CHARACTERIZATION OF POLYCHLORINATED BIPHENYL AND BROMINATED FLAME RETARDANTS IN SOIL AND SEDIMENT FROM DIFFERENT LAND-USE AREAS IN FIJI

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Introduction

Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) are classified as brominated flame retardant (BFRs) chemicals and have been used in an array of products, including electronic products, furniture, upholstery, textiles and other household products[1] to reduce flammability. Studies on animal and humans have identified that PBDEs and PBBs are able to accumulate in human adipose tissue and have the potential to cause adverse health effects[2]. Both groups of BFRs (PBDEs and PBBs) are structurally similar to polychlorinated biphenyls (PCBs), are fat-soluble and hydrophobic[3,4]. PBDEs and PBBs have shown similar characteristics to persistent organic pollutants (POPs) and both commercially relevant pentabromodipnenyl ether and octabromodiphenyl ether have been included as new POPs under the Stockholm Convention (SC)[5]. POPs are banned or severely restricted group of hazardous chemicals that are persistent, bioaccumulate in food chains and have the potential to impact at all levels of the trophic system. The Stockholm Convention is a global environmental treaty on elimination of persistent organic pollutants (POPs) which came into force in May 2004. Most countries in the Pacific Island Region (PIR) have ratified the Stockholm Convention, including Fiji. Fiji is one of the 22 Island Countries within the PIR and is an archipelago of more than 300 islands which lies between 15°-22.5°S latitude and 174°E-177°W longitude, spread over a total area of 709 700km^2 of which 97% is ocean[6]. Most island nations in the PIR have limited land-mass and agricultural or industrial development is mainly located along the coastlines, it is here where pollution related problems are most likely to occur[6]. None of the island nations in the PIR manufacture PCBs and PBDEs, but there is an increasing use of source items such as from electronics. Electronic waste is typically collected together with other waste and is subject to open burning at municipal dumps, hospital incinerators or households. Soils play an important role in the distribution and biogeochemical cycling of PCBs and PBDEs as they are a major reservoir and sink for PCBs and PBDEs due to their large sorption capacity[7]. The aim of this study was to provide new information on a wide range of PCB congeners and to establish baseline data on concentration and distribution of selected BFRs in soils and sediments collected from Fiji Islands. The study also was designed to investigate the importance of any local anthropogenic sources of PCBs and BFRs by relating data to land-use types.

Materials and methods

Four soil and eleven sediment sampling locations representing different land-use types on Fiji Islands were selected to cover a geographical representation of Fiji (Table 1). About 10 cm of the top soil was dug out at each soil sampling site with a clean shovel. Sediment samples were collected from near shore at a water depth of 5 m using a grab sampler made from aluminium. Three replicate subsamples from each site were combined and homogenized. These composite samples were freeze dried, sieved through a 2 mm sieve and placed in individual solvent washed amber jars. Samples were then transported to the National Measurement Institute (NMI) in Sydney, Australia and the National Research Centre for Environmental Toxicology (EnTox) in Brisbane, Australia for analysis. Analysis for PBDEs was carried out at NMI, an accredited laboratory using methods adopted from the USEPA Method 1614 (i.e. isotope dilution technique and quantified using HRMS)[8]. A total of 26 PBDE congeners and BB 153 were screened. Analysis for PCBs was carried out at EnTox/QHFSS using in-house standard operating procedure (i.e internal standards technique and quantified using GCMS). A total of 34 PCB congeners were screened. For QAQC, a laboratory blank was included and recoveries of the internal/surrogate standard were calculated for all samples. The PCBs and BFRs detected in soils and sediments were reported on a dry weight (dwt) basis.

Results and discussion

The internal / surrogate standards for spiking to calculate recovery and instrument calibration standards were used for quality control and quality assurance purpose. The recoveries of surrogate standards were between 60 - 136%. A number of PCB congeners were detected, including the indicator PCBs (i.e PCB 28,101,105,118,138,153,180). However, certain PCBs were not detected especially at a remote site (RE_MS23) that had low concentrations of detectable PCBs. For comparison of $\Sigma PCBs_{34}$ for land-use types the results are presented as "middle-bound" or including half the limit of detection (LOD). The $\Sigma PCBs_{34}$ value for all sediment samples analysed were found in a range of 20 pg g^{-1} – 10000 pg g^{-1} (SD = 2870 pg g^{-1}; median = 4130 pg g^{-1}) dwt. Principal Component Analysis (PCA) was conducted to identify clustering of various sediment samples that could characterize contamination sources of PCBs from various land-use areas. It is noteworthy that sediment samples from similar land-use areas clustered together in three distinct clusters (Figure 1). A study on estuarine sediments from coastal areas in Fiji also reported low levels of PCBs with elevated concentrations detected in surface sediments collected near urban land-fill sites[6].

