EVALUATION OF POP LEVELS IN SOIL AND SEDIMENTS FROM SITES REPRESENTING VARIOUS LAND-USE TYPES IN THE FIJI ISLANDS

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Introduction

The Stockholm Convention, a global treaty on elimination of persistent organic pollutants (POPs), came into force in May 2004. Fiji was the second country after Canada to ratify the Stockholm Convention, thereby agreeing to formulate a national implementation plan to monitor and control the release of POPs in the country. POPs are hazardous chemicals that are persistent, bioaccumulate in food chains and have the potential to impact at all levels of the trophic system. Fiji 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[2]. The current population of Fiji is estimated at about 824,700[11]. The larger islands in Fiji are quite mountainous, but also contain significant flat plains; it is on these flat plains that most agricultural and commercial activities are located and where pollution problems are most likely to occur[2]. Fiji, like many developing countries in the world, has limited or no monitoring data on POPs concentration in the environment and on the exposure of wildlife and humans to these chemicals[1]. Only a few studies on pesticide levels have been carried out in the South Pacific region, including Fiji, and relatively little is known on the occurrence of organochlorine chemicals[2]. The problem is exacerbated by the lack of proper waste management practices, most untreated sewage are discharged into the sea while other waste are typically dumped in open dump sites. Soil and sediment are considered important sinks for dioxin-like chemicals in the environment and their analysis have been used to evaluate potential emission sources of these chemicals[3]. There is currently no scientific data on polybrominated diphenylethers (PBDE), dioxin (PCDD), furan (PCDF) and dioxin-like PCB (dl-PCBs) concentrations in soil and sediment and sources from the Fiji Islands[1]. In this paper we report concentrations for dioxins, furans, a range of polychlorinated biphenyls (PCBs), PBDEs and organochlorines, in soil and sediment samples taken from various sites representing different land-uses in the Fiji Islands.

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 Research Centre for Environmental Toxicology (EnTox) laboratory in Brisbane and to the National Measurement Institute (NMI) in Sydney, Australia for analysis. Analysis for dioxin-like chemicals (PCDD/PCDF/dl-PCBs) and PBDEs was carried out at NMI, an accredited laboratory using methods adopted from the USEPA (ie isotope dilution technique and quantification using HRMS)[5]. Duplicate analysis for organochlorine pesticides and seven indicator PCBs were done at the Institute of Applied Sciences (IAS) and EnTox/QHFSS laboratory. Analytes of interest targeted in this study included the 2,3,7,8-chlorine substituted polychlorinated di-benzodioxin and polychlorinated di-benzofuran (PCDD/PCDFs) as well as the $C1_4$ to $C1_7$ PCDD/PCDF homologue groups, dioxin-like PCBs (dl-PCBs), the seven indicator PCBs, a range of PBDEs (>30 congeners) and organochlorine pesticides including DDTs, lindane, heptachlor, aldrin, dieldrin, endrin and heptachlor epoxide. Recoveries of the internal/surrogate standard were calculated for all samples. A soil sample used during the 8th round of international intercalibration study (Dioxins 2003) was used as a QCQA sample to assess the methodology.

Results and Discussions

The soil reference sample, isotopically labeled standards for spiking to calculate recovery and instrument calibration standards were used for quality control and quality assurance purpose. The recoveries of the isotopically labeled internal and surrogate standards were between 70-90%. The WHO-TEQ_{DFP} in the Dioxin 2003 report[9] for the 8th round of international intercalibration study for the sample B soil was 81 pg/g dwt (%RSD = 53), the value for WHO_{05} - TEQ_{DFP} obtained in this study was 62 pg/g dry weight (dwt) and was within that requirement. A number of contaminants including 2,3,7,8-chlorine substituted PCDD/PCDFs as well as the $C1_4$ to $C1_7$ PCDD/PCDF homologue groups, dioxin-like PCBs and a range of PBDEs (>30 congeners) were detected.

