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Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue

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The context, needs and state-of-the-art of passive air sampling techniques for atmospheric persistent organic pollutants are discussed.

Abstract

There have been a number of developments in the need, design and use of passive air samplers (PAS) for persistent organic pollutants (POPs). This article is the first in a Special Issue of the journal to review these developments and some of the data arising from them. We explain the need and benefit of developing PAS for POPs, the different approaches that can be used, and highlight future developments and needs.

Keywords: Passive air sampling; Persistent organic pollutants; Pesticides

1. The context – why develop passive air sampling techniques for POPs?

'Persistent organic pollutants' (POPs) is a generic term, encompassing many organic contaminant classes, including polynuclear aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and several other industrial and agricultural chemicals. Concerns about POPs centre around their persistence, bioaccumulation and sub-chronic toxicity potential, and propensity to undergo long-range atmospheric transport (LRAT). National and international controls on the production and use of POPs have been (or are being) introduced, notably through the Stockholm Convention (SC) administered with the UN Environment Programme (UNEP) and the LRTAP Protocol of the United Nations Economic Commission for Europe (UNECE). The role of the atmosphere in supplying POPs to terrestrial and aquatic foodchains, and in their global recycling is of key importance. This may follow emissions from obvious and strong point sources (e.g. PCDD/Fs from poorly operated incinerators), or from diffusive primary (e.g. PAHs from numerous combustion sources such as vehicles, domestic heating, etc.) and secondary sources (e.g. 'old' pesticides emitted from soils). This has focussed international regulation on reducing emissions to air (UNECE, 1998; UNEP, 1998), and risk assessment/modelling efforts on their ambient distribution (Klecka et al., 2000).

Air monitoring for POPs has conventionally been conducted at a very limited number of sites using 'active' or high volume air samplers. These are expensive, require electricity and a trained operator. For example, in the United Kingdom, the Toxic Organics Micro-Pollutants (TOMPs) air monitoring

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network operated on behalf of the UK Department of the Environment, Food and Rural Affairs (Defra) uses only six such sites nationally, while other pollutants – such as NO_x and ozone – are routinely sampled at tens–hundreds of locations nationally/regionally, using much cheaper sampling technologies, such as passive diffusion tubes. Regulatory and other developments mean that there will be a pressing need to obtain more POPs data for air, in a much more routine and cost-effective way, to ensure compliance. This provides the incentive to develop new and cheaper passive air sampler (PAS) options.

Some major developments, driving the development of PAS for POPs are as follows:

a. Under the SC, signatory countries must conduct source inventories, identify ongoing sources, and provide environmental monitoring evidence that ambient levels of POPs are declining. Developing countries, in particular, require cost effective and simple approaches that can operate in the absence of power. Generally, they lack the money to buy equipment (both sampling and analytical), to build the laboratories, to train their personnel, to finance the regular monitoring campaigns. PAS offer the opportunity to solve several of these problems, in the short-term. Such inexpensive and easy-to-handle devices also offer the option of shipping samplers and filters for exposure, and returning the filters for final analysis. In addition, a 'Global Monitoring Network' is being designed, with the objective of establishing baseline trends at global background sites (see UNEP, 2003 and paper by Harner et al., 2006);
b. In the EU, an air quality standard is to be adopted for PAHs, because of health concerns over the carcinogenic properties of this compound class (European Commission, 2001). There has been much discussion over the limit to be adopted, because of concerns over exceedances, even in rural areas where coal/wood are used for space heating, or near roadsides. Air quality standards for 1,4-butadiene have also been proposed, and limits for POPs may follow in the future. Once an air quality standard is adopted, there will be the requirement for local authorities to test for compliance.
c. Attention is focusing on occupational and indoor exposure to airborne POPs, because this can be an important source to workers and the general public. PAS can be used to unobtrusively sample indoor air, helping to identify sources/hotspots.
d. National Environment Agencies increasingly need to identify 'less obvious' diffusive sources of POPs, as they seek to further reduce emissions, now that more obvious primary sources have been/are becoming better controlled. PAS can be used to conduct 'screening/reconnaissance surveys', and are sensitive to site-/source-specific compound fingerprinting. They can therefore be used to help identify sources, and be used to help direct/target cost-effective active air sampling campaigns (see papers by Klánová et al., 2006; Čupr et al., 2006; Paschke et al., 2006).
e. There is considerable interest in mapping the ambient distribution of POPs, to support national/international air monitoring networks, and to yield input data for regional distribution models. Studies have been conducted to demonstrate the feasibility of such 'national' or 'continental scale' measurement/modeling programmes, by preparing and supplying PAS to be deployed simultaneously across large areas – even at the continental and global scale (see Jaward et al., 2004; Shen et al., 2005, 2006; Farrar et al., 2006). The samplers are then 'harvested', sealed and returned to the laboratory for analysis, data interpretation and modeling.
f. Besides their obvious usefulness for monitoring, mapping and source identification, PAS can also serve as tools in scientific investigations, by for example recording changes in atmospheric POP concentration and composition along environmental gradients (e.g. urban–rural; latitudinal; altitudinal; chiral signatures).
g. Passive air sampling techniques are particularly suited to complement and serve in the evaluation of compartmental multimedia fate and transport models, such as those exemplified by the fugacity approach (Mackay, 2001). Like these models, PAS are specifically designed, and therefore most appropriate, for persistent organic chemicals (Wania and Mackay, 1999), and tend to provide information on the long term average conditions in the atmosphere and ignore variability on a shorter time scale. Passive samplers have not yet reached a stage of maturity, which would allow the measurement of volumetric air concentrations with an accuracy approaching that of pumped samplers. The progress towards quantitative calibration notwithstanding, the strength of PAS lies in their ability to provide compositional information, such as parent/metabolite ratios, chiral signatures (Shen et al., 2004, 2005) and congener compositions of complex mixtures, such as the PCBs (Ockenden et al., 1998; Shen et al., 2006). As long as the chemicals being compared are not approaching equilibrium between sampler material and atmospheric gas phase, even changes in PAS uptake kinetics with wind speed – as has been observed for some sampler designs – will not affect the relative abundance of isomers, enantiomers and congeners. Incidentally, multimedia fate and transport models are also much better suited to predict compositional and relative information than absolute concentrations, because the latter depend on knowledge of the absolute emission rate, which for POPs is hardly ever known with high precision or accuracy (Wania and Mackay, 1999).

2. What approaches can be used?

As just indicated, there are considerable incentives to develop passive air sampling techniques. These should be simple to use, cheap, versatile and capable of being deployed in many locations concurrently. Passive samplers can be designed and calibrated, to allow reliable estimates of air concentrations to be made, or to allow semi-quantitative comparisons of the levels and patterns of POPs. Several designs are possible