A number of PBDE congeners were detected, however, PBDE 47 and PBDE 209 congeners were found in highest concentrations. Certain PBDE congeners were not detected especially at remote sites that had low concentrations of detectable PBDEs (Table 2 and Table 3). For comparison of $\Sigma PBDE_{26}$ for land-use type the results are presented as "middle-bound". The concentrations of $\Sigma PBDE_{26}$ found in the soil samples from the four sampling locations are summarized in Table 2. The $\Sigma PBDE_{26}$ value for all soil samples analysed were found in a range of 370 pg g^{-1} dwt to 2700 pg g^{-1} dwt (SD = 1100 pg g-1 dwt ; median = 800 pg g^{-1} dwt). The concentration range for PBDE 47 and PBDE 209 detected in the soil samples taken from the various sampling sites was 97 pg g^{-1} to 402 pg g^{-1} (SD = 150 ; median = 120) dwt and 97 pg g^{-1} to 2000 pg g^{-1}(SD = 950 ; median = 160) dwt, respectively.

The current study on soil from different land-use areas in Fiji indicates a chemical profile where PBDE 209 is the dominant PBDE congener detected. PBDE 209 contributes on average 31% but up to 75% towards the total concentration of PBDE present in the soil samples from different sampling sites. The highest levels for PBDE 209 shown in Table 2 were detected at PU_S02, followed by IN_SO15 (Table 2). With respect to PBDE 47 congener, the most contaminated soil sample was found to be from an industrial site (IN_SO15 at 402 pg g^{-1}dwt) followed by soil from a peri-urban site (PU_SO2 at 132 pg g^{-1}dwt). Both these sampling sites (PU_S02 and IN_S015) are close to open waste disposal sites. It is noteworthy that in soil samples BB 153 correlates with PBDEs in terms of higher concentration found in urban and industrial land-use types in comparison to sampling location in remote land-use areas (Table 2). The behaviour of BB153 in relation to PBDE accumulation in soil samples indicates some unknown local anthropogenic source rather than just a contribution from long range atmospheric transport (Table 2). The concentrations of PBDE compounds found in sediment samples from the seven sampling locations are summarized in Table 3. The concentration range for $\Sigma PBDE_{26}$ was 300 to 530 pg g^{-1} (SD = 90; median =380) dwt. The PBDE congener profile in sediments from all the seven sampling sites shows PBDE 209 and PBDE 47 concentrations being dominant and contributing up to 65% and 30% towards the total $\Sigma PBDE_{26}$, respectively. The brominated compound BB 153 (60% FIREMASTER) was found in all soil and sediment samples from the various land-use sites. The concentration of BB 153 was detected in a range of 0.1 pg g^{-1} dwt to 14 pg g^{-1} dwt in soil (SD = 7 ; median = 0.7) and 0.1 pg g^{-1} dwt to 11 pg g^{-1} dwt in sediment (SD = 4 ; median = 0.5) from various land-use sites across Fiji . The highest concentration of BB 153 was found at a peri-urban site (PU_SO2 at 14 pg g^{-1} dwt) followed by an agricultural site (AG_ES11 at 11 pg g^{-1} dwt).

A recent study from Australia reports that for aquatic sampling sites, the highest concentration of PBDE was from estuaries with the highest degree of urbanization and industralisation[10]. The compound BB 153 (60% FIREMASTER) is not manufactured in Fiji Islands, however, similar to PBDEs they are being brought in by imported products, mainly electronic appliances, computers and paints with fire retardant capacity. The presence of BB 153 in soil and sediment from Fiji indicates aerial deposition through long range atmospheric transport and global dispersion of brominated flame retardant contaminants to remote areas. The dominance of PBDE 209 in the congener profile could also be related to contamination through burning of electronic wastes that have been used in Fiji. A recent study into landfills in China indicates that for the PBDE profile, higher PBDE 209 concentrations were found at waste disposal sites where electronic waste was being dumped[7]. A study from

Australia reported PBDE 209 as the dominant PBDE congener in sediment samples[11]. Another study in the USA also found PBDE 209 as the dominant PBDE congener in sediments from the Great Lakes area[12]. Generally, the soil and sediment PCB and PBDE concentrations at all sampling sites were low. Sources of the elevated levels (PBDE 209) at the peri-urban (PU_S02) and the industrial sites (IN_S015 and IN_MS5) are not known, but the differences between sites can probably be explained by local diffusive sources such as open waste dump sites. A pilot study on POPs levels in ambient air in the Fiji Islands found that spatial and seasonal variability were not significant[13].

Acknowledgements
The authors gratefully acknowledge the University of the South Pacific and the Australian Agency for International Aid (AusAid) for funding this study. EnTox is co-funded by Queensland Health.

