Chemosphere 160 (2016) 280–286

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Utilizing the partitioning properties of silicone for the passive sampling of polychlorinated biphenyls (PCBs) in indoor air

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HIGHLIGHTS

- The silicone-indoor air partitioning of PCBs is an air-side rate-limited process.
- Varying air velocity can affect silicone-indoor air partitioning of PCBs.
- PCBs reach equilibrium between air and silicone-coated paper within two weeks.
- Silicone disks allow time-integrating sampling of PCBs with constant uptake rates.
- The prototype samplers show high sensitivity and precision.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form
20 May 2016
Accepted 12 June 2016
Available online 6 July 2016

Handling Editor: Caroline Gaus

Keywords:
Air velocity
Buildings
Calibration
Equilibrium
Kinetics
Sampling rates

ABSTRACT

The former use of polychlorinated biphenyls (PCBs) in construction materials can lead to elevated indoor air concentrations. We studied the partitioning of PCB congeners between indoor air and silicone with a view to establish passive sampling of PCBs. The release of PCB congeners from silicone followed first order kinetics and confirmed air-side rate-limited mass transfer. Logarithmic elimination rate constants decreased linearly with the $\log K_{OA}$ values of the PCB congeners, but varied in a non-linear way with air velocity. Linear uptake of PCBs was found for silicone disks (0.5 mm thickness) in a petri dish, while PCBs reached equilibrium in silicone-coated paper sheets (0.001 mm silicone on each side) exposed to indoor air for 1–2 weeks. The ratios of equilibrium concentrations in silicone and conventionally measured air concentrations were roughly comparable with silicone-air partition coefficients, but further research is required for the determination of silicone-air partition coefficients. Avoiding performance reference compounds (PRCs) because of the indoor setting, the two formats were calibrated against conventional active measurements. Comparisons of air concentrations derived from active and kinetic passive sampling showed a divergence by factors of 2.4 and 2.0 (median values) for the petri dishes and the silicone-coated paper, respectively. With promising results for sensitivity and precision, the calibration of kinetic passive samplers remains the main challenge and will need suitable, non-hazardous PRCs. Equilibrium sampling indicated promising alternatives.

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http://dx.doi.org/10.1016/j.chemosphere.2016.06.054
0045-6535/

1. Introduction

Polychlorinated biphenyls (PCBs) were produced in quantities of at least 1.3 million tons in several industrial countries until their general phase out in the 1970s and 1980s (Breivik et al., 2002). Since 2004, PCBs have been included in the Stockholm Convention on Persistent Organic Pollutants (POPs) which aims to reduce and ultimately eliminate the production and use of POPs. Due to their persistence in the environment and adverse effects, environmental and human levels of PCBs are monitored in several international programs, such as those of the Oslo-Paris Commission for the Protection of the North-East Atlantic (OSPAR), the Arctic Monitoring and Assessment Programme (AMAP) and the United Nations Environment Programme (UNEP). While PCB concentrations have generally decreased, concentration changes have been minor in the last ten years, suggesting ongoing PCB emissions to the environment (Diamond et al., 2010; Vorkamp et al., 2011; Vorkamp, 2016).

Amongst these, the former use of PCBs in construction materials may be a non-negligible source of PCB emissions, and consequently, human exposure. PCBs were used in sealants, paints, flooring materials and associated finishing products and double-glazed windows (Andersson et al., 2004; Kohler et al., 2005; Rudel et al., 2008; Jartun et al., 2009). In Denmark and possibly other countries, the main PCB use occurred in the 1950s–1970s and coincided with a period of high construction activity, leading to a potentially high number of buildings with PCB containing materials (Frederiksen et al., 2012). Indoor air measurements in Denmark have documented that elevated PCB levels can occur in the indoor environment (Frederiksen et al., 2012), some of these exceeding the action limits of 300 and 3000 ng/m^3 recommended by the Danish Health Authority (DHA, 2013).

While most indoor air measurements of PCBs rely on low volume active sampling, i.e. a defined volume of air pumped through a sorbing material, passive sampling might offer some practical advantages such as easy handling and cost-effectiveness (Saini et al., 2015). In addition, time-integrating or equilibrium sampling might provide more direct links to exposure assessments. Passive sampling experiences with PCBs in indoor air exist for different materials and formats, e.g. semipermeable membrane devices (SPMDs), glasses coated with ethylene vinyl acetate (EVA), polyurethane foam (PUF) and sorbent-impregnated PUF (SIP) (Shoeib and Harner, 2002; Harner et al., 2003; Hazrati and Harrad, 2007; Genualdi and Harner, 2012). For some of these as well as PCB sampling in outdoor air, a variable and at times inconsistent sorption behavior has been observed, indicating complexities beyond factors like temperature and air flows which are known to influence sampling rates (Wania et al., 2003; Hazrati and Harrad, 2007; Armitage et al., 2013).

