Environmental Pollution 193 (2014) 269–276

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Levels and profile of several classes of organic contaminants in matched indoor dust and serum samples from occupational settings of Pakistan

Nadeem Ali [a, b], Toufeer Mehdi [c], Riffat N. Malik [d], Syed A.M.A.S. Eqani [e], Atif Kamal [d], Alin C. Dirtu [a], Hugo Neels [a], Adrian Covaci [a, *]

[a] Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[b] Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah, Saudi Arabia
[c] Microbiology Division, Agriculture and Agri-Food Canada, Lacombe, Alberta, Canada
[d] Environmental Biology and Ecotoxicology Laboratory, Department of Environmental Sciences, Quiad-i-Azam University, Islamabad 45320, Pakistan
[e] Department of BioSciences, COMSATS Institute of Information Technology, Park Road, Islamabad, Pakistan

ARTICLE INFO

Article history:
Received 18 April 2014
Received in revised form
28 June 2014
Accepted 1 July 2014
Available online 26 July 2014

Keywords:
Organic contaminants
Occupational settings
Serum
Dust
Pakistan

ABSTRACT

Dust ingestion is an important route of human exposure to organic contaminants, especially for flame retardants (FRs) in occupational settings. Several classes of organic contaminants were analyzed in matched dust and serum samples from academics and workers in electronics and clothing stores of Faisalabad, Pakistan. The concentrations of contaminants varied in dust as follow: organophosphate FRs (∑PFRs) > novel brominated FRs (∑NBFRs) > polybrominated diphenyl ethers (∑PBDEs) > organochlorine pesticides (∑OCPs) > polychlorinated biphenyls (∑PCBs), while, in serum, concentration varied: ∑OCPs > bromophenols (∑BPs) > ∑PCBs > ∑HO-PCBs ≈ ∑PBDEs. Two NBFRs, namely 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) and bis(2-ethylhexyl) tetrabromophthalate (TBPH), were detected in <10% of the serum samples. *p,p′*-DDE was the major contaminant in serum contributing to ~75% of the total contaminant burden. Levels of Penta-BDE congeners in serum and dust were significantly correlated ($r = 0.64$, $p < 0.01$) for the academics, suggesting dust ingestion as an important determinant for their serum levels.

1. Introduction

Organic contaminants including polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs), are widely occurring in the environment and animal tissues (Dirtu and Covaci, 2010; Law et al., 2008; Srogi 2008). Recent reports on the occurrence of novel brominated flame retardants (NBFRs) and organophosphate flame retardants (PFRs) in different environmental compartments, including the indoor environment (Covaci et al., 2011; Stapleton et al., 2011; Van den Eede et al., 2011) provided critical information about their current status and ecological risks. Many of these contaminants are lipophilic, highly stable in the environment and can induce adverse health effects to both wildlife and humans due to mutagenic, teratogenic and carcinogenic properties (ATSDR, 2000, 2002; 2004). Considered as an international issue, the use of many of these chemicals has been restricted and several are listed under Stockholm Convention, e.g. PCBs, most OCPs and Penta- and Octa-BDEs (Stockholm Convention on POPs, 2009).

While the importance of various routes of human exposure is still unclear, studies have shown that humans are exposed to these chemicals *via* food, air and dust intake (Dirtu and Covaci, 2010; Mercier et al., 2011). Indoor dust is often used as a marker of indoor exposure due to its importance as a sink and repository for semi volatile organic compounds and particle-bound matter (Butte and Heinzow, 2002). Recently, the role of dust as potential human non-dietary exposure source to organic contaminants has been suggested as an attractive area of research (Ali et al., 2013a; Dirtu et al., 2012; Mercier et al., 2011). Human exposure to organic contaminants *via* indoor dust ingestion and food consumption has been the focus of several studies from North America (Imm et al., 2009), Europe (Dirtu and Covaci, 2010) and Japan (Inoue et al., 2006).

* Corresponding author.
E-mail address: adrian.covaci@uantwerpen.be (A. Covaci).

http://dx.doi.org/10.1016/j.envpol.2014.07.009
0269-7491/

To date, there has been no to limited information on organic contaminants in Pakistan or an evaluation of correlations between dust intakes and concentrations in humans (Ali et al., 2013a,b; Eqani et al., 2012). Serum can be good biomarkers to assess human exposure, while indoor dust is a good indicator to indoor organic pollution (Ali et al., 2013a,b). Therefore, serum and indoor dust were considered to assess concentrations of several classes of legacy and emerging contaminants (Table 1) in different occupational settings of Faisalabad, Pakistan. The city of Faisalabad is located in the province of Punjab, Pakistan and in past decades was characterized by intensive industrial activities, such as textile industry, and urban development. Occupational settings have always been a source of chemical exposure to workers, but due to the dearth of information and lack of routine surveillance systems, large numbers of workers are routinely exposed to various indoor chemicals especially in developing countries like Pakistan (Kamal et al., 2012). Many of the organic contaminants are associated with human health effects, but few studies are available on their direct link with the health condition. For instance, hepatitis C has a high prevalence in Faisalabad, Pakistan (Ahmad et al., 2007).