The concentrations of 'dioxins' (including 2,3,7,8-chlorine substituted PCDD and PCDF, $C1_4$ to $C1_7$ PCDD/PCDF homologue groups and the dioxin-like PCBs) and PBDE compounds found in the soil samples from the four sampling locations are summarized in Table 2. The WHO_{05} - TEQ_{DFP} value for all samples analysed were found in a range of 0.49-8.7 pg TEQ g^{-1} dwt (SD = 2.4 ; median = 1). The concentration range (including half LOD for "non-detects") for ∑PCDD/PCDF detected in the soil samples taken from the various sampling sites was 63 to 5700 pg g^{-1} (SD = 2700; median = 540) dwt. The current study on soil from different land-use areas in Fiji Islands indicates a dioxin profile where the OCDD is dominant with the corresponding furan detected in lower concentration. The OCDD concentrations contributed 50-80% towards the total concentration of 'dioxins' present in the soil samples from different sampling sites. The highest levels for all the POPs shown in Table 2 were detected at PU_S02, followed by IN_SO15 (Figure 1). This is because both sites have a history of chemical misuse (PU_S02, where more than 2 tonnes of pesticides were buried and Dicidex was leaking and IN_S015, where transformer oil was found to have leaked from old transformers[4]). With respect to PBDE 209, the most contaminated soil sample was found to be from a peri-urban site (PU_S02 at 2000 pg g^{-1}dwt) followed by soil from an industrial site (IN_S015 at 210 pg g^{-1}dwt). Both these sampling sites (PU_S02 and IN_S015) are close to open waste disposal sites.

The concentrations of 'dioxins' and PBDE compounds found in sediment samples from the seven sampling locations are summarized in Table 3. The concentration range (including half LOD for "non-detects") for ∑PCDD/PCDF was 16 to 1000 pg g^{-1} (SD = 370; median = 63) dwt. The dioxin profile in sediment from all the seven sampling sites shows OCDD concentrations being dominant and contributing 24-90% towards the total concentration of 'dioxins' in samples from different land-use sites. The sediment sample with the highest level of ∑PCDD/PCDF (1000 pg g^{-1}) dwt was from AG_RS20, a site with intensive agriculture especially rice farming and a large scale timber industry. This site (AG_RS20) is also close to a government agricultural research station which acts as a distribution point for pesticides for farmers[4]. The dioxins profile at AG_RS20 (Table 2) is similar (OCDD concentration > 80% to ∑PCDD/PCDF, low dioxin-like PCBs concentrations compared to the sum of the homologue group) to the soil sample taken from the agricultural research station at PU_S02 (Table 1). With respect to ∑PBDE, the concentrations in sediments were in the range of 250 to 530 pg g^{-1} dwt (SD = 100; median = 340), with PBDE 47 and 209 congeners also detected in all sediment samples (Table 2). A range of soil studies in Queensland indicate the dominance of higher chlorinated PCDD, where the OCDD levels are higher and the corresponding furans are lower in concentration[5,7]. A faster degradation of the lower chlorinated PCDD/PCDF in the tropical environment may contribute to the observed shift in congener profile[5]. Moreover, the least volatile and most persistent PCDD may accumulate specifically in tropical environments, whereas the more volatile lower chlorinated PCDD/PCDF may be transported from these environments to colder climates where they accumulate[5]. The OCDD dominated dioxin congener profile could also be related to contamination or precursors in pesticides[10] 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[8].

The concentrations of organochlorine species were analysed using less sensitive techniques (LOD 10 ng g^{-1} dwt for pesticides and PCBs) at EnTox and IAS laboratories and could not be detected in any of the samples. This indicates a relatively 'less contaminated' terrestrial and marine environment for the organochlorine species tested. In comparison, a previous study on sediment samples within the rice irrigation channel at Lakena (close to PU_S02) recorded DDTs and dieldrin levels in a range of 0.75 to 2.2 ng g^{-1}dwt, and no PCBs were detected[2]. Generally, the soil and sediment concentrations of POPs at all sampling sites were low. Sources of the elevated levels (OCDD and PBDE 209) at the peri-urban (PU_S02) and the industrial site (IN_S015) 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[6].

