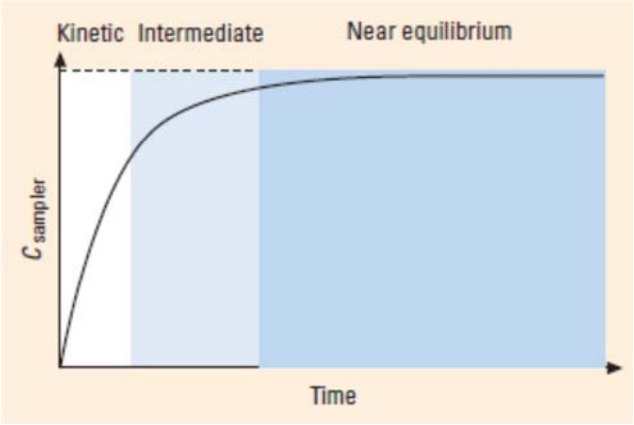


Figure 1. Three phases of uptake during passive sampling. From Mayer et al. (2003).

1.1.5 Excluding particle-bound PCB congeners

Basically, passive sampling only considers gas-phase transfer of contaminants and most devices are constructed in a way to prevent the settling of particles. Most of the devices in Table 1 are sheltered and additional steps have been described to remove particles, e.g. SPMD surfaces were brushed prior to extraction (Shoeib & Harner, 2002).

The current Danish instructions on PCB monitoring of indoor air, based on active sampling, include a sorbent and a filter, i.e. a set-up that includes gas-phase and particle-bound PCB congeners. For comparison purposes, it might appear desirable to include particle sampling in a passive sampling set-up, however, this conflicts with the diffusion based processes of passive sampling. In addition, other studies suggest that the sampling of particles will not produce much additional information, as PCB concentrations in indoor air are generally dominated by the lower chlorinated congeners due to their much higher volatility.

Of the 7 indicator PCB congeners (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, CB-180), CB-28 and CB-52 are generally the main contributors to the ΣPCB_7 value, and also CB 101 can give a significant contribution (Miljøstyrelsen, 2009). According to Shoeib & Harner (2002), these three congeners are mainly present in the gaseous form, since only higher chlorinated PCBs with octanol-air partition coefficients above > 10^{10} (i.e. log K_{OA} > 10, Annex 1) partition considerably onto particles. This observation is consistent with results from an active sampling campaign, where 89% of the total PCB amount passed the filter, i.e. was present in the gas phase (Balfanz et al., 1993). Other authors have also noted that PCB congeners in indoor air mainly are present in the unbound form, which is different from e.g. polybrominated diphenyl ethers (PBDEs) (Hazrati & Harrad, 2007).

In a study from the UK, glass fibre filters were added to the polyurethane foam disks (Table 1) in order to include particle-bound PBDEs in the sampling process (Abdallah & Harrad, 2010). However, this set-up was based on two different processes – gravitational deposition of particles and molecular diffusion of volatilised compounds – with different sampling rates, which essentially requires separate calibrations and produces two samples. In summary, passive sampling does not appear recommendable for quantitative analysis of particle-bound PCB congeners in this context, based on scientific as well as cost-benefit considerations.

1.2 Comparison and evaluation of passive sampling formats

1.2.1 Cost-effectiveness

The passive sampling device used within this screening context should be cost-effective, i.e. labour and materials needed for preparation, sampling and subsequent chemical analysis should be considerably below those of conventional analyses based on high-volume air sampling.

1.2.1.1 Purchase costs

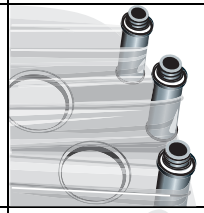
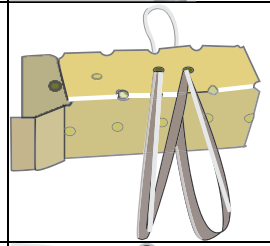
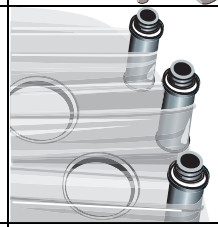
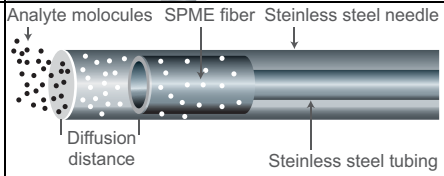
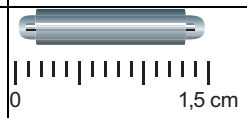
With the exception of the polymer-coated glass (POG), the PDMS-coated vials and the XAD-2 resins, all techniques described in Table 1 are commercially available in ready-to-use formats. Approximate prices are summarised in Table 2 – it has to be noted that other suppliers might exist and might give other prices and that Table 2 only includes the companies that the authors have been in contact with.

With regard to SPMD formats, classic SPMD applications are separated from more recently developed Mini-SPMDs, as described in Table 1. The costs of these two SPMD devices were compared by Goodbred et al. (2009), with the conclusion of Mini-SPMDs being cheaper than classic SPMD formats by one third to half, including compound extraction.

POGs have been specially made in the research laboratories studying POG applications. However, the procedure was very simple and can be copied by any chemical laboratory. Thus, the costs of this format will probably not exceed other formats, but for routine and large-scale applications, the supply has to be ensured. As described in Table 1, similar formats have been applied in other set-ups, e.g. sampling of PCB congeners from sediment (Mäenpää et al., 2011), here called PDMS-coated vials. These new devices use polydimethylsiloxane (PDMS, silicone) films, which also are cost-effective (Table 2).

XAD- 2 resins require a container as illustrated in Table 1. It is not described as particularly complicated, but it is not a standard product either, which probably limits its applicability in this context.

Table 1. Passive sampling techniques and formats potentially suitable for the screening of PCB concentrations in indoor air.

Format	Picture	Description	Reported sampling rates	Comments	References
Semipermeable membrane devices (SPMD), classic format		LDPE tube filled with triolein. PCB congeners cross the LDPE membrane and accumulate in the triolein. Typcially 91 cm length.	3-8 m^3/day (indoor air)	Can also be used without triolein (see below)	Shoeib & Harner (2002)
Mini-SPMDs		15 cm LDPE strip filled with triolein.	Expected sampling rate: About 1 m^3/day	Cheaper and smaller than classic SPMD devices	Goodbred et al. (2009)
Low density polyethylene (LDPE)		LDPE strips without triolein.	Comparable with SPMD		Booij et al. (2003)
Solid-phase micro extraction (SPME)		Stationary phase coated on a fused silica fibre inside a needle.	Not reported, but probably low for PCB congeners, < 0.005 m^3/day	The sensitivity is improved by thermal desorption (100 % of analyte reaches the GC detector).	
Stir bar sorptive extraction (SBSE); Twister		Small rod coated with polydimethylsiloxane (PDMS).	None reported. Based on outer surface area, they will be between the sampling rates for SPMD and SPME.	No application for air reported. Analysis by thermal desorption is fully automated, but requires specific and expensive equipment.	www.gerstel.com

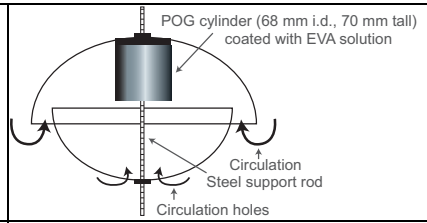
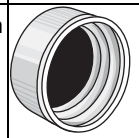
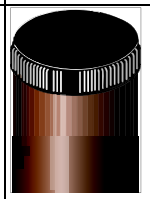
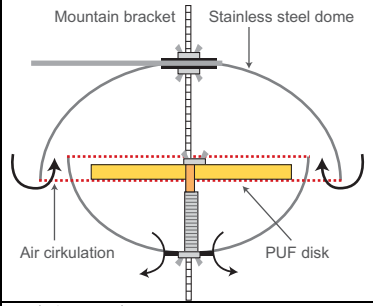
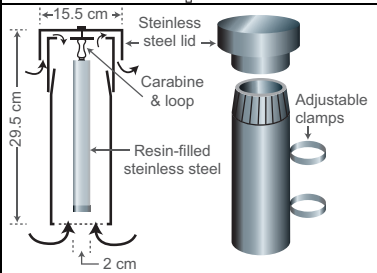
Polymer-coated glass (POG), classic format		Polymer film (e.g. ethylene vinyl acetate, EVA) coated on the inside surface of a glass cylinder or vial or on glass disks.	About 3 m^3/day (for 2.4 µm film of EVA on the inside and outside of a glass cylinder, indoor air)	Primarily used for equilibrium sampling, but kinetic sampling possible as well.	Harner et al. (2003); Farrar et al. (2005)
Immobilised liquid extraction (ILE)		Cap coated with polydimethylsiloxane (PDMS) or one of 3 other materials.	None reported	No application to air reported. Primarily used for absorptive sampling in complex aqueous samples.	www.ile-inc.com
PDMS-coated vials		Inside vertical walls of a glass jar are coated with polydimethylsiloxane (PDMS).	None reported for PCB congeners in air	Combines ILE and POG approaches. Primarily used for equilibrium sampling, but also applicable in kinetic regime.	Reichenberg et al. (2008); Mäenpää et al. (2011)
Polyurethane foam (PUF) disks		Adsorption on PUF, analogously to active sampling.	0.5-8 m^3/day (indoor air)	Not suitable for calibration with performance reference compounds.	Shoeib & Harner (2002); Hazrati & Harrad (2007)
XAD-2 resin		Stainless steel sampling container filled with XAD-2 (commonly used for active air sampling). Air exchange through a bottom opening and small holes in the top.	0.5-2 m^3/day (outdoor air)	Results reported for HCB and chlorinated pesticides, but not PCB. Described as semi-quantitative by the authors.	Wania et al. (2003)

Table 2. Approximate prices of the formats described in Table 1.

Format	Supplier	Tentative price	Incl. PRC?	Comment	Tentative price for the chemical analysis
SPMD, classic format	Exposmeter (Sweden), Environmental Sampling Technologies (EST) (USA)	About $ 160 (120 Euro) (EST), including the deployment device.	Yes, well-established	Well-established, but bulky. EST price of 2008 taken from Goodbred et al. (2009)	150 Euro when analysed by Exposmeter. EST: About $ 265 (200 Euro), according to Goodbred et al. (2009)
Mini-SPMDs	Exposmeter (Sweden) Environmental Sampling Technologies (EST) (USA)	50 Euro (Exposmeter); about $ 23 (18 Euro) (EST)	Yes	Exposmeter price includes pre-cleaning and spike with PRCs. EST price of 2008 taken from Goodbred et al. (2009)	150 Euro when analysed by Exposmeter. EST: About $ 185 (140 Euro), according to Goodbred et al. (2009)
LPDE	Exposmeter (Sweden)	50 Euro	To be tested	Price includes pre-cleaning	150 Euro when analysed by supplier
SPME	e.g. Supelco (Germany)	100 Euro (reusable 20-100 times)	To be tested	Automated analysis requires special hard ware (> 30 000 Euro)	Not available
SBSE	Gerstel (Germany)	Pack of 100: 30 000 DKK (approximately 4000 Euro) (reusable about 100 times)	To be tested	Automated analysis requires special hard ware (supplier information: 440 000 DKK, appr. 60 000 Euro). High end autosampler may be upgraded for 15 000–35 000 Euro.	Not available
POG, classic format	Can be made in a standard laboratory	Not known, but probably comparable with PDMS-coated vials.	Yes	-	Not available
PDMS-coated vials	Can be made in a standard laboratory	5 Euro in materials. Estimate of 10-30 Euro including technician time	To be tested	-	Not available
ILE	ILE Inc. (USA)	Pack of 20: $ 100, approximately 75 Euro	To be tested	-	Not available
PUF disks	Requires contact to users	Expected to be low to moderate	No	-	Not available
XAD-2 resins	Custom-made	Expected to be low to moderate	To be tested	-	Not available

1.2.1.2 Pre-sampling work, deployment and sampling

Pre-cleaning of the material is important to avoid analytical errors and to achieve comparable results. Both SPMD formats described in Table 1 are pre-cleaned by the supplier and will thus not require additional preparatory work in the laboratory. The commercially available SPME, ILE and SBSE

formats are also described as ready to use by their manufacturers. It is common practice to confirm this information in a few control measurements and subsequent blanks during sampling campaigns, including both laboratory and field blanks. Furthermore, the calibration of the sampler can be considered pre-sampling work, which will be studied during project phase 2 (see also section 1.2.5 "Accuracy and precision").

The deployment is a simple process and should not be time-consuming for any of the formats in Table 1. The SPMD formats can be provided with a deployment device (more expensive in the case of classic SPMDs, according to Goodbred et al., 2009). As illustrated in Table 1, PUF and POG devices have been placed into a metal shelter. This will not be necessary in indoor air applications, however, some device will be required for deployment. The SBSE and ILE devices as well as the PDMS-coated vials can be deployed easily, provided that a horizontal surface exists where they can be placed. The round PDMS-coated vials and ILE devices will be placed on the side to avoid particle deposition, and might thus require some stabilisation. SBSE devices are coated on the outside. Placed on e.g. a piece of aluminium foil, no PCB diffusion will occur on the part of the device's surface that touches the aluminium foil. This has to be taken into account during the calibration of the device.

1.2.1.3 Chemical analysis

Table 3 summarises how the compounds typically are extracted or desorbed from the sorbent, which additional steps have been described in the literature and what alternatives seem possible.

From a cost-effectiveness point of view, it is important to keep the method simple and to avoid multiple clean up and fractionation steps. In this respect, thermal desorption has an advantage over solvent extraction (in addition to sensitivity advantages, see below) as the entire PCB amount collected on the sampler is transferred to the gas chromatograph. However, solvent extraction and subsequent steps can also be carried out efficiently if kept simple. An advantage of solvent extraction is that it can be applied universally and does not require specific equipment that is limited to few laboratories.

Although most of the scientific studies on passive sampling of indoor air included – sometimes extensive – clean-up steps, these might not necessarily be required for this matrix and the compounds to be analysed. The objective of the clean-up procedures are usually to i) remove matrix components that may affect the instrumental analysis, ii) remove co-extracted compounds which also may interfere with the PCB congeners in the instrumental analysis (fractionation). Matrix effects are expected to be small for air analysis, but additional matrix effects might originate from the sampler itself in case of insufficient pre-cleaning. The risk of interference of other compounds (e.g. polycyclic aromatic hydrocarbons, PAH) cannot be completely ruled out, although the common PCB detection methods are rather specific.

The aspect of sensitivity is discussed in section 1.2.4. The most efficient way of improving the sensitivity of solvent based approaches is volume reduction of the extract by evaporation.

Table 3. Summary of the steps required to transfer PCBs from the sampler to a gas chromatograph, based on default procedures, literature descriptions and the authors' own experience.

Format	Extraction/ desorption	Clean up and/or fractionation	Possibility of thermal desorption	Comment	Reference
Classic SPMDs	Solvent extraction	Silica and/or alumina and/or gel permeation chromatography (GPC)	No	Several variations	Söderström & Bergqvist (2004); Booij et al. (2003)
Mini-SPMDs	Solvent extraction	Filtration	No	Method might also involve gel permeation chromatography (GPC)	Goodbred et al. (2009)
LDPE	Solvent extraction	Silica	No	Simpler than SPMD method as no triolein involved.	Booij et al. (2003)
SPME	Thermal desorption	Probably not needed for air samples	Yes	Automated injection of SPME fibres requires specific hardware (see Table 2).	-
SBSE	Thermal desorption or solvent extraction	Probably not needed for air samples	Yes	Thermal desorption requires specific equipment (see Table 2).	-
POG	Solvent extraction	Silica, silica/alumina	No	Precipitation of polymer requires additional step.	Harner et al. (2003)
ILE	Solvent extraction	Not known	No	-	-
PDMS-coated vials	Solvent extraction	Probably not needed for air samples.	No	No need to remove polymer (as for POG)	Mäenpää et al., 2011
PUF disks	Solvent extraction	Florisil	No	Additional back-extraction described in the reference.	Hazrati & Harrad (2007)
XAD-2 resins	Solvent extraction	Silica	No	Several solvent changes described in the reference.	Wania et al. (2003)

1.2.1.4 Conclusions with regard to cost-effectiveness

- Two types of SPMD devices are on the market of which the Mini-SPMDs are the more cost-effective ones. The disadvantage is a lower sampling rate and thus less sensitivity (to be discussed in section 1.2.4).
- Mini-SPMDs, SPME (reusable), SBSE (reusable), POG and PDMS-coated vials are comparable with regard to direct purchase costs. ILE will be cheaper, but might be less sensitive (to be discussed in section 1.2.4).
- Some commercially available devices are pre-cleaned.
- Deployment might be more difficult and time-consuming for PUF disks and POG than for the other formats.
- Thermal desorption is less laborious, but requires expensive hardware not universally available in chemical laboratories. Solvent extraction and subsequent clean-up should be kept very simple.

1.2.2 Robustness and easy handling

Passive samplers for indoor air measurements are generally designed to be relatively robust as measurement campaigns often run over weeks and months and different people might be involved in the deployment. Easy

handling is considered as a main advantage of passive sampling compared with active sampling (e.g. Brown, 2000). Therefore, this aspect usually receives much attention during the design phase, especially in formats developed for commercial use.

It is obvious that glass-based devices like POGs are more susceptible of breakage, but relatively thick glass can be chosen to increase stability, as has been the case with the PDMS-coated vials. For the other formats, accidental damage is unlikely, but the sampling can be disturbed if the sampler is not set up securely, especially if usual activities in the room continue during the sampling period.

1.2.2.1 Risk of contamination

All formats summarised in Table 1 have been optimised in terms of a rapid and efficient accumulation of PCB congeners and chemically similar compounds. Therefore, the contamination with PCB is possible if the device is not stored and deployed as described by the manufacturer or advised by scientists. It is essential that the device is stored – preferably sealed – and transported in an airtight container of glass, aluminium or stainless steel. The commercially available SPMD devices, SPME, SBSE and ILE are expected to fulfil these conditions of being stored in a PCB-free atmosphere. However, this will also have to be ensured on their transport back to the laboratory after deployment.

The PUF and POG devices have to be handled in a similar manner, as described in the literature (e.g. Farrar et al., 2005; Harner et al., 2006). PDMS-coated vials are coated only on the inside and closed with screw caps – which are lined with e.g. Teflon or aluminium foil – , so contamination can be avoided in a very simple way.

Once the container is opened, it is important to be able to move the device without touching the membranes or sorbents. Special care will have to be taken with the formats that are coated on the outside, such as SBSE and the classic POGs described in Table 1. It is common practice to work with field and laboratory blanks to assess potential contamination issues.

1.2.2.2 Risk of other errors

The risk of errors during deployment is generally small since the sampling process does not require any further work. The following conditions have to be met to avoid artefacts:

- The sampler should not be exposed to direct sunlight. This is less critical for sheltered formats, e.g. SPME, POG, ILE and other samplers that can easily be placed into a container. For PDMS-coated vials, amber glassware is typically used.
- A certain degree of ventilation should be ensured to avoid boundary layer effects. This is likely more critical for PUF disks than for tube-type samplers (Brown, 2000), and will be discussed under 2.3.2 “Boundary layer effects”.
- Local perturbation effects should be considered for all samplers.
- The deposition of particles should be avoided or particles should be removed after the deployment phase.

After the sampling period, the passive sampler has to be stored carefully again to avoid both contamination and loss of the PCB congeners. It has been described for PUF that they should be stored at 4°C until extraction (Harrad et al., 2006), and traditional SPMD samplers as well as Mini-SPMDs were stored frozen (Shoeib & Harner, 2002; Goodbred et al., 2009). However, given the high partition coefficients of PCBs for the passive sampler–air system, i.e. their strong tendency to partition from the air into the passive sampler phase, the risk of back diffusion after sampling is low, in particular at low temperatures.

For none of the formats in Table 1, a specific training is needed. However, the POG and PUF devices used with shelters as well as the classic SPMD devices may be considered as too bulky for easy and uncomplicated handling. Depending on the sampler eventually chosen for sampling campaigns, special care will have to be taken to e.g. avoid contamination, local perturbation effects and losses after sampling as well as to ensure secure deployment.

1.2.2.3 Laboratory standard procedures

Regarding procedures for sample processing and analysis in the laboratory, solvent extraction and extract purification on silica, alumina or Florisil (Table 3) can be considered standard procedures in laboratories offering PCB analyses. The thermal desorption of SPME and SBSE units, however, requires specific equipment for a gas chromatograph (Table 2). Gel permeation chromatography (GPC) is mainly used for lipid removal from lipid-rich samples and therefore not necessarily available either at laboratories primarily working with abiotic media (Wania et al., 2003).

1.2.2.4 Conclusions with regard to easy handling

- For glass-based samplers (e.g. PDMS-coated vials), thick glass should be chosen to minimise the risk of breakage.
- Classic SPMD, PUF disks, POG and XAD-2 resins might be too bulky for easy handling in a large-scale screening context.
- Transport to and from the sampling location should proceed in a closed, preferably sealed container of an inert material. This is the case for the commercial formats and glass devices coated on the inside (PDMS-coated vials).
- SBSE devices might require more attention (e.g. handling with forceps) when removed from their container because of their outside coating.

1.2.3 Robustness and easy interpretation

In addition to the physical robustness and practical handling discussed above, the passive sampler should also be robust in terms of easy interpretation of its collected PCB amount. This includes that the sampling rates should be constant and relatively stable during small changes in environmental conditions, e.g. temperature and boundary layer effects, if the sampler is operated in the linear uptake phase (Figure 1). This requires that the sampler is calibrated carefully, for instance by addition of performance reference compounds (PRCs). This concept is further described and discussed under "Accuracy" below.

1.2.3.1 Effects of temperature

Diffusion coefficients increase with temperature and will lead to increased sampling rates with increasing temperature (Górecki & Namieśnik, 2002;

Seethapathy et al., 2008). The variation of the sampling rate will be low in practice and was quantified to be approximately 0.2-0.4 % per °C (Brown, 2000). For SPMD and LDPE collecting PCB congeners from water, the sampling rate increased by a factor of 3 when the temperature was raised from 2°C to 30°C, leading to the conclusion that temperature is not a key factor that controls uptake rates unless large temporal variations are involved (Booij et al., 2003).

For passive samplers operated at equilibrium, it is important to note that the partition coefficient between the sorbent and air decreases with increasing temperature (Shoeib & Harner, 2002), i.e. the amount retained in the sampler becomes smaller.

1.2.3.2 Boundary layer effects

If the air movement is insufficient boundary layer effects can occur, i.e. the gas molecules close to the sampler surface are removed by diffusion and not replenished quickly enough. This is a particular problem for the passive sampling of PCBs, since the mass transfer of PCBs into the sampler generally is limited by diffusion through a stagnant boundary layer. Besides, air exchange in the indoor environment is limited and might lead to a requirement for additional ventilation (Brown, 2000).

According to Brown (2000), this effect is less problematic for tube-type passive samplers, such as the SPME formats (Table 1). All the other formats have optimized the surface area to volume ratio, i.e. created a large surface area which increases the sampling rate, but might also be more susceptible to boundary layer effects. Minimum air velocities of 0.2 – 0.5 m/s at the surface of the passive samplers are mentioned in the literature (Brown, 2000), but for organic compounds of low volatility, such as PCB congeners, there will most likely still be boundary layer effects. These effects must be considered during the calibration of the passive samplers, see section 1.2.5.

1.2.3.3 Other effects

Changes in humidity might also affect sampling rates. However, this is less critical for the hydrophobic sorbents that are generally used for passive sampling of PCBs. Condensation of water on the sorbent material should to be avoided, which can occur when a cold sampler is taken into indoor air (Brown, 2000).

1.2.3.4 Linear uptake phase vs. equilibrium

"Easy interpretation" also includes that it should be unambiguous whether the passive sampler is operated in the linear phase or at equilibrium (Figure 1). Sampling within the curvilinear portion between the linear uptake phase and equilibrium will result in greater complexity and uncertainty for deriving air concentrations (Harner et al., 2003).

It will also complicate interpretations if the PCB congeners to be analysed are not in the same uptake phase at the end of the deployment period, which can be the case in rapidly equilibrating devices (Farrad et al., 2005). At the time scales considered for indoor air monitoring of PCB congeners, i.e. hours or days, most of the formats in Table 1 would operate in the linear uptake phase. This has explicitly been stated for the XAD-2 resins (Wania et al., 2003) and will also be valid for classic SPMD formats, Mini-SPMDs and PUF disks.

Examples of the uptake of CB-52 and CB-101 by traditional SPMD and PUF devices are shown in Figure 2 (Shoeib & Harner, 2002). This figure shows that CB-52 enters the curvilinear phase much sooner than CB-101, however, it would still be in the linear phase over a period of hours and a few days. Ockenden et al. (2001) recommended using SPMD samplers in the linear portion of the uptake curve, which can be calibrated more easily.

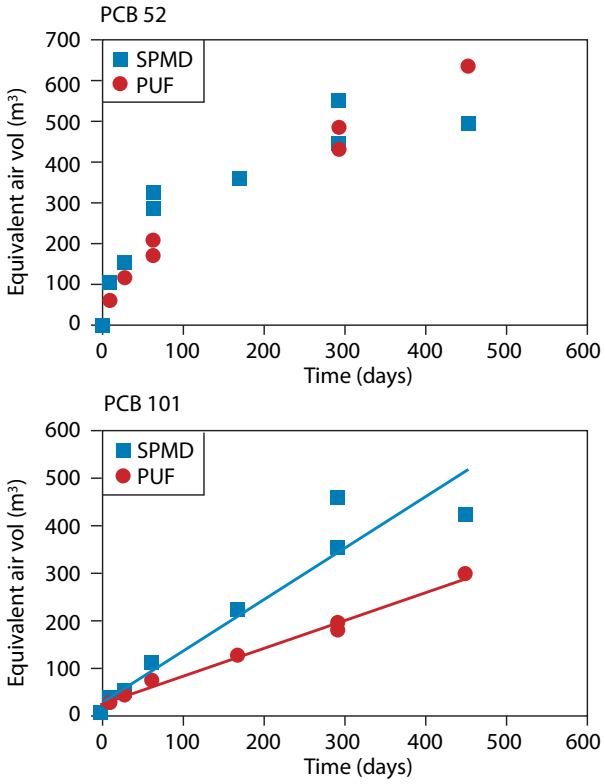


Figure 2. Sampling profiles of CB-52 and CB-101 by SPMD and PUF disks. From Shoeib & Harner (2002).

Little information is available on air applications of SBSE, and further experimental work would be required to establish its uptake profile and to calibrate the sampler. SPME and ILE are described as equilibrium devices, but can also be operated in the linear uptake phase. However, their sampling rates might be too low to reach detectable levels during collection (see 1.2.4 "Sensitivity").

POG and PDMS-coated vials can be operated in both modes, by varying the film thickness and exposure time (Farrar et al., 2005). The high surface-to-volume-ratio that can be achieved with these formats allows rapid equilibration (hours/days) of the compounds of interest. Varying the surface area or coating thickness can vary the sensitivity and sampling time, i.e. decreasing the film thickness will result in a shorter linear phase, which means that equilibrium is reached sooner. Uptake profiles of CB-28 and CB-153 are shown in Figure 3, based on POG cylinders with a 0.57 µm EVA film (Harner et al., 2003).

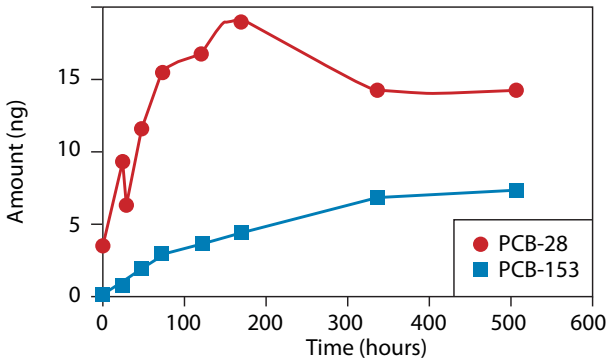


Figure 3. Uptake profiles of CB-28 and CB-153 by POG cylinders coated with 0.54 µm EVA. From Harner et al. (2003).

1.2.3.5 Conclusions with regard to easy interpretation

- The effect of temperature variations is expected to be small for kinetic sampling in the indoor environment.
- Boundary layer effects can hardly be avoided in PCB sampling from air and will have to be considered in the calibration of the device. The effect will be smaller for devices in motion, which can be achieved for the SBSE devices.
- The uptake profile also depends on the film thickness, i.e. a thicker film will result in a longer linear uptake phase.

1.2.4 Sensitivity

The sensitivity of the analysis is determined by the amount of PCB on the sampler, i.e. sampling rate and exposure time, and the analytical method, i.e. the percentage of the collected amount injected for analysis and instrumental detection limits. Quantifying PCB concentrations at low levels is the ideal approach, however, in specific situations, it might also be sufficient to state that concentrations are below detection limits and thus well below the cut-off values, i.e. produce a negative control.

1.2.4.1 Parameters affecting sensitivity

Calculation examples of different scenarios are shown in Table 4, to illustrate how the parameters are linked and which minimum air concentrations can be quantified with the different formats. In these calculations, an instrumental detection limit of 0.5 pg (0.0005 ng) has been used. This seems reasonable in standard PCB analyses, unless blanks, matrix effects or other analytical issues complicate the analyses. To account for such potential analytical challenges, it might be meaningful to consider a safety margin of 2-3 for instrumental detection limits. It should also be noted that the measurement uncertainty increases for concentrations close to detection limits.

Only a small part of the solvent volume used for the extraction of the PCB congeners is usually injected into the gas chromatograph for compound separation and detection. 1 µl is a typical injection volume, which often only is 0.1 % of the concentrated solvent extract (1 ml). Depending on other instrumental parameters, the injection volume can be slightly increased in standard analyses, however, a more efficient approach would be to reduce the volume of the final solvent extract, i.e. work with a final volume of 100 µl or 50 µl instead of 1 ml. This would increase the percentage injected to 1 % or 2 %, respectively. As can be seen from Table 4, this percentage affects detection limits considerably and an increase might be necessary to meet the target quantification limit of 0.1 ng/m^3 for individual PCB congeners.

A percentage of 100 stands for thermal desorption which is possible for SPME and SBSE formats and includes a complete transfer of the collected PCB amount onto the chromatographic column. Regarding sensitivity, this is a strong advantage compared with solvent extraction techniques, however, it requires additional hardware (Table 3) which is not commonly available in analytical laboratories.

Table 4. Parameters affecting the sensitivity of the analytical method. A typical instrumental detection limit of 0.5 pg (0.0005 ng) is used in the comparison. "Percentage injected" refers to the percentage of the collected amount injected into the gas chromatograph for analysis.

Format	Sampling rate (m^3/day)	Deployment time (hours)	Percentage injected (%)	Minimum quantifiable air concentration (ng/m^3)
SPMD classic	3	24	0.1	0.17
SPMD classic	3	24	1	0.017
Mini-SPMDs	1	24	0.1	0.5
Mini-SPMDs	1	24	1	0.05
Mini-SPMDs	1	8	1	0.15
SPME	0.005	24	100	0.1
SBSE	0.1	24	1	0.5
SBSE	0.1	24	100	0.005
SBSE	1	6	100	0.002
PDMS-coated vials	3	24	0.1	0.17
PDMS-coated vials	3	24	1	0.017
PDMS-coated vials	3	8	1	0.05
XAD-2 resins	2	24	0.1	0.25
XAD-2 resins	2	24	1	0.025

The deployment period can be varied easily, provided that the PCB sampling still occurs in the linear uptake phase. The authors were under the impression that the deployment period should be relatively short, which also agrees with the "easy handling" criterion. A period of 24 hours might be a suitable exposure time. Table 4 also includes three examples of shorter deployment periods. For Mini-SPMDs, this scenario would exceed the minimum quantifiable concentration of 0.1 ng/m^3, unless the shorter deployment period was counterbalanced by a higher percentage of the extract injected for analysis. For SBSE, the detection limits can only be met in this scenario if the sampling rate is relatively high (which might require movement of the sampler during sampling) and at least 5 % of the collected amount is injected.

As can be seen from Table 1, sampling rates are often > 1 m^3/day, which was the sampling rate for the active sampling of PCB with XAD-2 glass tubes in a study for the Danish Environmental Protection Agency (Miljøstyrelsen, 2009). The sampling rates for SPME might be too low to reach detectable levels within the desired deployment period. Sampling rates of ILE and SBSE are not known for PCB sampling in indoor air. For PDMS-coated vials, sampling rates depend on the film thickness and can thus be adapted to short-term measurements as well. This format is based on the same principle as ILE and has the same advantages with regard to easy handling, but adds some flexibility in terms of variable film surface area and thickness.

It has also been described in the literature that several SPMDs were combined for extraction and subsequent analysis (Ockenden et al., 2001). This will also be possible for other formats operated with solvent extraction, by either combining the devices for extraction or pooling several extracts for subsequent analysis. It has to be noted, however, that adding the PCB amounts from several samplers will also mean adding potential contaminations and thus increasing quantification limits.

1.2.4.2 Conclusions with regard to sensitivity

- Instrumental detection limits of 0.5 pg (for individual PCB congeners) seem reasonable, but a safety factor of 2-3 should be considered in case of analytical difficulties.
- Thermal desorption has a strong advantage in terms of sensitivity, but requires expensive hardware. This applies to the formats SPME and SBSE.
- For SPME, sampling rates will probably be too low for a reliable quantification of PCB congeners at the 0.1 ng/m^3 level after 24 hours of sampling.
- Solvent extraction is a common method, but the sensitivity is often substantially reduced when injecting only a minor percentage of the extract. An injection of only 0.1 % is not uncommon, whereas an injection of 1-4 % is easily achieved.
- Deployment periods of 24 hours seem reasonable. Shorter deployment periods might conflict with detection limits, but can produce negative controls.

1.2.5 Accuracy and precision

As mentioned above, the PCB amount collected on the passive sampler can be determined relatively accurately, using solvent extraction or thermal desorption and gas chromatographic analysis with mass spectrometric or electron capture detection. The analytical challenge is the back calculation of air concentrations, either as a time weighted average concentration (linear uptake phase of the passive sampler) or at equilibrium. Precision describes the variation between samples.

1.2.5.1 Calibration principles

As discussed above, most passive sampling formats are operated in the linear uptake phase. For accurate measurements, sampling rates have to be quantified accurately, including potential effects from variable environmental conditions, i.e. temperature or boundary layer effects. This requires a careful calibration of the sampler, under conditions as similar as possible to the real sampling set-up. The following two strategies can be used:

- Performance reference compounds (PRC), providing *in situ* calibration at the given mass transfer conditions.
- Standardising mass transfer conditions, e.g. by agitation of the passive sampler to minimise boundary layer effects.

1.2.5.2 Performance reference compounds

PRCs are added to the passive sampler and dissipate into the surrounding air under the same conditions as the target compounds are absorbed (e.g. Söderström & Bergqvist, 2004). Thus, the PRCs should be able to correct for differences in uptake rates due to environmental factors (Farrar et al., 2005). Table 5 summarises the PRCs used in scientific studies involving passive

sampling of PCB congeners. PRCs should have similar physical-chemical characteristics as the target compounds, but must not be present in the sample. These criteria can be fulfilled for PCB analysis, by choosing e.g. labelled compounds or some of the PCB congeners not present in the environment.

Table 5. Experiences with performance reference compounds (PRCs) published in the scientific literature.

