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Observations on persistent organic pollutants in indoor and outdoor air using passive polyurethane foam samplers

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ABSTRACT

Air quality data of persistent organic pollutants (POPs) indoors and outdoors are sparse or lacking in several parts of the world, often hampered by the cost and inconvenience of active sampling techniques. Cheap and easy passive air sampling techniques are therefore helpful for reconnaissance surveys. As a part of the Megacity Initiative: Local and Global Research Observations (MILAGRO) project in Mexico City Metropolitan Area in 2006, a range of POPs (polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs)) were analyzed in polyurethane foam (PUF) disks used as passive samplers in indoor and outdoor air. Results were compared to those from samplers deployed simultaneously in Gothenburg (Sweden) and Lancaster (United Kingdom). Using sampling rates suggested in the literature, the sums of 13 PAHs in the different sites were estimated to be 6.1–180 ng m^{-3}, with phenanthrene as the predominant compound. Indoor PAH levels tended to be higher in Gothenburg and outdoor levels higher in Mexico City. The sum of PCBs ranged 59–2100 ng m^{-3}, and seemed to be highest indoors in Gothenburg and Lancaster. PBDE levels (sum of seven) ranged 0.68–620 ng m^{-3}, with the highest levels found in some indoor locations. OCPs (i.e. DDTs, HCHs, and chlordanes) were widely dispersed both outdoors and indoors at all three studied areas. In Gothenburg all POPs tended to be higher indoors than outdoors, while indoor and outdoor levels in Mexico City were similar. This could be due to the influence of indoor and outdoor sources, air exchange rates, and lifestyle factors. The study demonstrates how passive samplers can provide quick and cheap reconnaissance data simultaneously at many locations which can shed light on sources and other factors influencing POP levels in air, especially for the gaseous fractions.

1. Introduction

Persistent organic pollutants (POPs) are chemicals for which indoor air assessment is of increasing interest. POPs have proven or potential health effects on humans and exposure to POPs in air can be an important pathway. Humans spend most of their time indoors, and concentrations indoors may also be higher than outdoors. A range of POPs such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) have frequently been monitored in outdoor air. However, data on indoor air are still sparse (Currado and Harrad, 1998; Leone et al., 2000; Wilford et al., 2004; Kohler et al., 2005; Strandberg et al., 2006; Gevao et al., 2007).

To assess the extent of human exposure to POPs from indoor air, easy and reliable sampling methods are

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necessary (Bohlin et al., 2007). Indoor air can be sampled for POPs actively and passively. Indoor active sampling can be intrusive, noisy and relatively expensive, in terms of both material and labour. These difficulties may explain the general lack of indoor air quality measurements of POPs, particularly in indoor private residences. It is therefore helpful if the method is based on passive sampling techniques. Passive samplers are cheap, simple to handle, relatively unobtrusive, and a large number can be deployed in different places simultaneously. Even so, there are still some drawbacks concerning existing passive air sampling techniques, such as the influence of environmental variables, and full understanding or control of uptake in indoor environments, that need optimisation before they can fully replace active samplers. The most widely used passive air sampler for POPs so far is the polyurethane foam (PUF) disk (Gouin et al., 2005; Harner et al., 2006). PUF disks are mainly used to collect the gaseous fractions of POPs. Uptake calibration studies have been conducted so that estimations of air concentrations can be derived. Most studies to date have focused on the use of PUF disks in outdoor applications, although some recent work has used them indoors for PCBs and PBDEs (Pozo et al., 2004; Wilford et al., 2004; Harrad et al., 2006). To our knowledge only one paper reports indoor air results from passive PUF disk sampling for PAHs (Gevao et al., 2007), while this paper may be the first using PUF disks to sequester the gaseous fraction of OCPs in indoor environments.