Therefore, the objectives of the study were: (i) to study the occurrence and profiles of selected organic contaminants in matched indoor dust and serum from different occupational settings, (ii) to study the dust ingestion as an exposure pathway for these contaminants, and (iii) to study the effects of organic pollutant on the marker for liver health. This investigation fills an existing gap related to the lack of routine surveillance systems in developing countries. It also sets fundaments for future biomonitoring studies on human exposure in occupational settings.

2. Materials and methods

2.1. Reagents and materials

Individual standards of OCPs, PCBs, PBDEs, HO-PCBs, and HO-PBDEs were obtained from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Standards of NBFRs, BPs were purchased from Wellington Laboratories (Canada), while PFRs standards, except for TCPP (Pfaltz & Bauer, Waterbury, CT, USA), were supplied by Chiron AS (Trondheim, Norway). Several internal standards (ISs) BDE 77 and BDE 128 (AccuStandard Inc, USA), $^{13}C_{12}$-BDE 209, ε-HCH, 2,2′,3,4,5,6′-hexachlorobiphenyl (CB 143), 4′,hydroxylated-2,3′,3,4,4′,6′-hexachlorobiphenyl (4′HO-CB 159) (Wellington Laboratories), tri-amyl-phosphate (TAP) (TCI Europe, Zwijndrecht, Belgium) and triphenyl-phosphate-d15 (TPP-d15) (Sigma, Aldrich) were used. All solvents and chemicals used during the analysis were of pesticide-grade purchased from Acros Organics (Geel, Belgium) and Merck (Darmstadt, Germany). Anhydrous sodium sulfate (Na_2SO_4) and silica gel (Merck) were washed with *n*-hexane and used after heating overnight at 160 °C. A positive pressure manifold (3M Company, St. Paul, MN, USA), Oasis® HLB extraction cartridges (6 mL/500 mg, Waters, Milford, MA, USA) and silica Bond Elut (3 mL/500 mg, Agilent Technologies, Palo alto, CA, USA) were used for solid-phase extraction (SPE). Empty polypropylene columns for clean-up (3 mL) were purchased from Supelco (Bellefonte, PA, USA).

Table 1
Organic contaminants studied in the indoor dust and human serum during present study.

NBFRs	1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), Hexabromobenzene (HBB), Decabromodiphenylethane (DBDPE), Hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO), 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), Bromophenols (mono–penta)
OCPs	Hexachlorobenzene (HCB), cis-Chlordane (CC), trans-Chlordane (TC), Oxychlordane (OxC), trans-Nonachlor (TN), Hexachlorohexane (α-HCH, β-HCH, γ-HCH), Dichlorodiphenyldichloroethane (*p,p′*-DDD), Dichlorodiphenyl-dichloroethylene (*p,p′*-DDE), Dichlorodiphenyltrichloroethane (*p,p′*-DDT).
PCBs	99, 101, 105, 118, 138, 153, 156, 170, 180, 183, 187, 194, 199, 206, 209
HO-PCBs	4′HO-CB 79, 4′HO-CB 120, 3HO-CB 118, 4′HO-CB 107, 4′HO-CB 146, 4′HO-CB 127, 3HO-CB 138, 3′HO-CB 153, 4HO-CB 130, 4HO-CB 163, 4′HO-CB 162, 4HO-CB 177, 4HO-CB 187, 4HO-CB 193, 4′HO-CB 172, 3′HO-CB 180, 4′diHO-CB 202, 4′HO-CB 208.
PBDEs	28, 47, 99, 100, 153, 154, 183, 196, 197, 203, 209
HO-PBDEs	3HO-BDE28, 5HO-BDE47, 6HO-BDE99
PFRs	Tri-ethyl-phosphate (TEP), Tris–(2-chloroethyl)-phosphate (TCEP), Tris–(1,3-dichloro-isopropyl)-phosphate (TDCPP), Tri–n-propyl-phosphate (T*n*PP), Tri-iso-butyl-phosphate (T*i*BP), Tris–(1-chloro-2-propyl)-phosphate (TCPP), Tri-(2-butoxyethyl)-phosphate, Tri-cresyl-phosphate (TCP), Tri-phenyl-phosphate (TPhP), Tri-n-butyl-phosphate (T*n*BP).

