Occupational and indoor air exposure to persistent organic pollutants: A review of passive sampling techniques and needs†

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Exposure to persistent organic pollutants (POPs) and related compounds such as PCBs, brominated flame retardants, organochlorine pesticides and PAHs is regarded as an important environmental risk factor for humans. Recently concerns about POPs resulted in the international protocol called the Stockholm Convention on POPs. Air quality standards (indoor, outdoor and occupational) for PAHs and other POPs will also be applied in the EU in the future. This will bring requirements for monitoring, to check for compliance and to reduce human exposures to POPs. This can occur from point sources and in various microenvironments, indoors, outdoors and in workplaces. Monitoring can be undertaken either by an active (pumped) method or using a passive (diffusive) air sampling (PAS) device. To date, PAS for POPs have mainly been used as integrating (long-term) samplers for ambient (outdoor) air. However, there are several reasons to develop PAS for monitoring of POPs in occupational and indoor environments. We discuss the potential advantages, limitations and developments needed, so that PAS can be used reliably and routinely indoors and in occupational settings for POPs.

Introductory remarks

The compounds

Persistent organic pollutants (POPs) and related compounds are groups of chemicals that include both man-made and natural chemical classes. POPs are of special concern since they can remain intact in the environment for long periods (persistent), accumulate through food chains into living organisms, have the ability to undergo long-range atmospheric transport (LRAT) and show toxicity potential. Among the compounds classified as POPs by the Stockholm Convention on POPs are industrial chemicals and by-products; polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins/furans (PCDD/Fs), and organochlorine pesticides (OCPs) such as DDT and its metabolites, chlordanes, dieldrin and hexachlorobenzene (HCB). Examples of POP related compounds are; brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs), and the combustion products polyaromatic hydrocarbons (PAHs). Even though not defined as POPs by the Stockholm Convention they need priority considerations since they exhibit POP-like characteristics of persistence, toxicity, long-range transport and bioaccumulation. They have been defined as potential candidate POPs and in addition PAHs are on the United Nations Economic Commission for Europe (UNECE) Protocol on POPs. Herein, we refer to all compounds above as POPs.

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Human exposure and health concerns

Exposure to POPs is recognized as an important environmental risk factor for humans. They have been variously linked to the following effects: cancer; nervous system damages; reproductive and immune system impairments; and hormonal imbalances.[1–20] As such, there have been concerns about the levels of exposure, identifying the pathways of exposure, and efforts to reduce exposures. It is often believed that the main route of exposure to POPs is *via* the diet, but there are several other possibilities. These include exposure to indoor air and dusts at home and in the workplace. For example, some OCPs have been used indoors, as pest control agents;[21,22] PCBs have been used as sealants, in paints and in electrical fittings;[20,23–27] PBDEs are flame retardants, used to treat computers, textiles, furnishings *etc.*,[28,29] and they may be released to air through volatilization from these field of applications and products and as a consequence levels may be elevated in indoor air. PAHs are released from incomplete combustion, and so can be emitted to indoor air from domestic fires, smoking, cooking *etc.*[16,30] As such, there is considerable scope for dietary exposure to be enhanced by these sources/pathways, and for such exposure to become highly variable between locations and individuals. The exposure to chemicals at work is often greater than the exposure in non-working situations but the duration for the exposure is often longer in non-working situations than the occupational. Therefore, also long time low level exposure may be important.

Legislative actions

International concerns about POPs have resulted in two protocols within the UN framework; the UNECE