Exposure related health concerns of POPs are of particular importance in densely populated urban regions where there may be a wide range of POPs and sources (e.g. industrial activities, heavy traffic and combustion sources). The number of mega cities (>10 million inhabitants) in the world is growing and the Mexico City Metropolitan Area (MCMA) is one of the most densely populated in the world. MCMA is also an interesting new area for POP studies since ambient monitoring data suggest Mexico to be a regional source of some POPs via long-range atmospheric transport (Shen et al., 2005) but there are still few or no studies showing data on POP levels in residential areas in Mexico City. A multi-pollutant study, the Megacity Initiative: Local And Global Research Observations (MILAGRO) project, was conducted during 2006 to study air pollutant exposure and health effects in Mexico City (http://www.eol.ucar.edu/projects/milagro/). As a part of this campaign PUF disks were used to sample POPs inside and outside homes. Comparative data using the same techniques were obtained for two European cities: Gothenburg, Sweden, and Lancaster, United Kingdom (UK), where indoor air data for some of the POP compounds are already available and of public health interest. These cities have smaller populations than Mexico City and outdoor air concentrations may therefore be expected to be lower. However, the situation indoors may be different since the colder climate in the two European cities gives different ventilation and living conditions than in Mexico City and there may also be national/regional differences in chemical usage.

In this paper we demonstrate how reconnaissance data concerning POPs can be obtained for a new area quickly, easily, and cheaply using passive air samplers. The deployment times and conditions were the same in each city, to allow observations on differences in the levels and patterns of POPs in indoor and outdoor air, differences in indoor/outdoor ratios for the three cities, and differences in indoor/outdoor ratios between chemicals.

2. Materials and methods

2.1. Design and deployment of the samplers

Air samples were collected using PUF disk samplers (14 cm diameter, 1.2 cm thickness, surface area 360 cm^2, density 0.035 g cm^{-3}, Klaus Ziemer GmbH, Germany). They were housed in two types of shelters, one for indoor sampling and one for outdoor sampling (Wilford et al., 2004). The indoor shelter consisted of one stainless steel dome on a tripod support. This design prevents the PUF disk from gravitational deposition of coarse particles but is open to air on all sides to minimize uptake restriction indoors, by encouraging air flow. The outdoor shelter consisted of two stainless steel bowls (20 and 30 cm e.d.) where air is allowed to flow over the PUF disks through a 1.5 cm gap between them.

Prior to deployment, virgin, untreated PUF disks were pre-cleaned by Soxhlet extraction for 24 h using dichloromethane (DCM), dried under vacuum and stored in multiple layers of solvent rinsed aluminium foil inside air tight polyethylene zip bags. The samplers were assembled at each deployment site to avoid contamination during transportation.

2.2. Sites

Air samples were taken in Mexico City (Mexico, population > 20 000 000). Simultaneous sampling was conducted in Gothenburg (Sweden, population ~ 490 000) and Lancaster (UK, population ~ 140 000). Sampling sites were chosen in convenient residential areas, representing different types of households. Three sampling areas within MCMA were chosen in accordance to the MILAGRO project; T0 – in Iztapalapa, near down town Mexico City, T1 – in Tecamac, in the state of Mexico NE Mexico City, and T2 – in San Pedro, in the State of Hidalgo N Mexico City. T0 is classified as urban and representative for the MCMA while T1 and T2 represent semi-rural areas. The sampling sites in Gothenburg and Lancaster were all in urban areas. Mean outdoor temperatures for the sampling period were 17 °C in Mexico City, 2 °C in Gothenburg and 6 °C in Lancaster. The temperatures indoors at all sites were roughly 20 °C.

2.3. Sampling

A total of 46 samplers were deployed simultaneously from March to April, 2006 (Table 1). Indoor samplers were placed in the main living area of the house at ~1 m height. Simultaneously, outdoor air samples were deployed at 11 of the homes (Table 1) at ~1.5 m height and some meters away from the house. The samplers were exposed for a 6–7 week period (42–50 days), the length of the exposure time differed slightly among locations, depending on collection possibilities. Two field blanks were taken in each country. After air sampling, the PUF disks were enveloped in new

Table 1
Sampler distribution between the sites

	In	Out	Total	Duplicate
Mexico City	13	5	18	–
Gothenburg	5	5	10	2
Lancaster	17	1	18	5

solvent rinsed aluminium foil, placed in air tight polyethylene zip bags and then brought back to the laboratory for storage at −20 °C until extraction.

A questionnaire was completed in each home with information on house characteristics, residents' lifestyle, etc. to attempt to identify factors affecting chemical loadings.

