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Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers

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Seasonal sampling of ambient POPs at global background sites is logistically feasible and highlights spatial difference in compound distribution.

Abstract

Polyurethane foam (PUF) disks were deployed at global background sites, to test logistical issues associated with a global monitoring network for persistent organic pollutants (POPs). α-HCH, exhibited relatively high and uniform concentrations (17–150 pg/m^3) at temperate and arctic sites with elevated concentrations associated with trans-Pacific inflow. Concentrations were much lower (<5 pg/m^3) in Bermuda, Chile and Cape Grim. Concentrations for γ-HCH, the main component of lindane, were spatially similar to the α-HCH pattern but lower in magnitude (typically, <10 pg/m^3). Chlordane concentrations (sum of *cis*-chlordane, *trans*-chlordane and *trans*-nonachlor) were also low (<10 pg/m^3). Dieldrin concentrations were in the range 2–25 pg/m^3 at most sites but elevated in Bermuda. Back trajectories suggest that advection from Africa and the US may contribute. Endosulfan, a popular current-use pesticide, exhibited highest concentrations ranging from tens to hundreds of pg/m^3. There was good agreement between duplicate samplers at each site and PUF disk-derived air concentrations agreed with high volume data. Few logistical/analytical problems were encountered in this pilot study.

Keywords: Passive air samplers; POPs; Persistent organic pollutants; Spatial trends

1. Introduction

On May 17, 2004, the Stockholm Convention on persistent organic pollutants (POPs) was ratified (Stockholm Convention on Persistent Organic Pollutants, 2005, http://www.pops.int/). This document which is coordinated through the United Nations Environment Program (UNEP) is intended to reduce or eliminate the use, discharges and emissions of POPs. Initially, a set of 12 chemicals were identified as priority POPs – they include: nine pesticide classes (aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, and DDT (dichlorodiphenyltrichloroethane), one industrial chemical class (PCBs, polychlorinated biphenyls) and PCDD/Fs (polychlorinateddibenzodioxins/furans) that are associated with various industrial/combustion emissions.

Article 16 of the Stockholm Convention deals with its ''effectiveness evaluation''. The intent is that after 4 years of entry into force, the effectiveness of the Convention will be assessed through a global monitoring program. Regional and global environmental transport of POPs will also be addressed. To assist member countries with this task, UNEP Chemicals published

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a guidance document for the global monitoring of POPs (Guidance for a global monitoring programme for persistent organic pollutants). In this document, four environmental media are recommended for investigating POP levels in the environment: air, bivalves (for monitoring water), other biota and human milk. The recommended strategy for air combines conventional high volume air samplers with passive air samplers (PAS). Conventional high volume samplers have been used in several international, long-term monitoring programs (e.g. Northern Contaminants program in Canada, European Monitoring and Assessment Program, and the Canada–US, Integrated Atmospheric Deposition Network (IADN), to name a few) which provide useful data for assessing temporal trends of POPs. However, because of the high financial costs and logistical requirements (e.g. need for electricity, trained operators) of running such networks, few examples exist on a global scale as evidenced by the scarcity of air concentration data for POPs in most parts of the world. PAS can help to fill this data gap. PAS are small, relatively inexpensive, simple to deploy and do not require electricity. Their use has already been demonstrated in several spatial studies at local, regional, and continental scales (Harner et al., 2004; Pozo et al., 2004; Jaward et al., 2004; Shen et al., 2004). Further, because PAS data continuously integrate the air burden of POPs, they have an added benefit and may complement the sometimes intermittent information provided by high volume air sampling networks.

Several passive air sampler types have been recently developed and applied to air monitoring of POPs. These include SPMDs (semipermeable membrane devices) (Ockenden et al., 2001 and references within), polyurethane foam (PUF) disks (Shoeib and Harner, 2002; Pozo et al., 2004; Jaward et al., 2004; Harner et al., 2004; Motelay-Massei et al., in press), samplers employing XAD-resin (Wania et al., 2003; Shen et al., 2004), and polymer-Coated Glass (POGs) (Harner et al., 2003; Farrar et al., 2005).