Based on promising results from other media (ter Laak et al., 2008; Jahnke and Mayer, 2010; Mäenpää et al., 2011), silicone, such as polydimethylsiloxane (PDMS), might be a suitable material for the passive sampling of PCBs in indoor air. The high permeability and rapid transfer of hydrophobic compounds into PDMS have contributed to widespread applications in the field of analytical chemistry, for example as stationary phases in gas chromatography and as a sorption material in solid phase micro extraction (SPME) (Seethapathy and Górecki, 2012). The purpose of our study was to (i) to determine the partitioning properties and kinetic characteristics of silicone for passive air sampling of PCBs. We hypothesized that silicone could serve as a passive sampling phase with ideal partitioning and mass transfer properties and that the mass transfer was rate-limited on the air side. (ii) Proof of principle testing of silicone-based passive air sampling, for operation in the kinetic and equilibrium regime. In this context, prototype passive samplers were applied in potentially contaminated buildings.

2. Materials and methods

The study included three main sets of experiments: Laboratory experiments with PCB spiked silicone and two field studies in PCB-containing buildings, as detailed below.

2.1. Laboratory experiments on PCB elimination from silicone

Elimination rates were determined for PCBs released from silicone at air flows of 0.1, 0.3 and 1 m/s. These experiments had the purpose of studying the partitioning between silicone and air for individual PCB congeners and to assess the effect of varying air velocities on the partitioning kinetics. The experiments were conducted for the following formats described in detail in the Supporting Information (Table S1): i) 2 mm silicone at the bottom of a 100 ml amber glass, ii) 0.25 mm silicone at the bottom of a 100 ml amber glass, iii) 0.1 mm silicone in a petri dish, iv) 2.5 mm silicone coating of a steel rod. In addition to experiment iv), the silicone-coated steel rods were also rotated on a magnetic stirrer.

Each format was spiked with 200 ng of individual PCB congeners (3500 ng for CB-3), which we expect to be clearly above equilibrium concentrations in the laboratory. The three different flows were established by placing the samples at different positions in a laboratory fume hood, partly shielded, as monitored by repeated flow measurements (HHF1001R, Omega Engineering Inc., Stamford, CT, USA). 2–3 spiked samples from each experiment defined start concentrations. The remaining samples, usually duplicates, were processed after pre-defined periods of time covering a total duration of four to eight weeks (Table S1). The elimination rate constant k is the slope of the regression line fitted to ln-transformed PCB concentrations over time (Equation (1)).

$$\ln C = \ln C_0 - k \cdot t \quad (1)$$

C_0: PCB amount at t_0 (ng); k: elimination rate constant (day^{-1}).

2.2. Time series in PCB-containing buildings

Two time series were conducted with silicone passive samplers to study the PCB uptake process, using the following formats (Fig. S1): A silicone disk of 0.5 mm thickness (Altec, St Austell, UK) in a 15 cm petri dish and a silicone-coated baking paper sheet (40 cm × 60 cm, double-sided coating of 0.001 mm silicone with 0.5 g Si/m^2, Metsä Tissue Corporation, Espoo, Finland). Only the silicone-coated paper was intended for passive sampling in the equilibrium regime. The silicone material used in the petri dishes was described in other studies (Rusina et al., 2007; Smedes et al., 2009).

Both silicone samplers were pre-cleaned in acetone, initially for 2 h. As this cleaning procedure was not sufficient for complete removal of interfering compounds in the gas chromatographic analyses, in particular for the silicone disks, their pre-cleaning time was extended to 130 h, following recommendations by Smedes and Booij (2012). The pre-cleaned silicone disks were placed in a petri dish, which then was closed with a glass lid and wrapped in aluminium foil. Both types of sampler were stored in sealed aluminium bags until sampling.

The sampling took place in a school (time series I) and the basement of an apartment building (time series II) over a period of one week, with sampling points after six hours, one, two and seven days. When the sampling was completed, 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. Gloves were worn at all times when the samplers were handled. All samples were duplicates, and non-