2.4. Sample extraction and analysis

All samples were Soxhlet extracted using DCM, cleaned and analyzed at Lancaster University according to a previously published method (Jaward et al., 2004a). Prior to extraction, the samples were spiked with 25 μL of recovery standard (RS) containing seven $^{13}C_{12}$-labelled PCB congeners (25 pg μL^{-1}), 25 μL of RS containing three PBDE congeners (25 pg μL^{-1}), and 20 μL of RS containing one PAH compound (20 pg μL^{-1}) to quality control the method performance during extraction and sample clean-up. A portion (20%) was taken for PAH analysis. The rest of each sample (80%) underwent further clean-up and analysis for PCBs, PBDEs, and OCPs (Jaward et al., 2004a; Moeckel et al., 2008). Samples were stored in a fridge prior to analysis.

2.5. Instrumental analysis

Analysis of PAHs was performed using a Perkin Elmer HPLC system with LC250 binary pump, LS40 fluorescence detector and ISS200 autosampler. A PAH Spherisorb column 15 cm × 4.6 mm i.d. (thermostatically controlled) was used to separate PAHs with an acetonitrile/water gradient at a flow rate of 1.5 mL min^{-1}. Samples were analyzed for 13 PAHs (see Table S2). Quantification was performed using external calibration curves.

PCBs and OCPs were analyzed by gas chromatography–mass spectrometry (GC–MS) on a Finnigan Trace GC–MS. The GC used splitless injection and was fitted with a CP-SIL 8CB capillary column (50 m, 0.25 mm i.d., Varian, USA). PCBs and OCPs (except hexachlorocyclohexanes (HCHs)) were determined with MS operated in positive electron ionisation impact mode using selected ion monitoring (EI-SIM). α- and γ-HCH were determined with MS using SIM but operated in negative chemical ionisation mode (NCI) with ammonia as reagent gas. PBDEs were analyzed separately with a Fisons MD 800 GC–MS system using NCI with ammonia as reagent gas and SIM mode. A total of 43 tri-octa PCB congeners, 11 OCPs (see Table S3), and 22 tri-octa PBDE congeners were quantified.

2.6. Quality assurance/quality control (QA/QC)

Field blanks (1 in ~7 samples) and lab blanks (1 in 12) were routinely included. Only minor residues of PCBs, OCPs, and PBDEs were found in the blanks while PAHs were occasionally detected. All samples were corrected for the blank by subtracting the mean blank value from the estimated amount in each sample. Limits of detection (LOD) were calculated as three times the standard deviation of the mean field blanks. When compounds were not found in the blanks, the concentration of the lowest calibration standard was taken as the LOD. LODs varied depending on compound/congener: 1.0–86 ng sample^{-1} for PAHs, 0.025–0.47 ng sample^{-1} for PCBs, 0.025–0.41 ng sample^{-1} for OCPs, and 0.063–0.097 ng sample^{-1} for PBDEs. Table S1 in Supplementary data gives LOD for each component/congener. The value of LOD/2 was used for further calculations when data were below LOD.

Recoveries were routinely monitored using the recovery standards. Recoveries ranged from 60 to 120% for all compound groups.

3. Results and discussion

3.1. Comments on the interpretation of PUF concentrations

The principles of passive air sampling with PUF disks have been thoroughly explained by others (Shoeib and Harner, 2002; Harner et al., 2004). Data can be reported and compared as the mass taken up per sampler per unit time, or converted to an estimated air concentration (mass per volume of air) using an uptake rate derived from field calibration studies. Recent studies have shown that the uptake rate may differ between compounds/congeners using the PUF disk (Hazrati and Harrad, 2007). Moreover, uptake rate can be affected by sampler design, type of shelter and sampling sites (due to different environmental conditions). However, average sampling rates derived for indoor air using the tripod shelter and for outdoor air using the bowl shelter are 2.5 and 3.5 m^3 day^{-1}, respectively (Shoeib and Harner, 2002; Wilford et al., 2004). These were applied here since other existing sampling rates are derived by using different shelter types which may affect the uptake (especially in stagnant indoor air) compared to our designs. Hence a six week sampling time corresponds to ~100 or 150 m^3 of air. Estimates of air concentrations derived in this way are generally reliable to within a factor of two compared to active sampling but the concentrations should be regarded as approximate estimates or semi-quantitative (Shoeib and Harner, 2002; Jaward et al., 2004b). More detailed calibration studies indoors and outdoors are needed to further improve the quantitative estimates.