Long-Range Transboundary Air Pollution (LRTAP) protocol on POPs and the United Nations Environmental Program (UNEP) POPs convention. The convention on LRTAP was first signed in 1979 and it resulted in a Protocol on POPs in 1998. The protocol includes fifteen chemicals and the objective is to control, reduce or eliminate discharges, emissions and losses of these compounds. The UNEP recently administrated the international protocol known as the Stockholm Convention on POPs, where a set of twelve chemicals was classified as priority POPs. The list includes nine OCPs, PCBs and PCDD/Fs. Signatory countries must perform source inventories and show that ambient levels are decreasing. In addition, specific air quality standards (indoor and outdoor) for PAHs and other POPs will be approved in the EU in future. Once an air quality standard is approved, there will be a requirement for local authorities to check for compliance with legislative actions to reduce risk to humans. This requires sampling methods which routinely can be applied as monitors of POPs to check for personal exposure of the general and worker population. Individual countries may also have occupational exposure limits. In addition, there can be limits on 'tolerable daily intakes' (*e.g.* for PCDD/Fs), where the combined contributions of dietary exposure, inhalation and other pathways need to be combined. All of these developments provide the motivation and incentive to monitor POPs in air, using simple, efficient, non-destructive and cost-effective sampling and monitoring tools, to check for compliance and to help identify sources. This review discusses the scope, opportunities and limitations for passive sampling techniques, indoors and at occupational settings of POPs.

Monitoring of POPs

Occupational and indoor air concentrations of POPs can be monitored by either stationary or personal monitors. A stationary sampler is often placed at a height resembling the breathing zone, in the living room for instance, or the most frequently used room of a workplace. The personal sampler is portable and should be carried by a person as close to the breathing zone as possible. Results from a recent study by Allen *et al*. showed that significantly higher concentrations of PBDEs can be obtained by personal compared to stationary samplers used in the same house.[29] Other studies also show that there can be a large discrepancy between concentrations measured by stationary and personal samplers which imply that results from stationary samplers may give an underestimation of the true personal air exposure of pollutants.[31,32] Personal monitoring is therefore the best choice to assess exposure for the general population and for workplaces. For both sampling strategies there is a choice between active and passive (diffusive) air sampler (PAS) approaches.

Active air samplers

Active air sampling of POPs are the most common method used today and are recommended by the EMEP Chemical Coordinating Center (http://www.emep.int/, http://www.nilu.no/projects/ccc/manual/index.html). Active, high-, medium- or low-volume (HiVol/MeVol/LowVol) samplers, have a sampling module which consists of two compartments; a glass, quartz fibre or Teflon filter which collects particle associated compounds and a solid adsorbent—either a polyurethane foam (PUF) plug, XAD resins or Tenax-which is located on line downstream from the filter to collect gas phase components that pass through the filter. The adsorbent can also retain those compounds that volatilize from the filter during sampling. A pump is necessary to force air through the sampling module and a flow meter is needed to measure the volume or flowing rate of air through the sampler. The pump and the flow meter requires power by electricity or battery. A known volume of air passes through the sampler, controlled by the flow meter, which enables precise quantitative measurements to be performed. The active sampler, dependent on sampler type (LowVol–HiVol), operates typically at flow rates ranging from 0.5–1400 L min^{-1}. The sampling time is normally a few hours up to one day and the provided results are snap-shots of the air concentration limited to the period of sampling. The results can be used to see peaks, ceiling and 8–24 h time weighted average (TWA) concentrations of pollutants but not integrating concentrations over longer periods. Stationary monitoring is the most commonly employed for Hi–MeVol active samplers. However portable personal battery power-driven LowVol pumps are available to collect both particulate but also vapour fractions of POPs.

Another type of active sampler is the Denuder sampler. This is a low-flow sampler that has a Denuder tube to collect the gas phase upstream of the filter. The collection of gas- and particulate phase is therefore reversed from the conventional sampler. It is not as widely used as the conventional sampler. A recent study showed discrepancies between the results from a Denuder sampler and a conventional sampler, implying that particulate PAH concentrations may be underestimated by a factor of two by using the conventional sampler.[33]

Passive air samplers (PAS)

