ASSESSMENT OF PCDD/F, DIOXIN-LIKE PCB AND PBDE INDOOR AIR BACKGROUND LEVELS USING PUF PASSIVE AIR SAMPLERS

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1. Introduction

PCDD/Fs, dl-PCBs and PBDEs are toxic, persistent, lipophilic chemicals which accumulate in biological tissues and are also present in water, air, soils and sediments. All these compounds can undergo long-range atmospheric transport, which means that POPs can be transferred from sources to the ambient environment in all areas.

Passive samplers can be used to accumulate organic compounds in the environment and allows for the estimate of the ambient concentrations in either homogenous or heterogenous media into which they are deployed. Examples include semipermeable membrane devices (SPMDs), Polyurethane foam (PUF) disks, Polymer coated glass (POG) and XAD resin cartridges. Passive air samplers (PAS) are being increasingly used to monitor persistent organic pollutants (POPs) in the atmosphere due to their high capacity to retain such compounds over the sampling period. The advantage they have over high-volume air samplers is that they do not use electricity and can be used in remote areas. They are generally small, easy to handle and operate, inexpensive, relatively non-intrusive can be used simultaneously in different locations and no maintenance is required during deployment[1-2].

In this study, PUF disk passive air samplers were used to investigate the accumulation of PCDD/Fs, dl-PCBs and PBDEs in the indoor air of a laboratory building. This study aimed to determine background concentrations of these persistent organic pollutants in air samples in five selected rooms within the laboratory building as sampled by PAS. The rooms chosen were predominantly the laboratory areas where dioxin analysis takes place; High Level Laboratory (Industrial samples > 10pg/g), Low Level Laboratory (Environmental and Food samples < 10pg/g), two Instrument rooms and a Library. The sampling medium was exposed to indoor air for a period of four months and analysis performed thereafter.

2. Materials and Methods

2.1 Sample collection

PUF-disk based air samplers were deployed at five locations within the NMI-Pymble Laboratory namely Low Level Laboratory (LLL), High Level Laboratory (HLL), HRMS Level 3, HRMS Level 4 and the Library. Samplers were deployed in a two-disk configuration per sampling chamber labelled (Top and Bottom). All PUF disks and stainless steel chambers were pre-cleaned with solvents. PUF disks were spiked with ^{13}C labelled surrogates for PCDD/Fs, dl-PCBs and PBDEs and housed in stainless steel chambers to protect the disks from coarse particle deposition, precipitation and sunlight.
The sampling media were exposed to a variety of indoor environments which include usage (as per above), flooring (carpet, non-carpet), presence of air conditioner, closeness to specific sources (eg. photocopier, instruments) and proximity to door. The air samples were collected after a period of 122 days.

Laboratory blank and two field blank samples were prepared. The field blanks consisting of clean PUF disks were spiked and placed in pre-cleaned amber jars. Jars were sealed and stored in fridge (4 °C) and these should not be opened or exposed to ambient air at any stage until time of analysis.

2.2 Sample extraction and analysis

The analytical methodology for the determination of PBDEs, PCDD/Fs and PCBs was based on the USEPA methods 1613, 1668 and 1614.
The PUF disks were individually spiked with isotopically labelled surrogate compounds (PCDD/Fs, PCBs and PBDEs) to act as internal standards prior to extraction by Accelerated Solvent Extraction (ASE - Dionex 100, Pressure 1700 psi, temperature 150°C) in Toluene. The extracts were concentrated and solvent exchanged to hexane. Samples were acid treated (H_2SO_4) for removal of matrix interference then purified and fractionated using an automated Fluid Management System (FMS) PowerPrep. The system utilises multi-layers Silica (acidic, neutral and basic), basic Alumina (for separation of Dioxins and dl-PCBs based on polarity) and Carbon dispersed on Celite (retains all of Dioxins and non-ortho PCBs). PCBs and PBDEs were eluted together in one fraction, with PCDD/F being eluted in a separate fraction. These were concentrated and solvent exchanged to Dichloromethane and evaporated to 'just dryness' by nitrogen blow-down prior to adding isotopically labelled Recovery Standards and Nonane. Instrumental analysis was performed using high resolution gas chromatography /high resolution mass spectrometry (HRGC/HRMS). An aliquot of the extract is injected into the GC, the analytes are separated by the GC and detected by the high-resolution (>10,000) mass spectrometer.

