

# New passive samplers for chlorinated semivolatile organic pollutants in ambient air

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## Abstract

Two new types of passive samplers were designed and tested on semivolatile organic compounds. The first type (a spiral-rod sampler) consists of a low-density polyethylene membrane acting as a permeation film and a silicone elastomer as the receiving material; the second (a stir-bar sampler) has the same membrane material but a polydimethylsiloxane-coated stir bar acting as the collector phase and installed radially symmetrically in the sampler. The advantages of the new samplers are their simple design, low costs, and their easy processing via thermodesorption coupled with capillary gas chromatography and mass selective detection. In both samplers, the uptake of selected analytes was integrative over exposure periods of up to 384 h. The sampling rates calculated from a laboratory calibration study using the chlorinated semivolatiles hexachlorobenzene, hexachlorocyclohexane isomers and polychlorinated biphenyls ranged from  $88.1 \text{ ml h}^{-1}$  for  $\delta$ -hexachlorocyclohexane to  $3443 \text{ ml h}^{-1}$  for 2,2',5,5'-tetrachlorobiphenyl. A field trial at a hazardous waste dump near Bitterfeld, Germany, for up to 21 days combined with periodical determinations of air concentrations using low-volume sampling indicated that the new samplers can in principle be used in the field, although the sampling rates derived from the field results differed considerably from the laboratory findings. Nevertheless the preliminary results suggest that the new sampler types are promising for the long-term air monitoring of semivolatiles. © 2004 Elsevier Ltd. All rights reserved.

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## 1. Introduction

Chlorinated semivolatile organic compounds (SVOCs), such as the pesticides hexachlorobenzene, lindane (and its isomers) and polychlorinated biphenyls once used extensively all over the world, are now ubiquitous air pollutants. They are relatively stable in the

atmosphere and can undergo medium- to long-range transport. In contrast to many other chemicals, these chlorinated substances have a high bioaccumulation potential and can directly or indirectly affect non-target plants, terrestrial and aquatic organisms, and even local human populations (Unsworth et al., 1999). Because the transport and fate of these substances (and thus their actual or time-integrated atmospheric concentrations) cannot be predicted with sufficient accuracy, persistent chlorinated SVOCs need to be extensively monitored. Air is commonly monitored by analysing grab air samples (taken in canisters, bulbs or bags) or by

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pumping/sucking defined air volumes through liquid adsorbers or solid sorbent tubes and quantifying the analytes sorbed. These techniques can only measure momentary pollutant concentrations or values representing short time periods (i.e. a matter of hours). Moreover, such sampling techniques require considerable manpower and technical facilities such as pumps, a power supply, etc. By contrast, passive samplers record for longer sampling periods by integrating the pollutant concentration over several weeks or even months. The long accumulation periods mean passive samplers enable very low concentrations of target analytes to be detected. In addition, they usually have a very simple design and have no infrastructural requirements. Passive samplers can be divided into two categories in terms of their design and the enrichment principle used: permeative samplers and diffusive samplers (Górecki and Namieśnik, 2002).

Only a few of the passive sampling systems reported can be used for SVOCs (Brown and Harper, 2000; Krupa and Legge, 2000). The semipermeable membrane device (SPMD) developed by Huckins and co-workers at the US Geological Survey (Huckins et al., 1990) is the only system so far to have been used to a significant extent (Prest et al., 1995; Ockenden et al., 1998; Lohmann et al., 2001). A SPMD consists of lay-flat low-density polyethylene tubing enclosing a thin film of triolein. Standardized SPMDs are nowadays commercially available and sampling rates have been published for a number of SVOCs (especially PCBs, PAHs and some organochlorine pesticides). The main disadvantages of SPMDs are their relatively high price and the complex sample preparation procedure required to recover the accumulated target analytes from the collecting phase (triolein). Sample preparation usually takes the form of dialysis using large amounts of organic solvents followed by preconcentration and the elaborate cleanup of extracts prior to chromatographic analysis (Petty et al., 2000).

A more recent development is the use of solid-phase microextraction (SPME) fibres as passive samplers. Early studies have shown that adsorption effects may occur on the steel needle (Khaled and Pawliszyn, 2000). Moreover, analysis should be performed immediately after the sampling period because the storage of SPME fibres for more than 24h after field exposure can cause significant analyte losses (Müller et al., 2000). Other factors restricting the use of SPME fibres are the lack of valid sampling rates for most of the main organic air pollutants and the variability in the sampling capacity of fibres with the same type of coating, an area which has hardly been addressed yet (Popp and Paschke, 1999; Paschke et al., 2002).

Shoeb and Harner (2002) investigated the enrichment of polychlorinated biphenyls and naphthalenes on several passive sampling phases. Wennrich et al.

(2002) tested two types of new integrative passive samplers using hollow fibre membranes 250 µm thick. These types are convenient for the long-term monitoring of semivolatiles organic air pollutants.

The passive samplers developed and tested in our present study consisted of a low-density polyethylene foil 50 µm thick containing a silicone elastomer or a polydimethylsiloxane-coated stir bar as the receiving phase. Both these devices feature a large exchange area and a high sampling capacity. The compounds sampled on the silicone rod and coated stir bar are analysed solvent-free and without further cleanup using a thermodesorption unit coupled with gas chromatography/mass spectrometry (GC-MS).

We tested the newly developed passive samplers on the field air sampling of chlorinated SVOCs at the Grube Antonie landfill in Bitterfeld (near Leipzig, Germany). This landfill, a former lignite-mining pit, contains about 70000t waste products from discontinued lindane production (i.e.  $\alpha$ -,  $\beta$ - and  $\delta$ -hexachlorocyclohexane (HCH)) as well as other forms of hazardous chemical waste (chlorobenzenes, DDT, etc.). Even though the dump is now covered with a layer of soil overgrown with grass, bushes and some trees, it may still be responsible for the elevated concentrations of HCHs in the air and airborne particulate matter in the Bitterfeld region (Popp et al., 2000).

## 2. Experimental

### 2.1. Chemicals and materials

Hexachlorobenzene, hexachlorocyclohexane isomers ( $\alpha$ -,  $\gamma$ - and  $\delta$ -HCH) and various polychlorinated biphenyls (PCB 28, PCB 52 and PCB 101) were purchased from Promochem (Wesel, Germany). The solvents methanol dichloromethane, *n*-hexane and acetone as well as sea sand were obtained from Merck (Darmstadt, Germany). The grain size of the sea sand was 0.1–0.3 mm. Low-density polyethylene film (300 × 300 mm, wall thickness 50 µm) and silicone elastomer rods (1.0 mm i.d.) were obtained from GoodFellow (Bad Nauheim, Germany). Stir bars (Twister™, PDMS coating: 20 mm long, 0.5 mm thick) and the Tenax TA tubes were supplied by Gerstel (Mülheim/Ruhr, Germany).

### 2.2. Preparation of the materials

To prepare the membrane material, LDPE foil was cut into pieces (51 × 75 mm) and heat-sealed to form tubes. These membrane tubes could be used for both samplers because their diameters were identical. Ten of the prepared tubing pieces were placed into a 250 ml glass flask with 130 ml *n*-hexane and agitated at 130 r.p.m. using a horizontal shaker (Gerhardt, Bonn,

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