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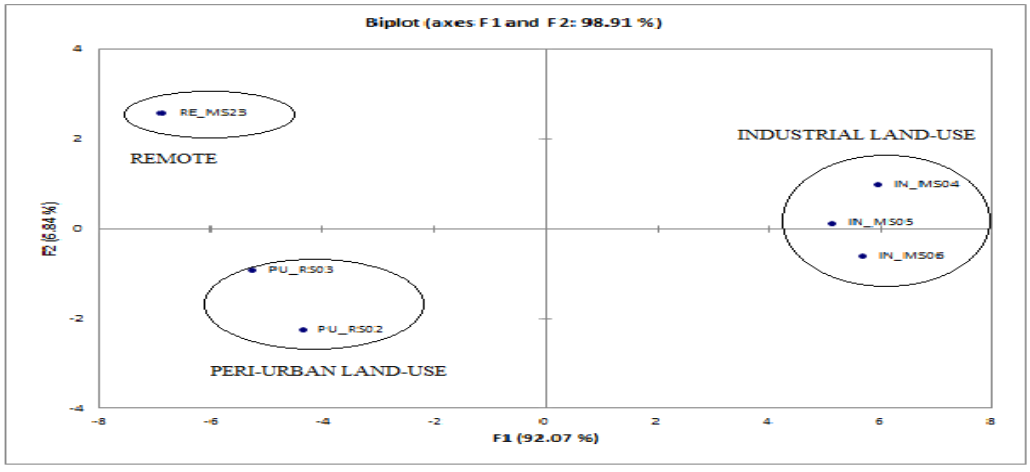

Figure 1: Biplot from PCA indicates correlation between land-use areas and PCB levels

Table 1: Sample nomenclature and description

Sample	Land-use	Sample type	Description
PU_S02	Peri-urban[1]	Soil	From Lakena agricultural research station compound
IN_S015	Industrial[2]	Soil	From Lautoka, FEA compound within industrial area
RE_S017	Remote[3]	Soil	From FEA hydro dam site in Monasavu highland
RE_S019	Remote	Soil	Mountain top soil close to ranger's station in Savusavu highland
AG_RS20	Agricultural[4]	River sediment	Collected near agricultural research station in Dreketi
AG_ES11	Agricultural	Estuarine sediment	Collected in the vicinity within the Sigatoka river estuary
RE_MS22	Remote	Marine sediment	Collected in the vicinity of the Levuka harbour
IN_MS05	Industrial	Marine sediment	Collected in the vicinity of the Vatuwaqa river mouth,close to the Laucala Bay industrial area
AG_RS03	Agricultural	River sediment	River sediment collected near the Wainibokasi jetty, Nausori
PU_MS18	Peri-urban	Marine sediment	Marine sediment collected at the Savusavu wharf near Savusavu town
IN_MS06	Industrial	Marine sediment	Marine sediment collected within vicinity of the Suva Harbour
PU_RS03	Peri-urban	River sediment	Collected at Nausori river adjacent to town centre
PU_RS02	Peri-urban	River sediment	River sediment collected from Labasa river near town
IN_MS04	Industrial	Marine sediment	Marine sediment collected from Walu Bay near city
RE_MS23	Remote	Marine sediment	Marine sediment collected outside of Savusavu town

[1] An area on the fringes of the urban and agricultural boundaries, close to coastal region
[2] An area dominated by industries and is > 5 km from any urban residential population
[3] An area > 60 km from any urban, industrial, agricultural or coastal boundaries
[4] An area > 15 km from any urban settlement, town or cities but close to coastal region

Table 2: Concentration data for PBDEs and BB 153 in soil from Fiji (pg g^{-1} dwt incl. ½ LOD)

	PU_SO2	IN_SO15	RE_SO17	RE_SO19
PBDE 209	2039	212	97	109
PBDE 206	12	7	8	4
PBDE 47	132	402	97	100
PBDE 99	67	157	52	62
$\Sigma PBDE_{26}$	2700	1200	400	370
BB 153	14	1	0.1	0.3

$\Sigma PBDE_{26}$ – The sum of 26 congeners of PBDE (includes half LOD).

Table 3: Concentration data for PBDEs and BB 153 in sediment from Fiji (pg g^{-1} dwt incl. ½ LOD)

	IN_MS5	IN_MS6	AG_ES11	PU_MS18	PU_MS22	AG_RS3	AG_MS20
PBDE 209	245	245	29	74	71	345	49
PBDE 206	9	2	2	1	2	8	4
PBDE 47	67	75	86	92	66	73	65
PBDE 99	32	40	46	51	42	42	44
$\Sigma PBDE_{26}$	500	350	330	300	440	530	380
BB 153	0.5	0.2	11	0.5	0.1	0.2	0.6

$\Sigma PBDE_{26}$ – The sum of 26 congeners of PBDE (includes half LOD).