3.2. Introductory remarks on the data

All compound groups were detected in all samples, indicating the presence of these contaminants in indoor and outdoor air in Mexico City, Gothenburg and Lancaster. No relationships between elevated levels and typical house features (e.g. age of furnishing, lifestyles) were found and further statistical testing was not undertaken due to the low sample numbers and wide ranges of values. Estimated indoor and outdoor concentrations (range, mean and median) are presented in Tables 2–4. Data are presented as

Table 2
Range, mean and median of estimated indoor and outdoor air concentrations for PAHs (ng m^{-3}) at each area obtained using sampling rates of 2.5 m^3 day^{-1} (indoors) and 3.5 m^3 day^{-1} (outdoors)

		$\Sigma_{3-4\ ring}$PAH			$\Sigma_{5-6\ ring}$PAH			Σ_{13}PAH		
		Range	Mean	Median	Range[b]	Mean	Median	Range	Mean	Median
Mexico City Urban	In	6.1–92	33	28	<LOD–0.53	0.10	0.034	6.1–92	34	28
	Out	32–64	47	44	<LOD–0.42	0.20	0.19	32–64	47	44
Mexico City Semi-rural	In	12–36	25	25	<LOD–1.0	0.19	0.024	12–37	25	25
	Out	72–92	82	82	0.36–0.43	0.40	0.40	72–92	82	82
Gothenburg	In	14–180	68	37	<LOD–1.6	0.33	<LOD	14–180	69	37
	Out	7.6–68	37	33	0.031–0.26	0.11	0.076	7.7–68	37	33
Lancaster	In	8.5–60	30	28	<LOD–0.45	0.052	<LOD	8.5–60	30	28
	Out[a]	6.5	6.5	6.5	0.25	0.25	0.25	6.8	6.8	6.8

[a] Based on one sampling site in this area.
[b] LODs are given in Supplementary data (Table S1).

range and median in further discussions since the values were not normally distributed. The ranges of sequestered amounts (mass per day) are given in Supplementary data (Tables S2 and S3). The agreement between duplicates for compounds primarily occurring in the gas phase was good; the deviations from their means were 5–25%, verifying the applicability of PUF disks to monitor gas phase POPs indoors and outdoors. Data for particle associated compounds both indoors and outdoors show inconsistent results between duplicate samples for PAHs; for example benzo(*a*)pyrene was often detected in only one of the two duplicate samples. More variable results for compounds mainly associated with the particulate phase of indoor duplicate samples have also been observed by Wilford et al. (2004), who reported that the indoor passive samplers mainly sample the gas phase with only a small contribution from particulates. Results from Klanova et al. (2008) indicate the same for outdoor sampling. The efficiency of particle trapping may be influenced by particle sizes and foam (PUF) densities.

3.3. Estimated levels, composition profiles and tracing sources

3.3.1. PAHs

The estimated levels of Σ_{13}PAH ranged from 6.1 to 180 ng m^{-3} in all samples. Phenanthrene was the predominant PAH compound and the 3–4 ring PAHs which are mainly in the gas phase contributed to >96% of Σ_{13}PAH. The indoor levels in Mexico City ranged from 6.1 to 92 ng m^{-3}, with median levels being 28 ng m^{-3} at the urban area, and 25 ng m^{-3} at the semi-rural area. The indoor levels of PAHs tended to be higher in Gothenburg (median 37 ng m^{-3}) than in Mexico City and Lancaster (median 28 ng m^{-3}). The highest indoor levels in Gothenburg were comparable to those found outdoors in Mexico City indicating elevated emissions of PAHs in these homes. The estimated levels from this study are in agreement with those estimated from PUF disk sampling in indoor air in Kuwait, both in terms of the composition profile and ΣPAHs (1.3–16 ng m^{-3}). The levels herein are also in agreement with estimated indoor air levels of PAHs from an area in Sweden where domestic wood burning is widespread (20–250 ng m^{-3}) (Strandberg et al., 2006).

