EMERGING CONTAMINANTS – INVESTIGATING BROMINATED FLAME RETARDANT LEVELS IN SOIL AND SEDIMENT FROM FIJI ISLANDS

Lal ,V.V[1]*., Mueller, J.F[2] ., Aalbersberg, W.G.L[1]., Symons, R[3]. and Stevenson, G[3]

[1]Institute of Applied Sciences, the University of the South Pacific, Fiji.
[2]The University of Queensland, National Research Centre for Environmental Toxicology, Brisbane, Australia.
[3]National Measurement Institute, Sydney, Australia
[*] Contact author. Ph: (679) 3232971: lal_v@usp.ac.fj

Abstract

No scientific data is available on emerging contaminants like brominated flame retardant (BFRs) including polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (BB 153) levels in the abiotic environment of Fiji Islands. Concentrations of PBDEs and BB 153 were determined in soil and sediment from various land-use types from Fiji Islands. Generally, total concentrations of PBDEs and BB 153 was <10 ng g^{-1} dwt, indicative of a relatively "low contaminated" environment. Total PBDE and BB 153 concentrations ranged from 300 - 2700 pg g^{-1} dwt and 0.1 -14 pg g^{-1} dwt, respectively. Noticeably, BDE 209 and 47 were typically the dominating congeners (up to 75% and 35% contribution to sum BDE, respectively). Comparatively higher levels of PBDE 209 and PBDE 47 were found near open dump sites within the vicinity of urban and industrial land-use areas. The presence of BB 153 in all soil and sediment samples and its correlation to BDEs in soil samples may indicate sources from some local anthropogenic activity.

Introduction

An "emerging contaminant" is a chemical or material that is characterized by a perceived, potential, or real threat to human health or the environment or a lack of published health standards[1]. A contaminant may also be "emerging" because a new source or a new pathway to humans has been discovered or a new detection method or treatment technology has been developed[1]. 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[2] 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). Certain PBDEs are being considered to be included as a POP.

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 Islands is one of the 22 Island Countries within the PIR and is an archipelago of more than 300 islands which lies between 15^{o}-22.5^{o}S latitude and 174^{o}E-177^{o}W longitude, spread over a total area of 709 700km^2 of which 97% is ocean[5]. 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[5]. None of the island nations in the PIR manufacture 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 PBDEs as they are a major reservoir and sink for PBDEs due to their large sorption capacity[6]. The aim of this study was to provide 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 BFRs by relating data to land-use types.

Material and methods

Four soil and seven 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 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. For QAQC, a laboratory blank was included and recoveries of the internal/surrogate standard were calculated for all samples. The BFRs detected in soils and sediments were reported on a dry weight (dwt) basis.

Results and Discussions

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 - 90%. 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 $\sum PBDE_{26}$ for land-use type the results are presented as "middle-bound" or including half the limit of detection (LOD).

The concentrations of $\sum PBDE_{26}$ found in the soil samples from the four sampling locations are summarized in Table 2. The $\sum PBDE_{26}$ 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 Islands indicates a chemical profile where the 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 BDEs 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 behavior of BB 153 in relation to BDE 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 $\sum PBDE_{26}$ 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 $\sum PBDE$, respectively. Comparatively, the sediment sample with the highest level of $\sum PBDE_{26}$ (pg g^{-1} dwt) was from AG_RS03, a site with a history of rice farming and recent dredging activity. 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 Islands. The highest concentration of BB 153 was found at a peri-urban sites (PU_SO2 at 14 pg g^{-1} dwt) followed by an agricultural site (AG_ES11 at 11 pg g^{-1} dwt). It is noteworthy that the estuarine sediment sample collected within the vicinity of agricultural land-use area (AG_ES11) had the highest concentration of BB 153 (11 pg g^{-1} dwt) of all sediments collected from various land-use types (Table 3). This finding stands out since BFRs are normally used more in urban and industrial areas rather than agricultural. And since it is difficult to exactly know where sediments at AG_ES11 originated from, the source that may have contributed towards comparatively higher concentration of BB 153 at AG_ES11 remains unknown. 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[9].

The compound BB 153 (60% FIREMASTER) is not manufactured in Fiji Islands, however, similar to BDEs 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 BDE 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[10]. Another study in the USA also found PBDE 209 as the dominant PBDE congener in sediments from the Great Lakes area[11].

Generally, the soil and sediment 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_SE5) 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[12].

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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
IN_SRB	Industrial	Soil	Dioxin 2003 international intercalibration soil sample[9]

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 Islands (pg g^{-1} dwt incl. ½ LOD)

	PU_SO2	IN_SO15	RE_SO17	RE_SO19	IN_SRB
PBDE 209	2039	212	97	109	4374
PBDE 206	12	7	8	4	223
PBDE 47	132	402	97	100	2348
PBDE 99	67	157	52	62	2610
$\sum PBDE_{22}$	450	422	146	95	2445
$\sum PBDE_{26}$	2700	1200	400	370	12000
BB 153	14	1	0.1	0.3	34

$\sum PBDE_{22}$ – The sum of all PBDE determined expect BDEs 209, 206, 47 and 99. (includes half LOD).

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

	IN_MS5	IN_MS6	AG_ES11	PU_ME18	PU_ME22	AG_RS3	AG_MS20
PBDE 209	245	110	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
BB 153	0.5	0.2	11	0.5	0.1	0.2	0.6
$\sum PBDE_{22}$	147	123	167	82	259	62	218
$\sum PBDE_{26}$	500	350	330	300	440	530	380

$\sum PBDE_{22}$ – The sum of all PBDE determined expect BDEs 209, 206, 47 and 99. (includes half LOD).