3. Results and discussion

In this study the concentrations of 7 PCDD and 10 PCDF congeners, 12 dl-PCB congeners and 33 tri through deca-brominated BDE congeners in ambient air were determined. The measured air concentrations of PCDD/Fs, PBDEs and PCBs are summarised in tables 1, 2 and 3 respectively. Results displayed are in pg/PUF for PCDD/Fs and pg/m^3 for PCBs and PBDEs for the total sampling period of 122 days. Blank and Field Blank samples showed no detectable amounts of PCDD/Fs and low PCB and PBDE concentrations (mean 2 pg/m^3 for ΣPBDEs).

Table 1: PCDD/Fs results reported in pg/PUF

	NMI ID LRN					
Congener	**LLL C#1**	**HRMSL3 C#2**	**HLL C#3**	**Library C#4**	**HRMSL4 C#5**	**Field Blank**
2,3,7,8-TCDF	<2	<4	<3	<3	<3	<2
2,3,7,8-TCDD	<2	<3	<3	<3	<3	<3
1,2,3,7,8-PeCDF	<2	<3	<2	<2	<1	<0.6
2,3,4,7,8-PeCDF	<0.9	<1	<2	<1	<1	<1
1,2,3,7,8-PeCDD	<1	<2	<3	<2	<2	<2
1,2,3,4,7,8-HxCDF	<1	<1	<1	<2	<1	<1
1,2,3,6,7,8-HxCDF	<2	<1	<1	<2	<1	<1
2,3,4,6,7,8-HxCDF	<0.8	<0.9	<1	<1	<1	<1
1,2,3,7,8,9-HxCDF	<0.7	<1	<1	<0.9	<1	<1
1,2,3,4,7,8-HxCDD	<2	<2	<3	<2	<2	<2
1,2,3,6,7,8-HxCDD	<2	<2	2.6	13	<2	<2
1,2,3,7,8,9-HxCDD	<1	<1	<2	5.0	<2	<1
1,2,3,4,6,7,8-HpCDF	<3	<3	<4	7.0	<2	<2
1,2,3,4,7,8,9-HpCDF	<1	<1	<1	<2	<1	<1
1,2,3,4,6,7,8-HpCDD	5	3	33	240	5	<3
OCDF	<2	<2	<3	5.0	<2	<1
OCDD	<10	<10	45	200	<10	<10
WHO_{05}-TEQ_{DF}						
Lower Bound [excluding LOD values]	0.050	0.030	0.47	4.1	0.050	0
Middle Bound [including half LOD values]	2.2	3.1	4.1	7.2	3.1	3.1
Upper Bound [including LOD values]	4.1	6.1	7.8	10	6.0	6.2

Most rooms showed WHO_{05}-TEQ_{DF} results for PCDD/Fs in the upper bound to be less than 10 pg/PUF reflecting the clean laboratory environment and instrument areas for ultra trace analysis. The levels of PCDD/Fs in the Field Blanks are comparable to those in the analytical areas; however the Library displayed some positive results for congeners 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDF 1,2,3,4,6,7,8-HpCDD, OCDF and OCDD respectively. The overall upper bound result however, was still low, 10 pg/PUF.This result was unexpected as the Library area is remote from the ultra trace laboratories and no obvious dioxin sources are present, although further studies would be required to investigate this observation.

Table 2: Results for major PBDE congeners in pg/m^3

Congener	LLL C#1	HRMS L3 C#2	HLL C#3	Library C#4	HRMS L4 C#5	Field Blank
TriBDE-28 + 33	160	710	300	18	200	<0.49
TeBDE-47	250	770	520	71	520	<4.4
PeBDE-99	48	97	120	23	83	<4.4
PeBDE-100	14	38	34	6.0	33	<0.99
HxBDE-153	1.9	1.6	4.7	1.6	1.3	0.43
HxBDE-154	1.7	2.1	4.1	1.3	1.6	0.39
HpBDE-183	0.20	0.19	0.33	0.79	0.15	<0.15
DeBDE-209	<4.9	<10	190	<10	<10	<4.9

The concentration of PBDEs as sampled by the PUF disk air samplers over the sampling period were approximately converted to pg/m^3 utilising the sampling rate of 1.66 m^3d^{-1} derived by Hazrati et Harrad (2007). A sampling rate of 1.66 m^3d^{-1} based on the average of R values determined for PBDEs 17, 28, 47, 49, 66, 99 and 100 could be applied to estimate airborne concentrations for other PBDEs[3]. Based on this sampling rate it was estimated that the PUF disks would have sampled 203 m^3 of air for the deployment period.