The outdoor levels in Mexico City ranged from 32 to 92 ng m^{-3}. Highest median levels (82 ng m^{-3}) were found in the semi-rural area where both point sources of PAHs (i.e. main roads, backyard burning and forest fires), and wind drift from the urban plume occur. As expected, outdoor levels tended to be lower in Gothenburg and Lancaster compared to Mexico City. The overall range of estimated outdoor PAH levels in this study is in good agreement with other studies in urban centres (e.g. Toronto and Manchester) (Coleman et al., 1997; Motelay-Massei et al., 2005).

3.3.2. OCPs

Some OCPs are still in use or were used until recently in Mexico while their use in Europe is banned or limited since many years. However, both old and new sources may account for the OCPs found in air.

Technical chlordane (CHL) consists of two major components: *trans*-chlordane (*t*-CHL) and *cis*-chlordane (*c*-CHL). Both CHL components were detected in all samples in this study. The estimated indoor levels in Mexico City ranged from 1.8 to 170 pg m^{-3} (median 12 and 3.2 pg m^{-3}), lower than reported for most houses from the US cornbelt (Leone et al., 2000). The highest indoor levels (83–170 pg m^{-3}) were found in the urban area. Indoor levels in Gothenburg (median 7.4) and Lancaster (median 6.5) were similar to most of the levels in Mexico City while somewhat elevated levels were found in some houses in Mexico City. The CHL levels outdoors in Mexico City ranged from 1.5 to 16 pg m^{-3}. Highest levels (7.3–16 pg m^{-3}) were found in the urban area. The outdoor levels in Gothenburg and Lancaster were lower (1 pg m^{-3}).

The two main components in technical-grade HCH are α-HCH (55–70%) and γ-HCH (10–18%). Purified γ-HCH (>99%) goes under the commercial name "Lindane" and is still used in parts of Europe (Jaward et al., 2004a). Technical HCH has an α-HCH/γ-HCH ratio ranging from 4 to 7, while low ratios point to the use of Lindane. The estimated levels of ΣHCH indoors in Mexico City ranged from 1.8 to 310 pg m^{-3} (median 15 (urban) and 3.0 pg m^{-3} (semi-rural)). Two indoor locations deviated from the general picture and showed high levels (230, 290 pg m^{-3}) for the γ-HCH component. The range of ΣHCH levels indoors in Lancaster was also large (47–1300 pg m^{-3}, median 260 pg m^{-3}) and almost half of the sites here showed levels exceeding 300 pg m^{-3} for the γ-HCH component. The indoor levels in Gothenburg tended to be lower

Table 3
Range, mean and median of estimated indoor and outdoor air concentrations for OCPs (pg m^{-3}) at each area obtained using sampling rates of 2.5 m^3 day^{-1} (indoors) and 3.5 m^3 day^{-1} (outdoors)

		ΣCHL			ΣHCH			ΣDDT			HCB			ΣOCP		
		Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Mexico City Urban	In	6.7–170	47	12	5.5–250	52	15	6.5–330	110	41	34–75	54	56	88–700	350	224
	Out	7.3–16	11	9.5	1.9–22	15	21	38–160	110	130	23–37	28	24	71–220	200	250
Mexico City Semi-rural	In	1.8–38	11	3.2	1.8–310	60	3.0	2.8–83	27	19	31–84	47	43	38–360	230	120
	Out	1.5–2.7	2.1	2.1	1.5–3.1	2.3	2.3	30–31	31	31	20–36	28	28	54–72	69	69
Gothenburg	In	4.3–9.3	7.1	7.4	3.3–64	43	50	63–260	190	240	48–100	67	67	180–490	370	440
	Out	0.93–4.7	1.9	1.1	1.0–3.6	2.5	2.2	2.2–57	15	3.4	49–58	53	54	55–120	78	65
Lancaster	In	1.6–27	8.0	6.5	47–1300	440	260	11–340	96	66	35–890	150	92	140–2300	680	410
	Out[a]	0.94	0.94	0.94	370	370	370	9.9	9.9	9.9	19	19	19	400	400	400

[a] Based on one sampling site in this area.