Format	PRC	Medium	Spike amount	Comment	Reference
SPMD	^{13}C-CB-28, ^{13}C-CB-52, ^{13}C-CB-101, ^{13}C-CB-138, ^{13}C-CB-153, ^{13}C-CB-180	Outdoor air	4 ng	No measurable depuration of CB-153 and CB-180 after 120 days.	Ockenden et al. (2001)
SPMD	^{13}C-CB-3, ^{13}C-CB-15, ^{13}C-CB-37, ^{13}C-CB-54	Outdoor air (Wind tunnel)	Not reported	Side effects of varying wind speed could be reduced by using PRCs.	Söderström & Bergqvist (2004)
POG	CB-6, CB-29, CB-40, CB-128, CB-155, CB-189	Outdoor air	2500 ng	Large variation in depuration rates. After 18 days of deployment, 0-87% of the PRC amount remained.	Farrar et al. (2005)
PUF disk	CB-19, CB-147 ("Sampling efficiency standards")	Indoor air	10 ng	No real PRC, used to provide a measure of contaminant loss during sampling.	Harrad et al. (2006); Hazarti & Harrad (2007)

According to Farrar et al. (2005), the ideal PRC undergoes moderate (30-70%) loss during the deployment period. This was not possible to achieve for the POGs used in the study, due to the large range in physical-chemical characteristics between the low molecular and the high molecular PCB congeners (Farrar et al., 2005). This general problem was also described for classic SPMDs, leading to the recommendation to use only those compounds as PRCs whose depuration rates fit with the desired deployment time (Ockenden et al., 2001). The Mini-SPMDs also include PRCs, but it will remain to be tested whether their depuration rates allow accurate calibrations in these screening applications. The PRC concept is not applicable to adsorption (in contrast to absorption) processes, such as the PCB collection on PUF disks.

While the PRC concept appears promising in theory, the studies published in the scientific literature indicate some issues, among these large variations in depuration rates between PCB congeners of different volatility. It is important that the depuration from the passive sampling device is measurable, i.e. exceeds the measurement uncertainty, but not so high that the amount of PRCs left on the sampler is below quantification limits, i.e. no depuration rate can be established. This balance should be studied experimentally, prior to sampling campaigns and is suggested for further work in project phase 2 (see section 1.4).

An additional challenge is the choice of suitable PRCs. As shown in Table 5, ^{13}C-labelled molecules were used in two of the studies, which are as similar to the target compounds as possible. Their analysis, however, requires mass spectrometric detection and excludes the use of electron capture detection. Farrar et al. (2005) used non-labelled PCB congeners which are not present in the environment. This might be a compromise between similarity to the target compounds and applicability of several detection methods.

A third item to be discussed is whether or not the release of potentially harmful chemicals into the indoor environment is acceptable, especially if usual activities in the rooms are maintained. The results published in the literature are from outdoor applications (Table 5), but in general, very low spike amounts have been used. Assuming a worst case scenario of the highest PRC application of 2500 ng, complete loss from the sampler and complete redistribution into indoor air, the volume of the room must not exceed 8 m^3 for a concentration above the lower cut-off value of 300 ng/m^3. The authors consider a spike amount of approximately 200 ng as sufficient, subject to experimental verification. Assuming a depuration of 80 %, 160 ng would be released into the surrounding air, which would lead to an indoor air concentration well below the cut-off values.

Table 2 includes some information on the use of PRCs with the different formats. The concept is well-established for SPMDs and also applied to the Mini-SPMDs in a commercially available format. The use of PRCs has also been reported for POG (Farrar et al., 2005) and will probably also include PDMS-coated vials. This will have to be tested, however, as will the use of PRCs with other formats, such as SBSE.

1.2.5.3 Other calibration methods

As described in section 1.2.3.2, air velocity around the sampler is a critical parameter as it determines the extent of boundary layer effects and thus the sampling rate. These effects have to be taken into account in the calibration, which has to be as close as possible to *in situ* conditions.

Some scientific studies have calibrated the passive samplers by parallel active sampling (e.g. Wilford et al., 2004). The uncertainty connected with this calibration principle can be reduced by standardising the uptake conditions, e.g. by keeping the sampler in motion. This can be achieved rather easily for the SBSE device which can be rotated on a magnetic stirrer. However, it will lose some of its advantages, i.e. noise-free operation and independence of power supply.

Alternatively, the sampling rates can be deduced from uptake profiles (Figure 2) and then applied to translate the PCB mass measured on the sampler into an air concentration (e.g. Shoeib & Harner, 2003).

1.2.5.4 Acceptable range of accuracy

The US National Institute of Safety and Health (NIOSH) accepts results with an accuracy of ± 25 % and a bias of ± 10 % for passive sampler applications in air. These accuracy criteria seem ambitious and are likely only met by organic compounds that are more volatile than the PCB congeners, i.e. collected under standardised uptake conditions with well-defined diffusion barriers. The PCB uptake is more difficult to control and accuracy can be expected to be within an order of magnitude. According to Shoeib & Harner (2002), passive samplers can provide air concentrations that are within a factor of 2 of the true values. Quantifications of achievable accuracy should be addressed in the project phases of experimental work, probably project phase 3.

1.2.5.5 Precision

PCB concentrations in indoor air vary in space and time, including an appreciable seasonal variation (Hazrati & Harrad, 2006). Parallel sampling has been conducted for most of the formats to establish the precision of the analytical procedure, i.e. the variation that can be attributed to the sampling and analysis step. In general, variations of approximately 20 % were found between replicates.

For classic SPMDs, an average difference of 19 % between replicate sampling was reported (Söderström & Bergqvist, 2004). A maximum variation of 20 % was also stated for Mini-SPMDs (Goodbred et al., 2009). For POG devices, variations of 18-31 % for individual PCB congeners were reported by Farrar et al. (2005), while somewhat lower variations of approximately 10-20 % were observed in the study by Harner et al. (2003). PUF devices were found to vary least, with an average variation of 7 % (Hazrati & Harrad, 2007). In contrast, XAD-2 resins had generally higher variations, confirming their semiquantitative nature. No data were available for PCB congeners, but DDT compounds varied between 20-50 % in the XAD-2 resin application (Wania et al., 2003).

1.2.5.6 Conclusions with regard to accuracy

- Accuracy is largely dependent on the calibration of the passive sampler.
- *In situ* calibration by performance reference compounds is the best solution in theory and has been applied to SPMDs (classic format and Mini-SPMDs) and POG.
- However, there might be issues about too high or low depuration rates of PRCs, limited choice of suitable PRCs and the release of these compounds into the indoor environment.
- Another strategy is to standardise the mass transfer conditions by agitation of the sampler. For SBSE, a battery driven magnetic stirrer could be used for this purpose
- Accuracy is typically within an order of magnitude. A factor of 2 has been reported in the scientific literature.

1.3 Conclusions and recommendations of project phase 1

Based on the assessment of the five criteria described in section 1.1.3 and the additional information in sections 1.1.4 and 1.1.5, the authors draw the following conclusions with regard to the development of a cost-effective screening tool:

- We expect the sampler to be operated in the linear uptake phase, which corresponds better than equilibrium sampling with the short deployment periods of a screening initiative.
- As the sampling profile might vary between compounds of different volatility, it will have to be verified experimentally that all PCB congeners of interest are collected in this phase.
- Passive sampling will generally be limited to the non-particle bound forms of the PCB congeners. Since the dominating PCB congeners in indoor air occur in the unbound form, this is not expected to be a significant limitation.
- Based on the easy handling criterion, classic SPMDs, PUF and POG were excluded from the screening study for being too bulky for this purpose.

- The five criteria point at Mini-SPMDs, SBSE and PDMS-coated vials as relevant for further work.
- Boundary layer effects should be considered with regard to the practical deployment.
- Performance reference compounds (PRCs) are the calibration of choice in theory, but some issues have been identified. It is not known either whether SBSE devices can be calibrated by PRCs.
- Alternatively, the mass transfer conditions could be standardised or controlled by some kind of agitation. This can probably be achieved most easily for SBSE, i.e. by using a battery-driven magnetic stirrer.
- Quantitative measurements within a factor of 2 of the true value will be a satisfactory range of accuracy.

In summary, we suggest further work with the following three formats:

Mini-SPMDs. Classic SPMDs have been applied successfully to monitor PCB in indoor air, but do not appear suitable for this purpose, as they are too bulky for easy handling and more expensive than some of the alternatives. Mini-SPMDs have the advantages of classic SPMDs with regard to effective PCB collection, but are smaller, easier to handle and relatively inexpensive. Their sampling rates will probably be sufficient for the target quantification limits. They are commercially available, including performance reference compounds for in situ calibration. The supplier Exposmeter (Umeå, Sweden) has shown interest in collaborating on the development of a customised product, i.e. a pre-cleaned Mini-SPMD with PRCs that is protected by a metal screen and connected to a mounting hook. This device can be supplied in an airtight metal can for storage and transport before and after deployment.

SBSE. This format uses a well-established PDMS coating and appears promising with regard to cost-effectiveness, handling and sensitivity. Automatic thermal desorption is an advantage in terms of sensitivity and will probably even allow sufficiently sensitive measurements at deployment times that are reduced to some hours. In addition, automated thermal desorption has the potential for high through-put analysis at a very low sample price. However, the thermal desorption requires specific and costly hardware, which is not commonly available in standard chemical laboratories. The use of performance reference compounds remains to be tested. Alternatively, standardised mass transfer conditions can probably be established by rotating the device on a magnetic stirrer.

PDMS-coated vials. This format combines advantages of POG and ILE formats and can be tailored to this specific screening application. It uses a PDMS film, like SBSE, which can be varied in thickness to optimise sampling rates. The vials are easy to handle and thick enough to be robust. They can probably also be used with performance reference compounds. This format has been developed by the project participants and co-workers and proved to be robust and simple in applications to other media. As the only one of the suggested formats, it can also be directed at equilibrium sampling of PCBs within a realistic time frame, which gives some additional possibilities for exposure assessments.

1.4 Perspectives: Further work suggested for project phase 2

For the second project phase, it is suggested to focus on experimental work with the three formats (SBSE, Mini-SPMDs, PDMS-coated vials), in order to develop a cost-effective screening tool for the analysis of PCB congeners in indoor air.

Elimination rates should be determined in elimination experiments for the three formats and different PCB congeners. The question of adequate calibration should be addressed, in particular the use of PRCs and the possibility of standardising the uptake conditions by e.g. stirring the SBSE device.

Furthermore, the authors suggest testing and optimising the selected formats with focus on some of the criteria discussed in this report, in particular sensitivity, precision and general practicability. This means that analyses should be conducted to determine and if possible further improve the relevant detection limits and that parallel deployments will give information on variation between samplers. Improvements of the practical handling should be considered as an integrated part of the experimental work. The question of accuracy will primarily be addressed in the project phase 3 when results from passive sampling will be compared with those of parallel active sampling.

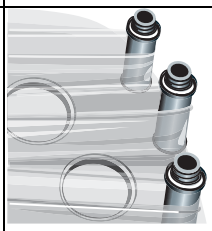
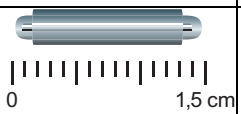
2 Laboratory tests of passive samplers for the detection of PCBs in indoor air (Project phase 2)

2.1 Introduction

2.1.1 Background

This chapter presents the continuation of previous work conducted in project phase 1. Phase 1 included a literature review of passive sampling methods and formats and a discussion of their suitability as a cost-effective screening tool for PCBs in indoor air. Based on these results, three formats were suggested (section 1.3) which appeared suitable for the purpose and should be further tested in project phase 2. These formats are summarised in Table 6.

Table 6. Passive sampling formats originally suggested for further work in project phase 2 (section 1.3).

Acronym	Illustration	Full name	Description	Commercial supplier	Reference
Mini-SPMD		Semipermeable membrane devices, small format	15 cm strips of low density polyethylene, filled with triolein.	Exposmeter, Sweden	Goodbred et al. (2009)
SBSE, Twister		Stir bar sorptive extraction	Small rod coated with polydimethylsiloxane.	Gerstel, Germany	www.gerstel.com
PDMS-coated vials		Polydimethylsiloxane (silicone)	Inner walls or bottom of the glass coated with PDMS	None	Reichenberg et al. (2008); Mäenpää et al. (2011)

In a subsequent meeting with the Danish Energy Agency, the conclusions from project phase 1 were discussed and the experimental work in project phase 2 was specified (Annex 2). The use of performance reference compounds (PRC) for calibration purposes, i.e. the addition of defined amounts of chemicals to the sampler, which are released during the sampling process, was discouraged and considered as unsuitable in an indoor measurement. Even though the resulting PRC concentrations in air would be substantially lower than the cut-off values, it will be problematic to work with a device which releases potentially harmful compounds to the indoor environment. As the routine use of Mini-SPMDs strongly depends on PRC calibration, the authors adjusted their plan and intensified their work with PDMS-coated vials instead, assuming that these will be less affected by variations in air movement. The new list of formats for project phase 2 is given in **Table 7**.

An alternative to calibration with PRC was the standardisation of air velocity during sampling. This might be achieved for SBSE relatively easily which can be set in motion on a magnetic stirrer, thus obtaining comparable sampling conditions between locations. This procedure, however, might conflict with the criteria of robustness and easy handling, described in project phase 1. SBSE have been included with and without movement in the experiments of this project phase (**Table 7**).

Table 7. Passive sampling formats included in project phase 2.

Acronym	Sorbent	Adjustments	Experimental variations	Experiment number
PDMS-coated vials	2 mm layer of PDMS	Silicone cast instead of coating	3 different flows	I
PDMS-coated vials	PDMS sheet of approximately 0.24 mm thickness	Thin PDMS sheet instead of coating	3 different flows	II
PDMS-coated vials	0.1 mm PDMS coating	Petri dish (15 cm diameter) with PDMS-coating.	3 different flows	III
SBSE, Twister	PDMS layer around a glass rod, housing a magnet	Not purchased from commercial supplier (for budget reasons). Custom made, length: 4.5 cm	3 different flows	IV
SBSE, Twister	PDMS layer around a glass rod, housing a magnet	Not purchased from commercial supplier (for budget reasons). Custom made, length: 4.5 cm	Magnetic stirring	V

2.1.2 Objectives of project phase 2

The overall objective of this project was to study, develop and use passive sampling for screening analyses of PCB concentrations in indoor air. Project phase 1 was concluded with a selection and recommendation of suitable passive sampling formats (Table 6; Table 7).

The objectives of the second project phase include further development, tests and optimisation of the selected formats, with the changes described above. More specifically, the following factors should be addressed:

- Influence of air velocity changes on the partitioning kinetics of PCBs between air and the sampler
- As a direct consequence, suitable calibration methods
- Risk of back diffusion of PCBs to air, after uptake of PCBs by the sampler
- Differences in elimination / uptake rates between PCB congeners
- Accuracy and precision
- Detection limits in relation to a desired sampling period of 24 hours.
- Practical handling.

2.2 Experimental approach

Most of the questions above were addressed in elimination experiments, i.e. the sampler was loaded with PCB congeners and their elimination over time was monitored. This approach has practical advantages compared with the alternative of an uptake experiment for which the ambient concentration would have to be controlled at a constant level. As previously agreed upon, the experiments were conducted with all 25 PCB congeners included in the laboratory's accredited method and hexachlorobenzene (HCB) as an additional volatile marker compound (Table 8).

Table 8. PCB congeners included in the experiments of project phase 2. In addition, HCB was used as a volatile marker compound.

MonoCBs	TriCBs	TetraCBs	PentaCBs	HexaCBs	HeptaCBs	OctaCBs	DecaCB
CB-3	CB-28	CB-40	CB-99	CB-128	CB-170	CB-194	CB-209
	CB-31	CB-44	CB-101	CB-138	CB-180	CB-198	
		CB-49	CB-105	CB-149	CB-187		
		CB-52	CB-110	CB-151	CB-188		
			CB-118	CB-153			
				CB-156			

For all experiments, an initial amount of approximately 200 ng was used for each PCB congener and HCB (approximately 3500 ng for CB-3, due to lower instrumental response). 2-3 spiked samples were retained from each experiment, to define start concentrations. The remaining samples were processed after pre-defined periods of time. As far as possible, the experiments were conducted with duplicate samples, to allow assessments of precision. Altogether, a total of 13 experiments with multiple combinations of samplers and flows have been run, as outlined in Table 9.

The PCB concentrations were plotted against time to study the PCB elimination from the silicone material. Elimination rates k_2 were calculated as the slope of the regression line fitted to log-transformed PCB concentrations over time (Figure 4). k_2 values were used to address the factors described in section 2.1.2, as well as for comparisons between experiments.

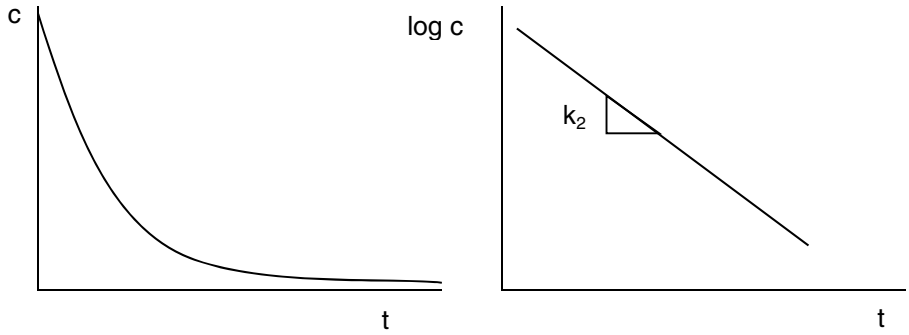
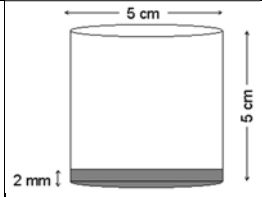
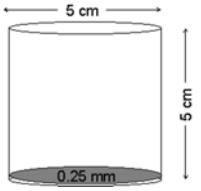
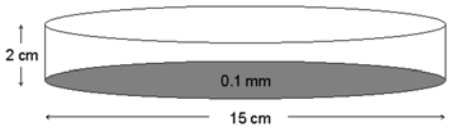
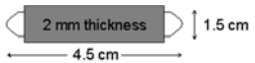


Figure 4. Concept of concentration decrease and resulting elimination rate k_2. c: Concentration. t: Time.

Table 9. Detailed descriptions of experiments in project phase 2.

Experiment	**I**	**II**	**III**	**IV**	**V**
Format	**Glass with silicone layer**	**Glass with silicone sheet**	**Petri dish with silicone coating**	**SBSE**	**SBSE**
Illustration					See IV
Air velocity	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	Magnetic stirrer; flow approximately 0.1 m/s
Sampling points (no. of replicates)	Start (3) ½ day (2) 1 day (2) 2 days (2) 4 days (2) 1 week (2) 2 weeks (1) 4 weeks (1) 8 weeks (1)	Start (3) ½ day (2) 1 day (2) 2 days (2) 4 days (2) 1 week (2) 2 weeks (1) 4 weeks (1) 8 weeks (1)	Start (3) 4 days (1) 1 week (1) 2 weeks (1) 4 weeks (1)	Start (2) 4 days (2) 1 week (2) 2 weeks (2) 4 weeks (1)	4 days (2) 1 week (2) 2 weeks (1) 4 weeks (1)

Furthermore, k_2 values were used in calculations of detection limits after a 24-hour-sampling. The concentration on the sampler can be estimated as

$$C_{Silicone} = C_{Air} \cdot \frac{k_1}{k_2} \cdot (1 - e^{-k_2 \cdot t}) \qquad \text{(Equation 1)}$$

where $C_{Silicone}$ and C_{Air} are concentrations on the sampler and in air, respectively, k_1 and k_2 are uptake and elimination constants, respectively (Figure 4), and t is the time. Thus, resulting sampler concentrations were calculated for air concentrations of 300 and 3000 ng/m^3.

Values for k_1 were taken from the literature (Petty et al., 1993; Esteve-Turrillas et al., 2009) and adjusted for the specific surface area of each of the samplers in Experiments I to V. k_1 will also depend on experimental conditions, amongst these changes in air velocity as discussed in detail below. However, these dependencies have not been taken into account in the calculations, i.e. a constant value has been used of k_1 for each type of sampler. An exception is Experiment V in which the sampler was rotated during the elimination experiment. In this experiment, k_1 was scaled up to account for differences in partitioning kinetics in comparison with Experiment IV, which used the same sampler geometry, but an immobile approach. Details are given in chapter 2.3.5 (Experiment V). In summary, it is important to note that these are estimations of sampler concentrations, not precise predictions.

For assessments of detection limits, (Equation 1 was re-arranged, so C_{Air} was calculated for a given PCB-amount on the sampler. An instrumental detection limit of 0.5 pg for individual PCB congeners was assumed, in accordance with estimations of detection limits in chapter 1.

2.2.1 Experiment I: Glass with a 2 mm silicone layer

This sampler consisted of amber glasses with a 2 mm silicone layer on the bottom. PCBs were added to the silicone layer as described above. 3 glasses were immediately closed and used for determination of start concentrations. Further samples were taken after ½ day, 1 day, 2 days, 4 days, 1 week, 2 weeks, 4 weeks and 8 weeks. Up to 1 week, the experiment was run in duplicate, beyond the 1 week data point, only single samples were analysed.

Air velocity was varied in terms of three different flows (approximately 0.1, 0.3 and 1 m/s) established by placing the samples at different positions in a laboratory fume hood, partly shielded.

The chemical analysis included the extraction of the PCB congeners with acetone, directly in the amber glasses used for the experiment. The compounds were extracted with 2 x 30 ml acetone with a total contact time of 3 days, to allow for complete re-diffusion of all PCB congeners into the solvent. The extracts were subsequently evaporated to < 1 ml including solvent change to iso-octane. Internal standards (CB-53 and CB-155) were added and the final extract volume was adjusted to 1 ml precisely.

2.2.2 Experiment II: Glass with a thin silicone sheet

This sampler consisted of the same amber glasses as tested in Experiment I, but with a thin silicone sheet of approximately 0.25 mm thickness (0.01 inch) placed in the bottom of the glass. The exact diameter was cut from a larger

sheet, i.e. adjustments to different glass sizes will be possible. Air velocity was varied in the same way as described for Experiment I.

After addition of the PCB mixture, 3 glasses were immediately closed for later determination of the start concentrations. The same time periods were used as for Experiment I, i.e. the remaining samples were analysed after ½ day, 1 day, 2 days, 4 days, 1 week, 2 weeks, 4 weeks and 8 weeks. As with Experiment I, the first five samples were run in duplicate, and single samples were analysed for the remaining data points. The chemical analysis was performed in the same way as described for Experiment I.

2.2.3 Experiment III: Petri dishes with a thin silicone coating

As part of the optimisation work in this project phase, a different sampler geometry was tested as well. This sampler consisted of a common petri dish with a thin layer of 0.1 mm silicone. The edge of the petri dish was approximately 2 cm high, i.e. providing less shielding of the sorbent than the glass vials. The larger diameter (15 cm) means a larger surface area and thus a larger air volume in contact with the sampler.

After addition of the PCB congeners, 3 samples were retained for determination of start concentrations. The remaining samples were analysed after 4 days, 1 week, 2 weeks and 4 weeks. No duplicates were run in this experiment, i.e. it will not be possible to assess precision of sampling and analysis. The PCB congeners were extracted using 2 x 30 ml of acetone. Due to the lower edge of the petri dish, the solvent was carefully taken up with a Pasteur pipette and transferred to a small container. The total contact time between the silicone and the solvent was reduced to 1 ½ hours, as the thinner silicone film allowed faster re-diffusion into the solvent.

2.2.4 Experiment IV: Custom-made SBSE samplers

For loading with PCBs, the samplers were placed in a rotating glass tube to which a PCB solution was added. The solvent evaporated while the PCBs diffused into the silicone layer. This procedure allowed a relatively equal distribution of PCBs on the sampler.

Two of the samplers were removed for determinations of start concentrations. The remaining samplers were placed on aluminium foil in the fume hood and shielded differently to create the same flows as for Experiments I to III. After the pre-defined intervals of 4 days, 1 week and 2 weeks, duplicate samples were analysed. For the last data point after 4 weeks, only a single sample was available for each flow.

The PCB congeners were extracted using 2 x 20 ml of acetone, added to the glass tubes which also contained the samplers. The same contact time was used as in Experiments I and II, i.e. a total contact time of 3 days. The further procedure was identical to that described for Experiment I and II.

2.2.5 Experiment V: Custom-made SBSE samplers on a magnetic stirrer

The samplers were loaded in the same way as described above. For start concentrations, the two samples of Experiment IV were used. The remaining six samplers were placed in glass beakers, which in turn were placed on the

magnetic stirrer. It was examined whether the sampler also could rotate directly on the magnetic stirrer, but this proved unstable.

Duplicate samples were analysed after 4 days and 1 week, further single samples were analysed after 2 weeks and 4 weeks. The air velocity in this experiment was approximately 0.1 m/s, i.e. comparable to the "low flow" settings in Experiments I to IV. The PCB congeners were extracted in the same way as described for Experiment IV.

2.3 Results

For each of the five experiments, data exist for a combination of 25 PCB congeners and three air velocities. Thus, a substantial amount of data has been produced during this project phase. It will not be possible to present all results in the following sections of the report. Instead, relevant examples have been chosen for the discussion of the factors described in section 2.1.2.

2.3.1 Experiment I: Glass with a 2 mm silicone layer

As expected, the release of PCBs from the silicone material proceeded slowly, as illustrated for CB-3, CB-28 and CB-52 in Figure 5. The figure clearly shows differences in elimination rates between the three PCB congeners, which reflect their differences in volatility: The higher the volatility of the compound, the higher its tendency to move from the solid phase (silicone) into air. In general, the volatility of PCBs decreases with the molecular weight of the congeners. For this experiment, only CB-3 (all flows) and HCB (low and medium flow) had statistically significant elimination rates, i.e. the slopes of the regression lines in the logPCB vs. time plot were statistically different from zero (Figure 5).

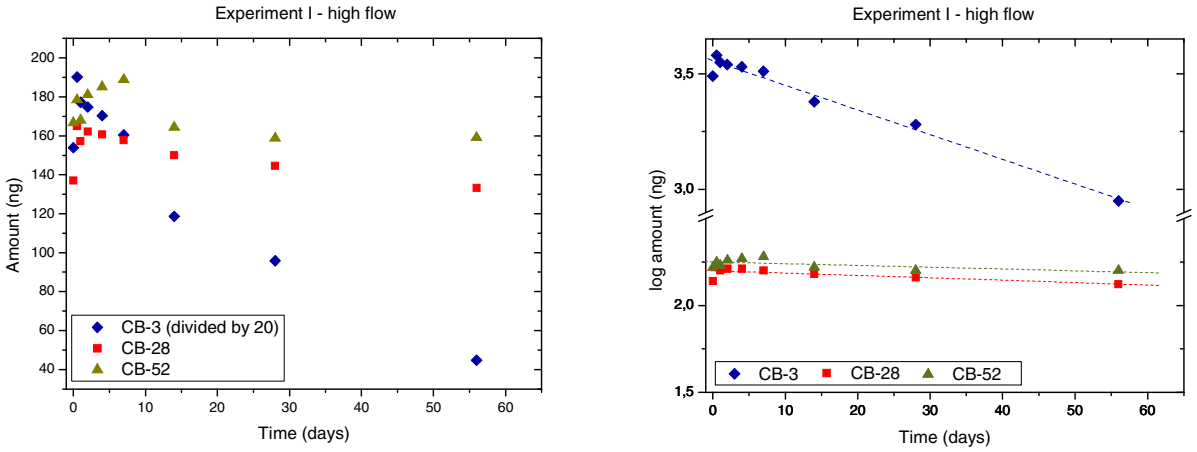


Figure 5. Results for CB-3, CB-28 and CB-52 in the high flow set-up of Experiment I (Glasses with a 2 mm silicone layer). Left: PCB amount over time. Results for CB-3 in this figure were divided by 20 to reach the same scale. Right: Log-transformed PCB amount over time and fitted regression lines. High flow: Approximately 1 m/s.

2.3.1.1 Risk of back diffusion

The slow decrease over time for all PCB congeners except CB-3 also reflects the high sorption capacity for hydrophobic compounds like PCBs of the 2 mm silicone layer. It can generally be stated that a thicker layer of silicone

retains the compounds more strongly, which will also become apparent in the comparison with Experiment II. With regard to the question of back diffusion into air during a sampling campaign, this also means that there is virtually no risk of back diffusion in Experiment I. For none of the PCBs analysed in this experiment, the mean concentration was significantly lower after 1 day than at the beginning of the experiment (one-tailed Student's t-test with unequal variances; $p < 0.05$). 1 day was chosen in the statistical test as this was the desired sampling period in a screening campaign of indoor air. For CB-3 and HCB, the most volatile compounds, a 10 % loss due to back diffusion would be reached after 10 and 20 days, respectively.

2.3.1.2 Effect of air velocity / calibration

The elimination rates generally decreased with decreasing air velocity above the sampler (Figure 6), however, due to the extremely slow elimination process in this experiment, this effect is less apparent than it is in Experiment II (Figure 8). For CB-3 and HCB, the ratio between the highest and the lowest k_2 values is 4.8 and 3.9, respectively. For k_2 values at medium and low flows, the ratio is still 2.6 for both compounds, i.e. a considerable factor influencing accuracy unless air velocity can be defined and kept constant between individual samplings or the variation can be accounted for in the calibration of the sampler.

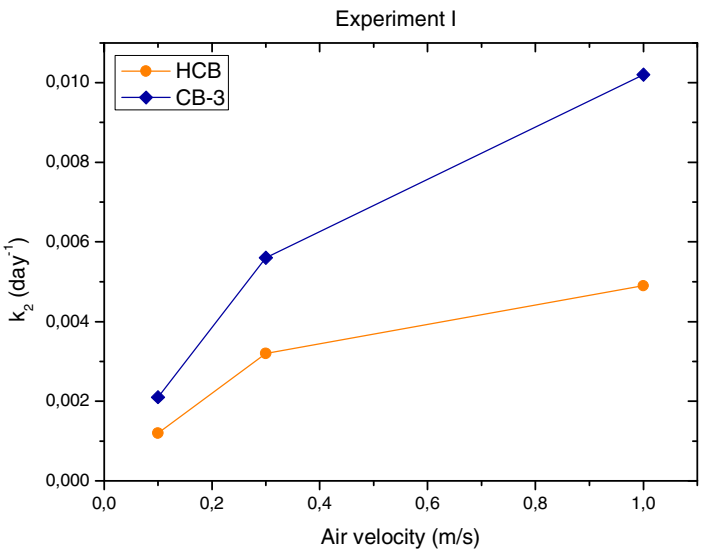


Figure 6. Dependence of elimination rates k_2 on air velocity above the sampler (Experiment I). For HCB, k_2 is not statistically significant at an air velocity of 0.1 m/s.

It was described in chapter 1 that several factors could affect sampling rates and should be accounted for in the calibration of the sampler, the most important ones being temperature and air velocity. While temperature variations affect sampling rates to a lesser extent and are easier to correct for, changes in air velocity were likely to influence sampling rates to a larger extent. This has now been confirmed experimentally. In addition, too low air exchange above the sampler can lead to a stagnating boundary layer with the risk of analyte depletion, i.e. the molecules can diffuse into the sampler more rapidly than they can be replaced in the boundary layer.

The calibration methods presented in chapter 1 to control the effect of air velocity include (i) the use of PRC which are released from the sampler and (ii) the standardisation of uptake conditions, e.g. by creating a constant and relatively high flow above the sampler. As mentioned above, PRC calibration means that PCB congeners or chemically similar compounds are released into the surrounding air, which is unfavourable in an indoor situation. In Experiment I, PCBs used as PRCs would also yield too low elimination rates to be usable for calibration purposes. The alternative of increased and standardised air velocity would be more promising.

2.3.1.3 Accuracy and precision

As mentioned above, non-standardised sampling conditions, in particular regarding air velocity, are likely to affect sampling rates and thus the amount of PCB congeners in the sampler. If the sampling rate cannot be determined for the specific sampling conditions, accuracy will likely be reduced. For this experiment, CB-3 varied by a factor of 2.6 between low and medium flow and by a factor of 4.8 between high and low flow.

Precision can be assessed on the basis of duplicate samples included in the experiment for the sampling points after ½, 1, 2, 4 and 7 days. Relative standard deviations were determined for HCB and CB-3, the only compounds with significant decreases over time, for each of the different flow set-ups. These standard deviations were compared with the concentrations of the initial sampling points at the start of the experiment (Table 10). The variation between the initial samples reflects the variation of the loading procedure, combined with the variation of the extraction and measurement process. For the subsequent duplicates, the total variation also includes the variability of the compound elimination. However, in all cases, the standard deviations were found to be lower than at the beginning of the experiment. In fact, precision can be regarded as extremely high.

Table 10. Minimum, maximum and average relative standard deviations of duplicates in Experiment I (½ day, 1 day, 2 days, 4 days, 1 week), compared with triplicates of the start concentrations. Only those compounds are listed that were found to decrease significantly during the course of the experiment.

	Start	High flow			Medium flow			Low flow		
	N=3	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
HCB	18%	0.14%	2.2%	1.0%	0.18%	7.0%	1.9%	-	-	-
CB-3	20%	3.7%	7.9%	6.0%	0.043%	8.2%	4.6%	0.047%	2.0%	0.63%

2.3.1.4 Uptake rates / detection limits

Estimated concentrations on the samplers for air concentrations of 300 and 3000 ng/m^3 and a sampling period of 24 hours are shown in Figure 7. The sampler concentrations were calculated according to Equation 1, using k_1 values from the literature (Petty et al., 1993; Esteve-Turrillas et al., 2009), adjusted to the surface area of the silicone layer in this experiment (Table 9). Due to the lack of significant k_2 data for all PCB congeners but CB-3, this calculation was limited to CB-3 and HCB. k_2 values were taken from the medium flow set-up.

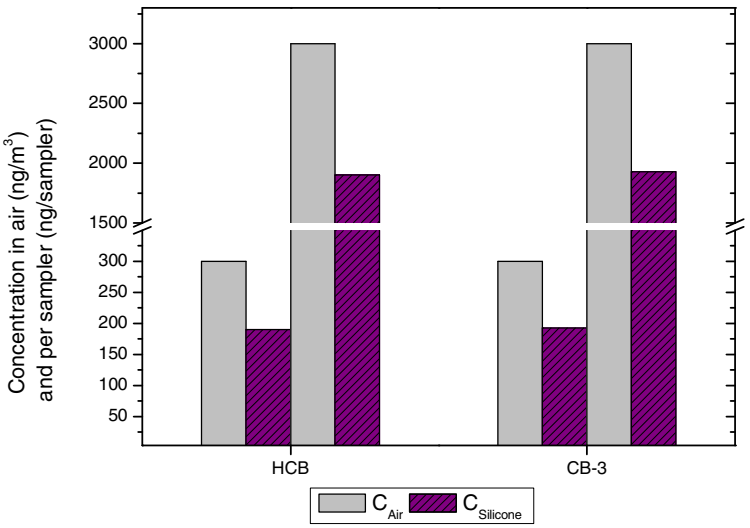


Figure 7. Assumed air concentrations C_{Air} of 300 and 3000 ng/m^3 and resulting estimates of sampler concentration $C_{Silicone}$ after 24 hours of sampling (Equation 1). Input values for HCB: k_1=0.6348 m^3/day; k_2=0.0032/day. Input values for CB-3: k_1=0.6446 m^3/day; k_2=0.0056/day.

For the calculation of detection limits, an instrumental detection limit of 0.5 pg was assumed. As described in section 1.2.4, the compounds are usually collected in an extract of which only a small part is used for the instrumental analysis. In the case of this experiment, it was 0.1 %, corresponding to 1 µl of a 1 ml extract. This percentage can be increased for lower detection limits: If, for example, the extract is concentrated to 100 µl and 1 µl is used for instrumental analysis, the percent injected increases to 1 %. Accordingly, a lower concentration in silicone would still be detectable. Therefore, different scenarios are included in Table 11. In summary, the detection limits of < 1 ng/m^3 can be considered acceptably low for a 24-hour-sampling period.