The use of PAS for indoor and workplace POP air monitoring is not as common as active sampling methods. PAS was introduced about 30 years ago as a sampling device for gaseous air pollutants and are frequently used for monitoring of other air pollutants, such as volatile organic compounds (VOCs), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone *etc*. but their use for POPs is still very limited.[34,35] Only a few studies have used PAS to measure POPs, such as PBDEs, PAHs and PCBs in residential indoor air with a stationary PAS.[26,28,36,37] The use of PAS as occupational monitors are scarce and to our knowledge only one PAS approach have been used as a personal monitor for the general population.[38] Although PAS have been sparingly used as a tool for measurements of POP in workplace and indoor air, they have been used more frequently outdoors.[39–44] Passive sampling techniques are also attracting a lot of use and attention for measurements in water and even soil.[45–49] Man-made PAS exist in several different designs, sizes and shapes. The passive sampling medium (adsorbent) can be solvent, polymer resin, chemical reagent or porous adsorbent and sampling is either based on permeation or diffusion. Other hydrophobic media such as vegetation,[50–53] organic films on window glass[54–57] and soil[58] have been used as surrogate PAS to

monitor spatial and temporal trends and the regional/global distribution of POPs.

Most man-made PAS work has focused on integrating samplers (weeks, months or even years) with a high capacity to sequester POPs. Uptake to these samplers is continuous (linear) over the sampling period, and it is necessary to know the sampling rate (*i.e.* volume of air 'seen' and sampled per unit time). Examples are semi-permeable membrane devices (SPMDs),[59–64] polyurethane foam disks (PUF),[47,65,66] XAD resin based samplers[67] and various membrane based samplers.[68,69] Another group of PAS are the low capacity samplers, where the principle is to allow gas phase POPs to reach equilibrium with the PAS. Examples of such samplers are polymer coated glass (POG),[70–72] solid phase micro extraction devices (SPME),[73,74] and glass disks.[75,76]

Principles of uptake

The theory of passive sampling has been described in detail by Shoeib and Harner[66] and Bartkow *et al.*[77] In brief, PAS techniques are based on free flow of analytes from the sample matrix to the passive sampling medium. The principles of uptake are to consider that the passive sampling medium is uniform and 'porous' and that it traps chemicals from the atmosphere by gaseous diffusion, and sorption. Once delivered to the sampler surface, compounds can permeate and dissolve in the medium or be physically adsorbed to the adsorbent by π–π interactions and/or van der Waal's forces. The flow continues until equilibrium between the atmospheric gas phase and the collection medium has been established or until the sampling is stopped by the user. The resistance to uptake may be from the air boundary layer or from the rate of diffusion into the passive sampling medium. For POPs the air–sampling medium partition coefficient is considered to be similar to the octanol–air partition coefficient (K_{OA}) which is a commonly used parameter to describe POP hydrophobic features. For compounds such as POPs with large K_{OA} values the mass transfer is air-side controlled. Wind is an important environmental parameter that can influence the uptake rate. Temperature is an important parameter that can effect air gas phase–sampler equilibrium partitioning. The effects of these environmental parameters are important to calibrate and/or control.

Active/passive sampler comparisons and requirements

Advantages with active samplers if they are correctly calibrated are that they show very good accuracy and precision. They also have the ability to provide information on short-term peaks and incidental point exposure situations since their sampling times can be short. However there are several recognized artefacts with active air sampling approaches. Examples include volatilization of compounds from the particulate matter held on the filter, breakthrough of substances from the adsorbent material and adsorption of gas phase species onto the filter material. The benefits of using PAS compared to an active method are many. They are: simpler and easier to handle; several places (or subjects) can be measured simultaneously; they are cheaper and do not need a pump. Pumps can be noisy and large, and require the use of electricity and a trained person to be operated. All of these features give the active sampler limited use in occupational and indoor studies.

If the sampler is supposed to be used for monitoring studies in workplaces it has to be easy to handle (simple to use), so it can be deployed away from the laboratory by a person without technical knowledge, preferably the trial person themselves. The treatment of the sampler after sampling has to be as simple as the deployment. It also has to be cheap, to make it possible to do large studies where sampling simultaneously in many different locations or over a geographical area is wanted.[78] An important feature for a PAS as a personal monitor is that they should be convenient for the subject to wear. The device should be small and light, and it is important that it does not affect the worker (subject) during his/her work. Noise from the pump can be disturbing for the subject and more cumbersome to carry. Studies have shown that wearing traditional sampling pumps could affect workers' behaviour and undermine the validity of occupational hygiene exposure measurements.[79]

All of the problems for an active sampler can be excluded by the use of a passive sampler. There are therefore several incentives to develop a passive sampler for monitoring of POPs in occupational and indoor environments.