(3.3–64 pg m^{-3}, median 50 pg m^{-3}). Reasons for elevated levels found at some indoor sites in our study (Mexico City and Lancaster) are unclear. The outdoor levels in Mexico City ranged from 1.5 to 22 pg m^{-3} for ΣHCH. Highest levels were found in the urban area. The outdoor levels in Gothenburg were as expected generally low (1.0–3.6 pg m^{-3}, median 2.2 pg m^{-3}) while the outdoor Lancaster site had high levels (370 pg m^{-3}). The α-HCH/γ-HCH ratios in all samples were low (<0.4), indicating regional use or air transport from adjacent regions of Lindane.

Estimated levels of ΣDDTs (*p*,*p*′-DDT, *o*,*p*′-DDT and corresponding metabolites DDD and DDE) showed a wide range from 2.8 to 330 pg m^{-3} indoors in Mexico City (median 41 and 19 pg m^{-3}). The ranges were similar indoors in both Gothenburg (63–260 pg m^{-3}, median 240 pg m^{-3}) and Lancaster (11–340 pg m^{-3}, median 66 pg m^{-3}). The levels outdoors in Mexico City (30–160 pg m^{-3}, median 130 and 31 pg m^{-3}) tended to be higher than outdoors in Gothenburg (2.2–57 pg m^{-3}, median 3.4 pg m^{-3}) and Lancaster (9.9 pg m^{-3}).

A low ratio of *p*,*p*′-DDE/*p*,*p*′-DDT indicates recent use of technical DDT while a ratio larger than 3 normally is expected for aged mixtures. The ratios outdoors in Mexico City were low (0.1–0.5) which in combination with moderate levels of DDT may indicate atmospheric transport from adjacent regions where the pesticide is still in use. Low ratios were also found indoors in both Gothenburg (<0.3) and Lancaster (1.5). This, together with indoor levels comparable to those in Mexico was unexpected, since DDT has been phased out in Scandinavia and the UK since the early 1970s. More studies are needed to look into this issue.

The estimated outdoor levels of CHLs, HCHs and DDTs at all sites are lower than Chiapas (Mexico), Belize and the Great Lakes region (Alegria et al., 2000; Buehler et al., 2001; Strandberg et al., 2001; Alegria et al., 2006), but comparable to those obtained in a north–south transect in Chile (Pozo et al., 2004).

Ambient levels of HCB are generally relatively constant around the world (Barber et al., 2005). Estimated outdoor levels at the studied regions conformed to this expectations: Mexico City (20–37 pg m^{-3}), Gothenburg (49–58 pg m^{-3}) and Lancaster (19 pg m^{-3}), and were similar to those reported as typical for the northern hemisphere (~50 pg m^{-3}) (Barber et al., 2005). Indoor samples in Mexico City and Gothenburg were also in a narrow range: 31–84 pg m^{-3} and 48–100 pg m^{-3}, respectively. A wider range was observed indoors in Lancaster and high levels were found at two houses, 400 and 890 pg m^{-3}, although the reasons are unknown.

3.3.3. PCBs

Europe is the region where PCBs have been used most extensively (Breivik et al., 2002) while information of use and levels in Mexican ambient and indoor air is sparse or lacking (Shen et al., 2006).

The estimated indoor levels of Σ_{tot}PCB ranged from 100 to 840 pg m^{-3} in Mexico City (median 460 and 160 pg m^{-3}), 330 to 1600 pg m^{-3} in Gothenburg (median 500 pg m^{-3}), and 150 to 2100 pg m^{-3} in Lancaster (median 620 pg m^{-3}). All the estimated indoor levels were lower than estimated indoors levels in Birmingham (average 2820 pg

Table 4
Range, mean and median of estimated indoor and outdoor air concentrations for PCBs and PBDEs (pg m^{-3}) at each area obtained using sampling rates of 2.5 m^3 day^{-1} (indoors) and 3.5 m^3 day^{-1} (outdoors)