Table 11. Estimates of detection limits, i.e. lowest detectable concentration in air, after 24 hours of sampling (Equation 1). Input values for HCB: k_1=0.6348 m^3/day; k_2=0.0032/day. Input values for CB-3: k_1=0.6446 m^3/day; k_2=0.0056/day.

Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m^3)
HCB	0.1	0.5	0.789
HCB	1	0.05	0.0789
CB-3	0.1	0.5	0.778
CB-3	1	0.05	0.0778

2.3.1.5 Conclusions Experiment I

The following conclusions can be drawn from Experiment I:

- The sampler is robust and easy to handle, both during sampling and in the subsequent chemical analysis.
- There is no risk of back diffusion during the desired sampling period.
- Elimination rates k_2 vary with changes in air velocity over the sampler, with a factor 2.6-4.8 for CB-3.
- Performance reference compounds (PRCs) are not advisable for calibration of the sampler, standardisation of uptake conditions might be an alternative.
- Changes in k_2 due to varying air velocity will affect accuracy. Precision, however, can be considered very high.

- For HCB and CB-3, detection limits of < 1 ng/m³ for a 24-hour-sampling have been estimated and can be considered very low.

2.3.2 Experiment II: Glass with a thin silicone sheet

This experiment used the same sampler geometry as Experiment I, but a silicone layer of a different thickness: Instead of casting a 2 mm layer into the glasses, circles were cut from a silicone sheet with a thickness of 0.25 mm. The experiment was conducted in the same way as Experiment I. As expected, the thinner silicone layer led to a faster elimination of the PCBs, as illustrated in Figure 8, for the same compounds as shown in Figure 5. No CB-3 was detectable on the sampler after 4 and 8 weeks in the high flow experiment, neither after 8 weeks in the medium and low flow experiments.

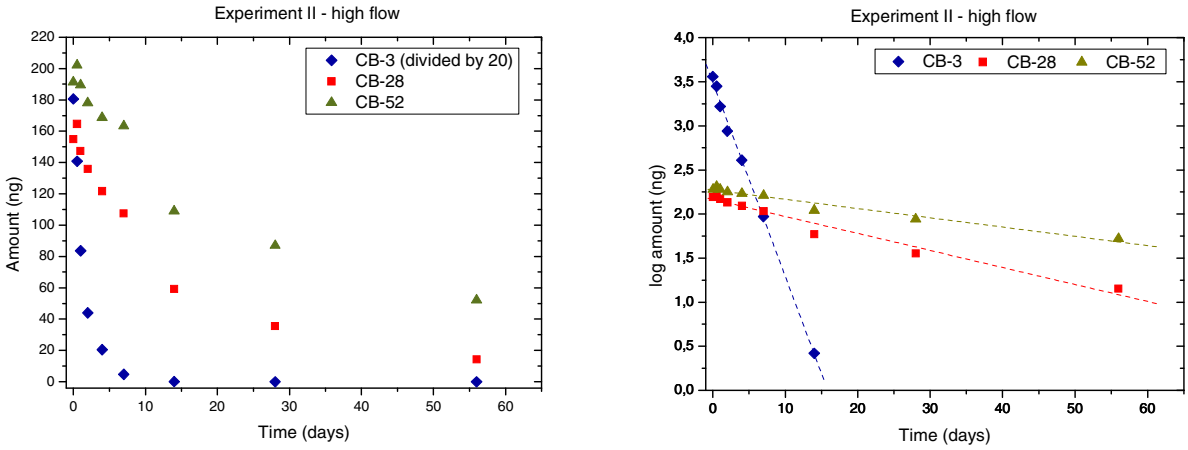


Figure 8. Results for CB-3, CB-28 and CB-52 in Experiment II (Glasses with a layer of 0.25 mm silicone). Left: PCB amount over time. Results for CB-3 in this figure were divided by 20 to reach the same scale. Right: Log-transformed PCB amount over time and fitted regression lines. High flow: Approximately 1 m/s.

While only HCB and CB-3 had significantly decreasing concentrations during Experiment I, several compounds had regression lines over time with statistically significant slopes in Experiment II. These are summarised in Table 12.

Table 12. Summary of compounds with significant decreases over time in Experiment II, based on statistically significant slopes ($p < 0.05$) of the regression lines in the logPCB vs. time plots

High flow	Medium flow	Low flow
HCB	HCB	HCB
CB-3	CB-3	CB-3
CB-28	CB-28	CB-28
CB-31	CB-31	CB-31
CB-40	CB-40	CB-40
CB-44	CB-44	CB-44
CB-49	CB-49	CB-49
CB-52	CB-52	CB-52
CB-99	CB-99	CB-99
CB-101	CB-101	CB-101
CB-110		

2.3.2.1 Risk of back diffusion

As Figure 8 indicates, the PCB congeners are less strongly retained by the thinner silicone sheet, compared with the 2 mm silicone layer in Experiment I. Higher elimination rates also mean a higher risk of undesired back diffusion after sorption of PCB congeners into the silicone phase. In order to quantify the extent of back diffusion, PCB amounts on the samplers were compared for the beginning of the experiments and after 1 day. These had decreased significantly after 1 day for CB-3 only, in the experiments with high and medium flow (one-tailed Student's t-test with unequal variances; $p < 0.05$).

Like for Experiment I, the regression lines were used to calculate the point of time at which 10% of the initial PCB amount had diffused back into air. For CB-28 and CB-31, this was reached after 2 days. For the tetra-CBs (Table 8), it was about 5 days. For the 1-day-sampling as planned in a screening survey, the back diffusion will still be negligible, but should be kept in mind.

2.3.2.2 Effect of air velocity / calibration

Given the higher elimination rates in this experiment, their dependence on changes in air velocity can be assessed for a higher number of compounds (Table 12). As described above, the elimination rates k_2 increased with increasing air velocity, i.e. air exchange above the sampler (Figure 9). With the exception of CB-99 and CB-101, k_2 values were statistically different (i.e. no overlap of 95% confidence limits) for the three flow conditions.

For all these compounds – except CB-40 -, the k_2 value did not increase linearly over the total range of air velocities, but increased more steeply from the low to the medium flow, than between medium and high air velocity (Figure 9). Flow variations in this range, i.e. between 0.1 and 0.3 m/s, might be more likely to occur in the indoor environment, than changes from the medium to the high flow. The k_2 ratios between the medium and the low flow are in the range of 1.4 (CB-40) to approximately 2.8 (CB-28), with a median value of 2.6 (for the compounds in Figure 9). Thus, variations in air velocity between 0.1 and 0.3 m/s might lead to a factor of 1.4-2.8 between elimination rates and thus uptake rates that determine the measured concentrations during passive sampling.

The variation of k_2 emphasises the importance of a calibration under realistic sampling conditions. The use of PRCs would probably be a scientifically sound solution and would produce k_2 values for a range of PCB congeners of different volatility (Table 12). However, less volatile congeners (e.g. CB-138, CB-153, CB-180) did not dissipate at a measurable rate. Standardising air velocity is a possible alternative, with the caveats described for Experiment I.

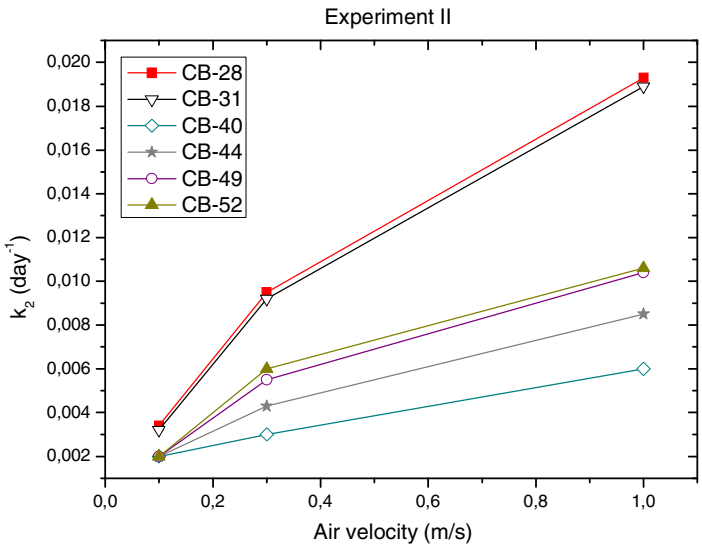


Figure 9. Dependence of elimination rates k_2 on air velocity above the sampler (Experiment II). Further PCB congeners with statistically significant k_2 values in Experiment II were CB-3, CB-99 and CB-101.

2.3.2.3 Accuracy and precision

As described above, a factor of 2.8 was observed for the k_2 value of CB-28 between the low and the medium flow of approximately 0.1 and 0.3 m/s, respectively. If the sampling rate changes over the same range between the calibration and the actual sampling, its quantification will be affected by a similar factor, i.e. accuracy will be within a factor of up to 3. For less volatile compounds, the factor will be smaller.

Precision has been addressed in the same way as described for Experiment I, based on the five duplicate samples of this experiment, analysed after ½, 1, 2, 4 and 7 days. Relative standard deviations were determined for those PCB congeners that declined significantly in this experiment, and compared with the standard deviations of the starting point of the experiment (Table 13). CB-3 and HCB have a relatively high standard deviation in the high flow experiment, in particular in the 7-days-sample. The remaining results show, however, that this seems to be an exception, one particular duplicate which deviates more than the rest of the samples. Again, precision can be considered as very high for the PCB congeners, perhaps with some exceptions for CB-3.

Table 13. Minimum, maximum and average relative standard deviations of duplicates in Experiment II (½ day, 1 day, 2 days, 4 days, 1 week), compared with triplicates of the start concentrations. Only those compounds are listed that were found to decrease significantly during the course of the experiment.

	Start	High flow			Medium flow			Low flow		
	N=3	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
HCB	5.8%	6.9%	50%	22%	0.57%	9.0%	4.6%	0.79%	6.3%	3.0%
CB-3	10%	12%	86%	40%	1.4%	15%	5.6%	0.18%	10%	4.3%
CB-28	6.3%	1.4%	17%	6.6%	1.3%	5.4%	2.6%	0.51%	8.7%	2.6%
CB-31	5.7%	0.49%	16%	7.3%	0.78%	6.7%	3.3%	0.26%	7.2%	2.7%
CB-40	8.3%	2.1%	10%	6.3%	1.7%	3.5%	2.7%	1,3%	7.1%	3.3%
CB-44	7.5%	0.68%	8.1%	4.9%	1.3%	5.0%	3.0%	0.13%	4.8%	1.7%
CB-49	5.0%	0.012%	8.7%	4.6%	0.073%	6.6%	4.2%	0.45%	5.8%	2.3%
CB-52	5.5%	0.046%	13%	6.1%	0.18%	14%	6.8%	1.5%	11%	4.6%
CB-99	6.5%	2.0%	11%	6.4%	1.2%	8.5%	4.6%	2.2%	6.2%	3.9%
CB-101	6.9%	1.2%	8.3%	4.2%	0.080%	3.8%	2.3%	0.0057%	12%	3.1%
CB-110	7.3%	0.80%	14%	4.9%	-	-	-	-	-	-

2.3.2.4 Uptake rates / detection limits

Equation 1 was applied to estimate the concentration in silicone for different air concentrations after 24 hours of sampling. For the cut-off value of 300 ng/m^3, the results for a number of PCB congeners are shown in Figure 10. The calculations include an estimate of uptake rates k_1 taken from the literature (Petty et al., 1993; Esteve-Turrillas et al., 2009) as well as k_2 values as determined in the experiment with medium flow. For these input values, the PCB amount in the sampler was approximately 190 ng/sampler, i.e. very well measurable.

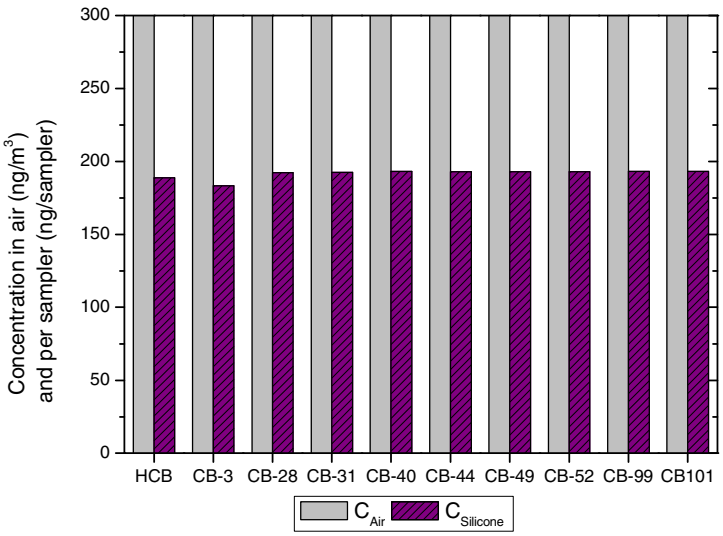


Figure 10. Assumed air concentrations C_{Air} of 300 ng/m^3 and resulting estimates of sampler concentration $C_{Silicone}$ after 24 hours of sampling (Equation 1). Input values: k_1=0.6446 m^3/day for HCB, k_1=0.6446 m^3/day for PCB congeners. k_2 values are taken from the medium flow set-up (see Figure 9).

As described above, Equation 1 and the same input parameters as in Figure 10 were also used for assessments of detection limits, i.e. the lowest air concentration still detectable at an instrumental detection limit of 0.5 pg (Table 14). Based on these estimates, low air concentrations of 1 ng/m^3 will easily be detectable with this method of sampling, even with a classical extraction method which only uses 0.1 % of the extract for instrumental analysis.

Table 14. Estimates of detection limits, i.e. lowest detectable concentration in air, after 24 hours of sampling (Equation 1). Input values: k_1=0.6348 m^3/day for HCB, k_1=0.6446 m^3/day for PCB congeners. k_2 values are taken from the medium flow set-up.

Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m^3)
HCB	0.1	0.5	0.794
CB-3	0.1	0.5	0.819
CB-28	0.1	0.5	0.779
CB-31	0.1	0.5	0.779
CB-40	0.1	0.5	0.777
CB-44	0.1	0.5	0.777
CB-49	0.1	0.5	0.778
CB-52	0.1	0.5	0.778
CB-99	0.1	0.5	0.776
CB-101	0.1	0.5	0.776

2.3.2.5 Conclusions Experiment II

The following conclusions can be drawn from Experiment II:

- The sampler is robust and easy to handle, both during sampling and in the subsequent chemical analysis.
- The PCB congeners are sufficiently retained to minimise the risk of back diffusion during the desired sampling period.
- Elimination rates k_2 vary with changes in air velocity over the sampler, with a factor of 1.4-2.8 between the low and medium flow conditions, which appear realistic for indoor air measurements.
- PRCs might be a way of calibrating these samplers, but the release of PCB compounds into the indoor environment is undesired.
- Standardisation of uptake conditions by sampler movement might be an alternative.
- Changes in k_2 due to varying air velocity will affect accuracy. Precision, however, can be considered very high, slightly less for CB-3.
- Detection limits of < 1 ng/m^3 for a 24-hour-sampling have been determined for a range of PCB congeners and can be considered very low.

2.3.3 Experiment III: Petri dishes with a thin silicone coating

This experiment combined a large diameter (15 cm) with a thin coating of silicone (0.1 mm). Based on the findings in Experiments I and II this should increase the exchange of PCBs between air and silicone. In contrast to the previous experiments, Experiment III did not include duplicate samples and only covered a period of 4 weeks.

As can be seen from Figure 11, the PCB congeners were released from the silicone in the high flow experiment, but not as fast as expected based on the sampler's geometry. Rates were generally lower than in Experiment II and fewer congeners dissipated at a rate which was statistically significant from zero. However, there was some variability between the different flows, indicating a larger uncertainty which cannot be assessed or compensated by replicate measurements in this experiment. The fact that this experiment does not include duplicates might have influenced elimination rates as single outliers or deviating results will have a stronger impact on the regression analysis.

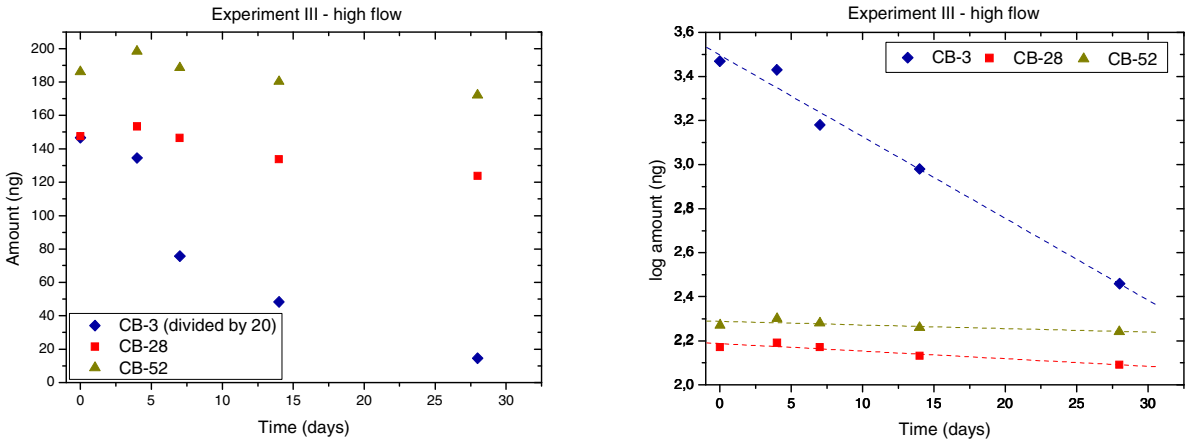


Figure 11. Results for CB-3, CB-28 and CB-52 in Experiment III (PDMS-coated petri dishes). Left: PCB amount over time. Results for CB-3 in this figure were divided by 20 to reach the same scale. Right: Log-transformed PCB amount over time and fitted regression lines. High flow: Approximately 1 m/s.

Furthermore, the shorter experimental period has to be born in mind as longer experiments might have led to a higher number of compounds with statistically significant regression lines. As several congeners were close to being significant, with regard to the slopes of their regression lines, additional data points might have changed the overall result.

2.3.3.1 Risk of back diffusion

Like in Experiments I and II, the risk of back diffusion was quantified on the basis of the regression lines. The time was calculated at which 10% of the initial PCB amount had diffused into the surrounding air. For the marker compounds HCB and CB-3, a 10 % decrease was reached within 1.5 and 2 days. For CB-28 and CB-31, the initial amount had decreased by 10 % after approximately 18 days. In summary, the risk of back diffusion can be considered low.

2.3.3.2 Effect of air velocity / calibration

The effect of varying air velocity over the sampler was less clear than in Experiment II, probably also as a result of higher variability between the experiments at different flows. HCB, CB-3, CB-28 and CB-31 had statistically significant k_2 values at all three air velocities, CB-99 for the high and the low flow. These k_2 values are shown in Figure 12. It can clearly be seen that the values for CB-3 and HCB are an order of magnitude higher than those of CB-28, CB-31 and CB-99.

For CB-28 and CB-31, an almost linear increase was observed for k_2 with increasing air velocity, and the lines run almost parallel. A similar tendency was found for CB-99: If the non-significant middle point at 0.3 m/s was disregarded, the line would be nearly parallel to those for CB-28 and CB-31, meaning that k_2 increased by the same factor as for CB-28 and CB-31. Linear increases in k_2 over a range of air velocities would reduce the calibration challenges because extrapolation between air velocities would be possible. Consequently, k_2 ratios for medium/low flow and high/medium flow were very similar (1.3-1.6 for CB-28 and CB-31).

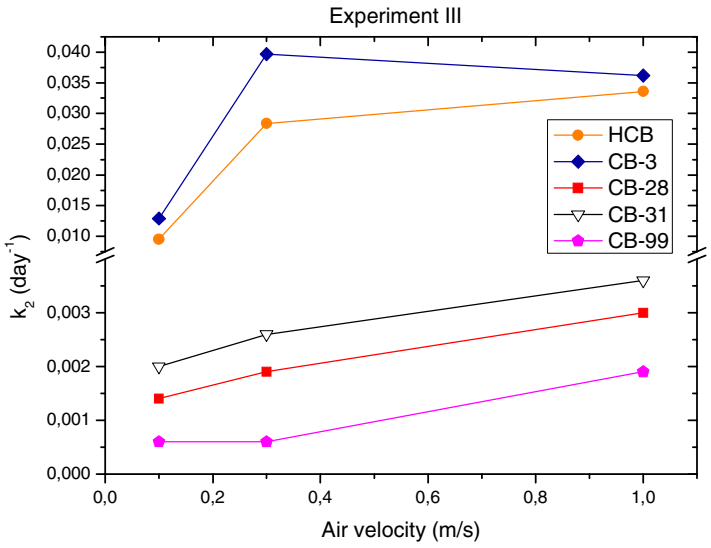


Figure 12. Dependence of elimination rates k_2 on air velocity above the sampler (Experiment III). Note that for CB-99, the medium flow k_2 value is not statistically significant.

Furthermore, the k_2 ratios for CB-28 and CB-31 were in the order of 1.3-1.6, i.e. considerably smaller than in Experiments I and II. This means that the

inaccuracies possibly introduced by different experimental conditions between calibration and sampling are smaller than in Experiments I and II. Unfortunately, this promising result was not confirmed by HCB and CB-3 for which k_2 increased sharply between the low and middle air velocity, but less steeply towards the high air velocity. In summary, the smaller k_2 ratios are promising and might enable measurements with an acceptable accuracy. However, variability between flows was relatively high, and more data would be needed to fully assess this format.

2.3.3.3 Accuracy and precision

As illustrated for CB-28 and CB-31 in Figure 12, varying air velocities only affect the elimination rate with a factor of 1.3-1.6, i.e. considerably lower than in Experiments I and II. This is a promising result, which, however, cannot be extended to other PCB congeners from the currently available data. Precision cannot be assessed in this experiment as it did not include duplicate samples. There are indications of larger variability between flows, but this would have to be verified experimentally.

2.3.3.4 Uptake rates / detection limits

As described for Experiments I and II, literature values of k_1 (Petty et al., 1993; Esteve-Turrillas et al., 2009) were adjusted to the surface area of this sampler and combined with k_2 values of this experiment (medium flow set-up). Compared with Experiments I and II, the uptake rates k_1 of this experiment are considerable higher, due to the larger surface area of the sampler (Table 9). With these input values, concentrations were calculated for the sampler, assuming 24 hours sampling and an air concentration of 300 ng/m^3 (Figure 13). Figure 13 shows a very efficient uptake process, with high PCB amounts on the sampler after only 24 hours of sampling.

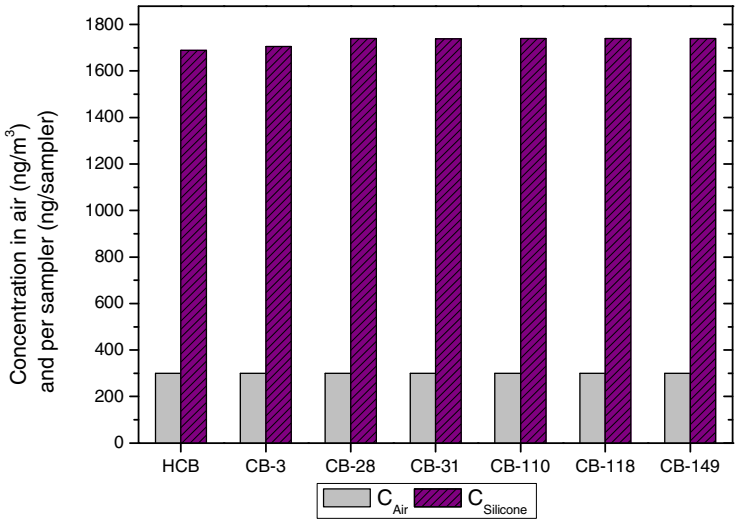


Figure 13. Assumed air concentrations C_{Air} of 300 ng/m^3 and resulting estimates of sampler concentration $C_{Silicone}$ after 24 hours of sampling (Equation 1). Input values: k_1=5.713 m^3/day for HCB, k_1=5.801 m^3/day for PCB congeners. k_2 values are taken from the medium flow set up (see Figure 12).

Equation 1 was also used to estimate a detection limit, i.e. the air concentration which corresponds to an instrumental detection limit of 0.5 pg and an injection percentage of 0.1 %, and thus a concentration $C_{Silicone}$ of 0.5 ng/sampler, collected after 24 hours of sampling. Due to the high uptake rates of this sampler, detection limits are even lower than in the Experiments I and II, by approximately an order of magnitude. As can be seen from Table 15, air concentrations below 0.1 ng/m^3 will be detectable.

Table 15. Estimates of detection limits, i.e. lowest detectable concentration in air, after 24 hours of sampling (Equation 1). Input values: k_1=5.713 m^3/day for HCB, k_1=5.801 m^3/day for PCB congeners. k_2 values are taken from the medium flow set-up.

Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m^3)
HCB	0.1	0.5	0.0888
CB-3	0.1	0.5	0.0879
CB-28	0.1	0.5	0.0863
CB-31	0.1	0.5	0.0863
CB-110	0.1	0.5	0.0862
CB-118	0.1	0.5	0.0862
CB-149	0.1	0.5	0.0862

2.3.3.5 Conclusions Experiment III

The following conclusions can be drawn from Experiment III:

- The sampler is practical and easy to handle. For routine applications, the glass petri dish could be exchanged with a metal container, to improve robustness.
- The PCB congeners are sufficiently retained to minimise the risk of back diffusion during the desired sampling period.
- Elimination rates k_2 vary with changes in air velocity over the sampler, but the factor of 1.3-1.6 was considerably smaller than for the other experiments.
- Thus, measurements with an acceptable accuracy might be possible without further calibration using PRCs or standardising uptake conditions. However, more data would be needed to verify these indications.
- Precision could not be assessed in this experiment, due to lack of replicate samples.
- The combination of a high surface area and a thin silicone coating makes compound uptake very efficient.
- Detection limits of < 0.1 ng/m^3 for a-24 hour-sampling have been determined for a range of PCB congeners and are lower than for the other formats.

2.3.4 Experiment IV: Custom-made SBSE samplers

This experiment used silicone-coated magnetic rods spiked with PCB congeners and placed on aluminium foil under the same flow conditions as tested in Experiments I to III, i.e. the samplers were not rotated in this experiment. PCB congeners were extracted and analysed over a period of 4 weeks, in a combination of duplicate and single samples.

Figure 14 shows that the elimination of PCBs proceeds very slowly, even for the high flow set-up. The curves are similar to those in Experiment I, taking into account the shorter experimental period of 4 weeks in this experiment versus 8 weeks in Experiment I, but indicate even lower elimination rates than those of Experiment I. Of all compounds analysed, only HCB at high and medium flow and CB-3 at high flow had significantly decreasing amounts over time, as reflected by statistically significant slopes in the logPCB vs. time curve (Figure 14). During the low flow experiment, none of the target compounds decreased significantly.

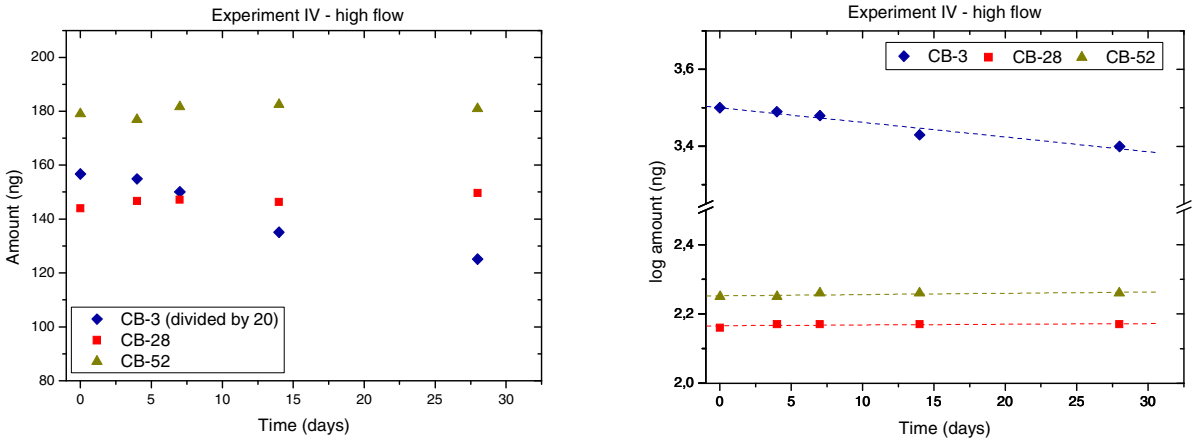


Figure 14. Results for CB-3, CB-28 and CB-52 in Experiment IV (Custom-made SBSE samplers, kept immobile). Left: PCB amount over time. Results for CB-3 in this figure were divided by 20 to reach the same scale. Right: Log-transformed PCB amount over time and fitted regression lines. High flow: Approximately 1 m/s.

2.3.4.1 Risk of back diffusion

As discussed for Experiment I, the low elimination rates show that the PCB congeners are retained strongly by the silicone material. Consequently, the risk of back diffusion will be low. The regression analysis has been used to calculate the time span required for a diffusion of 10 % of the initial amount. For HCB and CB-3, the only compounds with significantly decreasing concentrations, 10 % reduction of the initial amount was reached after 10 and 12 days, respectively. The risk of back diffusion is therefore virtually non-existent.

2.3.4.2 Effect of air velocity / calibration

Due to the extremely slow release of PCBs in this experiment, no data other than HCB and CB-3 at two and one flow situations, respectively, were available for assessment of air velocity effects (Figure 15). For HCB, a clear dependence of k_2 on air velocity was observed, with a k_2 ratio of 3.3 between the high and the medium flow. No other compounds could be assessed due to the insignificant elimination from the samplers over the experimental period of 4 weeks.

As described for Experiment I, one way of calibrating the samplers is the addition of PRCs, which dissipate into the surrounding air during the sampling process. A strong dependency of k_2 on air velocity, as indicated for HCB, suggests inaccuracies in the quantification process if air velocities are not comparable between the calibration and sampling situations. However, Figure 14 also indicates that for this format, elimination rates would be too low to be quantifiable, for nearly all PCB congeners. Alternatively, uptake conditions can be standardised, for instance by moving the sampler in a defined way. For the custom-made SBSE format, this has been tested by magnetic stirring, see Experiment V.

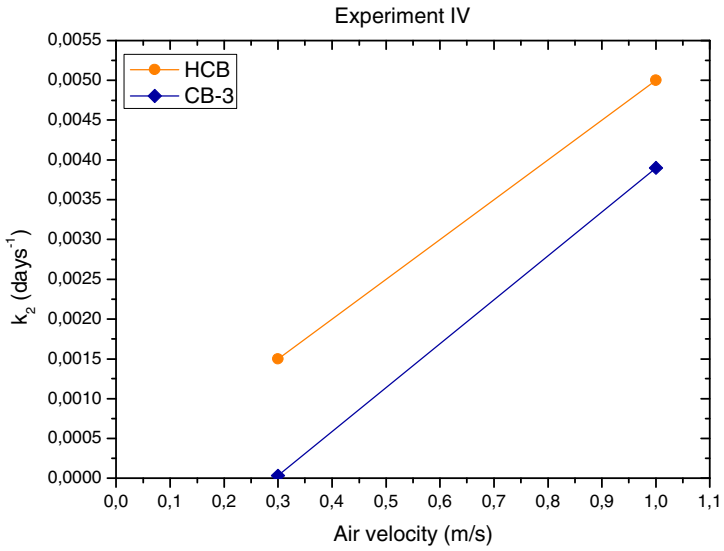


Figure 15. Dependence of elimination rates k_2 on air velocity above the sampler (Experiment IV). For CB-3, the k_2 value at the medium air velocity (0.3 m/s) is not statistically significant.

2.3.4.3 Accuracy and precision

As discussed above, it is not quite possible to assess accuracy of this sampling method due to lack of adequate data. Based on the very limited information available on flow-dependent changes in k_2, a factor of 3.4 was determined between k_2 values of HCB at medium and high flow. This indicates a rather substantial inaccuracy if air velocity varies in this range between calibration and actual sampling, but it would have to be verified by corresponding data for PCB congeners.

Experiment IV included 3 sets of duplicate samples for each of the three flows, i.e. at 4 days, 1 week and 2 weeks, allowing an assessment of data precision, however, only for HCB and CB-3, as other PCB congeners did not decrease during the course of the experiments. Relative standard deviations were calculated for these two compounds and compared with the variation at the start of the experiment (Table 16). For the high flow experiments, precision is high. For the medium flow experiment, however, HCB varies more strongly, caused by the duplicate 1 week sample. As discussed for Experiment II, this can also be an exception. It should also be noted that the duplicates in Experiment IV cover a larger temporal range than those of Experiments I and II, where uncertainty might increase. In summary, precision can also be considered satisfactory in Experiment IV.

Table 16. Minimum, maximum and average relative standard deviations of duplicates in Experiment IV (4 days, 1 week, 2 weeks), compared with duplicate samples at the start of the experiment. Only those compounds are listed that were found to decrease significantly during the course of the experiment.

	Start	High flow			Medium flow			Low flow		
	N=2	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
HCB	8.9%	3.4%	6.3%	4.5%	0.31%	27%	11%	-	-	-
CB-3	10%	1.1%	9.8%	4.0%	-	-	-	-	-	-

2.3.4.4 Uptake rates / detection limits

As for the other formats, silicone concentrations were estimated according to Equation 1, for air concentrations of 300 and 3000 ng/m^3 and a sampling period of 24 hours (Figure 16). Uptake rates k_1 for HCB and PCB congeners, respectively, were taken from the literature (Petty et al., 1993; Esteve-Turrillas et al., 2009) and adjusted for the surface area of this sampler. It has to be noted, however, that this likely includes an overestimation of actual uptake rates, because the surface area available for compound uptake is reduced by the contact area with the aluminium foil on which the sampler was placed in this experiment. This reduction of the actual surface area has not been taken into account in the calculations. Since only few significant k_2 values were available from this experiment, the calculation was limited to CB-3 and HCB, using k_2 values of the high flow experimental set-up.

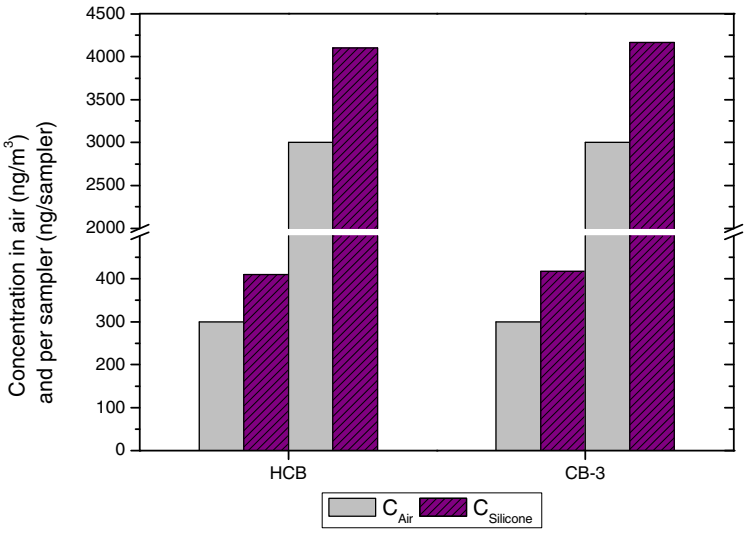


Figure 16. Assumed air concentrations C_{Air} of 300 and 3000 ng/m^3 and resulting estimates of sampler concentration $C_{Silicone}$ after 24 hours of sampling (Equation 1). Input values for HCB: k_1=1.371 m^3/day; k_2=0.0050/day. Input values for CB-3: k_1=1.392 m^3/day; k_2=0.0039/day. In contrast to the other experiments, k_2 values were taken from the high flow set-up (see Figure 14).