Challenges and possibilities

Despite the potential advantages of PAS just identified, there is still much development work needed, and no consensus on the best or 'accepted' techniques. Improvements are needed. Most of the PAS are currently applied to outdoor environments and none of the existing types have been fully calibrated for use in indoor and occupational settings. Further calibration also needs to be done for outdoor environments. Key questions are: Is it possible and/or necessary to develop PAS to be as 'good' as the active sampler? Should they be used semi-quantitatively for initial 'screening', to be supplemented by active sampling, or can they reliably replace active samplers as a quantitative tool completely?

Quantitative methods

At present PAS can enable estimations of air concentrations typically within a factor of 2–3 of the "true" concentrations.[40] For many situations, this may be an acceptable level of accuracy. However, further improvements may be possible, although PAS will probably always be inherently less reliable than active methods. Continuing improvements can be made to calibrate PAS, including the linearity of uptake at different contaminant concentrations, to assess interference/interactions between compounds, and the effects of relative humidity, wind speed, and temperature. Ultimately, it is envisaged that there should be recommended procedures and standardised methods for the deployment, handling and analysis of PAS.

Semi-quantitative method

PAS when appropriately applied in large field studies can be a highly sensitive semi-quantitative screening tool, able to provide valuable estimates of both POP contamination loads and POP profiles which are indicative of likely sources.[39,80–83] It

can even be possible to differentiate between such contamination loads when samplers are separated by just a few meters. PAS therefore already offers scope as a valuable screening tool in indoor and occupational settings.

Personal samplers

As discussed above the best exposure and risk assessments for POPs, for the general population and the working population can be done using personal monitors. Ideally, this should consider a sampling time relevant to exposure scenarios, and hence be representative for possible health effects (*i.e.* short exposure time for acute effects and longer exposure times for chronic/cumulative effects). Averaging exposure over 8 h reflects the duration of a typical work shift and air quality standards or limits are often set to this exposure time.[84] However molecular diffusion is a slow process and consequently sampling rates of PAS are low. This can hamper reliable analytical detection. Many PAS designs today (used as personal monitors for VOCs) have a relatively small uptake area and may therefore not be suitable as personal monitors when short exposure times are required. There is therefore a challenge to test new sampler types, geometries and adsorbents with larger uptake surface areas that can meet these demands. For example the required sampling time could be a working day, or an integrated working week (*e.g.* 8 h during 5 consecutive days). The latter would require a more complicated design, since the sampler would have to be closed/sealed during non-working hours. It would also be interesting to test such an open/close design for working shifts, where the sampler is opened (few minutes to hours), only when the exposure is expected to be high.

Stationary indoor samplers in private residences and workplaces

A stationary sampler as an exposure monitor in private residences and workplaces can sometimes be preferable, since the geometry and size of such sampler is less critical. Such a sampling design can be optimised, to give a large active uptake area and thus higher sampling rates which can shorten the sampling time. It can sometimes be a problem in indoor studies to find a representative place in the room where the stationary sampler best reflects the time integrated levels, since there can be significant variations within a room, dependent on distance to sources and air movement *etc.*[31] It is therefore important to develop sampling strategies for indoor measurements and test the validity of such strategies. Moreover, possible variations in uptake rates at the low air velocities typical for indoor air also need to be fully tested and evaluated.

Tracing point sources and microenvironment exposures

As discussed earlier exposure to POPs can occur from various microenvironments and point sources, both in- and outdoors and at workplaces. In these cases the exact concentration is not so important and it may therefore be sufficient to use PAS as simple, semi-quantitative screening tools, to help assess and trace point sources, levels in microenvironments and the degree of volatilisation of POPs from contaminated materials or products.[85]