2.2. Study participants, serum and indoor dust sampling

A total of 61 paired samples of blood and dust were collected from Faisalabad, Pakistan in December 2011. Of these, 30 paired samples were collected from people (age ranged 17–55 years, mean 30 years) working in old and new electronic (computer, home appliances and mobile) stores. The rest of the samples included people (age ranged 17–55 years, mean 29 years) working in old and new clothing stores ($N = 15$), and academics (age ranged 18–32 years, mean 25 years) ($N = 16$, young lecturers and post graduate students) from the University of Agriculture, Faisalabad, Pakistan. All individuals participating in this study were volunteers who signed an informed consent. For blood samples, baseline data, including age, gender and occupational history were collected from each participant. A volume of 7–8 mL blood was collected by venipuncture at a local clinic following overnight fasting. Blood was collected into sterile glass collection tubes without anticoagulant and after 1 h at room temperature; the serum was separated by centrifugation at 4000 g for 10 min, transferred to new tubes and kept at −20 °C until analysis. The serum lipid content was determined from enzymatic measurements of cholesterol and triglycerides (Phillips et al., 1989), which were done at the same clinic. Serum glutamic-pyruvic transaminase (SGPT) and serum glutamic oxaloacetic transaminase (SGOT), clinically a marker for liver health, were also measured to study the pollutants burden in people with normal and elevated enzymes. The study was approved by the Quiad-i-Azam University-Ethical Review Committee.

Dust samples were collected by brushing the floor surface (4–8 m^2) and, to avoid cross contamination, the brushes from the respective store/office/hostel room were used to collect samples. After brushing, dust was swept onto the aluminum foil, rapped and sealed in polyethylene zip bags. General information about the indoor inventories (details of electronics, foam chairs and other possible emission articles for chemicals) and date of last cleaning were collected. Before transfer to the laboratory, samples were kept in the dark to avoid photo-degradation. Each dust sample was sieved through a 500 μm mesh sieve pre-cleaned with acetone and stored in polypropylene recipients in a dark place. To prevent cross-contamination, sieves were scrubbed with acetone between homogenization of the samples.

2.3. Sample preparation and instrumentation

The procedure for extraction and clean-up for serum was used with minor modifications of previously described method (Covaci and Voorspoels, 2005; Dirtu et al., 2010). Details about the serum sample preparation are given in Ali et al. (2013b) and briefly in supplementary information (SI). The extraction and purification method of dust is described in detail in Van den Eede et al. (2012) and briefly in SI.

Details about the instrumental analysis of dust samples are described elsewhere (Ali et al., 2012; Van den Eede et al., 2012). Briefly, the analysis of PCBs, OCPs, NBFRs and PBDEs was performed by 6890 Agilent (Palo Alto, CA, USA) gas chromatography (GC) coupled to a 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI). A DB–5 column (15 m × 0.25 mm × 0.10 μm) was used for separation and the MS was deployed in selected ion monitoring (SIM) mode. The ion source, quadrupole and interface temperatures were set at 200, 150 and 300 °C, respectively. The analysis of PFRs was performed by GC–MS in electron ionization (EI) mode. A HT–8 column (25 m × 0.22 mm × 0.25 μm) was used and the MS was operated in SIM mode with two characteristic ions acquired for each compound. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively.

For 1st fraction of serum samples, the analysis was performed on GC-ECNI/MS using a DB-5 column (15 m × 0.25 mm × 0.10 μm) was used. The ion source, quadrupole and interface temperatures were set at 170, 150 and 300 °C, respectively. For 2nd fraction of the serum samples, a DB-5ms column (30 m × 0.25 mm × 0.25 μm) was used. The ion source, quadrupole and interface temperatures were set at 200, 150 and 300 °C, respectively. More details about method are available in Ali et al. (2013b), the quantification and identification ions for analytes and their corresponding ISs are given in SI (Table S1).

2.4. Quantification and quality assurance

Multi-level calibration curves were created for the quantification and good linearity ($r^2 > 0.995$) was achieved for the whole concentration range found in the samples. The analytes identification was based on relative retention times and ion chromatograms to the standards. A deviation of the ion intensity ratios within 20% of the mean values of the calibration standards was considered acceptable. Method