As for the other formats, detection limits will be sufficiently low after a 24-hour-sampling (Table 17), according to Equation 1 and the input parameters described above. Actual detection limits might be slightly higher as the surface area of the sampler has not been corrected for its contact area with the aluminium foil on which it was placed. However, there is still the possibility of increasing the percent injected if lower detection limits are desired.

Table 17. Estimates of detection limits, i.e. lowest detectable concentration in air, after 24 hours of sampling (Equation 1). Input values for HCB: k_1=1.371 m^3/day; k_2=0.0050/day. Input values for CB-3: k_1=1.392 m^3/day; k_2=0.0039/day.

Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m^3)
HCB	0.1	0.5	0.366
HCB	1	0.05	0.0366
HCB	100	0.0005	0.000366
CB-3	0.1	0.5	0.360
CB-3	1	0.05	0.0360
CB-3	100	0.0005	0.000360

Commercial SBSE formats offer the possibility of thermal desorption in the injector of the gas chromatograph, i.e. the total amount on the sampler is transferred to the instrumental analysis and the "percent injected" will increase to 100%. This would decrease detection limits substantially (Table 17). However, as explained in section 1.2.4, this method requires specific and costly hardware, which is not commonly available in chemical laboratories.

2.3.4.5 Conclusions Experiment IV

The following conclusions can be drawn from Experiment IV:

- The sampler is robust and easy to handle, however, the loading with e.g. PRCs is not trivial.
- There is no risk of back diffusion during the desired sampling period.
- Elimination rates k_2 vary with changes in air velocity over the sampler, with a factor of 3.4 for HCB between the medium and the high flow.
- Due to their low elimination rates, PRCs are not advisable for calibration of the sampler, standardisation of uptake conditions might be an alternative.
- Changes in k_2 due to varying air velocity will affect accuracy. Precision, however, can be considered high.
- For HCB and CB-3, detection limits of < 1 ng/m³ for a 24-hour-sampling have been determined and can be considered very low. Thermal desorption can reduce detection limits to < 1 pg/m³ for HCB and CB-3 under the assumptions of this calculation.

2.3.5 Experiment V: Custom-made SBSE samplers on a magnetic stirrer

The same samplers as those of Experiment IV were rotated on a magnetic stirrer. They had to be placed in glass beakers for reasons of stability, however, this set-up was not as robust as required according to the criteria described in section 1.1.3. Several glass beakers broke during this experiment, which makes the present version of this set-up unsuitable for screening purposes. In addition, its operation was not noiseless. If a format like this is chosen for further work, it will require technical refinement, based on the experience with Experiment V.

The flow in this experiment was measured to be approximately 0.1 m/s. The PCB congeners decreased clearly more quickly than in any of the flow variants of Experiment IV (Figure 14; Figure 17), but not as fast as they did in Experiment II, also considering the different time frames (Figure 8). The list of compounds with statistically significant decreases includes both low and higher chlorinated PCB congeners (Table 18). Several other PCB congeners were close to being statistically significant in their decrease over time (slope of the regression line in the logPCB vs. time plot). Compared with the immobile use of the same samplers in Experiment IV, the list of compounds has increased considerably.

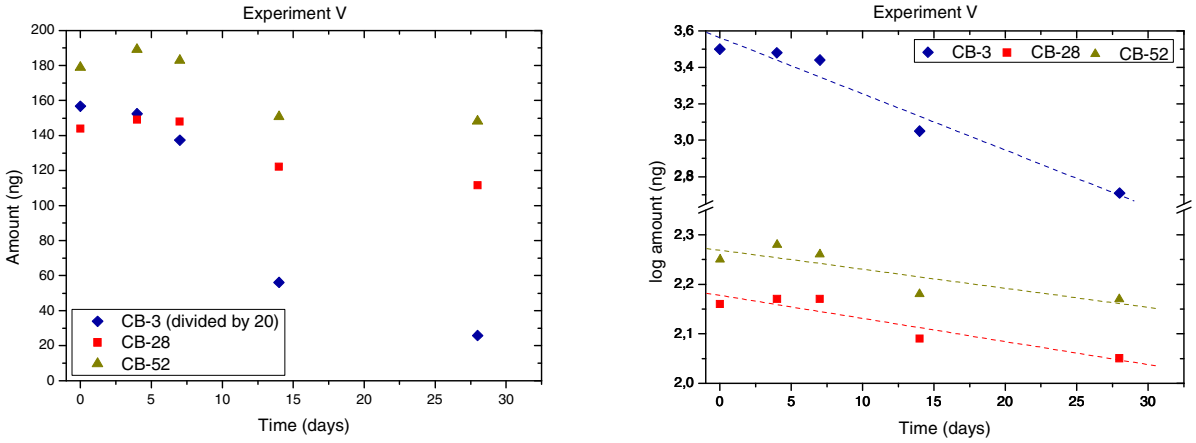


Figure 17. Results for CB-3, CB-28 and CB-52 in Experiment V (Custom-made SBSE samplers on a magnetic stirrer). Left: PCB amount over time. Results for CB-3 in this figure were divided by 20 to reach the same scale. Right: Log-transformed PCB amount over time and fitted regression lines. Only one flow was tested in Experiment V.

Table 18. Summary of significant decreases over time in Experiment V, based on statistically significant slopes ($p < 0.05$) of the regression lines in the logPCB vs. time plot (Figure 17).

Compound	k_2 value
HCB	0.041
CB-3	0.046
CB-28	0.0070
CB-49	0.0058
CB-52	0.0062
CB-128	0.0043
CB-153	0.0029
CB-180	0.0033

2.3.5.1 Risk of back diffusion

Given the higher elimination rates in this experiment compared with Experiment IV, the risk of back diffusion theoretically increases. It has been quantified in the same way as described for Experiments III and IV, i.e. the regression lines were used to calculate the point of time at which 10% of the initial amount had left the sampler. This point of time was calculated for the PCB congeners listed in Table 18 and ranged from approximately 3 days (CB-3) to over 18 days (CB-153). For CB-28 and CB-52, the duration of a 10 % reduction of initial amounts was 10 and 12 days, respectively. None of these results are critical in relation to the desired sampling period of 1 day if sampling conditions are comparable to that of the experiment.

2.3.5.2 Effect of air velocity / calibration

As the air velocity was not varied in this experiment, no direct dependencies of elimination rates on air velocity can be shown. However, the results of this experiment can be compared with those of Experiment IV where the same samplers were used without rotation. For HCB and CB-3, k_2 values were an order of magnitude higher in this experiment than in Experiment IV (Table 18, Figure 15). k_2 values for the tri- and tetrachlorinated PCB congeners CB-28, CB-49 and CB-52 were still slightly higher than those for HCB

and CB-3 in Experiment IV. This comparison shows that differences in uptake rates due to air velocity changes can be avoided by actively moving the sampler.

2.3.5.3 Accuracy and precision

Unlike the other experiments, Experiment V did not include any data which were suitable for discussions of accuracy. Precision can be assessed on the basis of duplicate determinations for 4 days and 7 days sampling points, for the PCB congeners with significant k_2 values. Relative standard deviations were calculated and compared with the variation at the beginning of the experiment (Table 19). The 7-day-sample showed a slightly higher standard deviation than the 4-day-sample, but in agreement with the other experiments, precision can generally be considered high.

Table 19. Minimum, maximum and average relative standard deviations of duplicates in Experiment V (4 days, 1 week), compared with a duplicate sample at the start of the experiment. Only those compounds are listed that were found to decrease significantly during the course of the experiment.

	Start (N=2)	Min	Max	Mean
HCB	8.9%	2.5%	4.4%	3.4%
CB-3	10%	0.72%	0.87%	0.80%
CB-28	8.7%	1.3%	7.0%	4.2%
CB-49	6.4%	1.0%	6.2%	3.6%
CB-52	4.9%	0.086%	6.4%	3.2%
CB-128	2.0%	3.6%	10%	6.9%
CB-153	3.5%	0.88%	6.7%	3.8%
CB-180	5.2%	2.4%	4.2%	3.3%

2.3.5.4 Uptake rates / detection limits

More PCB congeners had significant k_2 values in this experiment compared with Experiment IV. For these, silicone concentrations have been estimated according to Equation 1, resulting from air concentrations of 300 ng/m^3, uptakes rates from the literature (Petty et al., 1993; Esteve-Turrillas et al., 2009) and a sampling period of 24 hours. However, given the large difference in k_2 values between Experiment IV and V, k_1 has been scaled up as well. On average, k_2 values of HCB and CB-3 have increased from Experiment IV to Experiment V by a factor of 10. The same factor was used to upscale k_1, to approach more realistic k_1 values.

Due to the same sampler geometry and the upscaling of k_1 by a factor of 10, the detection limits calculated according to Equation 1 are an order of magnitude lower than those of Experiment IV (Table 17; Table 20). Like for all samplers tested in this project phase, detection limits can be considered low. They can even be decreased further be thermal desorption of the compounds collected on the sampler, which means that 100% of the collected amount is injected for instrumental analysis. This approach, however, would require specific hardware, which is not usually available in chemical laboratories.

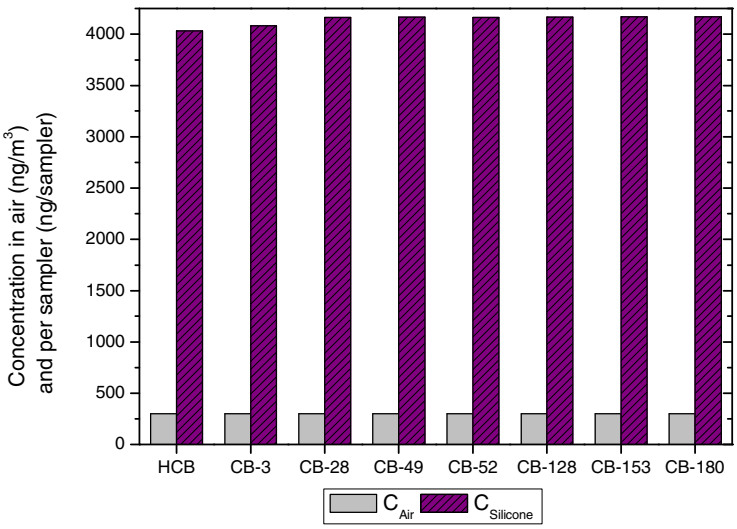


Figure 18. Assumed air concentrations C_{Air} of 300 ng/m^3 and resulting estimates of sampler concentration $C_{Silicone}$ after 24 hours of sampling (Equation 1). Input values: k_1=13.71 m^3/day for HCB, k_1=13.92 m^3/day for PCB congeners. Thus, k_1 values have been scaled up by a factor of 10 compared with Experiment IV.

Table 20. Estimates of detection limits, i.e. lowest detectable concentration in air, after 24 hours of sampling (Equation 1). Input values: k_1=13.71 m^3/day for HCB, k_1=13.92 m^3/day for PCB congeners.

Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m^3)
HCB	0.1	0.5	0.0372
HCB	100	0.0005	0.0000372
CB-3	0.1	0.5	0.0367
CB-3	100	0.0005	0.0000367
CB-28	0.1	0.5	0.0360
CB-28	100	0.0005	0.0000360
CB-49	0.1	0.5	0.0360
CB-49	100	0.0005	0.0000360
CB-52	0.1	0.5	0.0360
CB-52	100	0.0005	0.0000360
CB-128	0.1	0.5	0.0360
CB-128	100	0.0005	0.0000360
CB-153	0.1	0.5	0.0360
CB-153	100	0.0005	0.0000360
CB-180	0.1	0.5	0.0360
CB-180	100	0.0005	0.0000360

2.3.5.5 Conclusions Experiment IV

The following conclusions can be drawn from Experiment V:

- The experimental set-up as chosen for Experiment V is not sufficiently robust and will need technical refinement for routine applications.
- There is no risk of back diffusion during the desired sampling period.
- Elimination rates k_2 increased considerably compared with the immobile approach of Experiment IV.
- Experiment V has demonstrated that increases and standardisation of uptake rates by movement of the sampler might be a suitable way of calibration.
- Precision can be considered high.
- For a range of PCB congeners, detection limits of < 0.1 ng/m^3 for a 24-hour-sampling have been determined and can be considered very low.

Thermal desorption can reduce detection limits to < 0.1 pg/m³ under the assumptions of this calculation.

2.4 Conclusions from project phase 2

In general we can draw the following conclusions from the experiments in project phase 2:

- The samplers are generally robust, easy to handle and practical, both during sampling and in the subsequent chemical analysis. The magnetic stirring, however, would have to be refined as the set-up of this experiment will not be suitable for routine applications. The glass petri dishes could be replaced by metal containers of approximately the same dimensions.
- The risk of back diffusion is negligible for all sampler types and a sampling period of 24 hours.
- Elimination rates depend on air velocity, i.e. changes in air velocity will strongly affect accuracy. The effect seems to be smallest for the petri dishes with their high uptake rates, despite the risk of stagnating air layers above the silicone.
- A suitable calibration method should account for influences of varying air velocity. The use of PRCs is not supported since the release of PCB congeners to indoor air is undesirable. Furthermore, some of the experiments showed too low elimination rates to provide k_2 values beyond the most volatile PCB congeners.
- An alternative would be the standardisation of air velocity, either by moving the sampler or by providing constant flow (ventilation).
- Another possibility to overcome the air velocity effect could be a different concept, equilibrium sampling instead of kinetic sampling.
- While accuracy is affected by varying air velocities, precision is generally high.
- Detection limits can be considered low. Based on the estimates of this project phase, individual PCB congeners can be detected at concentrations of 0.1 – 1 ng/m³ after 24 hours of sampling, with several technical offering possibilities of further decreasing detection limits.

2.5 Suggestions for project phase 3

The objective of project phase 3 is to carry out a passive sampling with one or several of the samplers developed so far, in parallel with an active air sampling in buildings with suspected PCB sources. This comparison will serve an assessment of accuracy, and a validation of the sampler and its calibration method. Based on the results of project phase 2, the authors suggest the following tests for project phase 3:

- Due to the relatively small effect of flow variations and high uptake rates, petri dishes with a thin silicone coating should be tested in a real contamination situation. The glass dishes might be replaced by metal containers to increase robustness. This format is simple, easy to handle and robust. Its detection power will be sufficient, however, accuracy might be lower than desired for this purpose. The sampling format is not commercially available, but can be produced relatively easily in a chemical laboratory.
- One of the other samplers could be tested under standardised uptake conditions, in particular constant and reproducible air velocity. This could be achieved by moving the sampler or the surrounding air, e.g. by placing the sampler next to or directly onto a small fan. This format

might not be as simple as planned, but would produce more accurate data. Detection limits will be sufficiently low and might allow shorter sampling periods than the 24 hours anticipated in this report.

- As an alternative to kinetic sampling, equilibrium sampling should be tested. Equilibrium between the sampler and the surrounding air can be achieved by extremely high uptake rates, consequently applying a sampler with a large surface area and very thin silicone layer. This could for example be silicone-coated paper sheets ("baking paper"). Detection limits would be low as well. Instead of uptake rates, a partition coefficient will be required to translate the PCB amount on the sampler into an air concentration (see section 1.1.4).

3 Measurements of PCBs in indoor air for the calibration and validation of the passive sampler (Project phase 3)

3.1 Introduction

3.1.1 Background

A total amount of approximately 1.3 million tons of PCBs was produced and used in the 20th century (Breivik et al., 2002). In the construction sector, PCBs were commonly used between the 1950s and 1970s. As this period coincides with one of high construction activity in Denmark, the use of PCBs in buildings might be widespread and lead to gradual emissions to the environment. This includes both private residences and buildings of public use (schools etc.) and might present a source of PCB exposure for inhabitants or users of these buildings. For their protection, concentrations of 300 and 3000 ng PCB/m^3 air have been set as limit values that require renovation actions. Due to the potentially high numbers of buildings with PCB sources, fast and inexpensive screening tools are required, which allow an assessment of PCB concentrations in indoor air in relation to the cut-off values.

This chapter presents the results of the third and final phase of the project developing a cost-effective screening tool based on passive sampling techniques. Results of the first two phases, as reported in chapters 1 and 2, are briefly summarised in Table 21.

Table 21. Brief summary of project phases 1 and 2. SBSE: stir bar sorptive extraction. PDMS: polydimethylsiloxane (silicone).

Project phase	Work description	Outcome	Feedback from the Danish Energy Agency
1	Literature review of passive sampling formats potentially suitable for indoor air screening, discussion of their cost-effectiveness, handling, interpretation, sensitivity, accuracy and precision.	Suggestion of three formats for further work.	PCBs as performance reference compounds as well as movement of the passive sampler for standardized uptake conditions to be avoided.
2	Test and optimisation of two formats (SBSE, PDMS-coated vials), with particular focus on the influence of air velocity changes on the PCB partition kinetics between air and sampler. In addition, assessments of risks of back diffusion of PCBs to air, differences in elimination rates between PCB congeners, sensitivity, accuracy and precision.	Elimination rates depend on air velocity, i.e. changes in air velocity will affect accuracy.	Further work to include petri dishes (most promising results in phase 2) and PDMS-coated paper (with a view to equilibrium sampling instead of kinetic sampling).

Following project phase 2, the Danish Energy Agency invited representatives of companies and institutions working in the field to a meeting for discussions of results obtained so far and future steps towards a cost-effective screening tool. The presentation of results of project phases 1 and 2 given at this meeting is available from Annex 3 of this report. One of the outcomes of project phase 2 was a relatively smaller effect of variations in air velocity on the "petri dish" sampler, i.e. the format with a large surface area, a relatively

thin PDMS film and consequently, high uptake rates of PCBs. Taken this observation further, the parameters surface area and film thickness would be further optimised if the PDMS was applied to a large sheet of paper. Theoretically, PCB uptake rates might increase to the effect that the passive sampler could reach equilibrium with the PCB content in the surrounding air (Figure 1).

The participants at the meeting were supportive of the idea of testing the promising format of phase 2 (petri dishes with a thin silicone layer, sampling PCB congeners in the kinetic mode) and silicone-coated paper (potentially applicable for equilibrium sampling) in project phase 3.

3.1.2 Objectives of project phase 3

Project phase 3 had the specific objectives of field tests of the passive sampling formats, i.e. applying them in potentially contaminated buildings. For this purpose, the passive samplers were applied alongside conventional active sampling measurements, which sample PCBs by pumping a defined air volume through a PCB-adsorbing material.

As previously described, the PCB content on the passive sampler can be determined with a relatively high degree of accuracy and precision. The challenging step is the determination of the air volume which the passive sampler has sampled and which will be required to convert the PCB amount on the sampler to a PCB concentration in air. This volume depends on sampling rates for the individual PCB congeners (kinetic sampling) or their equilibrium partition coefficients (equilibrium sampling). As demonstrated in section 2.3, sampling rates are influenced by sampling conditions, such as air velocity and temperature.

The PCB concentrations available from active measurements alongside the passive sampling have the main purpose of i) providing a calibration of the passive sampler (i.e. determination of sampling rates) in the field and ii) assessments of accuracy in the field.

3.2 Measurements

3.2.1 Work plan for project phase 3

The work plan for project phase 3 as approved by the Danish Energy Agency is included as Annex 4. It consists of 2 time series and 10 individual measurements, i.e. 12 locations for PCB measurements. The time series were chosen to obtain more information about the sampling process, in particular in relation to the sampling stages shown in Figure 1. The individual measurements took approximately 24 hours. Of the 10 individual measurements, the first 5 were supposed to serve calibration purposes, while the remaining 5 measurements could be used to assess accuracy. Precision could be further evaluated on the basis of duplicates analysed for each sampling point. The overall work plan is summarised in Table 22 and Table 23.

Table 22. Details of the time series analysed with the passive samplers (silicone layer in a petri dish and silicone-coated paper). The number of replicates (in brackets) refers to the petri dish and paper each.

Time series	Location	Time period	Sampling points (No. of replicates)	Supporting measurement	Quality assurance	Collaborator
A	Hvalsø	19-26 June 2013	6 hours (2) 1 day (2) 2 days (2) 7 days (2)	Temperature	Blanks (petri dish and paper)	Rambøll
B	Nærum	9-16 July 2013	6 hours (2) 1 day (2) 2 days (2) 7 days (2)	Temperature	Blanks (petri dish and paper)	Grontmij A/S

The passive sampling took place concurrently with conventional active PCB sampling as described in section 3.1.2. The active sampling campaigns were undertaken by the consulting companies Rambøll and Grontmij A/S (Table 22 and Table 23) who kindly made their measurement results available to this project. Furthermore, the companies assisted the project by deploying the passive samplers and returning them to our laboratory, for all locations with the exception of the time series. This will be detailed below, but it is worth noting that the "easy handling" criterion discussed in previous project phases (section 1.2.2) was convincingly confirmed by this collaborative approach.

Table 23. Details of the individual measurements conducted for approximately 24 hours with the passive samplers (silicone layer in a petri dish and silicone-coated paper). At all locations, temperature was measured as a supporting parameter. Each test was accompanied by a blank for petri dish and paper, respectively.

Test	Location	Date	No. of samples	No of replicates per sample	Purpose	Collaborator's sample name	Collaborator
I	Horsens	10/11 July 2013	2	2 petri dishes 2 papers	Calibration	L11, L12	Rambøll
II	Haderslev	22/23 August 2013	3	2 petri dishes 2 papers	Calibration	L16, L17, L18	Rambøll
III	Haderslev	30/31 October 2013	2	2 petri dishes 2 papers	Validation (accuracy)	L1, L3	Rambøll
IV	Viborg	26/27 March 2014	3	2 petri dishes 2 papers	Validation (accuracy)	L8, L11, L12	Rambøll

3.2.2 Preparation of the passive samplers

Silicone sheets were purchased from Altec Products Ltd. (www.altecweb.com). For the petri dish sampler, silicone disks were cut from these larger sheets. The disks had a thickness of 0.5 mm and a diameter of 15 cm to fit into the petri dish. The silicone disks were pre-cleaned with acetone for 2 hours, in order to remove compounds that could interfere with the chemical analysis of PCBs. As this cleaning procedure did not seem sufficient for complete removal of interfering compounds (see below), a cleaning time of 139 hours was applied in test IV.

After cleaning, the silicone disk was placed into the petri dish, which then was closed with a glass lid and wrapped in aluminium foil. Following this

preparation, the petri dishes were stored in aluminium bags sealed with tape (Figure 20).

The silicone-coated paper [40 cm x 60 cm, 1 µm silicone thickness] was purchased from Metsä Tissue Corporation (www.metsatissue.com). It was a "grade 602" paper with a silicone coating of 0.45-0.5 g/m² on each side. For pre-cleaning, single sheets were loosely folded and placed in a glass container with acetone for 2 hours. The sheets were unfolded for drying and then re-folded and placed into aluminium bags which were sealed with tape. Photographs of the two samplers are shown in Figure 19.

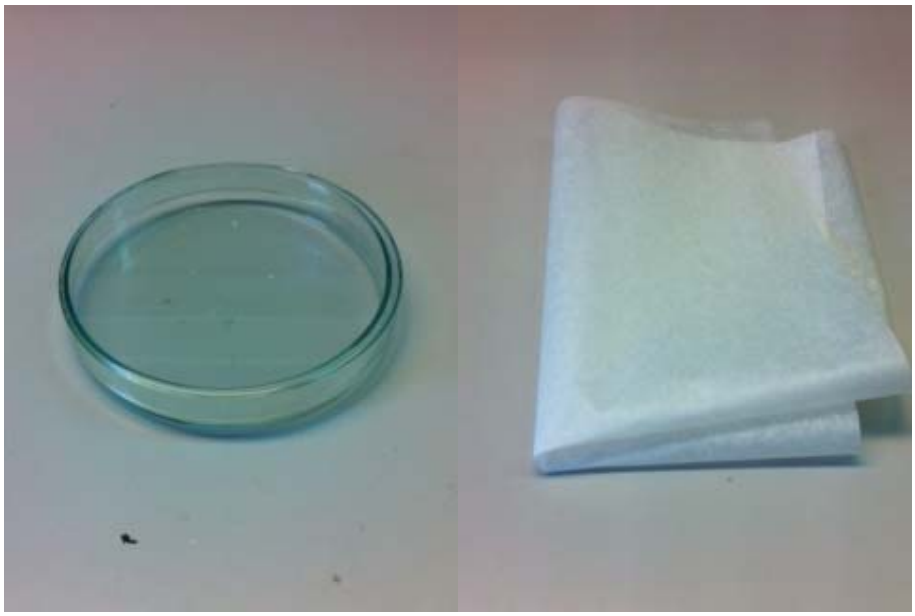


Figure 19. Petri dish with a layer of silicone (left) and folded silicone-coated paper (right).

3.2.3 Shipment and sampling

As described above, sampling was coordinated with the consulting companies Rambøll and Grontmij A/S. For the time series, the project participants (Katrin Vorkamp, Philipp Mayer, Annegrete Ljungqvist) visited the locations and took care of the sampling themselves. In all other cases, i.e. for the 10 individual measurements (Table 23), the passive sampling equipment was sent to the collaborators by ordinary post. Placed in the aluminium bags (Figure 20), the equipment could be mailed easily. The collaborators were advised to re-use the aluminium bags for return of the samples to the laboratory. However, it was not important to place each sampler into the same bag as before, as all samplers had been prepared equally. The aluminium bags could be easily labelled with sample information.

For the actual measurement, the samplers were removed from the aluminium bags and placed in the room to be sampled. The petri dishes were typically placed on a table or a cupboard, and the sampling started when the lid was removed. The papers were attached to cords available in the room or to a clothes drying rack. For attachment, pegs wrapped in aluminium foil were used. Alternatively, metal clips could be used. An example of a sampling set-up is given in Figure 21. The figure shows several paper sheets and petri dishes because all samples in this project phase consisted of several repli-

cates (Table 23), to allow assessments of precision and to strengthen the overall dataset.

After completion of the passive sampling, the process was reversed. The petri dishes were closed with their respective lids, wrapped in aluminium foil and placed in the aluminium bags. The papers were loosely folded and placed in the aluminium bags. All samples were returned to the laboratory by ordinary post. Gloves were worn at all times when the samplers were handled, to avoid contamination by e.g. dust.

Figure 20. Aluminium bag containing the passive samplers (petri dish or paper).

As discussed in project phase 2, sampling rates and partition coefficients depend on temperature. For this reason, temperature was monitored during all measurements. The temperature logger was an ACR Smart Button data logger from ACR Systems Inc. (www.arcsystems.com), which had been programmed to log the temperature every 30 seconds. The temperature loggers are very small and were therefore placed into a clear bag for easier handling. They were sent to the collaborators together with the samples, and returned accordingly. In test II, the temperature logging failed and was replaced by the average temperature measured by the collaborators during their measurement.

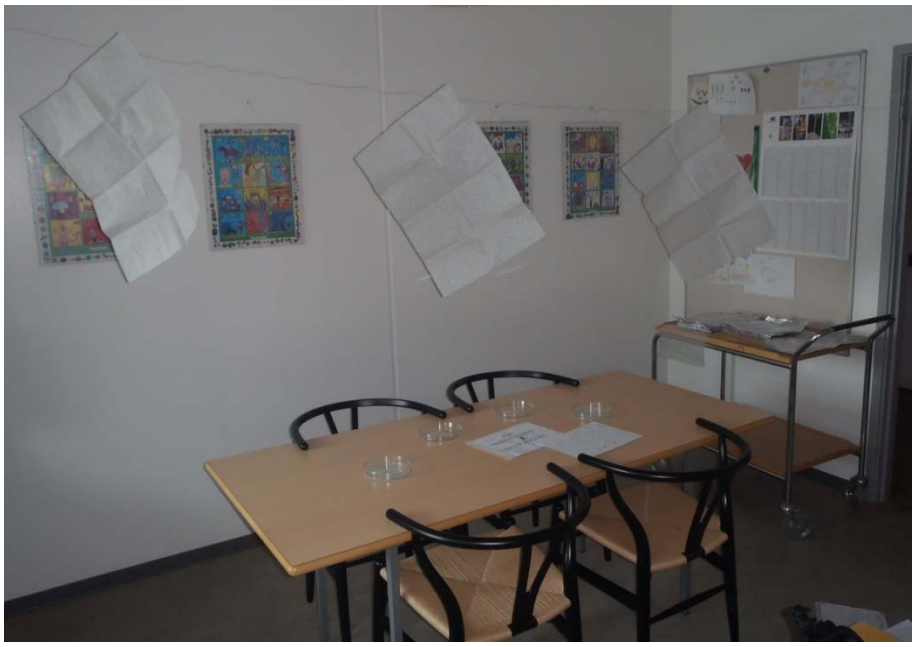


Figure 21. Example of a passive sampling set-up. For quality assurance purposes, the sampling campaign included several replicates of petri-dishes and silicone-coated paper. Photograph taken by RambøII.

3.2.4 PCB analysis

Upon receipt of the samples at the laboratory, the sealed aluminium bags were stored at 4°C until analysis. PCB extraction usually occurred within a few days after sample receipt, details are given in Annex 5.

The silicone disk was removed from the petri dish and placed into a glass container with 100 ml acetone. After 24 hours, a second extraction step took place with fresh acetone (100 ml), to ensure complete re-diffusion of the analytes into the solvent. The extracts were combined and reduced in volume to < 1 mL, while changing the solvent to iso-octane. After addition of the internal standards (CB-53 and CB-155), the extracts were adjusted with iso-octane to a precise volume of 1 mL. The same extraction procedure was chosen for the paper samples, however, the extraction time was only 2x 2 hours.

The PCB congeners were analysed by gas chromatography (GC) with electron capture detection (ECD). The GC was equipped with two 60 m capillary columns of different polarity (J&W Scientific DB-5 and DB-1701, 0.25 mm inner diameter, 0.25 µm film thickness). Quantification was based on a duplicate 7-point-calibration. The PCB congeners included in this method are identical with those in project phase 2 (Table 8). Due to higher background signals in the chromatograms combined with very low concentrations of the analytes, CB-170, CB-194, CB-198 and CB-209 were not studied further.

3.2.5 Data treatment

As two capillary columns were used in the instrumental analysis, each sample produced two results. Following the laboratory's quality assurance / quality control guidelines established for accredited PCB analyses in biota, one result or an arithmetic mean was used for further data analysis. As further described in section 3.3, interferences appeared in the chromatograms, in particular of the petri dish samplers, possibly owing to incomplete cleaning of the silicone prior to sampling. Visual inspections of chromatograms and comparisons of relative retention times identified peaks which likely in-

terfered with the PCB congeners to be quantified. In these cases, peak signals of the interfering peaks were subtracted from signals of the target peaks.

The temperature logs were used to calculate an average temperature for the sampling period. For the time series, average temperatures were calculated between the start and the respective data point of the time series.

For the time series, PCB concentrations of the passive samplers were plotted against time. For the PCB uptake profiles on the silicone-coated paper, a curve was fitted to each PCB congener of the time series (Equation 2):

$$C = C_{\infty} \cdot (1 - e^{-k \cdot t}) \qquad \text{(Equation 2)}$$

C∞: PCB concentration at equilibrium (ng/sampler) k: rate constant (hours^{-1}).

These curves were also used to estimate the time to equilibrium for the specific congeners:

$$t_{90\%} = \frac{\ln 10}{k} \qquad \text{(Equation 3)}$$

$$t_{50\%} = \frac{\ln 2}{k} \qquad \text{(Equation 4)}$$

Equations 3 and 4 describe the time (in hours) that is required to reach 90% and 50% equilibrium, respectively.

The actual sampling period of the 24-hour-measurements ranged from roughly 14 hours (test III) to 26 hours (test I). The PCB concentrations were therefore normalized to a precise sampling period of 24 hours to be comparable among tests.

For the calibration of the passive samplers, linear relationships were established between the concentration on the sampler and the concentration in air:

$$C_{PS} = R_S \cdot C_{Air} \qquad \text{(Equation 5)}$$

C_{PS} is the concentration of each PCB congener measured by passive sampling (ng/sampler/24 hours) and C_{Air} is the air measurement (ng/m^3) as provided by Rambøll (Table 23). The slope of this line is the congener-specific sampling rate R_S (m^3/sampler/24 hours).

In the validation of the passive sampler, Equation 5 was used to calculate an air concentration C_{Air} from C_{PS}, which was then compared to the measured concentration as provided by Rambøll.

3.3 Results

3.3.1 Introductory remarks

As described above, the chromatograms of laboratory and field blanks showed a number of peaks which were not PCB congeners, but other compounds potentially interfering with the PCB quantification. The likely expla-

nation for this observation is an insufficient cleaning of the silicone. The cleaning process, as described in section 3.2.2, had the purpose of removing interfering compounds that could possibly be released from the silicone during extraction. These are not PCB congeners, but more likely fractions of the silicone polymer.

The interferences were more pronounced in the petri dishes than in the silicone-coated paper. This observation is consistent with a thinner silicone layer (1 µm) on the paper from which potentially interfering compounds diffuse into the solvent more quickly than from the thicker silicone layer (0.5 mm) used in the petri dishes. For both samplers, the same cleaning procedure had been applied. It has to be concluded that for routine use of the silicone-based passive samplers, a reduction of interfering compounds will be advisable. This can be achieved by a more effective pre-cleaning of the material or a dilution of the extracts. In test IV, the cleaning period was increased to 139 hours, which produced blank samples with fewer and lower values.

3.3.2 Time series

As described in Table 22, the time series covered a period of one week, during which 4 samplers were analysed (6 hours, 1 day, 2 days, 7 days). For each sampling point, two samplers were analysed to provide data on precision.

3.3.2.1 Petri dishes

In time series A, linearly increasing concentrations were observed for the congeners CB-28, CB-31, CB-40, CB-49, CB-52, CB-99, CB-101, CB-105, CB-110 and CB-118 (Figure 22). For the more highly chlorinated congeners, deviations between duplicates or inconsistent time trends increased the uncertainty about the true value and made the time series questionable. The reasons are most likely i) lower sampling rates for the highly chlorinated and less volatile congeners, resulting in lower amounts on the sampler and thus smaller peaks in the chromatogram, ii) lower air concentrations of the highly chlorinated and less volatile congeners, iii) interfering peaks in the chromatogram, as described in section 3.3.1.

In time series B, concentrations were generally lower than in time series A. According to the active measurements at the same locations, the PCB_{total} concentration was only 48 ng/m³ as the location of time series B, while it was 660 ng/m³ for the location of time series A (both calculated as 5x ΣPCB_7). The lower concentrations made the quality assurance of the chemical analysis more challenging (see factor iii) discussed above), but it still was possible to establish linear relationships between concentrations of some PCB congeners and time. Figure 23 shows the results for most of the same congeners as presented in Figure 22. Some of the congeners seem to approach a plateau after about one week of sampling, but are clearly linear in the 24 hours the regular measurements should last.