Methodology concerns

Analytical procedures

POP laboratory analysis work today is often laborious and expensive. It can be labour intensive and require large volumes of organic solvents. Specifically with regard to PAS, typical analytical steps can include exterior cleaning (SPMDs), extraction by means of organic solvent dialysis (SPMD and other membrane technologies) or Soxhlet extraction (PUF and XAD resins) or repeated rinsing/soaking (POG). Sample fractionation and enrichment procedures are usually done with several steps, for instance mixed silica gel columns (neutral, basic or acidic) and size exclusion chromatography systems such as gel permeation chromatography (GPC). Finally analysis and quantification is performed by solvent injection to a gas chromatography/mass spectrometry (GC/MS) system. Improvements on the extraction steps can be made by using an ultra sonication extraction system or a microwave-assisted extraction, which can reduce both the time needed for accomplishment of the isolation step and use of extraction solvents.[86–89] Another possibility may be pressurized liquid extraction (PLE) which can shorten the extraction step for POPs but it has so far mainly been used for extraction of solid material (food, soil, sediments, organisms) and to our knowledge not on PAS.[90] However, ideally, for a fast and cost-effective sampling, the sampling step could be directly integrated with the analytical step with elimination of solvent use. In this context, the SPME device is an interesting technique, since the sampling time can be as short as a few minutes up to at least 24 h and they can be used as both time weighted average (TWA) samplers and equilibrium samplers.[91] Quantification of target analytes can be performed using the sampling rates which the gas phase pollutants load onto the fibers. SPME can be directly injected to a GC system. A drawback is that the adsorption area is small for many pollutant level situations and more work to test their robustness and influence on environmental parameters, such as temperature and face velocity is needed. Other possibilities would be if the sampler or the adsorption material was directly compatible with thermal desorption equipment (ATD). This method is used for other types of pollutants such as VOCs[92] but only a few studies has been done on POPs.[38,93] This is less labour intensive than traditional solvent extraction methods and can be favourable since it yields lower detection limits since the entire sample can be transferred to the GC/MS system. An interesting study by Vrana and co-workers demonstrated an integrative sampler that consists of a bar coated with poly (dimethylsiloxane), enclosed in a dialysis membrane bag that can pre-concentrate organic compounds such as PAHs and PCBs from aqueous matrices.[69] Instrumental analysis was performed in a thermal desorption tube. However, a problem with ATD may be that most thermal desorbers and thermal desorption conditions have been created for analysing VOCs and may not be appropriate for POP analysis and that there are limited possibilities to re-run the sample after the first shot. Problems with recovery for higher molecular weight PAHs (such as fluoranthene and pyrene) due to thermal heterogeneity in the ATD system have been reported.[38] Thus there is a need to further test and validate ATD systems or improve

liquid extraction methods to shorten and simplify the extraction and enrichment processes, in order to make the method simple and cost-efficient.

After analysis, the sampler should ideally be reusable, after both ATD and after liquid extraction for further cost-effectiveness of the sampling.

Compound uptake by PAS

The uptake of a compound by a PAS occurs in three different stages; initial linear (kinetic or time integrated) uptake, curvilinear uptake as equilibrium is approached, and the equilibrium phase (Fig. 1). The amount of compound sequestered by the PAS depends on the air concentration, exposure time, sampler design and the environmental conditions during sampling. A PAS can either operate in the linear phase of uptake or when equilibrium has been achieved. Thus, for a certain compound and sampler design, it is important to know the time to reach those phases, respectively. Shoeib and Harner reported that tri-CBs and tetra-CBs reached equilibrium after 50–75 and 200–400 days with PUF and SPMD samplers, respectively, while the uptake of penta- and hexa-CBs was linear during the entire 450 day sampling.[66] Thus most POP compounds stay in the linear uptake phase during a sampling time of up to *ca*. 6 weeks. Typically, high capacity PAS, such as SPMD and PUF, operate in the linear phase of uptake before equilibrium has been reached and knowledge of the compound sampling or uptake rate is needed for quantification. There are to date only a few calibration uptake rates available in the literature. Shoeib and Harner reported indoor uptake rates for PUF of PCBs to be usually in the range 3 to 5 m^3 day^{-1}.[66] Bartkow *et al*. found similar uptakes for SPMDs of PAHs in air ranging from 0.6 to 6.1 m^3 day^{-1}.[60] Uptake rates derived from an indoor calibration study for PUF and PBDEs presented similar values—2.5 m^3 day^{-1}.[82] Recently Hazrati and Harrad showed somewhat lower sampling rates for PCBs and PBDEs measured indoor with PUF and a different chamber design. These sampling rates ranged from 0.57 to 1.9 m^3 day^{-1}.[94] Although all of the reported sampling rates are in the same range more calibration work is needed from both indoor and outdoor studies, to further validate the samplers and improve confidence in their use for fully quantitative approaches.

