POPs IN DEVELOPING COUNTRIES: KEY FINDINGS FROM A BASELINE STUDY ON PCDD/Fs IN SOIL AND SEDIMENT FROM 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 ^{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[2]. The current population of Fiji is estimated at about 837,231[17]. 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 very limited scientific data on dioxin (PCDD), furan (PCDF) and dioxin-like PCB (dl-PCB) concentrations in soil and sediment and sources from the Fiji Islands[1]. In this paper we investigate concentration data for total dioxin-like compounds (PCDD/Fs) from soil and sediment samples taken from various sites representing different land-uses in the Fiji Islands in an attempt to find contamination sources in this region.

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 dioxin-like chemicals (PCDD/PCDF/dl-PCBs) was carried out at NMI, an accredited laboratory using methods adopted from the USEPA Method 1613B and 1668A (ie isotope dilution technique and quantification using HRMS)[5]. 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 and dioxin-like PCBs. 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 labelled standards for spiking to calculate recovery and instrument calibration standards were used for quality control and quality assurance purpose. The recoveries of the isotopically labelled internal and surrogate standards were between 70 - 90%. The WHO_{05}-TEQ_{DFP} in the Dioxin 2003 report 6 for the 8th round of international intercalibration study for the sample B soil was 81 pg g^{-1} dwt (% RSD = 53), the value for WHO_{05}- TEQ_{DFP} obtained in this study was 62 pg g^{-1} 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 and dioxin-like PCBs were detected. The concentrations of ΣPCDD/Fs (total of 2,3,7,8-chlorine substituted PCDD and PCDF, $C1_4$ to $C1_7$ PCDD/PCDF homologue groups and the dioxin-like

PCBs) found in the soil samples from the four sampling locations are summarized in Table 2. The concentration range for ΣPCDD/F 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 83 - 96% towards ΣPCDD/Fs present in the soil samples from different sampling sites. The highest concentration of OCDD was detected at PU_S02, followed by IN_SO15 (Table 2). At PU_S02, there is a history of chemical misuse (2 tonnes of pesticides were buried and Dicidex was leaking) and at IN_S015, transformer oil was found to have leaked from old transformers[4]. A report by Secretariat of the Pacific Regional Environment Programme (SPREP) indicated that ash and debris that contained Dicidex at Dreketi agricultural research station was contaminated with PCDD/Fs, with OCDD found in highest concentration 140 ng kg^{-1} (SPREP, 2003). Ash samples in the above study resulted from burning of containers that held Dicidex. This was done to get rid of stockpiles of old or obsolete pesticides. Improper disposal of pesticide wastes can lead to environment contamination. It is therefore noteworthy that a key finding of this study was that sediment samples (AG_RS20) collected near Dreketi agricultural station in this study also indicated PCDD/F contamination with OCDD being the congener. Soil and sediment samples were also investigated for contamination by pentachlorophenol (PCP). This was done based on information from a survey on stockpiles of POPs in Pacific Region that highlighted that PCP has been imported for use in Fiji[4]. However, the ΣPCDD/ΣPCDF concentration ratio (D/F) in soil samples in this study ranges 13 to 8758. This indicates that OCDD contamination in soil from various land-use types in Fiji is not due to the use of pentachlorophenol (PCP), the D/F ratio for contamination by PCP ranges from 1 – 109. The concentrations of ΣPCDD/Fs found in sediment samples from the seven sampling locations are summarized in Table 2. The concentration range for ΣPCDD/F 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 58 - 95% towards ΣPCDD/Fs from different sampling sites. The sediment sample with the highest level of ΣPCDD/F (1000 pg g^{-1}) dwt was from AG_RS20, a site with intensive agriculture especially rice farming and a large scale timber industry. The site (AG_RS20) is also close to a government agricultural research station which acts as a distribution point for pesticides for farmers[4]. The ΣPCDD/ΣPCDF concentration ratio (D/F) in sediments ranges 4 to 404. Another key finding of this study is that the sites with ΣPCDD/ΣPCDF concentrations ratio (D/F) within the PCP range included AG_ES11 (4), AG_RS03 (7.3) and PU_MS18 (7.9). However, due to very little contribution by PCDF towards total concentration of PCDD/F it indicates some other source for OCDD abnormality than contamination by PCP[10]. Further, 1,2,3,6,7,8-HxCDD is usually present as the dominant isomer among the toxic HxCDDs in PCP10. The congener 1,2,3,4,7,8-HxCDD is dominant among the 2,3,7,8-substituted HxCDDs in sediments from Fiji Islands. The similarities in PCDD/F profiles in all soil and sediment from Fiji Islands suggests that PCDD source or formation process in similar in all samples. Further, the OCDD congener represents 73 – 92% towards ΣPCDD/F in various land-use areas in Fiji Islands. This is an interesting find since sampling area covers an area of about 709,700km^2 of which 97% is ocean and includes a variety of anthropogenic and terrestrial influences[2,11]. Studies in Queensland[11], Missisippi in USA[12], Yellow Sea[13], East China Sea[13], the Pacific Ocean[13] and kaolinite samples analysed in Germany[14] have highlighted the dominance of OCDD towards ΣPCDD/F and having similar HxCDD isomer patterns and high ΣPCDD/ΣPCDF concentration ratios (D/F) in sediment samples. Moreover, these studies highlight that known anthropogenic sources for high concentration of PCDDs (particularly OCDD) were not evident. A widespread source that is natural in origin may be responsible for the OCDD abnormality in soil and sediment samples from Fiji Islands. A number of studies indicate natural formation which include biogenic or geogenic formation processes[15,16]. Further, environmental processes such as the local climate conditions may be responsible. 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. Generally, the soil and sediment concentrations of ΣPCDD/F (including OCDD) at all sampling sites were low. Sources of the elevated levels (OCDD) at the peri-urban (PU_S02) and the industrial site (IN_S015) are not known, but the differences between sites can probably be due to local sources. However, the overwhelming representation towards total PCDD/F concentration in all soil and samples across Fiji Islands indicates that the source is widespread and of significance. At this stage, the source or formation process responsible for high concentration of OCDD towards ΣPCDD/F in soils and sediments from various land-use areas in Fiji remains unknown.