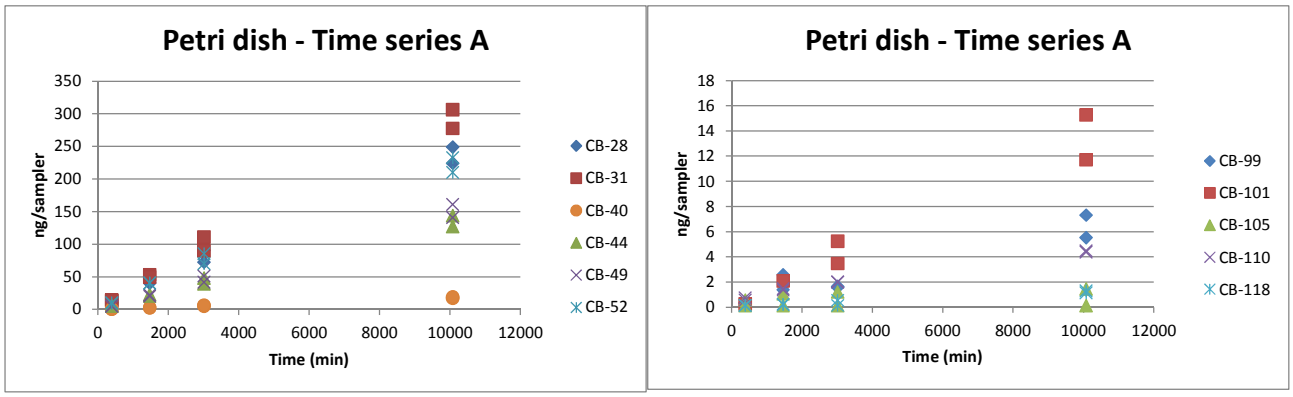


Figure 22. Results for CB-28, CB-31, CB-40, CB-44, CB-49, CB-52, CB-99, CB-101, CB-105, CB-110 and CB-118 in petri dishes of time series A (see Table 22 for details). Duplicate samples are not averaged, but given as individual measurements.

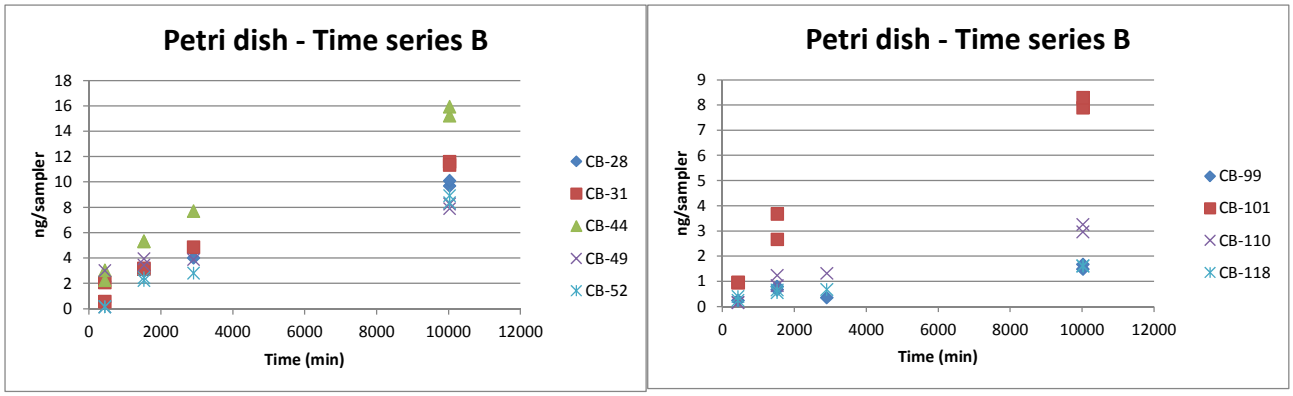


Figure 23. Results for CB-28, CB-31, CB-44, CB-49, CB-52, CB-99, CB-101, CB-110 and CB-118 in petri dishes of time series B (see Table 22 for details). Duplicate samples are not averaged, but given as individual measurements.

Despite their high volatility, no time series could be established for CB-3. As this compound should have relatively high sampling rates, the reasons ii) and iii) given above most likely apply to this compound.

3.3.2.2 Silicone-coated paper

The paper format, which had not been tested in project phase 2, worked satisfactorily in terms of PCB absorption. In contrast to the petri dishes, the results for the silicone-coated paper show a convergence to equilibrium concentrations during the course of the experiment. This was expected as the thinner silicone layer and the large surface area increase the PCB uptake and equilibrium will be established sooner than in the case of the petri dishes.

Figure 24 shows examples for CB-28, CB-44, CB-52 and CB-101, i.e. data measured in the time series A and the curves fitted according to Equation 2. As described above for the petri dishes, the PCB concentrations at the location of time series B were more than 10 times lower than those for time series A. Consequently, it was more ambiguous to determine the correct, but low PCB peaks in the chromatogram and thus establish the kinetics for time series B. CB-52 and CB-101 are shown in Figure 25, as examples of time series B. Corresponding plots for the remaining PCB congeners are given in Annex 6, for time series A and B.

Table 24 gives the fitted parameters for C_∞, i.e. the concentration at equilibrium (still in the unit ng/sampler), and for the rate constant k as well as $t_{90\%}$,

i.e. the time until equilibrium is reached by 90% (Equation 3). These values confirm that the sampling until equilibrium will not be reached as quickly as anticipated, but will take about one week. This also becomes apparent from Figure 24 and Figure 25. This result has implications for the 24-hour-measurements (Table 23), which will probably not reflect equilibrium sampling and which therefore cannot be converted to air concentrations by means of equilibrium partition coefficients.

Table 24 also shows that for some of the most pronounced PCB congeners, e.g. CB-52, rate constants *k* are similar for the two time series. This indicates similar kinetics, even though the concentration levels are very different between the two time series. As the kinetics for phase partitioning into silicone are independent of concentrations (Seethapathy & Gorecki, 2013), the observed differences between the *k* values of the two time series are likely related to the experimental conditions (temperature, air velocity) as well as the larger uncertainty in the quantification of time series B.

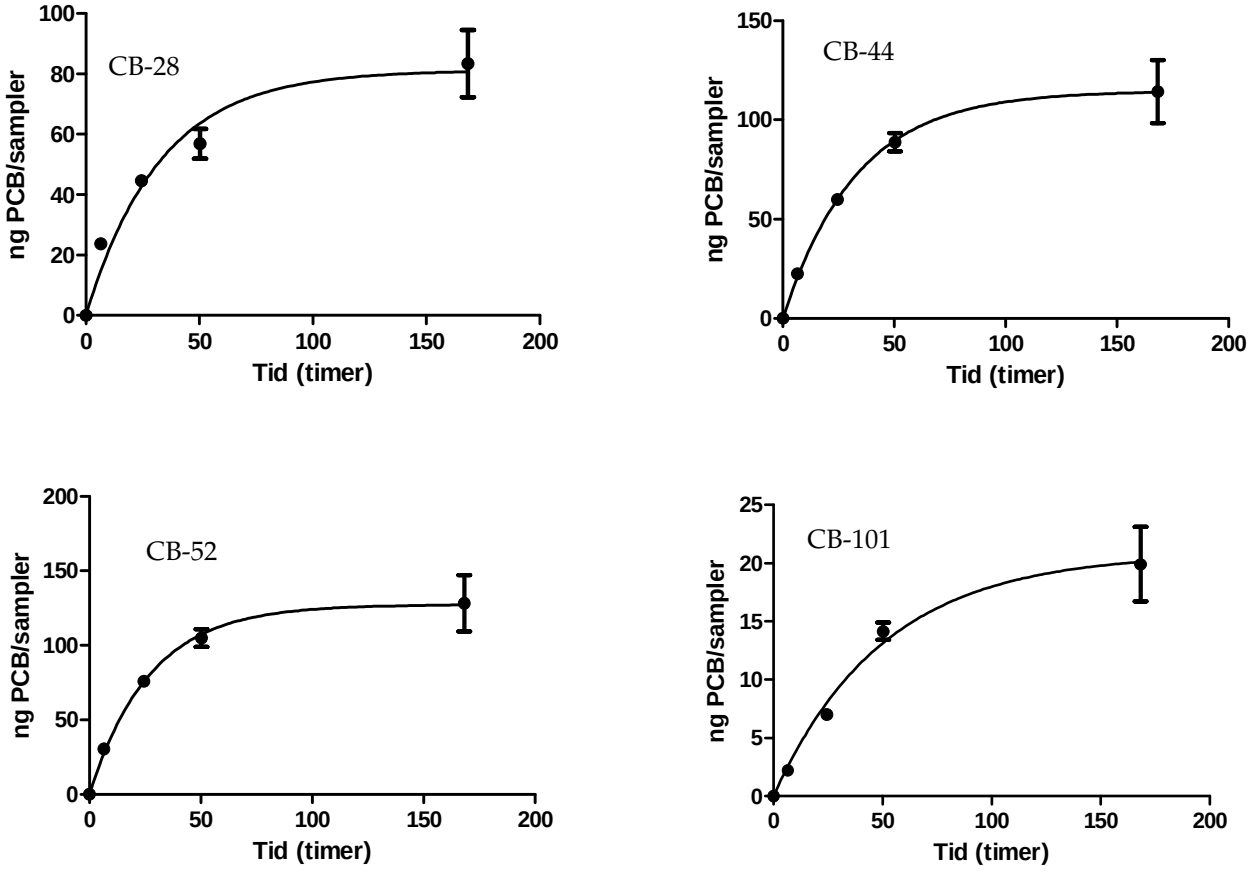


Figure 24. Results for CB-28, CB-44, CB-52 and CB-101 sampled with silicone-coated paper in time series A (see Table 22 for details) and curves fitted according to Equation 2. The figure shows means and standard deviations.

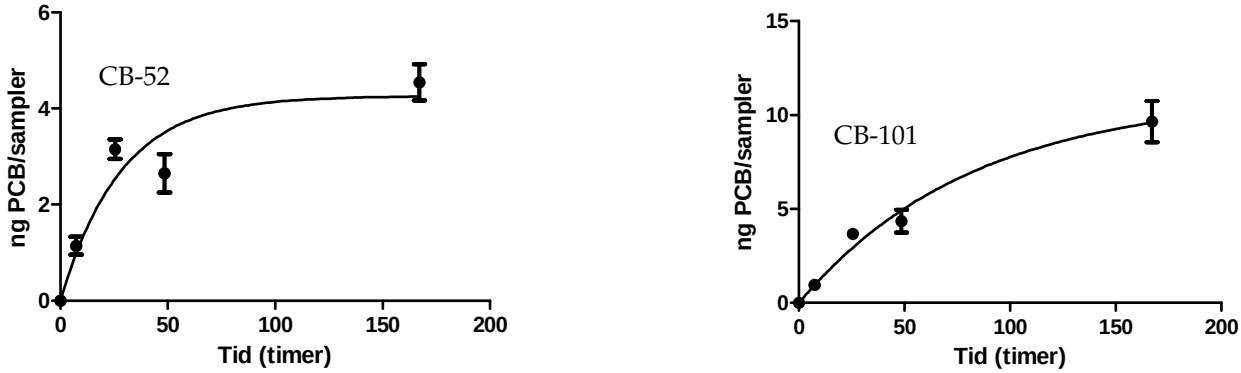


Figure 25. Results for CB-52 and CB-101 sampled with silicone-coated paper in time series B (see Table 22 for details) and curves fitted according to Equation 2. The figure shows means and standard deviations.

Table 24. Calculated parameters for PCB concentrations at equilibrium (C_∞), rate constant *k* and time until 90% equilibrium is reached, according to Equation 3. n.s.: not significant, i.e. 95% confidence intervals included zero. The full data set including standard errors is given in Annex 7.

	Time series A			Time series B		
	C_∞ (ng/sampler)	k (hours^{-1})	$t_{90\%}$ (days)	C_∞ (ng/sampler)	k (hours^{-1})	$t_{90\%}$ (days)
CB-28	81.2	0.03046	3.1	1.66	0.1118	0.9
CB-31	96.1	0.03339	2.9	2.12	0.1082	0.9
CB-40	13.6	0.04082	2.4	0.59	0.01998	4.8
CB-44	114.6	0.03029	3.2	3.53	0.02447	3.9
CB-49	80.0	0.03556	2.7	1.84	0.03618	2.7
CB-52	127.3	0.03679	2.6	4.26	0.03563	2.7
CB-99	14.3	0.02061	4.7	n.s.	n.s.	-
CB-101	20.9	0.01983	4.8	11.0	0.01215	7.9
CB-105	4.02	0.009619	10.0	n.s.	n.s.	-
CB-110	14.9	0.01390	6.9	20.4	n.s.	-
CB-149	2.42	0.009342	10.3	n.s.	n.s.	-
CB-153	1.11	0.01468	6.5	n.s.	n.s.	-

3.3.2.3 Precision

All measurements were performed as duplicates, providing data for assessment of precision. This point was also addressed in the laboratory experiments of project phase 2 where relative standard deviations between replicates generally was < 10%, often even < 5% (Section 2.3). Although neither petri dishes nor silicone-coated paper were tested specifically, relatively high precision can be expected under controlled laboratory conditions, based on the results of project phase 2.

Figure 26 shows averaged standard deviations for duplicates of time series A and B, respectively. The results for time series A show low standard deviations (< 10%) for the PCB congeners with relatively high concentrations. The standard deviations increase as concentrations approach the analytical detection limit. This was the case for the higher chlorinated PCB congeners in time series A and for all congeners in time series B. In general, higher precision can be expected for concentrations at equilibrium as opposed to the kinetic phase shown in Figure 26 because the equilibrium sampling devices are designed for maximised rather than well controlled mass transfer conditions (Mayer et al., 2003).

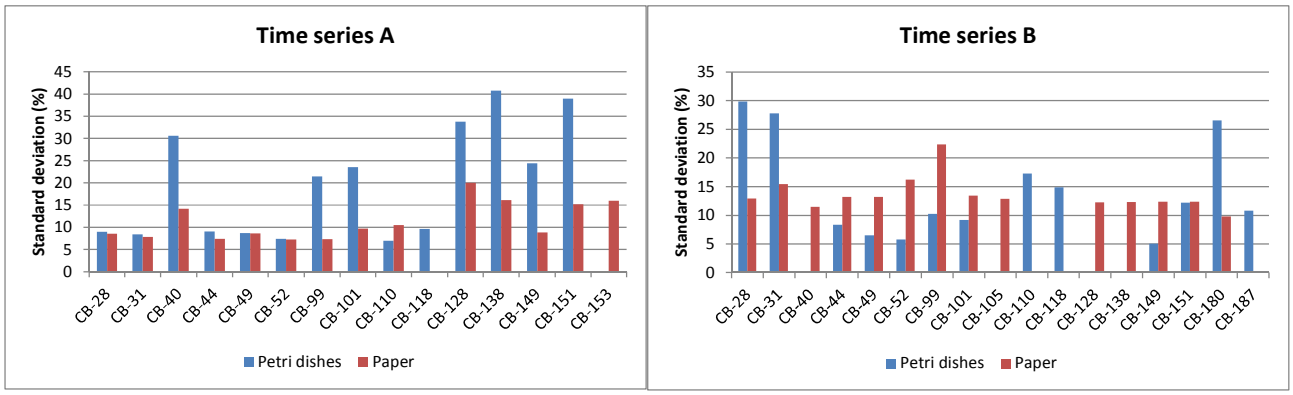


Figure 26. Standard deviations (%) between duplicates, averaged over the time series. Precision can be expected to improve when equilibrium is reached for the silicone-coated paper (Mayer et al., 2003).

3.3.2.4 Conclusions time series

- The results show that silicone is a suitable material for the kinetic sampling (petri dishes) as well as equilibrium sampling (paper).
- PCB concentrations in petri dishes increase linearly with time. This could be established for the more volatile compounds (CB-28 up to CB-118), which are assumed to be the main congeners in indoor air.
- The PCB congeners reach equilibrium on silicone-coated paper, but the equilibration time is in the order of several days or about one week.
- The kinetics can be derived more clearly at locations with higher concentrations, here 660 ng/m^3 (time series A) rather than 48 ng/m^3 (time series B) for PCB_{total}.
- Standard deviations of < 10% can be achieved for duplicates. Standard deviations increase as concentrations approach the analytical detection limits, but will decrease at equilibrium.

3.3.3 24-hour-measurements

As described above, ten individual measurements were conducted over the course of approximately 24 hours, each with duplicate sampling to provide data on precision (Table 23). The first five measurements (tests I and II) had the purpose of calibrating the samplers, i.e. determining uptake rates for the PCB congeners. This calibration used the results of the active measurements conducted by Rambøll, which are given for each test in Table 25. They cover a wide concentration range, which is favourable for calibration purposes.

Table 25. Results in ng/m^3 of active measurements provided by Rambøll at the same time and locations as the passive sampling. Values in bold were below the detection limits in the active measurements, but the compounds were detectable by passive sampling.

	Test I		Test II			Test III			Test IV	
	L11	L12	L16	L17	L18	L1	L3	L8	L11	L12
CB-28	22	18	159	180	51	**< 1.2**	**< 1.2**	30	28	67
CB-52	33	19	210	260	110	5.9	2.7	30	45	79
CB-101	8.8	5.4	33	40	48	1.6	**< 1.2**	**< 1.2**	6.3	6.5
CB-118	2.0	**< 1.2**	4.4	6.1	9.4	**< 1.2**	**< 1.2**	**< 1.2**	**< 1.2**	**< 1.2**
CB-138	**< 1.2**	**< 1.2**	**< 1.2**	**< 1.2**	4.4	**< 1.2**	**< 1.2**	< 1.2	**< 1.2**	**< 1.2**
CB-153	**< 1.2**	**< 1.2**	**< 1.2**	1.6	4.5	**< 1.2**	**< 1.2**	**< 1.2**	**< 1.2**	**< 1.2**
CB-180	< 1.2	**< 1.2**	< 1.2	**< 1.2**	**< 1.2**	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2
ΣPCB_7	65.8	42.4	397	488	227	7.5	2.7	60	73	146
PCB_{total}	329	212	1987	2439	1137	37.5	13.5	300	365	730

3.3.3.1 Passive sampler performance

The PCB_{total} concentrations in the ten locations ranged from 13.5 to 2439 ng/m^3, and increased in the order test III < test I < test IV < test II (Table 25). This order could be reproduced by both types of passive samplers (Table 26).

Table 26. Results for PCB_{total} in ng/sampler of passive measurements. PCB concentrations were normalised to a sampling period of 24 hours. PCB_{total} was calculated in the same way as in Table 25, i.e. 5x ΣPCB_7.

	Test I		Test II			Test III			Test IV	
	L11	**L12**	**L16**	**L17**	**L18**	**L1**	**L3**	**L8**	**L11**	**L12**
PCB_{total} Petri dish	141	86	743	686	381	82	76	144	239	588
PCB_{total} Paper	314	188	1853	3171	1593	69	96	533	1256	1699

CB-180 was below detection limits in all of Rambøll's measurements. CB-138 and CB-153 were below detection limits in 90 and 80 % of the samples, respectively. It is indicated by bold values in Table 25 which compounds below detection limits in active measurements could still be detected by the passive samplers (petri dish or paper). This confirms the high sensitivity of these methods, which is in agreement with results of project phase 2 (section 2.3). In general, the sensitivity was higher for paper than for the petri dishes.

As the calibration is based on Rambøll's measurements, it will be limited to those congeners in Table 25 which were above detection limits in the active sampling. The higher chlorinated congeners generally play a minor role, with regard to their presence in indoor air (Miljøstyrelsen, 2009), which is also confirmed by the results in Table 25. Given the high sensitivity of the passive samplers, it will be desirable to develop sampling rates for the higher chlorinated congeners as well. However, with regard to an evaluation of indoor air concentrations in relation to the cut-off values of 300 and 3000 ng/m^3, the higher chlorinated congeners will likely be of minor importance.

3.3.3.2 Calibration of the petri dishes

Test I and II were used for the calibration of the petri dishes. For this purpose, the PCB concentrations measured in the petri dishes and normalised to 24 hours were plotted against the corresponding concentration measured in air according to Equation 5. Lines were forced through the origin. A linear relationship could be established for CB-28, CB-52 and CB-101 (Figure 27). The slopes can be considered a constant sampling rate, in units of m^3/sampler/24 hours (Equation 5). Deviations from the straight line are likely related to experimental conditions (temperature, air velocity, boundary layer effects) as discussed in section 2.4, and analytical uncertainties. For CB-118 it was not possible to establish a linear relationship. The results of the calibration are summarised in Table 27, data for the petri dishes are given in Annex 8.

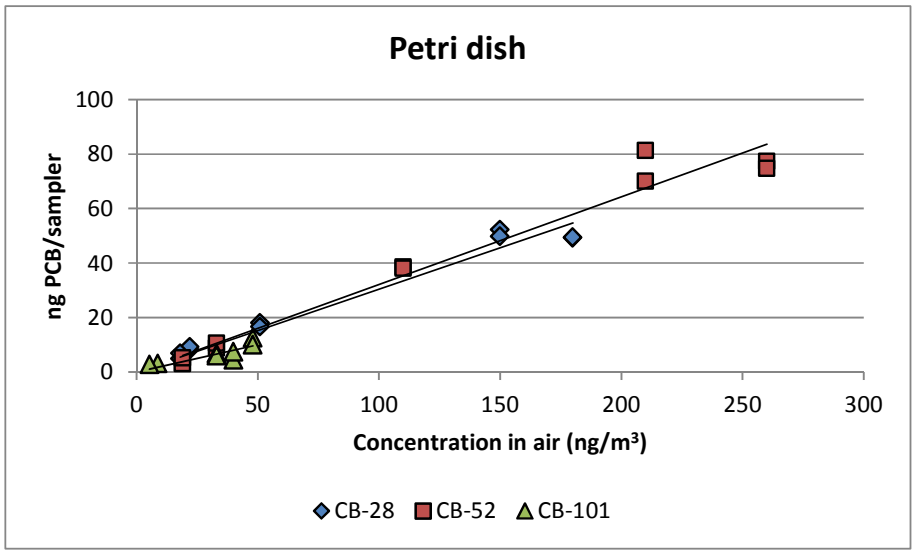


Figure 27. Linear relationships between concentrations in air (ng/m^3) and in the sampler (ng /sampler/24 hours) for CB-28, CB-52 and CB-101 sampled with the petri dishes. Data for petri dishes were available as duplicates, with the exception of two samples for CB-101.

Table 27. Results of the calibration of the petri dishes, according to Equation 5 and concentrations in Table 25.

	Sampling rate R_S (m^3/sampler/24 hours)	R^2
CB-28	0.304	0.96
CB-52	0.3216	0.96
CB-101	0.2007	0.69

3.3.3.3 Calibration of the silicone-coated paper

The time series indicated that the PCB congeners had probably not reached equilibrium with the silicone of the paper during the 14-26 hours of the individual measurements. Table 24 shows that $t_{90\%}$ < 1 day was only given for CB-28 and CB-31 in time series B. As differences in experimental conditions (e.g. temperature, air velocity) may affect uptake kinetics, this result (which is not confirmed by time series A) cannot be generalised. As the time series show that most congeners will still be in the kinetic uptake phase after 24 hours, the silicone-coated paper was calibrated in the same way as the petri dishes.

Linear relationships could be established for CB-28, CB-52, CB-101 and CB-118, between the concentration of the silicone-coated paper and the measured concentration in air (Figure 28). The higher chlorinated PCB congeners could be detected in the paper as well, but their concentrations below detection limits in the active measurements limit this calibration to four congeners. CB-153 could also be included, based on the two data points of L17 and L18 (Table 25) and the origin as a third value. Thus, CB-153 is included in the results in Table 28, but it has to be considered uncertain. The PCB concentrations used in the calibration of the paper format are given in Annex 9.

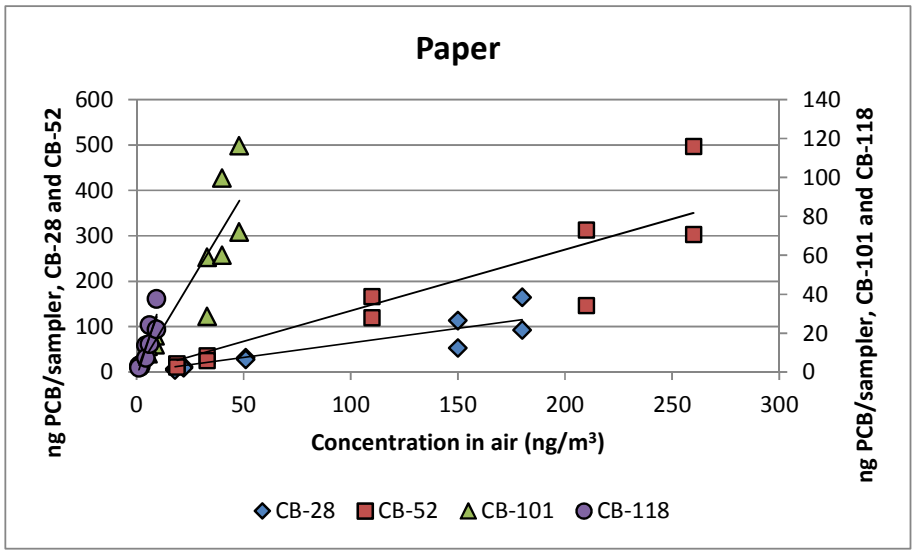


Figure 28. Linear relationships between concentrations in air (ng/m^3) and in the sampler (ng/sampler/24 hours) for CB-28, CB-52, CB-101 and CB-128 sampled with silicone-coated paper. CB-101 and CB-118 refer to the secondary y-axis. Data for paper were available as duplicates.

Table 28. Results of the calibration of the silicone-coated paper, according to Equation 5 and concentrations in Table 25. CB-153 has to be considered uncertain because of only two values for air concentrations (see Table 25).

	Sampling rate R_S (m^3/sampler/24 hours)	R^2
CB-28	0.6412	0.81
CB-52	1.3477	0.81
CB-101	1.8345	0.78
CB-118	3.0046	0.82
CB-153	2.6147	0.75

3.3.3.4 Validation of the petri dishes

Tests III and IV were used to validate the passive sampling measurements, i.e. to convert the passive sampling measurement (ng/sampler/24 hours) to an air concentration (ng/m^3) as described in Equation 5 and to compare this with the results of the active measurements provided by Rambøll. The sampling rates were those given in Table 27. Tests III and IV again spanned a relatively large concentration range (Table 25), which is beneficial for this validation purpose. The passive sampling data of tests III and IV are given in Annex 10.

The results for tests III and IV are shown in Figure 29 and Figure 30, respectively. In general, the petri dishes tend to overestimate the actively sampled air concentration. The difference is particularly large in test III where CB-28 in the petri dishes exceeds the air concentration of the active measurements by a factor 10 or more. The concentrations in the petri dishes and the active measurements as well as their ratios are summarised in Table 29.

The agreement is generally better for test IV, with excellent agreement for CB-52 in L8 and ratios of 1.3-2.8 for the remaining measurements (Table 29). The large difference from actively sampled concentrations in test III might partly be explained by the low concentration in this test. As discussed for the time series, the measurements become more precise and most likely also more accurate for higher concentrations. The results of test III could for instance have been affected by the settlement of dust particles on the petri dishes. Given the low PCB concentration at this location, even small particle adsorption could have a large effect on the measured concentration.

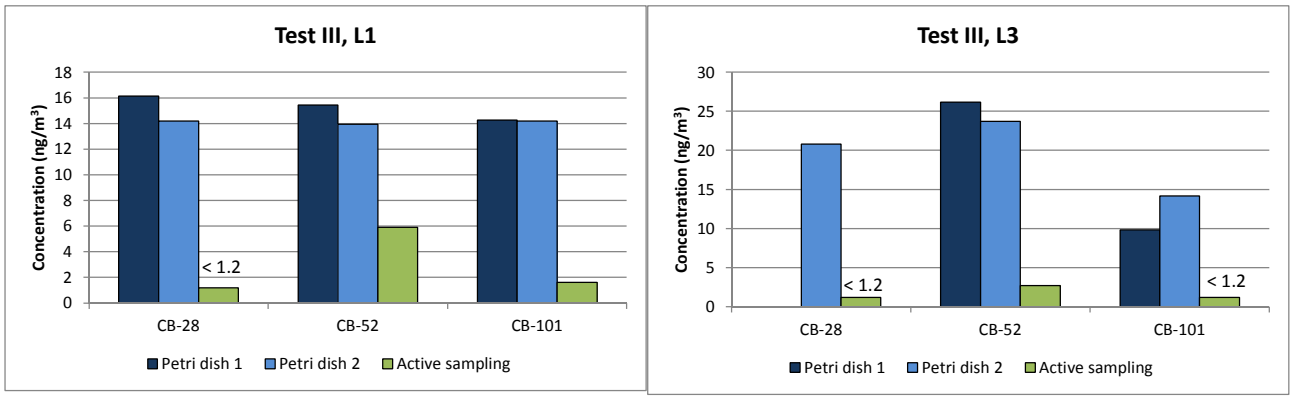
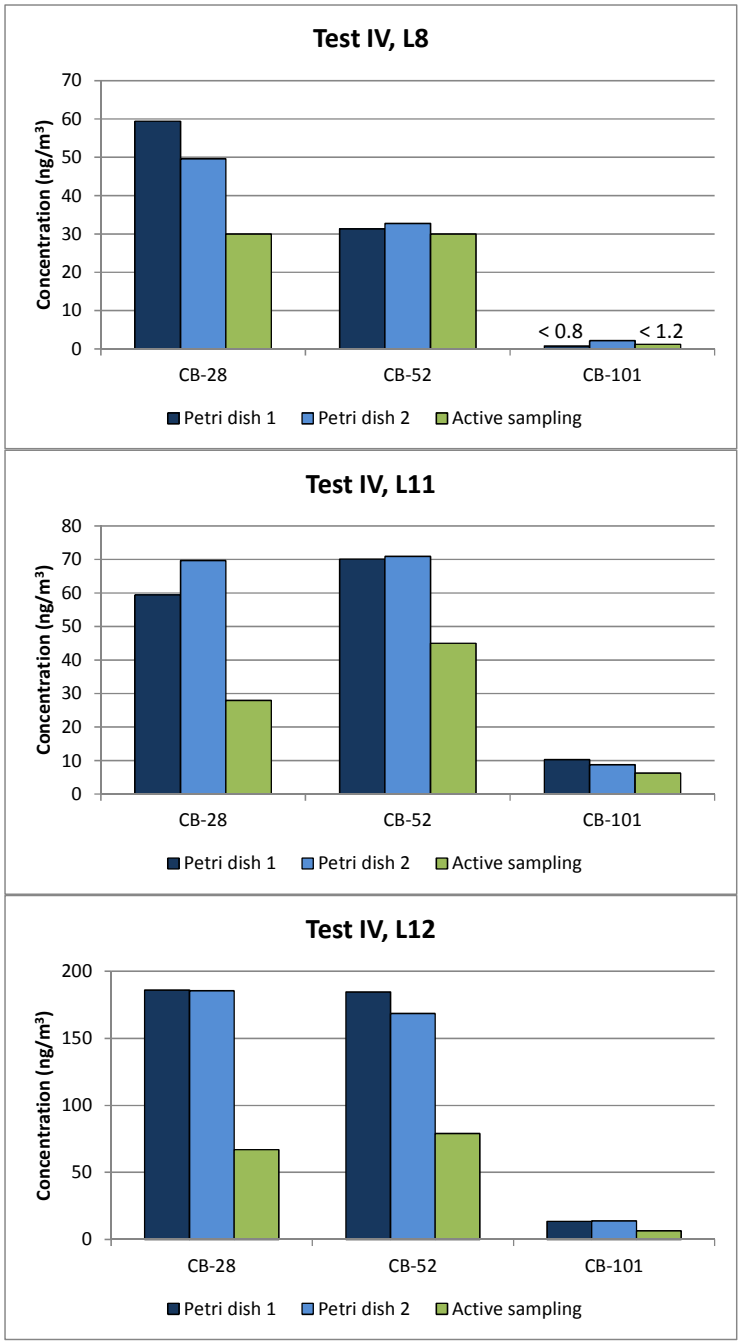


Figure 29. Calculated PCB concentrations in air (ng/m^3) for petri dishes of test III compared with the results of the active sampling (Table 25). For L3, no concentration could be determined for CB-28 in petri dish 1.

Figure 30. Calculated PCB concentrations in air (ng/m^3) for petri dishes of test IV compared with the results of the active sampling given in Table 25.



Achievable accuracy of passive samplers was discussed in section 1.2.5 on the basis of literature data. It was concluded that accuracy could be expected to be within an order of magnitude because PCB uptake is difficult to control. A factor of 2 between the passive sampling result and the true values had also been reported in the literature (Shoeib & Harner, 2002). Following project phase 1, it was decided to abandon common calibration methods for passive sampling applications, i.e. the use of performance reference compounds or the standardisation of uptake conditions to overcome boundary layer effects (section 2.1.1). As discussed in section 1.2.3, the latter in particular can have a significant effect on uptake rates. Considering the uncertainties thus connected with the passive sampler calibration, the accuracy achieved in this simple set-up can probably be considered acceptable. Even for test III, accuracy is still roughly within an order of magnitude, and for test IV, accuracy is much higher, i.e. within a factor of 2.8.

Table 29. Calculated air concentrations for petri dishes (ng/m^3) and their ratio to concentrations obtained from active sampling. PCB_{total} was calculated in the same way as in Table 25, i.e. 5x ΣPCB_7. n.a.: no data available.

	CB-28	CB-52	CB-101	PCB_{total}
Test III, L1				
Active sampling (ng/m^3)	< 1.2	5.9	1.6	37.5
Petri dish 1 (ng/m^3)	16.1	15.4	14.3	229
Petri dish 2 (ng/m^3)	14.2	14.0	14.3	212
Ratio 1	> 10	2.6	8.9	6.1
Ratio 2	> 10	2.4	8.9	5.7
Test III, L3				
Active sampling (ng/m^3)	< 1.2	2.7	< 1.2	13.5
Petri dish 1 (ng/m^3)	n.a.	26.2	9.9	284
Petri dish 2 (ng/m^3)	20.8	23.7	14.2	293
Ratio 1	n.a.	9.7	> 8	21.1
Ratio 2	> 17	8.8	> 10	21.7
Test IV, L8				
Active sampling (ng/m^3)	30	30	< 1.2	300
Petri dish 1 (ng/m^3)	59.4	31.4	< 0.8	458
Petri dish 2 (ng/m^3)	49.6	32.4	2.2	423
Ratio 1	2.0	1.1	consistent	1.5
Ratio 2	1.7	1.1	> 1.8	1.4
Test IV, L11				
Active sampling (ng/m^3)	28	45	6.3	365
Petri dish 1 (ng/m^3)	59.4	70.1	10.3	699
Petri dish 2 (ng/m^3)	69.6	70.9	8.8	746
Ratio 1	2.1	1.6	1.6	1.8
Ratio 2	2.5	1.6	1.4	1.9
Test IV, L12				
Active sampling (ng/m^3)	67	79	6.5	730
Petri dish 1 (ng/m^3)	186	185	13.4	1920
Petri dish 2 (ng/m^3)	185	168	14.0	1839
Ratio 1	2.8	2.3	2.1	2.5
Ratio 2	2.8	2.1	2.2	2.4

Table 29 also includes calculated concentrations for PCB_{total}, in comparison with the concentrations obtained from active sampling. For test III, the passive sampling concentrations are closer to the cut-off value of 300 ng/m^3 than the active measurements. This might lead to false positive measurements. However, the higher sensitivity of the passive samplers could influence PCB_{total} towards higher values as concentrations below detection limits are considered as zero in the calculation of ΣPCB_7 and subsequently, PCB_{total}. As the passive samplers produce more values above detection limits ΣPCB_7 and PCB_{total} will become higher.

It is important to note that the passive sampling measurement is intended to be used as an initial screening tool, which will be followed up by more accurate active sampling if cut-off values are exceeded. For this purpose, potentially false positives are less critical than potentially false negatives would be.

3.3.3.5 Validation of the silicone-coated paper

The PCB amounts sampled with the silicone-coated paper in tests III and IV were converted to air concentrations using the sampling rates of Table 28. The original passive sampling data in ng/sampler/24 hours is given in Annex 11. The results were evaluated in the same way as described for the petri dishes, but also included CB-118 and CB-153. Figure 31 and Figure 32 show the calculated concentrations in comparisons with the active sampling (Table 25). The results are summarised in Table 30, including ratios between the concentrations obtained with passive samplers and active sampling.