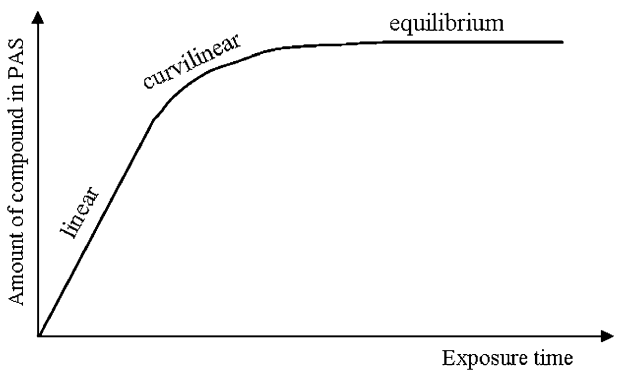

Fig. 1 The three phases of uptake of POPs by a PAS as a function of exposure time.

The equilibrium samplers, such as POGs and SPMEs can reach equilibrium after just a few days or even hours, depending on the compound.[72,91,95] However, the time to reach equilibrium depends on the film thickness, and can be controlled—or at least manipulated—by varying it. A thicker film needs longer time to reach equilibrium, although a higher method sensitivity can be achieved since more amount of compound will be taken up. Importantly film thickness must be uniform, and standardised/certified for a commercially available design. However, the time to reach equilibrium for a PAS also depends on the environmental conditions, and the user has to demonstrate that steady state has been achieved. Eventually the equilibrium type PAS may be promising, when the sampling situation is quite constant, such as in indoor environments. If equilibrium has been attained, the air concentration can simply be calculated if the sampler to vapour phase partition coefficient, $K_{PAS-air}$, is known. A drawback with equilibrium samplers in occupational studies may be that they do not provide time integrated average (TWA) concentrations for instance a working day or week and the results are more comparable to momentary sampling.

Sampler performance and adsorbing material

There is a need to test new adsorbents and sampler geometries with sufficient adsorption area to improve sampling rate. These need to be sensitive enough for POPs in various environmental settings including ambient and occupational. Optimal characteristics are: an adsorbent material that has a strong affinity for POPs; low or negligible influence of temperature, relative humidity (RH), face velocity (wind), back diffusion, and storage; and calibrated at different exposure times and possible to be analysed on an ATD. When PAS are deployed outdoors it is important to provide shelter/buffering from the wind (since a high wind speed reduces the thickness of the boundary layer and hence increases the uptake rate), while in low wind situations it is important to allow sufficient air to circulate around the sampler to ensure that uptake rates are not reduced. Different chamber designs have been used for some PAS and the design of the chamber has been shown to be important for how the effect of the environmental conditions on the samplers are dampened.[47,96] In indoor situations there is likely to be less variation in the environmental variables and there is a greater concern about sufficient air movement in the low wind velocities characteristic of indoor environments.[94] A personal sampler used in occupational settings will be exposed to both indoor and outdoor environments. Thus, there is a need to account for the possible variations in uptake rates at the low air velocities typically encountered in indoor environments, just as the effects of high air velocities often found outside must be accounted for in studies of outdoor environments. This can probably be aided by the use of performance reference compounds (PRCs)[63,96,97] added to the sequestration phase before use. The design of a chamber device for indoor PAS should ideally protect the sampling surface from deposition of dust particles settling from above, whilst still letting adequate air move around the sampler. A design of a personal PAS monitor should be robust and intended for both in- and outdoor situations, small and light

weight and should manage both high and low wind situations and temperatures, and also be sufficiently protected against rain and UV sunlight. Reportedly some PAH components have a tendency to photodegrade under UV sunlight.[47] Every new PAS and protective chamber device will therefore need to be sufficiently calibrated and harmonized in order to facilitate its use as a universal chamber. So the samplers need to be tested both in laboratory experiments and in the field. Laboratory test atmosphere chambers may be useful to help in such testing.