This paper reports PUF disk-derived air concentrations for organochlorine pesticides (OCPs) from a pilot study where duplicate PUF disks were deployed at several global remote/background sites for periods of 2–7 months. The purpose of the study was to test logistical issues and other practical requirements for conducting a global sampling campaign. This was in preparation for a larger scale deployment at over 50 sites under the Global Atmospheric Passive Sampling (GAPS) Study which is now in progress (Pozo et al., 2005). Results from this pilot study also address scientific questions concerning the detection of target compounds and reproducibility of the samplers. Lastly, seasonality in air concentrations of OCPs was also evaluated at stations where samplers were deployed over consecutive periods.

2. Material and methods

2.1. PUF disks samplers

These samplers consist of a foam disk (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}; PacWill Environmental, Stoney Creek, ON) positioned in a stainless steel sampling chamber consisting of two domes (Fig. 1). This "flying saucer" design protects the foam disks from direct precipitation, sunlight and coarse particle deposition. Air is allowed to flow over the sampling surface through a ~2.5 cm gap between the two domes. The uptake of POPs by PUF disks has been previously characterized (Shoeib and Harner, 2002; Pozo et al., 2004) and shown to sample mainly the gas-phase at ~3–5 m^3/day although chemicals associated with very fine particles may also be collected. Tuduri et al. (in this issue) showed a small wind dependency on sampling rates at low wind speeds (less than 5 m/s) with increasing wind dependency at higher wind speeds. This wind effect was also observed by Pozo et al. (2004) in the field deployment of PUF disks samplers in mountainous regions of Chile. In this study sampling rates determined using depuration compounds (isotopically labelled chemicals that are spiked into the PUF disks prior to deployment to assess mass transfer kinetics) were $\sim 4 \pm 1.1$ m^3/day except at one extremely windy mountain site where duplicate samplers showed sampling rates about two times higher.

2.2. Sampler deployment

Beginning in 2002, duplicate PUF disk samplers were deployed at several remote sites (see Table 1, Fig. 2). Deployment times varied from 2 to 7 months depending on logistical constraints such as availability of site contacts to retrieve samplers. Deployment periods are summarized in Table 2. Prior to exposure, PUF disks were pre-cleaned by Soxhlet extraction for 24 h using acetone and then for another 24 h using petroleum ether. PUF disks were stored in amber glass jars with Teflon-lined lids. Field blanks were also collected by installing them in the sampler chambers and then immediately removing and storing as a sample. Duplicate samplers were deployed at each site for all deployment periods.

2.3. Analysis

Samples were analyzed for 19 OCPs including: α-, β-, γ-, δ-HCHs, aldrin, heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, endosulfan I, endosulfan II, endosulfan sulphate, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT (Ultra Scientific, North Kingstown, RI, USA). Analysis of PUF disk extracts was by gas chromatography–mass spectrometry (GC–MS) on a Hewlett-Packard 6890 GC-5973 MS. OCPs were determined in negative chemical ionization (NCI). Conditions for NCI analysis and selection of target/qualifier ions are described in Pozo et al. (2004).

3. Results and discussion

3.1. Quality assurance quality control

Method recoveries previously determined for OCPs were satisfactory (Pozo et al., 2004) and no recoveries were applied to the data. Field blanks were treated as samples and analyzed for the suite of OCPs. Results were below instrument detection limits (Table 2) so no blank correction was necessary.

3.2. Air parcel back trajectories

To aid in the interpretation of the data, air parcel back trajectories were calculated using the Canadian Meteorological Centre Trajectory Model (2005). Three-day back trajectories at 100 m above ground level were calculated daily during the deployment periods. Results were compiled into "spaghetti plots" that help to identify the frequency with which air arrived at the sampling site from particular sectors or