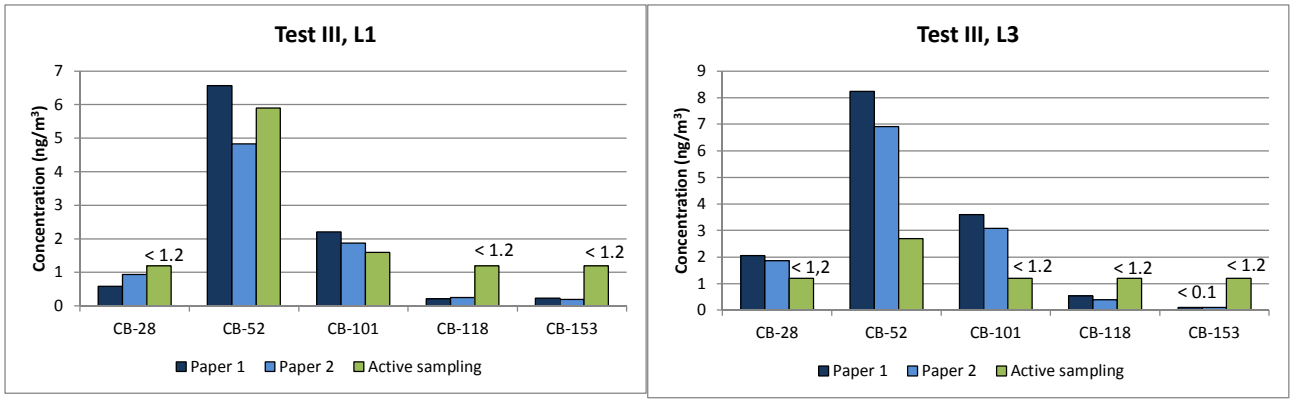


Figure 31. Calculated PCB concentrations in air (ng/m^3) for silicone-coated paper of test III compared with the active measurements given in Table 25.

Compared with the petri dishes, test III shows better agreement between the concentrations obtained from passive and from active sampling. While the ratios between passive and active measurements were > 10 for CB-28 in test III, L1, this test shows very good agreement between the two methods, with ratios close to 1. The ratios were somewhat higher for test III, L3, with a maximum of about 3 (Table 30).

As discussed previously, measurable concentrations could be produced from passive sampling for the concentrations below detection limits after active sampling. These were generally consistent with the active sampling results. This was also the case for CB-153 although the calibration only was based on two data points. The obvious uncertainty of this calibration, which was highlighted in the discussion of the calibration, seems to be less prob-

lematic than anticipated as all results of CB-153 were consistent with the concentration below detection limits obtained from active sampling.

Test IV also agrees with the results of the active measurements, within a factor of about 3. Good agreement exists for CB-28 and CB-52 in test IV, L8 and for test IV, L12. However, the duplicate samples of the L11 and L12 measurements deviate more than usually observed for the silicone-coated paper, leading to different ratios to the active samples (Table 30). As also observed for the petri dishes, the passive sampler generally tends to overestimate the air concentration measured with active sampling.

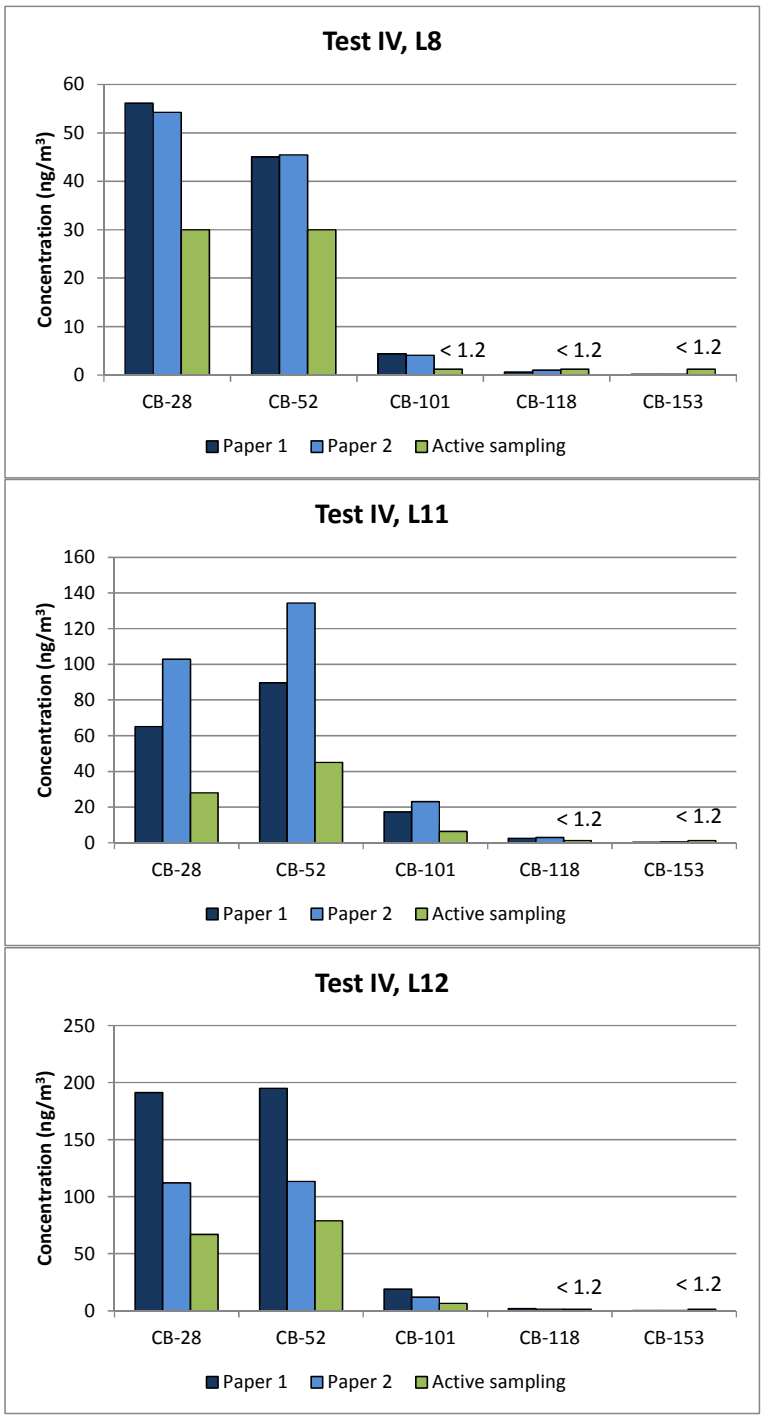


Figure 32. Calculated PCB concentrations in air (ng/m^3) for silicone-coated paper of test IV compared with the active measurements given in Table 25.

Comparisons with Table 29 show very similar concentrations for the petri dishes and the silicone-coated paper and consequently, very similar ratios to the concentrations obtained from active sampling. It is interesting to note that the petri dishes and the paper samples basically arrive at the same air concentrations despite large differences in sampling rates (Table 27 and Table 28). Combined plots of the two passive samplers are given as Annex 12.

Table 30. Calculated air concentrations for silicone-coated paper (ng/m^3) and their ratio to active sampling. PCB_{total} was calculated in the same way as in Table 25, i.e. 5x ΣPCB_7.

	CB-28	CB-52	CB-101	CB-118	CB-153	PCB_{total}
Test III, L1						
Active sampling (ng/m^3)	< 1.2	5.9	1.6	< 1.2	< 1.2	37.5
Paper 1 (ng/m^3)	0.6	6.6	2.2	0.2	0.3	49
Paper 2 (ng/m^3)	0.9	4.8	1.9	0.2	0.2	40
Ratio 1	consistent	1.1	1.4	consistent	consistent	1.3
Ratio 2	consistent	0.8	1.2	consistent	consistent	1.1
Test III, L3						
Active sampling (ng/m^3)	< 1.2	2.7	< 1.2	< 1.2	< 1.2	13.5
Paper 1 (ng/m^3)	2.1	8.2	3.6	0.5	< 0.1	73
Paper 2 (ng/m^3)	1.9	6.9	3.1	0.4	< 0.1	62
Ratio 1	> 1.5	3.1	> 3.0	consistent	consistent	5.4
Ratio 2	> 1.5	2.6	> 2.6	consistent	consistent	4.6
Test IV, L8						
Active sampling (ng/m^3)	30	30	< 1.2	< 1.2	< 1.2	300
Paper 1 (ng/m^3)	56.1	45.1	4.4	0.6	0.1	531
Paper 2 (ng/m^3)	54.2	45.4	4.1	1.0	0.1	524
Ratio 1	1.9	1.5	> 3.5	consistent	consistent	1.8
Ratio 2	1.8	1.5	> 3.5	consistent	consistent	1.8
Test IV, L11						
Active sampling (ng/m^3)	28	45	6.3	< 1.2	< 1.2	365
Paper 1 (ng/m^3)	65.1	89.6	17.3	2.5	0.3	874
Paper 2 (ng/m^3)	103	134	23.1	2.9	0.4	1318
Ratio 1	2.3	2.0	2.7	> 2.0	consistent	2.2
Ratio 2	3.7	3.0	3.7	> 2.4	consistent	3.3
Test IV, L12						
Active sampling (ng/m^3)	67	79	6.5	< 1.2	< 1.2	730
Paper 1 (ng/m^3)	191	195	19.0	2.0	0.3	2038
Paper 2 (ng/m^3)	112	113	12.1	1.5	0.2	1196
Ratio 1	2.9	2.5	2.9	> 1.5	consistent	2.7
Ratio 2	1.7	1.4	1.9	> 1.2	consistent	1.6

3.3.3.6 Precision

Precision was discussed for the time series in section 3.3.2 for both petri dishes and paper and it is not expected to be principally different for the 10 individual measurements. In the validation chapters 3.3.3.4 and 3.3.3.5, the duplicate samples were presented individually, which gives a good indication of their variation. Deviation between duplicates is generally small and in line with conclusions of section 3.2.3.

However, Figure 32 indicates some variation between duplicates of silicone-coated paper, which exceeds the value of 10 % discussed in section 3.3.2.3. Figure 33 therefore shows the standard deviation between duplicates of test

IV. This test included measurements in three rooms (L8, L11, L12) of which only L11 and L12 exceeded the standard deviations observed in previous measurements. This can likely be explained by the fact that the silicone-coated papers had not yet reached the equilibrium sampling regime, which for equilibrium sampling devices is characterizes by improved precision (Mayer et al., 2003). The reason for this is that equilibrium sampling devices are designed to reach equilibrium within a reasonable time, which implies maximized but not necessarily very well controlled mass transfer conditions.

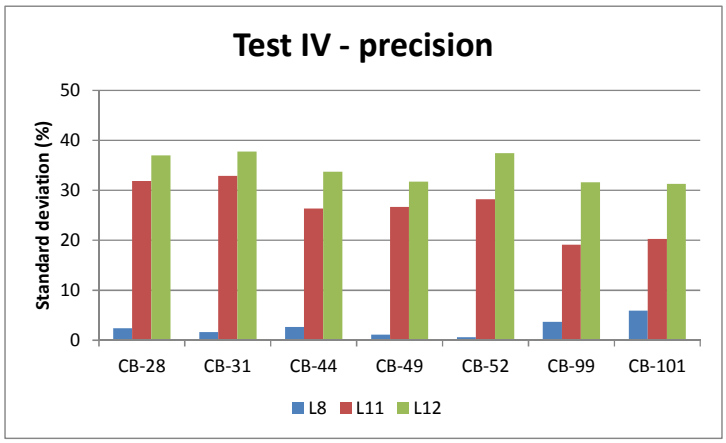


Figure 33. Standard deviations between duplicates of silicone-coated paper of test IV, illustrating two measurements (L11 and L12) with lower precision than usual.

3.3.3.7 Conclusion 24-hour-measurements

- Both passive sampling formats are very sensitive and could detect congeners which were below detection limits in the active sampling. This agrees with the findings of project phase 2 (section 2.4).
- Calibration of the passive sampler succeeded for CB-28, CB-52 and CB-101 (petri dishes) as well as CB-28, CB-52, CB-101, CB-118 and CB-153 (silicone-coated paper) in terms of linear relationships between passively and actively measured concentrations.
- The petri dishes tend to overestimate the air concentration obtained from active sampling, in particular at low concentrations. The accuracy is roughly an order of magnitude, with highest frequencies for ratios of 2-3 between active and passive sampling.
- The silicone-coated paper also tends to overestimate the air concentrations obtained from active sampling. The accuracy is roughly within a factor of 3. Concentrations could be produced for congeners which were below detection limits in active sampling.
- This overestimation might produce false positives. Considering the main purpose of the passive sampling technique for initial PCB screening, this can be regarded as less critical than false negatives would be.

3.4 Conclusions from project phase 3

In general we can draw the following conclusions from the measurements in project phase 3. The overall conclusions are also summarised in **Table 31**, including the criteria established in project phase 1 and indicating where more development work will be needed.

- The samplers are inexpensive, based on material costs and preparation time of the samplers.
- The samplers are generally robust, easy to handle and practical, with regard to shipment, sampling and the subsequent chemical analysis.

- Silicone works well as a sampling material for PCB congeners in indoor air. Thorough pre-cleaning of the material prior to use in passive sampling improves chromatography and thus unambiguous PCB determination.
- The passive samplers are precise and sensitive and can detect several congeners which were below detection limits in active sampling. These results confirm findings of project phase 2 (section 2.4).
- Under the conditions of the sampling campaign of this project phase, both passive samplers absorb PCB congeners in the kinetic phase. Time series indicate that the equilibrium sampling envisaged for the silicone-coated paper would require sampling periods of approximately one week.
- Linear uptake could be established for a large number of PCB congeners with IUPAC numbers ≤118 (petri dishes).
- Sampling rates could be determined for CB-28, CB-52 and CB-101 (petri dishes) as well as CB-28, CB-52, CB-101, CB-118 and CB-153 (passive samplers). The calibration was limited by the data available from active sampling as it only included seven PCB congeners several of which were below detection limits.
- In comparison with data from active sampling, the passive samplers tended to overestimate air concentrations by up to a factor of 3. For two measurements with petri dishes, air concentrations from active sampling were overestimated by roughly a factor of 10.
- Considering the limited data material for calibration and the likelihood of varying experimental conditions (in particular regarding air velocity and potential boundary layer effects), this agreement with active sampling is considered acceptable.
- Overestimations might produce false positives. Given the main purpose as a screening tool, this can be regarded as less critical than false negatives would be.

Table 31. Summary of conclusions from project phase 3, including the criteria established in project phase 1 (section 1.1.3).

	Petri dishes	**Silicone-coated paper**
Cost-effectiveness[a)]	+ < 100 kr.	+ Very low, but was not quantified.
Robustness and easy handling	+ As shown in this report.	+ As shown in this report.
Robustness and easy interpretation	(+) Interferences in the chromatograms, which might require more effective pre-cleaning of the silicone or dilution of extracts.	(+) Interferences in the chromatograms, although to a lower degree than for petri dishes, which might require more effective pre-cleaning of the silicone or dilution of extracts.
Sensitivity	+ As shown in this report.	+ As shown in this report.
Precision	+ As shown in this report.	+ As shown in this report.
Accuracy	(+) Tendencies of overestimating active measurements by up to a factor 3, in some cases up to a factor 10.	(+) Tendencies of overestimating active measurements by up to a factor 3.

[a)]A price estimate was prepared in June 2012, which is attached to this report as Annex 13.

4 References

Abdallah, M.A.-E.; Harrad, S. (2010). Modification and calibration of a passive air sampler for monitoring vapour and particulate phase brominates flame retardants in indoor air: Application to car interiors. Environmental Science & Technology 44, 3059-3065.

Balfanz, E.; Fuchs, J.; Kieper, H. (1993). Sampling and analysis of polychlorinated biphenyls (PCB) in indoor air due to permanently elastic sealants. Chemosphere 26 (5), 871-880.

Booij, K.; Hofmans, H.E.; Fischer, C.V.; van Weerlee, E.M. (2003). Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. Environmental Science & Technology 37, 361-366.

Breivik, K.; Sweetman, A.; Pacyna, J.M.; Jones, K.C. (2002) Towards a global historical emission inventory for selected PCB congeners – a mass balance approach. Science of the Total Environment 290, 181-198.

Brown, R.H. (2000). Monitoring the ambient environment with diffusive samplers: theory and practical considerations. Journal of Environmental Monitoring 2, 1-9.

Esteve-Turrillas, F.A.; Pastor, A.; de la Guardia, M. (2009) Use of semipermeable membrane devices for monitoring pesticides in indoor air. Journal of AOAC International 92 (5), 1557-1565.

Farrar, N.J.; Harner, T.J.; Sweetman, A.J.; Jones, K.C. (2005). Field calibration of rapidly equilibrating thin-film passive air samplers and their potential application for low-volume air sampling studies. Environmental Science & Technology 39, 261-267.

Goodbred, S.L.; Bryant, W.L.; Rosen, M.R.; Alvarez, D.; Spencer, T. (2009). How useful are the "other" semipermeable membrane devices (SPMDs); the mini-unit (15.2 cm long)? Science of the Total Environment 407, 4149-4156.

Górecki, T.; Namieśnik, J. (2002). Passive sampling. Trends in Analytical Chemistry 21 (4), 276-291.

Harner, T.; Farrar, N.J.; Shoeib, M.; Jones, K.C.; Gobas, F.A.P. (2003). Characterization of polymer-coated glass as a passive air sampler for persistent organic pollutants. Environmental Science & Technology 37, 2486-2493.

Harner, T.; Shoeib, M.; Diamond, M.; Ikonomou, M.; Stern, G. (2006). Passive sampler derived air concentrations of PBDEs along an urban-rural transect: Spatial and temporal trends. Chemosphere 64, 262-267.

Harrad, S.; Hazrati, S.; Ibarra, C. (2006). Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: Implications for human exposure. Environmental Science & Technology 40, 4633-4638.

Hazrati, S.; Harrad, S. (2007). Calibration of polyurethane foam (PUF) disk passive air samplers for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): Factors influencing sampling rate. Chemosphere 67, 448-455.

Mäenpää, K.; Leppänen, M.T.; Reichenberg, F.; Figueiredo, K.; Mayer, P. (2011). Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment – comparison of two approaches to determine equilibrium partition concentrations in lipids. Environmental Science & Technology, in press.

Mayer, P.; Tolls, J.; Hermens, J.L.M.; Mackay, D. (2003). Equilibrium sampling devices. Environmental Science & Technology May 1, 185A-191A.

Miljøstyrelsen (2009). Sundhedsmæssig vurdering af PCB-holdige bygningsfuger. Orientering fra Miljøstyrelsen nr. 1.

Ockenden, W.A.; Corrigan, B.P. Howsam, M.; Jones, K.C. (2001). Further developments in the use of semipermeable membrane devices as passive air samplers: Applications to PCBs. Environmental Science & Technology 35, 4536-4543.

Petty, J.D.; Huckins, J.N.; Zajicek, J.L. (1993) Application of semipermeable membrane devices (SPMDs) as passive air samplers. Chemosphere 27 (9), 1609-1624.

Reichenberg, F.; Smedes, F.; Jönsson, J.-Å.; Mayer, P. (2008). Determining the chemical activity of hydrophobic organic compounds in soil using polymer coated vials. Chemistry Central Journal 2, 8.

Seethapathy, S.; Gorecki, T. (2013) Applications of polydimethylsiloxane in analytical chemistry: A review. Analyical Chimica Acta 750, 48–62.

Seethapathy, S.; Górecki, T.; Li, X. (2008). Passive sampling in environmental analysis. Journal of Chromatography A 1184, 234-253.

Shoeib, M.; Harner, T. (2002). Characterization and comparison of three passive air samplers for persistent organic pollutants. Environmental Science & Technology 36, 4142-4151.

Söderström, H.S.; Bergqvist, P.-A. (2004). Passive air sampling using semipermeable membrane devices at different wind-speeds in situ calibrated by performance reference compounds. Environmental Science & Technology 38, 4828-4834.

Wania, F.; Shen, L.; Lei, Y.D.; Teixeira, C.; Muir, D.C.G. (2003). Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmosphere. Environmental Science & Technology 37, 1352-1359.

Wilford, B.H.; Harner, T.; Zhu, J.; Shoeib, M.; Jones, K.C. (2004). Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. Environmental Science & Technology 38, 5312-5318.

5 Annexes

Annex 1: PCB in indoor air

PCB was used commercially as technical mixtures of various PCB congeners. Depending on the manufacturer, marketed products were named Arochlor, Chlophen, Kanechlor, Pyralene etc. and varied in their composition and consequently, in their chlorine content. PCB mixtures were extensively used as plasticisers in elastic sealant materials, often exceeding concentrations of 1%, mainly between the mid 1950s to the mid 1970s (Balfanz et al., 1993; Kohler et al., 2005).

A study from Switzerland identified the technical PCB mixtures predominantly used in joint sealants as medium chlorination mixtures, e.g. Chlophen A50 or Arochlor 1248/1254 (Kohler et al., 2005). 70% of the samples studied could be traced back to these mixtures which mainly contain tetra- and pentachlorinated congeners. This is consistent with the results from a German study according to which Chlophen 30 was employed very rarely (Balfanz et al., 1993), while a British study found closer resemblance of air samples to the lower chlorinated mixtures Arochlor 1016 and Arochlor 1242 (Hazrati & Harrad, 2006). The use of PCB in sealants was also reported from the USA where Arochlor 1254 was identified as the main PCB formulation (Herrick et al., 2004).

The release of PCB congeners into the indoor environment has been documented in several studies, including the occurrence of some high PCB concentrations in indoor air of several $\mu g/m^3$. Studies from Switzerland and the USA found significantly elevated PCB levels in air of those buildings where PCB containing joint sealants were present (Herrick et al., 2004; Kohler et al., 2005). In 5% of the cases in Switzerland, levels were higher than 3000 ng/m^3, the higher cut-off value of the National Board of Human Health in Denmark. Highest PCB concentrations in indoor air have generally been found in buildings constructed (or refurbished) between 1955 and 1980 (Kohler et al., 2005; Hazrati & Harrad, 2006).

Also without distinct PCB sources in the indoor environment, the concentrations typically exceed those in outdoor air by an order of magnitude, probably because of widespread diffuse secondary PCB contamination (MacLeod, 1981; Wallace et al., 1996; Shoeib & Harner, 2002; Kohler et al., 2005; Harrad et al., 2006). Higher indoor than outdoor air concentrations were also found in buildings constructed after 1980 (Hazrati & Harrad, 2006). Similarly, some sealant samples contained PCB at levels well below those used for plasticising, probably also a result of contamination, e.g. by using the same equipment as for PCB-containing sealants (Kohler et al., 2005).

The PCB transfer from sealants to air depends, among other factors, on their volatility, and will lead to a congener profile in indoor air which deviates from the original one in the sealant (Balfanz et al., 1993). Studies on PCB concentrations in indoor air have generally found a predominance of PCB congeners with a low molecular weight which are the most volatile ones (Benthe et al., 1992; Balfanz et al., 1993). In fact, sealants appeared to be de-

pleted in these congeners when compared to the commercial mixtures (Kohler et al., 2005).

The current analytical method includes the seven PCB congeners CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180. For estimates of a total PCB concentration, the sum of these seven congeners is multiplied with a factor of 5. Consistent with procedures in other countries, the cut-off values of 300 and 3000 ng PCB/m^3 indoor air are also based on this selection of congeners, although indoor air typically only contains the most volatile compounds (Benthe et al., 1992; Balfanz et al., 1993).

An interesting correlation with outdoor temperature has been found in several studies, even though the indoor temperatures were nearly constant. Thus, higher PCB concentrations were found in indoor air in summer than in winter, possibly an effect of higher volatilisation rates at higher outdoor temperatures (Benthe et al., 1992; Balfanz et al., 1993; Hazrati & Harrad, 2006). This observation might have implications for measuring campaigns, including compliance checks with the cut-off values.

The long-term exposure to PCB from e.g. indoor air will increase the accumulation of PCB in the body which originate from other sources, e.g. certain food items. As the concentration of PCB in the environment has decreased in the last 20-30 years (e.g. Bignert et al., 1995; Vorkamp et al., 2009), PCB exposure from other sources has gained significance. PCB exposure has been associated with cancerogenic effects, as well as adverse effects on the immune system, neurodevelopment and reproductive success.

PCB congeners are globally regulated through the Stockholm Convention, with the objective for parties to take measures to eliminate and reduce the release of PCB and other persistent organic pollutants. In addition to being a public health issue, emissions from the indoor to the outdoor environment are likely to occur, followed by environmental transport and incorporation into the food chain (Hazrati & Harrad, 2006).

Table A.1. Brief characterisation of the seven PCB congeners chosen for analysis, with regard to indoor air occurrence. LogK_{OW} data from Hawker & Connell (1988). Log K_{OA} data from Shoeib & Harner (2002).

	CB-28	CB-52	CB-101	CB-118	CB-138	CB-153	CB-180
Homologue group	Tri-CB	Tetra-CB	Penta-CB	Penta-CB	Hexa-CB	Hexa-CB	Hepta-CB
Molecular mass	257.6	292.0	326.4	326.4	360.9	360.9	395.3
Log K_{OW}	5.50	5.84	6.38	6.74	6.83	6.92	7.36
Log K_{OA}	8.12	8.43	9.19	9.96	10.10	9.91	n.a.

References (Annex 1)

Balfanz, E.; Fuchs, J.; Kieper, H. (1993). Sampling and analysis of polychlorinated biphenyls (PCB) in indoor air due to permanently elastic sealants. Chemosphere 26 (5), 871-880.

Benthe, C.; Heinzow, B.; Jessen, H.; Mohr, S.; Rotard, W. (1992). Polychlorinated biphenyls. Indoor air contamination due to Thiokol-rubber sealants in an office building. Chemosphere 25 (7-10), 1481-1486.

Bignert, A.; Litzén, K.; Odsjö, T.; Olsson, M.; Persson, W.; Reutergårdh, L. (1995). Time-related factors influence the concentrations of sDDT, PCBs and shell parameters in eggs of Baltic Guillemot (Uria aalge), 1861-1989. Environmental Pollution 89, 27-36.

Hawker, D.W.; Connell, D.W. (1988). Octanol water partition-coefficients of polychlorinated biphenyl congeners. Environmental Science & Technology 22, 382-387.

Harrad, S.; Hazrati, S.; Ibarra, C. (2006). Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: Implications for human exposure. Environmental Science & Technology 40, 4633-4638.

Hazrati, S.; Harrad, S. (2006). Causes of variability in concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in indoor air. Environmental Science & Technology 40, 7584-7589.

Herrick, R.F.; McClean, M.D.; Meeker, J.D.; Baxter, L.K.; Weymouth, G.A. (2004). An unrecognised source of PCB contamination in schools and other buildings. Environmental Health Perspectives 112 (10), 1051-1053.

Kohler, M.; Tremp, J.; Zenneg, M.; Seiler, C.; Minder-Kohler, S.; Beck, M.; Lienemann, P.; Wegmann, L.; Schmid, P. (2005). Joint sealants: an overlooked diffuse source of polychlorinated biphenyls in buildings. Environmental Science & Technology 39, 1967-1973.

MacLeod, K.E. (1981). Polychlorinated biphenyls in indoor air. Environmental Science & Technology 15, 926-928.

Shoeib, M.; Harner, T. (2002). Characterization and comparison of three passive air samplers for persistent organic pollutants. Environmental Science & Technology 36, 4142-4151.

Vorkamp, K.; Thomsen, M.; Møller, S.; Falk, K.; Sørensen, P.B. (2009). Persistent organochlorine compounds in peregrine falcon *(Falco peregrinus)* eggs from Southern Greenland: Temporal changes from 1986 to 2003. Environment International 35, 336-341.

Wallace, J.C.; Bau, I.; Hites, R.A. (1996). Sampling and analysis artefacts caused by elevated indoor air polychlorinated biphenyl concentrations. Environmental Science & Technology 30, 2730-2734.

Annex 2: Minutes of the project meeting at the Danish Energy Agency (Energistyrelsen) 17th January 2011

Project participants (Katrin Vorkamp and Philipp Mayer) are referred to as "DMU" in the text below.

Mødets formål var at diskutere resultaterne af fase 1 med udgangspunkt i udkast til delrapport modtaget den 10. december 2010 samt at aftale det videre arbejde i fase 2.

Aftalt på mødet

Selv om både styrelsen og DMU ser en del væsentlige udfordringer i projektets videre forløb i relation til projektets overordnede formål, anser styrelsen – og DMU - en fortsættelse af projektet at være fornuftigt.

Styrelsen har ikke behov for ændringer til udkastet af delrapporten, men der skal tilføjes et resumé på dansk. Delrapport med resumé tilsendes styrelsen.

Regning for fase 1 kan sendes til styrelsen.

Da dele af afrapportering af fase 2, ligesom for fase 1, med fordel kan drøftes med udenlandske producenter af passive målere, accepteres, at også denne afrapportering skrives på engelsk med et dansk resumé. Inden opstart af en fase 3 aftales sprog for delrapport 3. Offentliggørelse af den endelige samlede rapport aftales senere.

DMU har haft kontakt til en tysk myndighed og bedt om deres erfaringer med screeninger med passiv målinger af PCB. Når DMU modtager dem, får styrelsen kopi. Øvrige indhentede baggrundsrapporter til delrapporten har styrelsen ikke behov for at modtage.

Diskussionspunkter fra mødet

- Cost-effectiveness. Delrapporten angiver målet for pris for en passivmåling til ca. halvdelen af pris for en gængs måling eller mindre. Dette følger op på tidligere drøftelser af hvordan formuleringen "til en brøkdel af prisen for hvad en aktiv måling koster" i projektbeskrivelsen skal forstås. Styrelsen specificerer, at den ser potentialet for screening med passiv måling begrænset, hvis prisen pr. måling alene reduceres med 50 pct.
- Robustness and easy handling. Styrelsen vurderer, at også problematikken om forsendelse indgår.
- Robustness and easy interpretation. Styrelsen ser gerne, at metoden ikke begrænses til måling af de i styrelsens vejledning om måling nævnte 7 kongener. DMU oplyser, at i projektfasen måler man som udgangspunkt for 22 kongener – samme som i SBI-undersøgelsen for MST – og vil tage stilling til hvorvidt metoden kan anvendes til andre end de 7 indikatorkongenerer
- Sensitivity. Styrelsen er enig i formålet med screening: at vurdere om PCB-indholdet ligger langt under de udmeldte aktionsværdier, ligger tæt på eller meget over. Styrelsen specificerer, at det ikke har højeste prioritet at opnå en detektionsgrænse på 0,1 ng/m^3, men at andre parametre (bl.a. pris, robusthed) er vigtigere.
- Include particle sampling. DMU gør opmærksom på, at passiv måling er en diffusions-styret proces og derfor alene kan måle PCB i gasfasen. Ud fra litteraturen og resultaterne fra SBI-undersøgelsen for MST har DMU

vurderet i rapporten, at hovedparten af PCB i indeluften vil forekomme i gasfasen og at en partikelopsamling derfor ikke vil tilføre væsentlig mere information. Det er styrelsens vurdering, på baggrund af det i 2010 afholdte stormøde i styrelsen om udkast til vejledning om måling, at der var bred enighed om, at PCB på små støvpartikler ikke var uvæsentligt i en sundhedsmæssig henseende. Projektets fase 3 indeholder parallelle målinger med passiv og aktive metoder, og det vil kunne give viden om dette spørgsmål. DMU forklarer, at en kvantitativ opsamling af partikler ikke kan foretages med samme metode, men vil kræve en ekstra indsats, hvilket sandsynligvis vil slå sig ned i prisen per analyse.

- Risk of errors – boundary layer effects. Generelt skal der være en vis luftbevægelse omkring den passive måler for at undgå at luftfasen direkte ovre målerens overflade bliver "tømt" for PCB-molekyler. Hvis dette sker, kan der ikke opnås en konstant opsamlingsrate. Der er nævnt lufthastigheder på 0,2 – 0,5 m/s som eksempler fra litteraturen og nævnt visse mekaniske apparater opstillet i forbindelse med måleren. Styrelsen vurderer, at de angivne lufthastigheder er uacceptable i såvel boliger som skoler og institutioner, og behov for mekaniske apparater – små ventilatorer eller roterende plader – vil kunne besværliggøre og fordyre screeningen. DMU oplyser, at andre kalibreringsmetoder ("performance reference compounds") kan tage højde for effekten, se nedenstående punkt.
- En af de foreslåede 3 målemetoder til at indgå i fase 2 – SBSE – kræver muligvis en mere omhyggelig behandling før, under og efter måling i felten. DMU har kontaktet den tyske producent og afventer tilbagemelding. Derudover har DMU rettet henvendelse til en tysk myndighed for at få deres erfaringer med denne type opsamler. Så måske er der intet praktisk problem.
- Effects of temperature. Da diffussionskoefficienter stiger med stigende temperatur optræder en temperaturafhængig målefejl. Fejlen er dog begrænset i forhold til de øvrige fejlkilder ved målingerne.
- Sampling rate – deployment time. De 3 foreslåede målemetoder forventes alle at kunne opnå en detektionsgrænse på 0,1 ng/m^3 i en 24 timers periode, og alle vil sandsynligvis kunne "nøjes" med en måletid på 6 – 8 timer, som vil være relevant i en skole -, muligvis dog med en højere detektionsgrænse.
- For 2 af de 3 foreslåede metoder er der etableret et kalibreringsprincip ("performance reference compounds") som muliggør en forholdsvis præcis og nøjagtig måling, idet kalibreringen finder sted samtidig med målingen og dermed tager højde for de aktuelle betingelser. Performance reference compounds skal ligne de stoffer så meget som muligt som ønskes målt. Derfor er der i litteraturen brugt andre PCB kongenerer (som ikke forekommer i indeluften). DMU har i rapporten inkluderet et "worst case" regneeksempel, baseret på den højeste koncentration der er brugt som performance reference compound i litteraturen. Frigivelsen af denne mængde vil ligge langt under grænseværdien på 300 ng/m^3 i et almindeligt lokale. Styrelsen vurderer, at frigivelse af selv en lille dosis PCB i indeklimaet ved en måling kan blive et politisk problem, så metoderne vurderes uegnede, hvis der ikke findes et andet "kalibreringsstof".
- Acceptable range of accuracy. Delrapporten angiver, at målenøjagtigheden på nuværende videnniveau kan forventes at være "an order of magnitude" - betyder en usikkerhedsfaktor på 10. En udenlandsk rapport angiver dog, at passiv måling kan angive luftkoncentrationer med en usikkerhedsfaktor på 2 fra den sande værdi. Med en faktor på 10 betyder det,

at en sand værdi på 300 ng/m³ forventes angivet i intervallet 30 – 3000 ng/m³, og med en usikkerhedsfaktor på 2 forventes resultatet angivet i intervallet 150 – 600 ng/m³. Usikkerhedsfaktoren på 2 ses at svare til det dobbelt af måleusikkerheden ved aktiv måling ved en koncentration på 300 ng/m³. DMU har angivet i rapporten, at spørgsmålet om nøjagtighed vil indgå i det videre arbejde, primært i fase 3 når aktive og passive målinger udføres parallelt. Derudover er der noteret i projektbeskrivelsen "En konkret vurdering af mulige overskridelser af disse aktionsværdier anbefales fortsat at blive baseret på konventionel aktiv opsamling", dvs. den passive opsamler har en screeningsfunktion, med de delformål der er listet op i projektbeskrivelsen (hurtig identificering af bygninger med høj PCB-belastning, identificering af "hot spots" indenfor en større bygning, vurdering af langtidseksponering).