Sampling concerns

In water, biofouling can influence the uptake rate of compounds over time.[98] While the effect of biofouling is expected to be negligible in air, compounds associated to particles or aerosols can be trapped on some PAS surfaces and influence the amount accumulated by the PAS. This effect has been widely reported for PUF, where the porous surface will enhance the effect, and also for SPMDs.[94,95,99] For many POPs, the atmospheric burden is predominantly in the gas phase. Warmer indoor temperatures may also enhance ambient POP distribution towards the gas phase. However, some POP compounds, including some PAHs, PBDEs and PCDD/Fs are almost exclusively present on aerosols.[99,100] If they are present on ultrafine particles, they can move through the air very much like gases and can be trapped by some PAS. Aerosol types, sizes and abundance can be different in occupational settings from ambient aerosols. It is therefore important to have an appreciation of the influence of particulate-borne POPs on what is sampled/retained by the PAS. It may be a problem if PAS collect particles, since it is not known to what extent this collection occurs. The 'best' sampler would presumably collect both gas and particulate phase in a quantitative way. Exposure markers that exist primarily in the gas phase may be helpful to this discussion (see below).

Compounds sampled and sampling time

PAHs in non-occupational settings are sometimes at 2–3 orders of magnitude lower levels (ng m^{-3}) than in occupational settings (μg m^{-3}). For OCPs, PCBs and PBDEs the ambient background levels are sometimes even one magnitude lower than those (pg m^{-3}).[101] It is important that passive air sampling and analysis combinations can provide sufficient sensitivity to be used reliably at such concentrations. In order to monitor industry atmospheres, private homes and personal exposures it would be valuable to have samplers (probably a range of samplers) to integrate air concentrations over various time scales as short as hours, days, weeks, months or even years. Tracer compounds can be selected, which 'represent' particular groups or sources, or because they are of particular health concern. For example, PAHs in ambient air are dominated by 3–4 ring PAHs such as phenanthrene, pyrene and fluoranthene (*ca.* 80–95% in the vapour phase at 20 °C).[61,100] They may be helpful as marker compounds and suitable indicators for PAH contamination and overall human exposure. Traditionally benzo(*a*)pyrene (BaP) is the main indicator of carcinogenic PAHs.[2] However BaP is typically a small fraction (*ca.* 1% of the total amounts of PAHs measured) and >90% is associated on particles.[100] Therefore, there is a need for other health and emission relevant PAH markers, for comparisons and evaluation of trends. In ambient air, BaP and fluoranthene are typically the major contributors to carcinogenic equivalents.[2] Thus, of the volatile PAHs, fluoranthene (>80% in the vapour phase) could be a suitable indicator for carcinogenic risk. More than 90% of the total PCB burden in air is typically the tri- to tetra homologues and a major fraction of the OCPs mentioned herein are associated with the gas phase and for PBDE the most abundant congener BDE-47 about 80% are in the gas phase.[24,100,101]

Sampler concerns

It would be helpful to develop a protocol for the minimum PAS exposure time necessary for reliable quantification of analytes. Such a protocol should include the instrumental detection limit, typical PAS blank levels, uptake rates and typical atmospheric concentration for a particular tracer compound. Available sampling rates (m^3 day^{-1}) in the literature for the PAS reviewed in this paper are different, because they have different surface areas available for POP uptake. However, if the uptake rate is calculated on a standardised area basis (*e.g.* cm^2) they are very similar; *ca.* 0.01 m^3 day^{-1} cm^2.