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Table 1: Sample nomenclature and description

Sample	Land-use	Sample type	Description
PU_S02	Peri-urban[1]	Soil	Lakena agricultural station near Nausori
IN_S015	Industrial[2]	Soil	Lautoka industrial area, close to Fiji Electricity
RE_SO17	Remote[3]	Soil	Monasavu highland, forest area near dam
RE_SO19	Remote	Soil	Savusavu highlands forest area near rangers station
AG_RS20	Agricultural[4]	Sediment	Dreketi river, near agricultural research station
AG_ES11	Agricultural	Sediment	Sigatoka river estuary opposite agricultural areas
RE_MS22	Remote	Sediment	Levuka harbor near PAFCO fisheries
IN_MS05	Industrial	Sediment	Vatuwaqa industrial areas in vicinity of Laucala Bay
AG_RS03	Agricultural	Sediment	Wainibokasi jetty, Nausori
PU_MS18	Peri-urban	Sediment	Savusavu wharf within vicinity of town
IN_MS06	Industrial	Sediment	Suva harbor
IN_SRB	Industrial	Sediment	Dioxin2003 Inter-calibration study soil B sample

[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 ΣPCDD/F, OCDD and OCDF concentration (pg g^{-1} dwt) in soils and sediments from various land-use sites studied across Fiji Islands**

Sample	ΣPCDD/F	OCDD	OCDF
PU_S02	5700	5000	200
IN_S015	950	910	14
RE_SO17	63	52	3
RE_SO19	120	110	<0.1
AG_RS20	1000	905	2
AG_ES11	16	12	<0.1
RE_MS22	39	34	1
IN_MS05	62	59	1
AG_RS03	19	16	1
PU_MS18	120	69	10
IN_MS06	76	65	2