The major PBDE congeners were detected in all air samples in the analytical rooms including the Library. The major congeners included TriBDE-28 + 33, TeBDE-47, PeBDE-99, PeBDE-100, HxBDE-153 and HxBDE-154. The ΣPBDE ranged from 130 pg/m^3 to 1600 pg/m^3 with the mean concentration of 860 pg/m^3.

Congener DeBDE-209 was not detected in any of the rooms except for the High Level Laboratory (HLL). A possible reason for the absence of BDE-209 may be owing to its association with aerosol particles at ambient temperatures. Most passive samplers are designed to sample gas phase chemicals[4].

The reason for the detection of BDE-209 in HLL room is unclear. NO confirmation was made in regards to this result.

The lowest ΣPBDE concentration (130 pg/m^3) was found in the Library, a room with carpet, air-conditioner and foam padded furniture. The highest ΣPBDE concentration (1600 pg/m^3) was found in the instrument room HRMS L3, a small size room with two air conditioning systems, some sound proofing foam, instruments, one computer and a printer. Similar ΣPBDE concentrations (880and 1200 pg/m^3) were found for two rooms, HRMS L4 and HLL respectively. The ΣPBDE concentration found in the LLL room was 490 pg/m^3, lower than all other analytical rooms. This would be expected, being a room with less furnishing and electrical/electronic appliances than all other analytical rooms.

The differences in the PBDE concentrations in air in the selected rooms may be related to distinct sources within each given room. Studies have suggested that PBDE concentrations in any room will be affected by specific sources and complicated by factors such as ventilation rate, proximity of the sampler to potential sources and age of those sources rather than building characteristics[5].

The congener profile from the indoor air samples was similar for all rooms with dominance by BDE-47, followed by BDE-28 + 33, BDE-99, BDE-100 and BDE-154 ≈ BDE-153 respectively, suggesting that the major sources of PBDEs indoors, in this case, is likely due to volatization from Penta treated products as well as retention /ventilation[4].

Table 3: PCB results in pg/m^3

Congener	LLL C#1	HRMSL3 C#2	HLL C#3	Library C#4	HRMSL4 C#5	Field Blank
TePCB-77	0.55	1.7	1.7	1.8	0.65	0.037
TePCB-81	0.024	0.11	0.090	0.12	0.043	0.0024
PePCB-105	25	41	63	12	13	2.0
PePCB-114	1.7	3.2	4.3	0.93	1.0	0.17
PePCB-118	67	110	160	35	37	5.5
PePCB-123	0.86	5.7	8.5	4.4	0.63	0.13
PePCB-126	0.046	0.074	0.069	0.032	0.051	0.018
HxPCB-156	6.9	9.8	18	2.3	3.1	0.60
HxPCB-157	1.4	2.0	3.7	0.47	0.62	0.19
HxPCB-167	2.2	3.5	6.0	0.83	1.1	0.19
HxPCB-169	0.012	0.013	0.0078	0.0092	0.0060	0.018
HxPCB-189	0.12	0.22	0.44	0.092	0.11	0.10

The calculated air concentrations of PCBs are summarised in Table 4. A sampling rate of 0.89 m^3d^{-1} as derived by Hazrati et Harrad (2007) was used to calculate the air concentrations of PCBs in indoor air in the selected rooms. The volume of air estimated was 109 m^3 for the sampling period.
PCB congeners were detected in all rooms, however, some were at lower levels compared to the analytical blank. The dominant congeners in all the selected rooms were PePCB-118, PePCB-105 and HxPCB-156 respectively.
The rooms which contained the highest concentrations of PCBs were the HLL and the HRMS L3; the LLL had lower levels of PCB concentrations than these two rooms. The LLL is under positive pressure, although the results still showed traces of contamination. The Library and the HRMS L4 displayed similar patterns despite being in well separated areas. The Library contains mostly books and furnishings and the HRMS L4 has all new equipment; analytical instruments, new office furniture and computers. This may be indicative of the background levels within the building.
The air concentrations do not account for the different actual airflows at each location.
These results were not necessarily what was anticipated and may reflect a more complex system, and require further investigation to confirm these initial findings.

Acknowledgement

NMI – Pymble DAU would like to thank the National Research Centre for Environmental Toxicology (EnTox) for providing the Passive Air Samplers for this experiment.

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