Table 1 presents a calculation exercise, where the size of sampler surface area and exposure times needed are calculated, for two typical background air pollutant concentrations. The aim is to see if a sampler can be made small enough to be used as personal sampler. In addition, two GC introduction techniques—solvent injection and ATD—are compared. The following assumptions are made; the instrumental limit of detection is 5 pg, the blank values are zero, 2 μL of a final sample extract volume of 40 μL is injected in the solvent injection mode and the whole sample is injected in the ATD mode. As can be seen, a required sampler surface area of only 1.5–3 cm^2 is needed for a compound with an air concentration of *ca.* 0.5 to 1 ng m^{-3}, if these conditions can be met. A

Table 1 A calculation exercise aimed to illustrate the size of sampler needed for different air concentrations and exposure times. Traditional solvent or ATD mode sample introduction for GC/MS analysis is compared. A sampling rate of 0.01 m^3 day^{-1} cm^{-2} calculated from literature PAS sampling rates was used

	Mass compound needed in sample/pg	Air concentration/ pg m^{-3}	Required volume of air/m^3	Exposure time/h	Required surface area/cm^2
ATD	5	1000	0.005	8	1.5
ATD	5	10	0.5	8	150
ATD	5	1000	0.005	40	0.3
ATD	5	10	0.5	40	30
Solvent injection	100[a]	1000	0.1	8	30
Solvent injection	100	10	10	8	3000
Solvent injection	100	1000	0.1	40	6.5
Solvent injection	100	10	10	40	600

[a] In 40 μL of solvent.

Table 2 Estimated features of PAS used for organic compounds (POPs and VOCs) in air

	Organic compound classes[b]	Published use for POPs in air	Availability	Cost	Analytical procedure	Published uptake rates	Blanks	Re-usable	Sampling time required
SPMD	PAH, OCP, PCB, PCDD/F, PBDE	Few	Commercially available sampling device	Expensive samplers, and analysis	Complicated, need several steps	Few	Intermediate	No	Weeks/months
PUF	PAH, OCP, PCB, PBDE	Intermediate	Commercially available material	Cheap samplers, expensive analysis	Complicated, need several steps	Intermediate	Low/ intermediate	?	Weeks/months
POG	PAH, PCB, PBDE	Sparse	Commercially available material	Expensive analysis	Complicated, need several steps	Sparse	Low/ intermediate	No	Days/weeks
XAD-2 resin based	PAH, PCB, OCP	Sparse	Commercially available material	Expensive sampling material, and analysis	Complicated, need several steps	?	Intermediate/ high	Yes	Months/years
SPME	PAH, VOC	Sparse	Commercially available sampling device	Cheap sampler and analysis	Simple	Sparse	Low	Yes	Hours/days
Radiello	VOC	None	Commercially available sampling device	Cheap sampler and analysisi	Simple	Intermediate (only VOCs)	Low	Yes	Hours/weeks
Badge types[a]	VOC	None	Commercially available sampling device	Cheap sampler and analysis	Simple	Intermediate (only VOCs)	Low/ intermediate	Yes	Hours/weeks
Perkin Elmer tubes	VOC	None	Commercially available sampling device	Cheap sampler and analysis	Simple	Plenty (only VOCs)	Low	Yes	Days/weeks
Fan-Lioy	PAH	One	Not commercially available	Cheap analysis	Simple	One	Low	Yes	Days/weeks

[a] SKC-Ultra, and 3M-OVM™. [b] According to published literature.

sampler surface area of <10 cm^2 would presumably be a reasonable size for a personal monitoring device. Hence, for a suitable marker compound, an 8 h exposure would theoretically yield enough material for analysis from background air. Of note, air quality standards or limits for ambient and workplace air are likely to be significantly higher than the calculation exercise exemplified herein which would favour the sampler limit of detection. On the practical side, it can often be difficult to ensure 'zero blanks', without the use of clean room and special handling facilities.

Table 2 summarize some PAS which are used for organic contaminants (POPs and VOCs) in air. It is not intended to be complete but should assist and guide throughout the large number of sampler types and designs and help the user to select a suitable sampler for a chemical group and study purpose.

In conclusion, monitoring of POPs in indoor air is an exciting and growing field. Current and future air quality standards/exposure limits mean that there is incentive to get new/better approaches for the monitoring. This article has reviewed the 'state of the art', and shows the advantages and disadvantages of different approaches but it is not yet clear which method/methods will find favour, and become 'industry standards'.

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