		Σ_7PCB			Σ_{tot}PCB			Σ_7PBDE		
		Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Mexico City Urban	In	70–220	130	140	210–840	470	460	23–460	120	49
	Out	68–190	130	130	230–660	440	430	31–64	50	55
Mexico City Semi-rural	In	29–89	57	46	100–320	190	160	24–200	72	55
	Out	27–61	44	44	87–210	150	150	15–30	23	23
Gothenburg	In	100–450	260	160	330–1600	890	500	8.5–52	39	17
	Out	20–54	37	36	59–170	120	120	0.68–2.3	1.7	2.0
Lancaster	In	43–1600	500	330	150–2100	860	620	4.7–620	52	16
	Out[a]	53	53	53	120	120	120	5.4	5.4	5.4

[a] Based on one sampling site in this area.

m^{-3}) (Harrad et al., 2006) even when applying the same uptake rates. Levels were also lower than in buildings believed to contain PCB-treated sealants in Switzerland (Kohler et al., 2005) which indicates no primary PCB sources in the studied homes.

The outdoor levels in Mexico City ranged from 87 to 660 pg m^{-3} and tended to be higher in the urban area (median 430 pg m^{-3}) than the semi-rural area (median 150 pg m^{-3}). Previous studies in North America also showed urban areas as sources of PCBs (Buehler et al., 2001; Strandberg et al., 2001; Harner et al., 2004). The median outdoor air levels in Gothenburg and Lancaster (120 pg m^{-3}) are somewhat lower than in Mexico City but showed good agreement to previous published ambient air results in Sweden and the UK, respectively (Lee et al., 1998; Backe et al., 2000).

3.3.4. PBDEs

This may be the first report on PBDEs in Mexico.

The estimated levels of Σ_7PBDEs (28, 47, 49, 99, 100, 153, 154) in all samples ranged from 0.68 to 620 pg m^{-3}. PBDE-47 and PBDE-99 were the dominating congeners, contributing on average 47 and 27%, respectively, to the Σ_7PBDE.

The indoor and outdoor levels in Mexico City ranged from 23 to 460 pg m^{-3} (median 49 and 55 pg m^{-3}) and 15 to 64 pg m^{-3} (median 55 and 23 pg m^{-3}). The median levels indoors and outdoors in Gothenburg (17 and 2.0 pg m^{-3}) and Lancaster (16 and 5.4 pg m^{-3}) were lower than in Mexico City, while the highest single value was found in a house in Lancaster (620 pg m^{-3}). Relatively high levels of PBDEs in the UK have been observed previously and were explained by stringent fire regulations and past manufacture of PBDEs (Jaward et al., 2004a).

The estimated indoor levels in this study are lower than in indoor air in Ottawa, Canada (median 100 pg m^{-3}) (Wilford et al., 2004), while the highest levels found (Mexico City and Lancaster) are similar to those of urban UK sites (Harrad et al., 2006). The outdoor levels in Mexico City are consistent with levels found in Chicago (Strandberg et al., 2001), and Gothenburg and Lancaster are in the same range as those found in other outdoor (winter) studies in Sweden (de Wit, 2002).

3.4. Indoor versus outdoor levels

Ratios between indoor and outdoor air concentrations (I/O ratios) may be used as a tool to indicate whether there are indoor sources (I/O $>$ 1) or outdoor sources (I/O $<$ 1). I/O ratios for the gaseous fraction of ΣPAHs, ΣPCBs, ΣPBDEs, and ΣOCPs in Mexico City and Gothenburg are presented in Fig. 1. Spatially and temporally consistent indoor and outdoor samples were taken at some sites in these cities; Lancaster is omitted in this assessment because of a lack of suitable outdoor data. The I/O ratios were considerably $>$1 in Gothenburg, and generally close to 1 in Mexico City.