Annex 3: Presentation of results of project phases 1 and 2 at a meeting at the Danish Energy Agency (Energistyrelsen) 4th December 2012

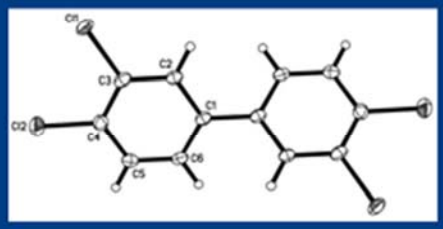
Møde i Energistyrelsen 4.12.2012

SCREENING AF INDELUFTEN FOR PCB-INDHOLDET VHA. PASSIVE OPSAMLERE

Katrin Vorkamp og Philipp Mayer

Aarhus Universitet

Institut for Miljøvidenskab



Møde i Energistyrelsen 4.12.2012

Baggrund

Behov for et hurtigt og effektivt screeningsværktøj, for at identificere bygninger/lokaler med høj PCB-belastning.

Ambitionsniveau:

- Ja/Nej svar i forhold til aktionsværdierne på 300 og 3000 ng/m^3. Positive resultater bør følges op med mere nøjagtige aktive målinger.
- Prøvetagningen med passive opsamlere skal være billigere end en aktiv måling.

Fordele med passive sampling:

- Simpelt udstyr, som ikke generer, når man opholder sig i lokalet.
- Tidsintegrerende målinger som også gør det muligt at vurdere langtidseksponeringen.

Formål

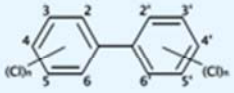
Undersøge, udvikle og udnytte passiv opsamling til screening af PCB-indholdet i indeluften.

Fase 1: Anbefaling af egnede metoder på basis af eksisterende viden.	☑
Fase 2: Udviklingen og optimering af opsamlerens håndtering og analysen i laboratoriet.	☑
Fase 3: Afprøvning og validering af den passive opsamler i kontaminerede bygninger.	

Møde i Energistyrelsen 4.12.2012

Fase 1

Review og anbefaling af egnede metoder



Forventning til den passive opsamler, defineret af EST:

- Opsamleren skal tillade målinger i kortere perioder (1 time) og over længere tid (langstidseksponering).
- Dvs. detektionsgrænserne skal være så lave, at en times måling er nok for at måle en kontaminering i henhold til aktionsværdierne.
- Opsamleren skal være robust og nem at opsætte.
- Opsamlingen skal kunne foretages til en brøkdel af prisen for en aktiv måling.

Fase 1 - Kriterier

Kost-effektiv: Mindst en halvering af udgifterne til en aktiv måling.

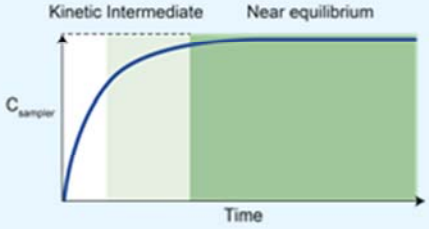
Robust og nem at håndtere: Kan bruges af lægmand. Lav risiko for kontaminering.

Robust og nem at tolke: Konstant optagelsesrate eller ligevægt.

Følsom: Tilstrækkelige detektionsgrænser efter kort tids opsætning.

Nøjagtig og præcis: Ja/Nej svar muligt i henhold til aktionsværdierne.

Fase 1 – Linear optagelse vs. ligevægt



Mayer et al. (2003), Environ. Sci. Technol. 184A- 191A

Kinetisk fase:

Luftkoncentrationen bestemmes ud fra

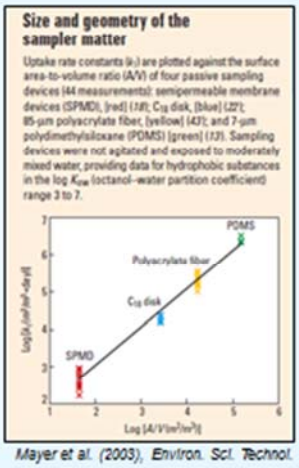
- Konc. på opsamleren
- Optagelsesraten

Konc. er en middelkoncentration over det undersøgte tidsrum.

Ligevægt: Luftkoncentrationen bestemmes ud fra

- Konc. på opsamleren
- Ligevægtsfordelingskoefficienten

Fase 1 – Linear optagelse vs. ligevægt



Mayer et al. (2003), Environ. Sci. Technol. 184A- 191A

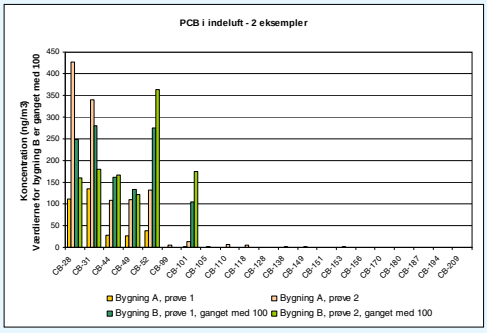
Optagelsesprocessen afhænger af tid, men også af opsamlerens design, f.eks. forholdet mellem overflade og volumen (A/V).

Højt A/V forhold

→ høj optagelsesrate

→ hurtig ligevægtsindstilling.

Fase 1 - Partikler



„89% af PCB i indeluften foreligger i gasfasen."

(Balfanz et al., 1993, Chemosphere 26, 871-880)

"Kun PCB congenerer med logK_{OA} værdier > 10 binder væsentligt til partikler." *(Shoeib & Harner, 2002, Environ. Sci. Technol. 36, 4142-4151)*

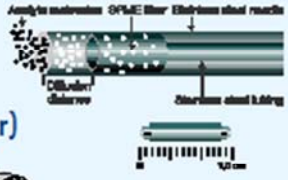
Miljøstyrelsen (2009). Orientering fra Miljøstyrelsen nr.1.

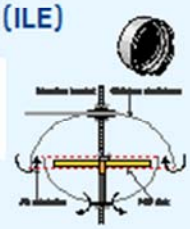
	CB-28	CB-52	CB-101	CB-118	CB-138	CB-153	CB-180
Homologue group	Tri-CB	Tetra-CB	Penta-CB	Penta-CB	Hexa-CB	Hexa-CB	Hepta-CB
Molecular mass	257.6	292.0	326.4	326.4	360.9	360.9	395.3
Log K_{OW}	5.50	5.84	6.38	6.74	6.83	6.92	7.36
Log K_{OA}	**8.12**	**8.43**	**9.19**	**9.96**	**10.10**	**9.91**	**n.a.**

Hawker & Connell (1988) , Environ. Sci. Technol. 22, 382-387; Shoeib & Harner (2002), Environ. Sci. Technol. 36, 4142-4151.

Fase 1 - Formater

- Semi-permeable membrane devices (SPMD)
  - Klassisk version (typisk 91 cm)
  - Mini-version (15 cm)
- Solid-phase micro extraction (SPME)
- Stirbar sorptive extraction (SBSE, Twister)
- Immobilised liquid extraction (ILE)
- PDMS coated vials
- PUF skiver
- XAD resins


Fase 1 – Kost-effektivitet

Format	Pris (Euro)	Bemærkning	Forhandler
Mini-SPMD	ca. 50	Materialet er renset.	Exposmeter (Sverige)
SPME	ca. 100	Kan genbruges. Automatiseret GC-analyse kræver specielt udstyr.	fx Supelco (Tyskland)
SBSE (Twister)	ca. 4000/100	Kan genbruges. Automatiseret GC-analyse kræver specielt udstyr.	Gerstel (Tyskland)
ILE	ca. 75/20	-	ILE Inc. (USA)
PDMS coated vials	ca. 15	Kan fremstilles i et kemisk laboratorium.	-
PUF skiver	moderat	-	fx Supelco (Tyskland)
XAD resins	moderat	-	-

Fase 1 – Robust og nem at håndtere

Den nemme håndtering er en vigtig konkurrencefordel for passive opsamlere. Derfor er der generelt lagt vægt på dette kriterium i designfasen.

Potentielle fejlkilder:

- Direkte eksponering til sollys. Mindre kritisk i formater hvor sorbenten er beskyttet (PDMS coated vials, ILE etc.)
- Boundary layer effects.
- Sedimentation af partikler.

Risiko for kontaminering generelt lav, hvis opsamlere håndteres rigtigt.

AARHUS UNIVERSITET
Møde i Energistyrelsen 4.12.2012

Fase 1 – Nem at tolke?

Udfordring: Konstante og reproducerbare optagelsesrater.

1. Temperatur

Optagelsesraten stiger med stigende temperatur

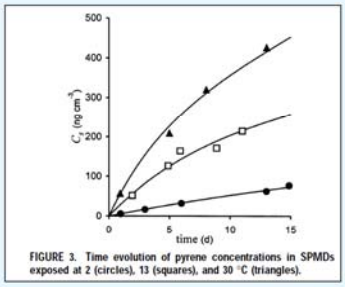


FIGURE 3. Time evolution of pyrene concentrations in SPMDs exposed at 2 (circles), 13 (squares), and 30 °C (triangles).

Booij et al. (2003). Environ. Sci. Technol. 37 (2), 361-366.

„Optagelsesrater varierer med ca. 0,2 – 0,4% per °C."

(Brown, 2000, Journal of Environmental Monitoring 2, 1-9)

Temperatureffekten kan forventes at være lille i indendørsmålinger.

AARHUS UNIVERSITET

Møde i Energistyrelsen 4.12.2012

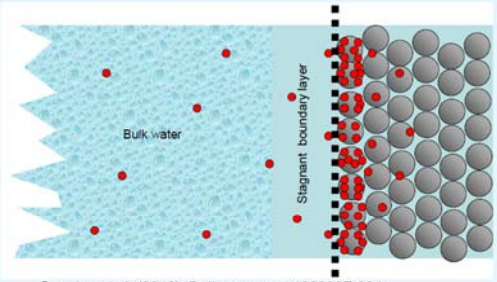
Fase 1 – Nem at tolke?

Udfordring: Konstante og reproducerbare optagelsesrater.

2. Boundary layer effects

Stabilt luftlag over sampleren som „tømmes" for PCB molekylerne.

En signifikant boundary layer fører til lavere optagelsesrater.



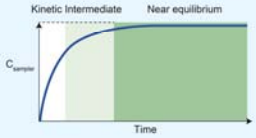
Smedes et al. (2010). Deltares report 1202337-004.

Opsamlere med store overflader er mest påvirket.

Der bør tages højde for denne effekt i kalibreringen af passive opsamlere til indendørs PCB målinger.

AARHUS UNIVERSITET

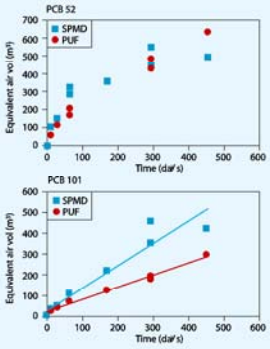
Møde i Energistyrelsen 4.12.2012



Fase 1 – Nem at tolke?

3. Linear optagelse vs. ligevægt

Optagelsesrater er forskellige for de enkelte PCB congenerer.



„Opsamlingen i intermediate fasen fører til større kompleksitet og usikkerhed i luftkoncentrationerne." *(Harner et al., 2003, Environ. Sci. Technol. 37, 2486-2493)*

Indenfor opsamlingsperioder på timer eller få dage vil de fleste formater være i den lineare fase. Ligevægten kan fremskyndes ved at øge A/V.

(Shoeib & Harner, 2002, Environ. Sci. Technol. 36, 4142-4151)

Fase 1 - Følsomhed

Instrumentel detektionsgrænse: ca. 0,5 pg/PCB congener.

Format	Sampling rate (m^3/day)	Deployment time (hours)	Percentage injected (%)	Minimum quantifiable air concentration (ng/m^3)
SPMD classic	3	24	0.1	**0.17**
SPMD classic	3	24	1	**0.017**
Mini-SPMDs	1	24	0.1	**0.5**
Mini-SPMDs	1	24	1	**0.05**
Mini-SPMDs	1	8	1	**0.15**
SPME	0.005	24	100	**0.1**
SBSE	0.1	24	1	**0.5**
SBSE	0.1	24	100	**0.005**
SBSE	1	6	100	**0.002**
PDMS-coated vials	3	24	0.1	**0.17**
PDMS-coated vials	3	24	1	**0.017**
PDMS-coated vials	3	8	1	**0.05**
XAD-2 resins	2	24	0.1	**0.25**
XAD-2 resins	2	24	1	**0.025**

„100% injiceret“ kræver specielt GC-udstyr.

Optagelsesrate for PDMS-coated vials kan øges gennem A/V forholdet.

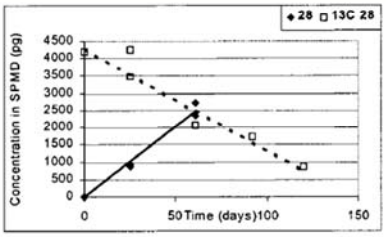
AARHUS UNIVERSITET
Møde i Energistyrelsen 4.12.2012

Fase 1 – Nøjagtighed og præcision

Udfordring: Bestemmelse af optagelsesrater.

Kalibreringsmetoder:

1. Performance Reference Compounds (PRCs)
   Frigives fra opsamleren → in situ kalibrering.
2. Standardiserede optagelses-betingelser
   Optagelsesrater er reproducerbare → kalibrering i laboratoriet.



Ockenden et al. (2001). Environ. Sci. Technol. 35, 4536-4543.

„Nøjagtighed indenfor en faktor 2 af den sande værdi kan opnås for passive opsamlere i luft.“ *(Shoeib & Harner, 2002, Environ. Sci. Technol. 36, 4142-4151)*

AARHUS UNIVERSITET

Møde i Energistyrelsen 4.12.2012

Fase 1 – Konklusioner

Kost-effektiv: Mindst en halvering af udgifterne til en aktiv måling. ☑

Robust og nem at håndtere: Kan bruges af lægmand. Lav risiko for kontaminering. ☑

Robust og nem at tolke: Konstant optagelsesrate eller ligevægt. ?

Følsom: Målbare PCB koncentrationer efter kort tids opsætning. ☑

Nøjagtig og præcis: Ja/Nej svar muligt i henhold til aktionsværdierne. ?

→ **Fase 2**

AARHUS UNIVERSITET

Møde i Energistyrelsen 4.12.2012

Overgang til fase 2

Kalibreringsmetoder:

1. **Performance Reference Compounds (PRCs)** 👎
2. **Standardiserede optagelsesbetingelser** 👎

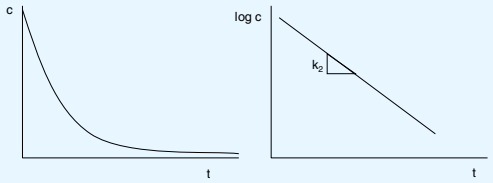
Undersøgelser af:

- **Effekt af varierende lufthastighed / boundary layer effekt.**
- **Følsomhed.**
- **Nøjagtighed og præcision.**
- **Rutinemæssig anvendelse.**
- **PDMS coated vials**

- **Stirbar sorptive extraction (SBSE, Twister)**

Fase 2 - Laboratorieforsøg

Bestemmelse af elimineringsrater, for forskellige
- formater / opsamlere
- lufthastigheder
- PCB congener.



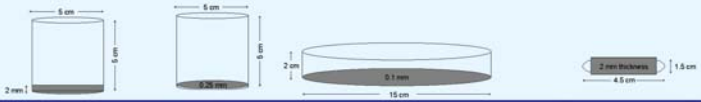
Estimering af koncentrationen på opsamleren:

$$C_{Silicone} = C_{Air} \cdot \frac{k_1}{k_2} \cdot (1 - e^{-k_2 \cdot t})$$

- k_2: elimineringsrate (dag^{-1}), bestemt eksperimentelt.
- k_1: optagelsesrate (dag^{-1}), fra litteraturen.
- C_{Air}: hhv. 300 ng/m³ og 3000 ng/m³.

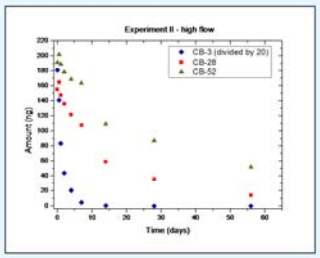
AARHUS UNIVERSITET
Møde i Energistyrelsen 4.12.2012

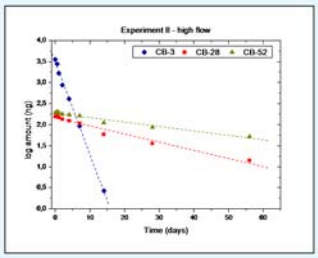
Fase 2 - Laboratorieforsøg

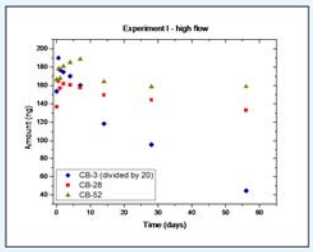


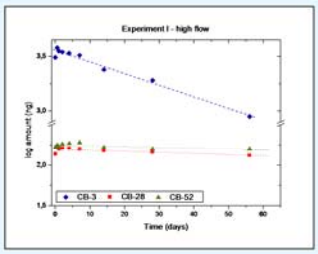
Experiment	I	II	III	IV	V
Format	Glass with silicone layer	Glass with silicone sheet	Petri dish with silicone coating	SBSE	SBSE
Illustration					See IV
Air velocity	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	0.1 m/s (0 - 0.2 m/s) 0.3 m/s (± 0.2 m/s) 1 m/s (± 0.2 m/s)	Magnetic stirrer; flow approximately 0.1 m/s
Sampling points (no. of replicates)	Start (3) ½ day (2) 1 day (2) 2 days (2) 4 days (2) 1 week (2) 2 weeks (1) 4 weeks (1) 8 weeks (1) 16 weeks (1)	Start (3) ½ day (2) 1 day (2) 2 days (2) 4 days (2) 1 week (2) 2 weeks (1) 4 weeks (1) 8 weeks (1) 16 weeks (1)	Start (3) 4 days (1) 1 week (1) 2 weeks (1) 4 weeks (1)	Start (2) 4 days (2) 1 week (2) 2 weeks (2) 4 weeks (1)	4 days (2) 1 week (2) 2 weeks (1) 4 weeks (1)

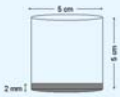
Fase 2 – Elimineringsrater, konstant flow









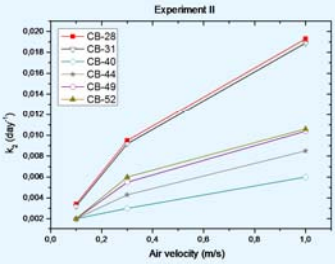


AARHUS UNIVERSITET
Møde i Energistyrelsen 4.12.2012

Fase 2 – Varierende flow

Stoffer med elimineringsrater som er statistisk forskellige fra nul:

High flow	Medium flow	Low flow
HCB	HCB	HCB
CB-3	CB-3	CB-3
CB-28	CB-28	CB-28
CB-31	CB-31	CB-31
CB-40	CB-40	CB-40
CB-44	CB-44	CB-44
CB-49	CB-49	CB-49
CB-52	CB-52	CB-52
CB-99	CB-99	CB-99
CB-101	CB-101	CB-101
CB-110		



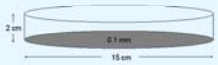
k_2 varierer med en faktor 1,4 (CB-40) til 2,8 (CB-28) for de to laveste lufthastigheder.

Stigning af k_2 ikke konstant.

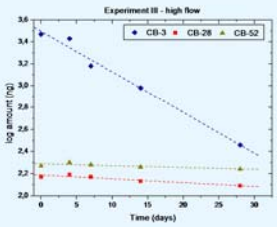
AARHUS UNIVERSITET

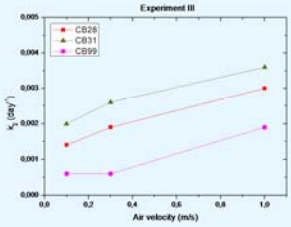
Møde i Energistyrelsen 4.12.2012

Fase 2 – Højt A/V forhold



Effekten af varierende flow er mindre end i forsøg II.





k_2 varierer kun med en faktor 1,3-1,6 for CB-28, CB-31 og CB-99.

Stigning af k_2 næsten konstant.

AARHUS UNIVERSITET

Møde i Energistyrelsen 4.12.2012

Fase 2 – Følsomhed

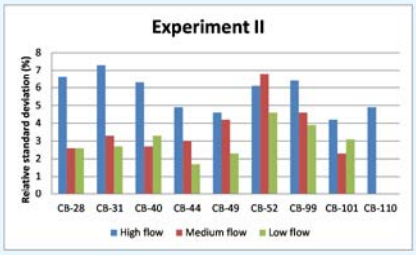
Målbare koncentrationer efter 24 timers opsamling

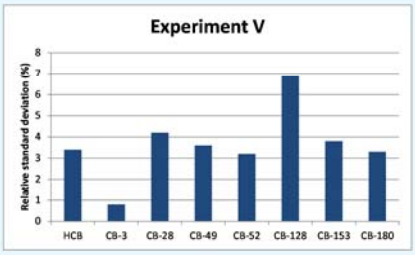
Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m³)
HCB	0.1	0.5	**0.794**
CB-3	0.1	0.5	**0.819**
CB-28	0.1	0.5	**0.779**
CB-31	0.1	0.5	**0.779**
CB-40	0.1	0.5	**0.777**
CB-44	0.1	0.5	**0.777**
CB-49	0.1	0.5	**0.778**
CB-52	0.1	0.5	**0.778**
CB-99	0.1	0.5	**0.776**
CB-101	0.1	0.5	**0.776**

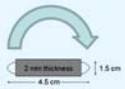
Compound	Percent injected	$C_{Silicone}$ (ng/sampler)	C_{Air} (ng/m³)
HCB	0.1	0.5	**0.0888**
CB-3	0.1	0.5	**0.0879**
CB-28	0.1	0.5	**0.0863**
CB-31	0.1	0.5	**0.0863**
CB-110	0.1	0.5	**0.0862**
CB-118	0.1	0.5	**0.0862**
CB-149	0.1	0.5	**0.0862**

Fase 2 – Præcision

Relative standardafvigelser for dobbeltbestemmelser

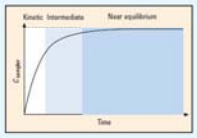






AARHUS UNIVERSITET
Møde i Energistyrelsen 4.12.2012

Fase 2 – Konklusioner

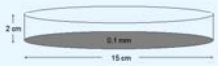


- Der foreligger praktiske og billige formater til passiv opsamling.
- Høj følsomhed og præcision.
- Optagelsesrater vil variere med en faktor 1,5 - 2 under forskellige flow forhold (indendørs).
- „Nøjagtighed indenfor en faktor 2 af den sande værdi kan opnås for passive opsamlere i luft."

  (Shoeib & Harner, 2002, Environ. Sci. Technol. 36, 4142-4151)
- Denne nøjagtighed er tilstrækkelig i forhold til det oprindelige ambitionsniveau. **(Ja/Nej svar i forhold til aktionsværdierne på 300 og 3000 ng/m³.)**

Forslag til fase 3

- **Standardiserede optagelsesbetingelser**
- **Formater med højt A/V forhold – fase 2 har vist mindre afhængighed af ændrede flowforhold.**



- **Ligevægtsopsamlingen → optagelsesrater er så høje at der kan opnås ligevægt indenfor opsætningstidsrummet.**

Annex 4: Work plan for project phase 3

Copy of "Notat til Energistyrelsen" of 19 March 2013

Fase 3 i projektet "Passive opsamlere til måling af PCB i indeluften"

På mødet den 4. december 2012 med Energistyrelsen og repræsentanter fra branchen blev der aftalt at undersøge to typer passive opsamlere i projektets tredje fase:

- Petriskåle med et tyndt lag silikone.
- Papir med et meget tyndt lag silikone på begge sider.

Petriskålen vil fungere som en kinetisk opsamler, dvs. stofferne opsamles over tid med en konstant optagelsesrate. Luftkoncentrationen skal bestemmes ud fra koncentrationen på opsamleren og optagelsesraten. Papiret vil blive testet til ligevægtsopsamling, hvor luftkoncentrationen bestemmes ud fra koncentrationen på opsamleren og en luft-opsamler-fordelingskoefficient.

Formålet med undersøgelserne i 3. projektfase er at optimere de passive opsamlere yderligere og teste dem med hensyn til præcision og nøjagtighed. Dette gøres samtidig med aktive målinger af PCB i indeluften, som udføres i anden sammenhæng, f.eks. i det nationale kortlægningsprogram. De aktive målinger vil blive brugt som referenceværdier til kalibrerings- og evalueringsformål.

Præcisionen undersøges ved at arbejde med dobbeltbestemmelser. I projektbeskrivelsen var der oprindeligt foreslået 3-5 replikater. Da resultaterne for projektfase 2 viste en god præcision mellem parallelle opsamlere, sættes antallet af replikater ned, til fordel for flere uafhængige målinger.

På alle lokaliteter er det vigtigt at måle temperatur (og luftfugtighed) under hele opsamlingsprocessen.

Ud fra resultaterne fra projektets 2. fase vælges en tidsperiode på 18-24 timer til opsamlingen, medmindre andet er anført i nedenstående beskrivelse.

I projektbeskrivelsen er der foreslået, at projektdeltagerne (Philipp Mayer og Katrin Vorkamp) tager ud til 1-2 lokaliteter, helst på Sjælland. Det virker hensigtsmæssigt at vælge de lokaliteter hvor der måles en tidsserie (se nedenstående beskrivelse), da tidsserien må forventes at være mest forskellig fra måleprocesserne under f.eks. det nationale kortlægningsprogram.

1. Petriskåle

Der vælges i alt 12 lokaliteter. Hvis der foreligger forhåndsviden om koncentrationerne, kunne der med fordel vælges lokaliteter med forskellige koncentrationer.

- 5 lokaliteter bruges til kalibreringen af den passive opsamler, dvs. bestemmelsen af opsamlingsrater ud fra resultaterne af den aktive måling.
- 5 lokaliteter bruges til uafhængig måling af PCB og vurdering af opsamlerens nøjagtighed ud fra sammenligningen med den aktive måling.

- 2 lokaliteter bruges til måling af en tidsserie som omfatter følgende tidsintervaller: 6-8 timer, 1 dag, 2 dage, 1 uge. Tidsserien vil give flere oplysninger om optagelsesprocessen.

2. Papir

Der vælges i alt 12 lokaliteter. Hvis der foreligger forhåndsviden om koncentrationerne, kunne der med fordel vælges lokaliteter med forskellige koncentrationer.

- 10 lokaliteter bruges til måling af PCB og vurdering af opsamlerens nøjagtighed ud fra sammenligningen med den aktive måling.
- 2 lokaliteter bruges til måling af en tidsserie som omfatter følgende tidsintervaller: 6-8 timer, 1 dag, 2 dage, 1 uge. Tidsserien vil give flere oplysninger om optagelsesprocessen, specielt hvornår der kan regnes med ligevægtsindstillingen.

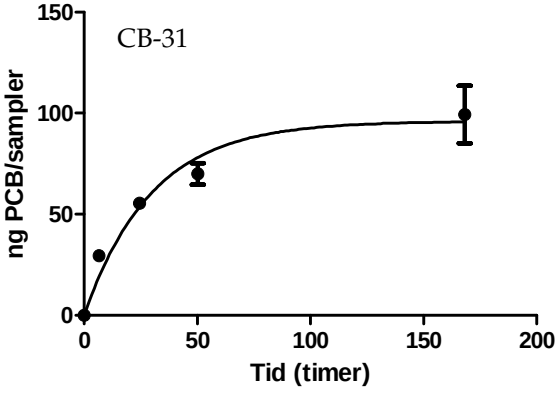
Annex 5: Overview over the samples received and analysed for PCBs in project phase 3

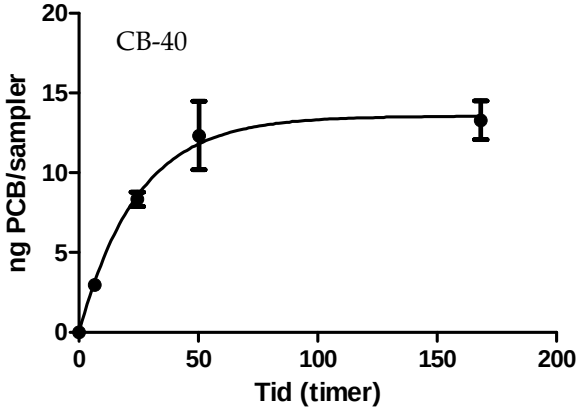
ENVS sample number	Collaborator's number	Sample	Date sample receipt	Date extraction	ENVS batch number
2013-12148	5429-P1	Petri dish	19-06-2013	26-06-2013	#13-08
2013-12149	5429-P1	Petri dish	19-06-2013	26-06-2013	#13-08
2013-12150	5429-P1	Petri dish	20-06-2013	26-06-2013	#13-08
2013-12151	5429-P1	Petri dish	20-06-2013	26-06-2013	#13-08
2013-12152	5429-P1	Petri dish	21-06-2013	26-06-2013	#13-08
2013-12153	5429-P1	Petri dish	21-06-2013	26-06-2013	#13-08
2013-12163	5429-P1	Petri dish	26-06-2013	26-06-2013	#13-08
2013-12164	5429-P1	Petri dish	26-06-2013	26-06-2013	#13-08
2013-12154	5429-P1	Paper	19-06-2013	26-06-2013	#13-08
2013-12155	5429-P1	Paper	19-06-2013	26-06-2013	#13-08
2013-12157	5429-P1	Paper	20-06-2013	26-06-2013	#13-08
2013-12158	5429-P1	Paper	20-06-2013	26-06-2013	#13-08
2013-12160	5429-P1	Paper	21-06-2013	26-06-2013	#13-08
2013-12161	5429-P1	Paper	21-06-2013	26-06-2013	#13-08
2013-12165	5429-P1	Paper	26-06-2013	26-06-2013	#13-08
2013-12166	5429-P1	Paper	26-06-2013	26-06-2013	#13-08
2013-12181	Rum_A	Petri dish	10-07-2013	17-07-2013	#13-09
2013-12182	Rum_A	Petri dish	10-07-2013	17-07-2013	#13-09
2013-12183	Rum_A	Petri dish	10-07-2013	17-07-2013	#13-09
2013-12184	Rum_A	Petri dish	10-07-2013	17-07-2013	#13-09
2013-12185	Rum_A	Petri dish	11-07-2013	17-07-2013	#13-09
2013-12186	Rum_A	Petri dish	11-07-2013	17-07-2013	#13-09
2013-12187	Rum_A	Petri dish	16-07-2013	17-07-2013	#13-09
2013-12188	Rum_A	Petri dish	16-07-2013	17-07-2013	#13-09
2013-12189	Rum_A	Paper	10-07-2013	17-07-2013	#13-09
2013-12190	Rum_A	Paper	10-07-2013	17-07-2013	#13-09
2013-12192	Rum_A	Paper	10-07-2013	17-07-2013	#13-09
2013-12193	Rum_A	Paper	10-07-2013	17-07-2013	#13-09
2013-12195	Rum_A	Paper	11-07-2013	17-07-2013	#13-09
2013-12196	Rum_A	Paper	11-07-2013	17-07-2013	#13-09
2013-12198	Rum_A	Paper	16-07-2013	17-07-2013	#13-09
2013-12199	Rum_A	Paper	16-07-2013	17-07-2013	#13-09
2013-12201	129496-L11-R4	Petri dish	17-07-2013	17-07-2013	#13-09
2013-12202	129496-L11-R5	Petri dish	17-07-2013	17-07-2013	#13-09
2013-12203	129496-L12-R4	Petri dish	17-07-2013	17-07-2013	#13-09
2013-12204	129496-L12-R5	Petri dish	17-07-2013	17-07-2013	#13-09
2013-12206	129496-L11-R1	Paper	17-07-2013	17-07-2013	#13-09
2013-12207	129496-L11-R2	Paper	17-07-2013	17-07-2013	#13-09
2013-12209	129496-L12-R1	Paper	17-07-2013	17-07-2013	#13-09
2013-12210	129496-L12-R2	Paper	17-07-2013	17-07-2013	#13-09
2013-12236	19422-L16-R4	Petri dish	27-08-2013	28-08-2013	#13-16
2013-12237	19422-L16-R5	Petri dish	27-08-2013	28-08-2013	#13-16
2013-12238	19422-L17-R4	Petri dish	27-08-2013	28-08-2013	#13-16
2013-12239	19422-L17-R5	Petri dish	27-08-2013	28-08-2013	#13-16
2013-12240	19422-L18-R4	Petri dish	27-08-2013	28-08-2013	#13-16
2013-12241	19422-L18-R5	Petri dish	27-08-2013	28-08-2013	#13-16
2013-12242	19422-L16-R1	Paper	27-08-2013	28-08-2013	#13-16
2013-12243	19422-L16-R2	Paper	27-08-2013	28-08-2013	#13-16
2013-12245	19422-L17-R1	Paper	27-08-2013	28-08-2013	#13-16
2013-12246	19422-L17-R2	Paper	27-08-2013	28-08-2013	#13-16
2013-12248	19422-L18-R1	Paper	27-08-2013	28-08-2013	#13-16
2013-12249	19422-L18-R2	Paper	27-08-2013	28-08-2013	#13-16
2013-12556	10508-L1-4	Petri dish	01-11-2013	01-11-2013	#13-23
2013-12557	10508-L1-5	Petri dish	01-11-2013	01-11-2013	#13-23
2013-12558	10508-L3-4	Petri dish	01-11-2013	01-11-2013	#13-23
2013-12559	10508-L3-5	Petri dish	01-11-2013	01-11-2013	#13-23
2013-12560	10508-L1-1	Paper	01-11-2013	01-11-2013	#13-23
2013-12561	10508-L1-2	Paper	01-11-2013	01-11-2013	#13-23
2013-12563	10508-L3-1	Paper	01-11-2013	01-11-2013	#13-23
2013-12564	10508-L3-2	Paper	01-11-2013	01-11-2013	#13-23
2014-12929	Viborg L8-1	Petri dish	31-03-2014	01-04-2014	#14-05
2014-12930	Viborg L8-2	Petri dish	31-03-2014	01-04-2014	#14-05
2014-12931	Viborg L11-1	Petri dish	31-03-2014	01-04-2014	#14-05
2014-12932	Viborg L11-2	Petri dish	31-03-2014	01-04-2014	#14-05
2014-12933	Viborg L12-1	Petri dish	31-03-2014	01-04-2014	#14-05
2014-12934	Viborg L12-2	Petri dish	31-03-2014	01-04-2014	#14-05
2014-12935	Viborg L8-1	Paper	31-03-2014	01-04-2014	#14-05
2014-12936	Viborg L8-2	Paper	31-03-2014	01-04-2014	#14-05
2014-12938	Viborg L11-1	Paper	31-03-2014	01-04-2014	#14-05
2014-12939	Viborg L11-2	Paper	31-03-2014	01-04-2014	#14-05
2014-12940	Viborg L12-1	Paper	31-03-2014	01-04-2014	#14-05
2014-12941	Viborg L12-2	Paper	31-03-2014	01-04-2014	#14-05

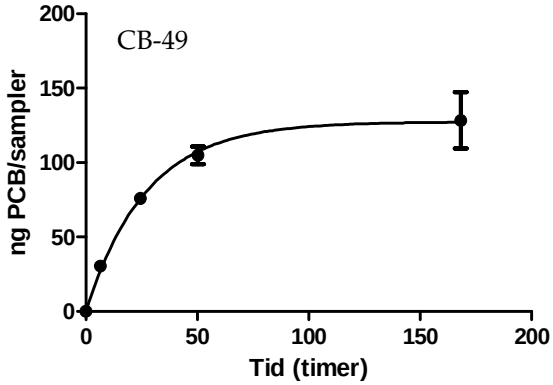
Annex 6: Results of time series A and B for silicone-coated paper and curves fitted according to equation 2 of the main report

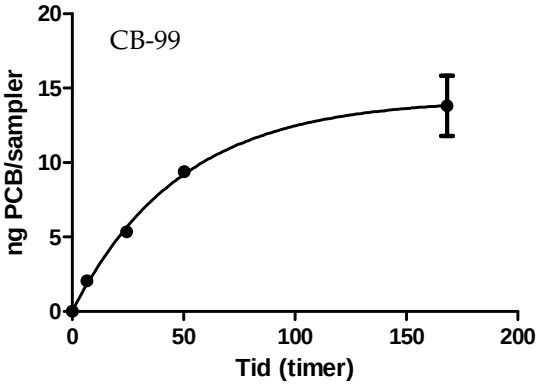
Time series A:

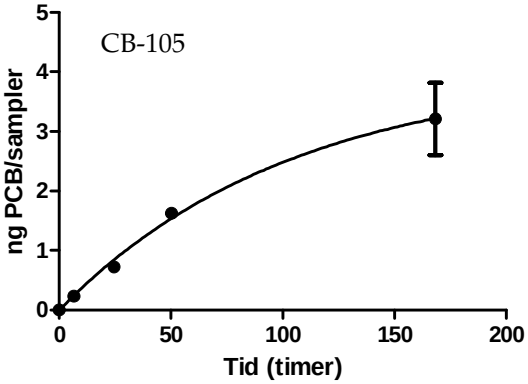
Data of CB-28, CB-44, CB-52 and CB-101 are shown in the main report. Congeners with non-significant results are not shown.