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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: Summary of WHO_{05}-TEQ_{DFP}, ∑PCDD/PCDF, ∑dioxin-like PCBs, ∑ $C1_4$ to $C1_7$ PCDD/PCDF, OCDD/F, ∑PBDE, PBDE 47 and 209 concentrations (pg g^{-1}) in soils from various land-use sites studied in Fiji

Site	PU_S02	IN_S015	RE_S017	RE_S019
Component (pg/g dwt)				
WHO_{05}-TEQ_{DFP}	8.7	1.3	0.87	0.72
∑PCDD/PCDF	5700	950	63	120
∑dioxin-like PCB	50	73	30	20
∑Homologue PCDD/PCDF	1000	95	12	4.8
OCDD	5000	910	52	110
OCDF	200	14	3	0.05
∑PBDE	2700	1200	400	370
PBDE 47	130	400	97	100
PBDE 209	2000	210	97	109

Table 3: Summary of WHO_{05}-TEQ_{DFP}, ∑PCDD/PCDF, ∑dioxin-like PCBs, ∑ $C1_4$ to $C1_7$ PCDD/PCDF, ∑PBDE, PBDE 47 and 209 concentrations (pg g^{-1}) in sediments from various land-use sites studied in Fiji

Site	IN_MS05	IN_MS06	AG_RS20	AG_ES11	PU_MS18	RE_MS22	AG_RS03
Component (pg/g dwt)							
WHO_{05}-TEQ_{DFP}	1.4	0.49	1.3	1.1	0.72	0.69	1
∑PCDD/PCDF	62	76	1000	16	120	39	19
∑dioxin-like PCB	170	190	10	15	40	11	23
∑Homologue PCDD/PCDF	19	27	84	3.2	62	15	8.4
OCDD	59	65	1000	12	69	34	16
OCDF	0.62	2.4	1.5	0.08	10	1	0.9
∑PBDE	500	340	340	250	290	410	440
PBDE 47	67	75	65	86	92	66	73
PBDE 209	240	110	49	29	74	1	340

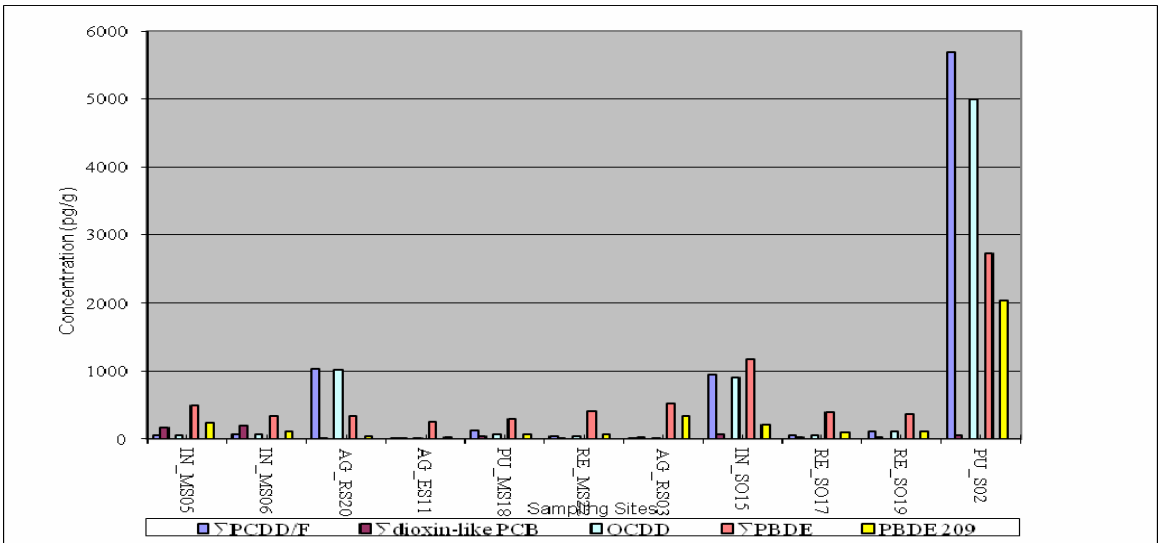

Figure 1: Concentration of ∑PCDD/PCDF, ∑dioxin-like PCB, OCDD, ∑PBDE and PBDE 209 in soil and sediment samples representing various land-use sites across the Fiji Islands