The high I/O ratios for ΣPAH in Gothenburg together with somewhat elevated indoor levels may indicate that PAH emissions in these homes are mainly from indoor sources while the opposite pattern was observed in Mexico City. An interesting observation was that low molecular weight PAHs in Gothenburg in general show an I/O ratio well above 1 while the 5–7 ring PAHs are found in more samples outdoors than indoors, giving an I/O $<$ 1. Lower I/O ratios for the 5–7 ring PAHs were also seen in Mexico City. This may indicate the presence of emission sources of mainly low molecular weight PAHs (vapour phase PAHs) indoors. It is believed that PCBs and PBDEs have significant indoor sources and the I/O ratios in Gothenburg (13 and 20) are consistent with this hypothesis while the I/O ratios in Mexico City show another pattern (Vorhees et al., 1997). However, the estimated indoor levels of PCBs and PBDEs are fairly low in the homes in Gothenburg so the elevated I/O ratios may have other explanations (e.g. secondary

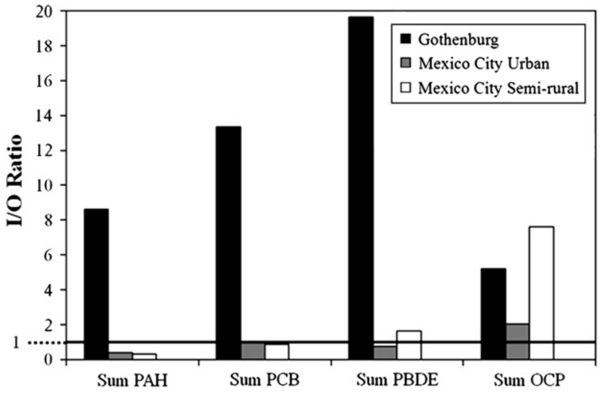

Fig. 1. Ratios of average indoor and outdoor concentrations (I/O) in Mexico City (urban and semi-rural) and Gothenburg. Solid line at I/O = 1 corresponds to equal concentrations indoor and outdoor while values above this means higher indoor concentrations and values below are higher outdoor concentrations.

sources). The high I/O ratios (>5) together with elevated estimated indoor levels for ΣOCPs in Gothenburg may indicate possible indoor sources in these homes. Mexico City has I/O ratios around 1 for ΣDDTs, ΣCHL, and HCB while ΣHCH is much higher indoors in one home giving elevated I/O ratio (~8) for ΣOCP in this area (Fig. 1).

The different pattern of I/O ratios between Gothenburg and Mexico City can be explained by a number of factors. The I/O ratios are based on present sources in the indoor and outdoor environments. This is complicated by other factors such as type of source (primary/secondary), age of the contaminant sources, and different climatic and housing factors such as air exchange rates. The rate of air exchange is an important factor and reduced air exchange rates and rates below one exchange per hour have been reported to give higher I/O ratios for fine particles (Bahadori et al., 1999; Rojas-Bracho et al., 2000). General air exchange rates are about five times higher in Mexico than in Sweden. Additionally, hydrophobic materials indoors may act as sinks for POPs (i.e. carpets, PUF containing fillings, furnishing, dust) and the POPs are more protected from degradation such as photodegradation and biodegradation in those than in outdoor sinks/sources (Vorhees et al., 1997). Thus, there might be a build up of POPs in these materials and they may act as secondary emission sources. Differences in home furnishing traditions between regions may therefore contribute to the I/O ratio differences.

Temperature may also affect the I/O ratio. Air concentrations of POPs are strongly correlated to atmospheric temperature (Buehler et al., 2001). For example, emissions of PCBs, OCPs, and PBDEs from secondary sources outdoors decrease during wintertime, while PAHs have emission sources during wintertime, because of increased industrial and domestic heating. Differences in temperature may also affect the gas-particle partitioning for PAHs and PBDEs, in turn affecting sequestration by the PUF disk. Temperature may result in 2–3 times higher concentrations outdoors in Mexico City (17 °C) than Gothenburg (2 °C), although the differences in I/O ratios herein are greater than this. More detailed studies are needed to verify sources indoors and outdoors and to what extent various factors imply on observed levels.

This study demonstrates the power of passive air sampling for reconnaissance studies. The trends and levels obtained here support previous active sampling studies, but with data obtained quicker, easier and at lower cost. Furthermore, the opportunity afforded to deploy many samplers simultaneously makes source identification and process-based studies more readily achievable. In future, the routine use of depurate compounds (DC) which deplete over time as a function of wind speed/exposure will help passive air sampling approach towards more quantitative estimates of “true” air concentrations.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2008.07.012.

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