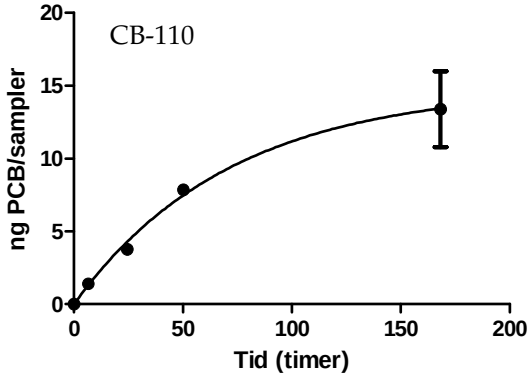


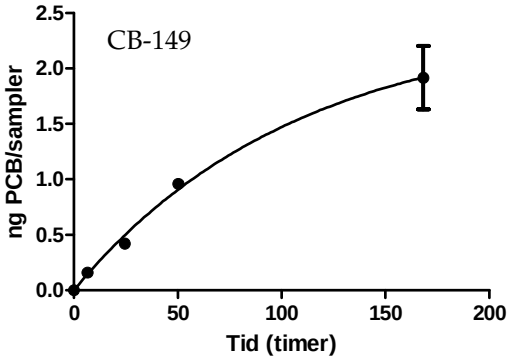


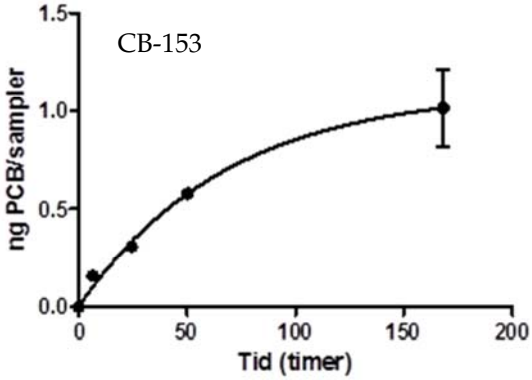






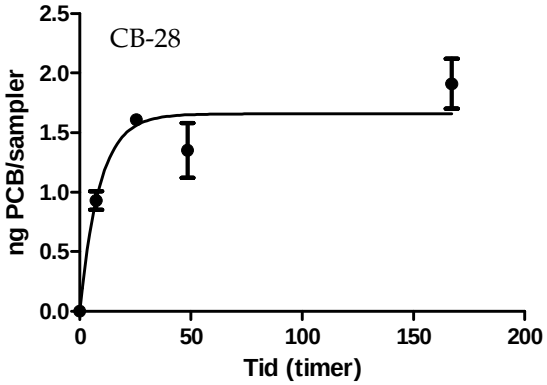


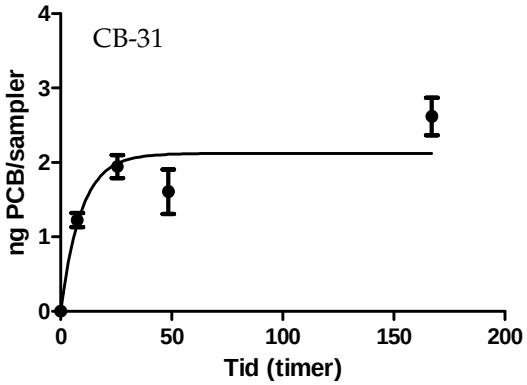

CB-149
ng PCB/sampler
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
Tid (timer)

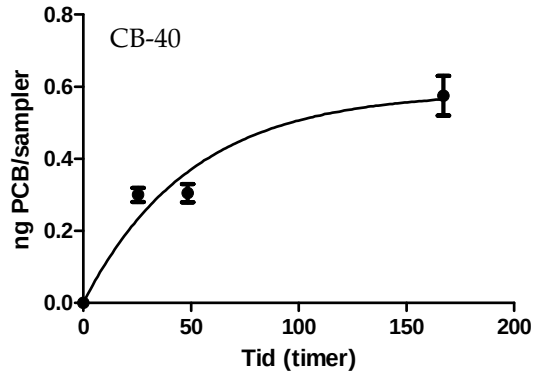

CB-153
ng PCB/sampler
1.5
1.0
0.5
0.0
0
50
100
150
200
Tid (timer)

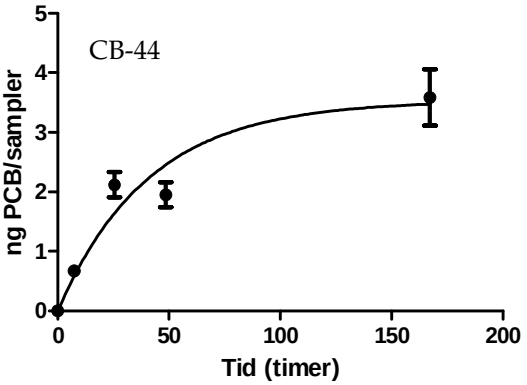
Time series B:

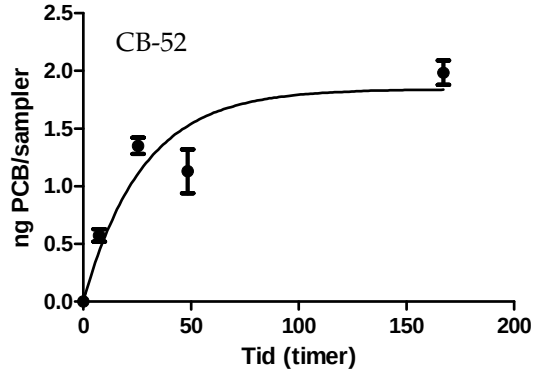
Data of CB-52 and CB-101 are shown in the main report. Congeners with non-significant results are not shown.











Annex 7: Additional results for PCB congeners collected on silicone-coated paperaccording to equation 2

Time series A:

	C_∞ (ng/sampler)	Standard error C_∞ (ng/sampler)	k (hours^{-1})	Standard error k (hours^{-1})	R^2
CB-28	81.2	6.17	0.03046	0.006246	0.93
CB-31	96.1	7.29	0.03339	0.007032	0.93
CB-40	13.6	0.865	0.04082	0.007797	0.95
CB-44	114.6	6.07	0.03029	0.004321	0.97
CB-49	80.0	4.67	0.03556	0.005890	0.96
CB-52	127.3	6.96	0.03679	0.005781	0.96
CB-99	14.3	0.927	0.02061	0.003283	0.97
CB-101	20.9	1.66	0.01983	0.003843	0.95
CB-105	4.02	0.739	0.009619	0.003379	0.94
CB-110	14.9	1.79	0.01390	0.003699	0.94
CB-149	2.42	0.396	0.009342	0.002886	0.96
CB-153	1.11	0.149	0.01468	0.004704	0.94

Time series B:

	C_∞ (ng/sampler)	Standard error C_∞ (ng/sampler)	k (hours^{-1})	Standard error k (hours^{-1})	R^2
CB-28	1.66	0.120	0.1118	0.03621	0.89
CB-31	2.12	0.197	0.1082	0.04462	0.83
CB-40	0.59	0.0583	0.01998	0.004899	0.93
CB-44	3.53	0.365	0.02447	0.006319	0.90
CB-49	1.84	0.193	0.03618	0.01061	0.87
CB-52	4.26	0.440	0.03563	0.01024	0.88
CB-101	11.0	1.25	0.01215	0.002877	0.96
CB-110	20.4	7.96	n.s.	-	0.97

Annex 8: PCB data (petri dishes) used for the calibration of the passive sampler (ng/sampler/24 hours)

All concentrations (ng/sampler) were normalised to a sampling period of 24 hours. The compounds in bold were those for which concentrations were available from Rambøll's measurements in ng/m^3, see Table 25.

	Test I				Test II					
Rambøll's sample ID	129496-L11-R4	129496-L11-R5	129496-L12-R4	129496-L12-R5	19422-L16-R4	19422-L16-R5	19422-L17-R4	19422-L17-R5	19422-L18-R4	19422-L18-R5
AU/ENVS sample ID	13-12201	13-12202	13-12203	13-12204	13-12236	13-12237	13-12238	13-12239	13-12240	13-12241
CB-28	**8.26**	**9.27**	**4.92**	**6.87**	**52.25**	**49.85**	**49.27**	**49.48**	**18.02**	**16.66**
CB-31	8.80	9.83	5.29	6.66	67.04	64.32	67.82	66.79	24.70	22.05
CB-40	0.29	0.29	0.29	0.29	7.48	5.91	7.40	6.36	2.44	2.36
CB-44	4.82	5.28	2.56	3.44	59.38	57.56	63.39	56.11	21.52	25.60
CB-49	3.69	4.77	1.16	1.75	49.97	44.42	52.49	43.88	16.41	19.45
CB-52	**8.86**	**10.59**	**2.99**	**5.27**	**81.35**	**70.11**	**77.34**	**74.66**	**38.57**	**38.13**
CB-99	2.31	0.90	1.06	1.07	2.93	2.77	3.23	3.39	5.81	4.74
CB-101	**3.08**	**7.48**	**2.75**	**7.38**	**6.84**	**6.03**	**4.51**	**7.41**	**12.56**	**9.99**
CB-105	< 0.12	< 0.12	1.09	0.86	17.06	13.10	11.09	11.48	11.76	10.81
CB-110	1.01	1.43	0.59	0.68	4.43	3.80	4.09	4.41	7.77	7.78
CB-118	**4.08**	**4.75**	**1.43**	**1.73**	**< 0.19**	**< 0.19**	**< 0.19**	**0.37**	**2.53**	**3.44**
CB-128	< 0.26	< 0.26	< 0.26	< 0.26	0.37	0.25	0.32	0.31	0.33	0.21
CB-138	**< 0.13**	**< 0.13**	**0.30**	**0.74**	**5.73**	**2.26**	**1.59**	**2.25**	**2.87**	**2.17**
CB-149	0.35	0.47	0.51	0.67	< 0.19	< 0.19	< 0.19	< 0.19	1.39	1.43
CB-151	0.97	1.04	1.49	1.08	< 0.18	< 0.18	< 0.19	< 0.18	1.25	1.71
CB-153	**< 0.28**	**< 0.28**	**< 0.28**	**< 0.28**	**14.73**	**8.23**	**2.84**	**4.64**	**3.93**	**3.58**
CB-156	< 0.14	< 0.14	< 0.14	< 0.14	< 0.20	< 0.20	< 0.20	< 0.20	0.27	0.21
CB-180	**< 0.15**	**< 0.15**	**< 0.15**	**< 0.15**	**< 0.21**	**< 0.21**	**< 0.21**	**< 0.21**	**< 0.21**	**< 0.21**
CB-187	< 0.13	< 0.13	< 0.13	< 0.13	0.57	2.12	2.21	0.73	0.80	1.35
CB-188	< 0.14	< 0.16	< 0.16	< 0.16	< 0.20	< 0.20	< 0.20	< 0.20	< 0.19	< 0.19

Annex 9: PCB data (silicone-coated paper) used for the calibration of the passive sampler (ng/sampler/24 hours)

All concentrations (ng/sampler) were normalised to a sampling period of 24 hours. The compounds in bold were those for which concentrations were available from Rambøll's measurements in ng/m^3, see Table 25.

	Test I				Test II					
Rambøll's sample ID	129496-L11-R1	129496-L11-R2	129496-L12-R1	129496-L12-R2	19422-L16-R1	19422-L16-R2	19422-L17-R1	19422-L17-R2	19422-L18-R1	19422-L18-R2
AU/ENVS sample ID	13-12206	13-12207	13-12209	13-12210	13-12242	13-12243	13-12245	13-12246	13-12248	13-12249
CB-28	**12.17**	**8.99**	**6.62**	**4.13**	**113.31**	**52.75**	**163.99**	**92.66**	**31.56**	**27.48**
CB-31	12.16	8.74	5.96	3.58	155.41	72.92	231.17	132.34	44.87	37.76
CB-40	1.22	0.85	0.63	0.43	43.26	21.36	74.54	44.17	19.60	13.75
CB-44	16.68	11.63	7.59	4.98	254.53	120.41	450.35	252.28	121.76	91.85
CB-49	10.51	7.30	4.89	3.11	194.10	87.02	294.13	190.88	76.61	56.55
CB-52	**35.32**	**24.81**	**17.21**	**10.89**	**312.39**	**145.96**	**495.88**	**302.14**	**165.64**	**119.31**
CB-99	6.64	4.89	4.62	3.21	27.23	13.65	45.57	27.82	41.31	26.52
CB-101	**18.58**	**13.92**	**13.20**	**9.27**	**58.85**	**28.61**	**99.58**	**59.98**	**116.22**	**72.00**
CB-105	1.38	1.06	1.65	1.21	7.53	4.09	12.83	7.74	16.05	9.49
CB-110	8.72	6.35	6.91	4.84	36.76	19.28	60.41	39.43	85.37	52.03
CB-118	**3.73**	**2.73**	**3.17**	**2.23**	**13.67**	**7.22**	**24.02**	**14.30**	**37.52**	**21.90**
CB-128	0.36	0.24	0.44	0.24	0.43	0.25	0.79	0.45	3.11	1.70
CB-138	**1.39**	**1.04**	**1.53**	**1.06**	**2.54**	**1.29**	**4.21**	**2.67**	**13.05**	**8.39**
CB-149	3.49	2.40	5.00	3.39	6.39	3.24	10.46	7.06	26.39	15.12
CB-151	1.22	0.89	2.63	1.71	2.49	1.12	4.80	2.58	6.76	3.95
CB-153	**1.76**	**1.36**	**2.81**	**2.14**	**3.15**	**1.45**	**5.25**	**3.24**	**14.68**	**8.81**
CB-156	< 0.14	< 0.14	< 0.14	< 0.14	< 0.20	< 0.20	< 0.20	< 0.20	0.32	< 0.20
CB-180	**< 0.15**	**< 0.15**	**0.58**	**0.46**	**< 0.21**	**< 0.21**	**0.42**	**0.23**	**0.32**	**0.21**
CB-187	< 0.13	< 0.13	0.98	0.69	0.59	0.26	1.46	0.73	0.72	0.33
CB-188	< 0.14	< 0.14	< 0.14	< 0.14	< 0.20	< 0.20	< 0.20	< 0.20	< 0.19	< 0.19

Annex 10: PCB data (petri dishes) used for the validation of the passive sampler (ng/sampler/24 hours)

All concentrations (ng/sampler) were normalised to a sampling period of 24 hours. The compounds in bold were those for which concentrations were available from Rambøll's measurements in ng/m^3, see Table 25. n.a.: no data available, due to interferences in the chromatogram.

	Test III				Test IV					
Rambøll's sample ID	10508-L1-4	10508-L1-5	10508-L3-4	10508-L3-5	Viborg-L-8-1	Viborg-L8-2	Viborg-L11-1	Viborg-L11-2	Viborg-L12-1	Viborg-L12-2
AU/ENVS sample ID	13-12556	13-12557	13-12558	13-12559	14-12929	14-12930	14-12931	14-12932	14-12933	14-12934
CB-28	**4.91**	**4.31**	**n.a.**	**6.32**	**18.06**	**15.09**	**18.07**	**21.17**	**56.53**	**56.36**
CB-31	8.16	2.49	n.a.	11.16	13.72	12.18	14.75	16.77	64.50	61.44
CB-40	< 0.26	< 0.26	1.34	0.99	2.03	1.47	3.31	4.76	8.20	8.12
CB-44	1.43	1.27	5.15	5.11	5.03	5.52	18.99	18.29	47.01	44.29
CB-49	5.38	5.71	6.76	6.80	5.41	6.19	12.94	12.53	36.81	34.01
CB-52	**4.96**	**4.49**	**8.42**	**7.63**	**10.09**	**10.53**	**22.54**	**22.80**	**59.35**	**54.18**
CB-99	9.12	5.54	4.67	10.16	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
CB-101	**2.86**	**2.85**	**1.98**	**2.84**	**< 0.16**	**0.44**	**2.06**	**1.76**	**2.70**	**2.80**
CB-105	1.11	1.25	1.24	1.23	< 0.26	< 0.26	< 0.27	< 0.27	0.26	0.42
CB-110	< 0.24	< 0.24	< 0.24	< 0.24	< 0.14	< 0.14	0.68	0.31	0.45	0.50
CB-118	**< 0.24**	**0.33**	**1.57**	**0.35**	**1.28**	**1.11**	**0.95**	**1.66**	**1.67**	**1.78**
CB-128	< 0.24	< 0.24	< 0.24	< 0.24	< 0.14	< 0.14	< 0.15	< 0.15	< 0.15	< 0.15
CB-138	**4.25**	**3.52**	**< 0.23**	**1.19**	**< 0.14**	**n.a.**	**2.14**	**1.56**	**< 0.14**	**< 0.14**
CB-149	1.76	1.62	2.00	2.00	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15	< 0.15
CB-151	< 0.46	< 0.46	< 0.47	< 0.47	< 0.28	< 0.28	< 0.29	< 0.29	< 0.28	< 0.28
CB-153	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**0.58**	**0.49**	**n.a.**	**n.a.**	**n.a.**
CB-156	< 0.51	< 0.51	< 0.52	< 0.52	n.a.	0.15	0.17	n.a.	n.a.	n.a.
CB-180	**< 0.27**	**< 0.27**	**< 0.27**	**< 0.27**	**< 0.33**	**< 0.33**	**< 0.34**	**< 0.34**	**< 0.33**	**< 0.33**
CB-187	< 0.48	< 0.48	< 0.48	< 0.24	< 0.29	< 0.29	< 0.30	< 0.30	< 0.29	< 0.29
CB-188	< 0.25	< 0.25	< 0.26	< 0.26	< 0.15	< 0.15	< 0.16	< 0.16	< 0.16	< 0.16

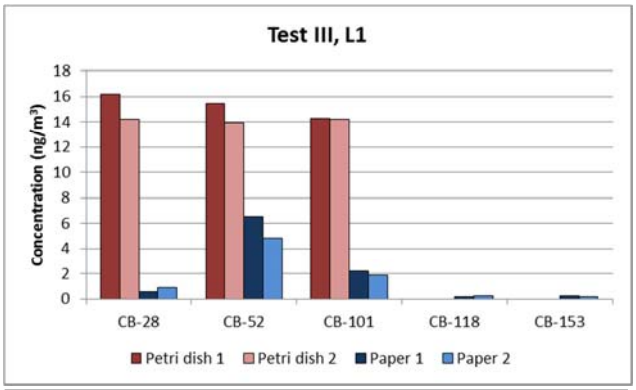
Annex 11: PCB data (silicone-coated paper) used for the validation of the passive sampler (ng/sampler/24 hours)

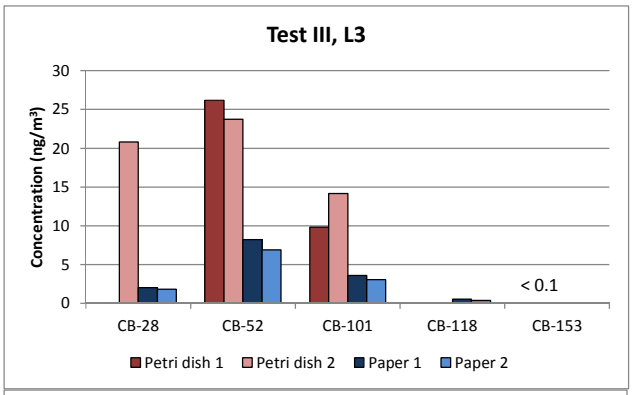
All concentrations (ng/sampler) were normalised to a sampling period of 24 hours. The compounds in bold were those for which concentrations were available from Rambøll's measurements in ng/m^3, see **Table 25**.

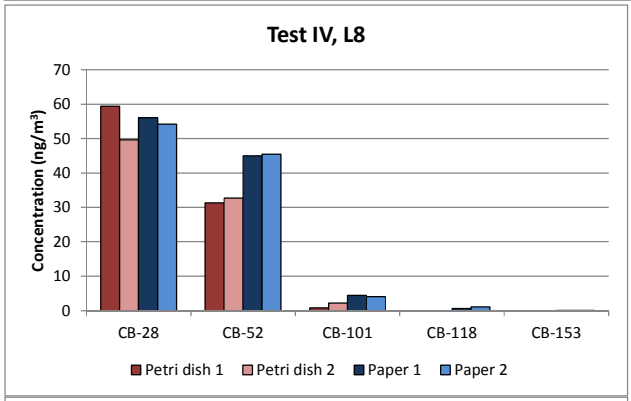
	Test III				Test IV					
Rambøll's sample ID	10508-L1-1	10508-L1-2	10508-L3-1	10508-L3-2	Viborg-L-8-1	Viborg-L8-2	Viborg-L11-1	Viborg-L11-2	Viborg-L12-1	Viborg-L12-2
AU/ENVS sample ID	13-12560	13-12561	13-12563	13-12564	14-12935	14-12936	14-12938	14-12939	14-12941	14-12942
CB-28	**0.38**	**0.60**	**1.32**	**1.19**	**35.96**	**34.77**	**41.74**	**65.99**	**122.70**	**71.86**
CB-31	2.41	1.86	3.48	3.24	44.28	43.28	51.67	82.94	151.73	87.84
CB-40	0.26	0.26	0.26	0.26	7.26	6.82	21.71	30.57	34.02	21.87
CB-44	3.77	3.34	5.36	5.14	52.53	50.61	121.83	177.55	224.93	138.38
CB-49	2.64	1.73	3.06	2.65	38.19	38.78	79.71	116.76	158.35	100.36
CB-52	**8.85**	**6.51**	**11.09**	**9.32**	**60.74**	**61.23**	**120.81**	**181.04**	**262.73**	**152.76**
CB-99	0.43	0.21	< 0.19	0.36	4.52	4.76	15.17	19.90	16.32	10.35
CB-101	**4.06**	**3.43**	**6.60**	**5.64**	**8.10**	**7.45**	**31.71**	**42.30**	**34.83**	**22.21**
CB-105	0.43	0.34	0.63	0.63	0.69	0.54	3.13	3.96	2.21	1.55
CB-110	2.21	1.74	3.30	2.75	4.28	3.61	20.92	27.46	18.95	12.26
CB-118	**0.65**	**0.76**	**1.61**	**1.16**	**1.85**	**3.11**	**7.49**	**8.80**	**6.06**	**4.41**
CB-128	< 0.24	< 0.24	< 0.24	< 0.24	< 0.14	< 0.14	< 0.15	< 0.15	< 0.15	< 0.15
CB-138	**0.71**	**0.55**	**0.29**	**0.26**	**< 0.14**	**< 0.14**	**0.34**	**0.45**	**0.24**	**0.26**
CB-149	0.42	0.52	0.70	1.23	< 0.15	< 0.15	2.07	2.65	2.32	1.40
CB-151	0.77	0.59	0.70	0.67	< 0.28	< 0.28	0.77	0.94	1.02	0.72
CB-153	**0.62**	**0.50**	**< 0.26**	**< 0.26**	**< 0.31**	**< 0.31**	**0.77**	**1.05**	**0.76**	**0.60**
CB-156	< 0.26	< 0.26	< 0.26	< 0.26	< 0.15	< 0.15	< 0.16	< 0.16	< 0.16	< 0.16
CB-180	**< 0.27**	**< 0.27**	**< 0.27**	**< 0.27**	**< 0.33**	**< 0.33**	**< 0.34**	**< 0.34**	**< 0.33**	**< 0.33**
CB-187	< 0.24	< 0.24	< 0.24	< 0.24	< 0.29	< 0.29	< 0.30	< 0.30	< 0.29	< 0.29
CB-188	< 0.25	< 0.25	< 0.26	< 0.26	< 0.15	< 0.15	< 0.16	< 0.16	< 0.16	< 0.16

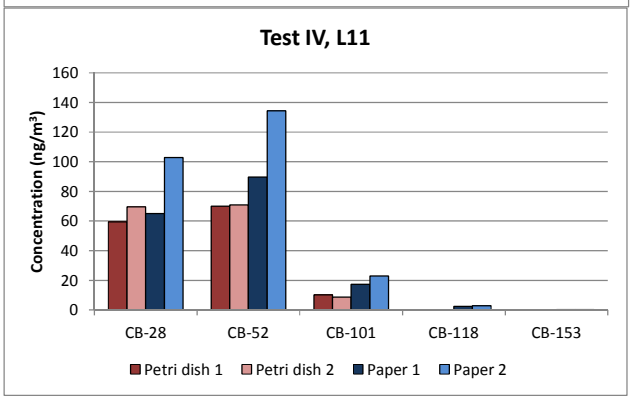
Annex 12: Plots of air concentrations (ng/m^3) calculated from passive sampling data

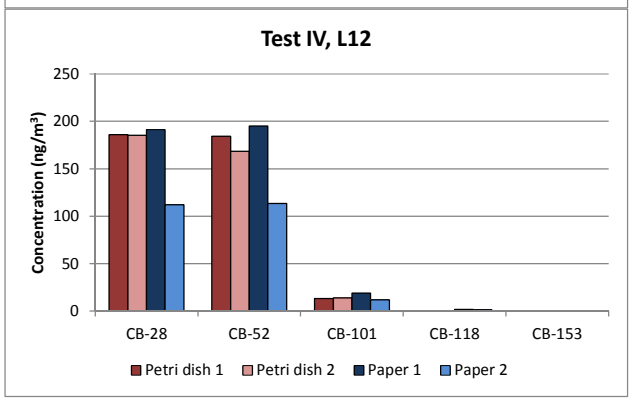
CB-118 and CB-153 could only be determined for silicone-coated paper because of a lack of calibration for the petri dishes.











Annex 13: Prisestimat, 7. juni 2012

Baggrund

Projektets anden fase havde til formål at teste og videreudvikle de typer af passive opsamlere der blev vurderet som potentielt egnede til en indendørs luftmåling af PCB efter projektets første fase. Blandt flere andre parametre undersøgte vi i fase 2 hvordan en frigivelsesrate, dvs. hastigheden af PCB'ernes overførsel fra silikonefasen til luft, er påvirket af ændringer i luftbevægelsen hen over opsamleren. Denne parameter kan få stor betydning for resultatets nøjagtighed, hvis optagelsesrater varierer under forskellige flowforhold. Eksperimenterne viste en tydelig effekt på de fleste opsætninger, som dog var mindst udpræget for en opsamler med en stor overflade (petriskåle med silikone) og dermed høje optagelsesrater.

På basis af resultaterne fra projektets anden fase blev der foreslået tre typer opsamlere til det videre arbejde i fase 3:

- Petriskåle med et tyndt lag silikone
- Standardiserede optagelsesbetingelser med konstante og reproducerbare lufthastigheder, dvs. opsamleren eller luften bevæges på en defineret måde, f.eks. kan opsamleren sættes direkte på en lille ventilator.
- Ligevægtsopsamling i stedet for kinetisk opsamling. Ligevægten kan opnås indenfor det ønskede tidsrum (ca. 8 timer) ved at kombinere en stor overflade med et tyndt silikonelag (f.eks. silikone på papir).

Formål med dette notat

For at kunne sammenligne de forventede udgifter af en passiv måling med konventionelle målinger har Energistyrelsen bedt om et prisestimat for de tre foreslåede formater. Dette notat gør et forsøg på at estimere udgifterne for den første (**petriskåle med silikone-skive**) og sidste (**ligevægtsopsamling på et silikone-lag på papir**) af de tre forslag. For det andet forslag (standardiserede betingelser) vil det være nødvendigt at konkretisere opsætningen, for at kunne indhente priser på udstyr og materialet.

Derudover estimeres udgifterne for **glas med et støbt silikone-lag** (forsøg I i projektets anden fase). Pga. meget lave elimineringsrater var det ikke muligt at vurdere indflydelsen af varierende flowforhold på denne opsamler i projektets anden fase. Da der også foreligger prisinformationer, er de også medtaget i dette notat.

Nedenstående beregninger og estimater fokuserer på materialet og tidsforbruget forbundet med fremstilling og ibrugtagning af de passive opsamlere. Analysearbejdet til bestemmelse af PCB-indholdet vil være den samme som i tilfælde af en fugeprøve, eller mindre.

Estimerede udgifter

Tabel 1 sammenfatter de forventede udgifter der er estimeret for de tre typer opsamlere. "Materialet" omfatter glasvarerne og silikonen, klargøringen dækker over støbeprocessen og rensningen af silikonen. For ligevægtsopsamleren vurderes der at kunne anvende almindeligt bagepapir uden forbehandling. Opsamlerens performance bør dog undersøges nærmere. De detaljerede beregninger der ligger til grunde for dette estimat fremgår af Bilag 1.

Tabel 1. Estimerede udgifter/stk. til tre typer passive opsamlere.

Opsamler	Materiale	Klargøring [a)]	Anvendelse	Samlede udgifter [b)]
Petriskåle med en tynd silikone-skive	Ca. 60 kr.	Ca. 30 kr.	Meget nem og hurtig	Ca. 90 kr.
Glas med støbt lag silikone	Ca. 20 kr.	Ca. 50 kr.	Meget nem og hurtig	Ca. 70 kr.
Ligevægtopsamling med silikone på papir	< 1 kr [c)]	Ingen	Nem håndtering og analyse. Performance skal undersøges nærmere.	Meget lave, men kræver nærmere undersøgelse.

[a)] Materiale og tid, se detaljer i Bilag 1.

[b)] Uden tidsforbrug til opsætning og nedtagning af opsamleren, som dog forventes at være lille.

[c)] Almindeligt bagepapir

Bilag 1: Beregninger i dette prisestimat

1. Petriskåle med en tynd silikone-skive

1.1 Materialeudgifter

Til projektet er petriskåle i glas købt hos VWR i Herlev (www.vwr.com). Indkøbsprisen var 26,04 kr. per petriskål (inkl. låg). Der er også angivet i rapporten, at glasskålene muligvis kan erstattes af dåser af metal som vil være mere robuste. For at undgå kontaminering vil det være vigtigt at vælge et materiale der ikke er behandlet med kemikalier, f.eks. i lak eller farver. Det er også muligt at der kan bruges andre typer petriskåler med lavere pris.

I projektet er der brugt silikoneplader med en tykkelse på 0,01 inch (ca. 0,25 mm) fra Speciality Silicone Products (SSP), Ballston Spa, NY, USA (www.sspinc.com). Pladerne har en størrelse af 12 inch x 12 inch, svarende til ca. 30,5 cm x 30,5 cm. Der antages derfor, at der kan produceres 4 skiver à 15 cm diameter for hvert ark silikone. Prisen for 1 ark silikone er $27 (ca. 137 kr). 1 skive vil dermed koste ca. 34,25 kr. i materialet.

Firmaet Mikrolab A/S i Aarhus (www.mikrolab.dk) er blevet kontaktet omkring et tilbud på fremstilling af skiver i den passende størrelse. Tilbuddet er sammenfattet i Tabel 2. På basis af en produktionsmængde på 200 stk. vil fremstillingen af 1 skive dermed koste ca. 8 kr. Prisen vil falde til ca. 3 kr. ved bestilling af 1000 stk.

Tabel 1. Vejledende priser i danske kroner (DKK) for fremstilling af silikoneskiver.

200 stk.	1000 stk.	Forhandler	Reference
1675	2687,5	Mikrolab, Aarhus, DK	E-mail fra Brian Nyborg, Mikrolab

1.2 Klargøring

Silikonen skal renses før ibrugtagning, f.eks. ved at lægge hver skive i 100-200 ml acetone. Opløsningsmiddel skal være af høj renhed og blev indkøbt til projektet til ca. 200 kr./2,5 l. 150 ml acetone koster dermed 12 kr.

I løbet af en arbejdsdag kan der renses ca. 100 skiver. Med en timesats på 332 kr. for laboranter og en effektiv arbejdstid på 6 timer svarer dette til ca. 20 kr. per opsamler.

2. Glas med et støbt silikone-lag

2.1 Materialeudgifter

I projektet er der brugt brune glas på 60 ml som er købt fra Apodan Nordic A/S i København (www.apodan.dk). Prisen på et glas var 5,67 kr.

Silikonen er købt hos Institut für Anaplastologie Velten & Hering GbR i Genthin, Tyskland (www.epithesen.de) og koster 165,50 Euro (ca. 1241 kr.) for en pakke på 454 g. Til hvert glas bruges ca. 5 g silikonen, hvilket svarer til ca. 14 kr. per opsamler.

2.2 Klargøring

Støbeprocessen af 200 opsamlere med efterfølgende hærdning og rensning af materialet vil tage ca. 4 arbejdsdage for en laborant. Med en timesats på 332 kr. for laboranter og en effektiv arbejdstid på 6 timer om dagen svarer dette til ca. 40 kr. per opsamler. Til rensningen af silikonen bruges der ca. 150 ml acetone som koster ca. 12 kr. (se 1.2).

3. Ligevægtsopsamlingen med et tyndt silikone-lag på papir

Som udgangspunkt vælges der almindeligt bagepapir som består af cellulose med et tyndt lag silikone på begge sider. En æske bagepapir med enkelte ark koster ca. 10 kr. (www.superbest.dk; www.abenaonline.dk), dvs. et enkelt ark vil koste < 1 kr. Der forventes ikke at materialet skal forbehandles. Denne form for opsamling har ikke været undersøgt i projektet endnu og er principielt forskellig fra den kinetiske opsamling, idet der ikke bestemmes en opsamlingsrate, men en fordelingskoefficient mellem opsamleren og mediet (luft).

PASSIVE SAMPLING OF POLYCHLORINATED BIPHENYLS (PCB) IN INDOOR AIR: TOWARDS A COST-EFFECTIVE SCREENING TOOL

PCBs were widely used in construction materials in the 1906s and 1970s, a period of high building activity in Denmark. The objective of this study was therefore to use passive sampling techniques to develop a simple and cost-effective screening tool for PCBs in indoor air. The study proceeded in three phases combining a literature review, laboratory experiments and measurements in buildings potentially containing PCBs in indoor air. The laboratory experiments showed a strong influence of air velocity on the PCB partitioning between air and the passive sampler. Based on the results of the first two phases and comments from experts in the field of PCB containing construction materials, a kinetic sampler (petri dish with silicone) and a potential equilibrium sampler (silicone-coated paper) were tested in buildings. Calibration and validation were based on conventional active sampling, for both methods in their kinetic sampling phase. The methods were sensitive and precise, but tended to overestimate the concentration obtained by active sampling. More work will be needed to test the silicone-coated paper under equilibrium sampling conditions.

ISBN: 978-87-7156-109-8
ISSN: 2245-0203