LEVELS AND SOURCES OF PCDDs AND PCDFs IN SUGARCANE AND PINEAPPLE AGRICULTURAL SOILS FROM HAWAII

Grant SC[1], Hermanussen S[1], Päpke O[2], Gaus C[1]

[1] National Research Centre for Environmental Toxicology (EnTox), University of Queensland, 39 Kessels Rd, Coopers Plains, Queensland 4108, Australia; [2] Eurofins-Ergo Forschungsgesellschaft mbH, Geierstrasse 1, D-22305 Hamburg, Germany

Introduction

Several studies over the last few decades have reported the contamination of Hawaii's aquatic systems and associated sediments and biota with organochlorine pesticides[1-4]. Pesticides have been used on the Hawaiian Islands since the mid-1900s in both agriculture, particularly for sugarcane and pineapple cultivation where herbicide usage can be up to 5 times higher compared to crops grown in temperate climates[2], and for wood treatment throughout the islands. The production processes for some of these organochlorine pesticides are known to result in contamination with dioxins and dioxin precursors[5-6]. Many pesticides were banned in the 1970s and 1980s, and their concentrations have been reported to have decreased in Hawaiian streambed sediments and biota[3]. However, their impurities, such as dioxins, are persistent in the environment and studies from elsewhere in the world have shown elevated levels of PCDD/Fs in agricultural soils with a history of pesticide usage. In particular, dioxin contamination has been reported in regions with land-use activities similar to that in Hawaii; for example, in sugarcane and pineapple growing areas in sub-tropical Queensland, Australia, where few other point sources of dioxins, such as industrial processes or waste incineration, occur[7-11]. However, due to a lack of information available on pesticide usage in Queensland, and the occurrence of transformation processes resulting in altered PCDD/F profiles compared to the original source, the source of PCDD/F contamination in Queensland agricultural soils has not been ascertained to date[12]. This study was undertaken to investigate whether sugarcane and pineapple soils from areas other than Queensland were contaminated with PCDD/Fs and to investigate the possible origin of the contamination using PCDD/F congener profiles and isomer patterns compared to those of known sources.

Materials and Methods

Soil samples were collected from five sites across three of the Hawaiian Islands, Hawaii, Maui and Oahu. Four sites were located on agricultural lands, where sugarcane or pineapple had been or was currently being grown. 3-5 subsamples of the top 5 cm of soil were collected within drainage channels or from the edge of cultivated fields and combined to form one composite sample. A further soil sample was collected from a site remote from agricultural activity in the vicinity of a conservation area, where recent lava activity had occurred.

Samples were analysed for PCDD/Fs at Eurofins-Ergo Forschungsgesellschaft mbH. The extraction method followed that described previously[7] and analysis of tetra- to octa-CDD/Fs was performed on a GC (DB5ms silica column, 60 m, 0.25 µm FT, 0.25 mm ID) interfaced to a Finnigan mass spectrometer operating on a resolution of approximately 6000-7000. Identification of 2,3,7,8-substituted PCDD/Fs was performed using retention times of 17 $^{13}C_{12}$ labeled internal PCDD/F standards and isotope ratios of the two most abundant isotopes. Non-2,3,7,8-substituted PCDD/Fs were determined using the relative retention times of these compounds by comparison to a known flyash sample. The quality control criteria followed for peak detection are documented elsewhere[7]. The recoveries of the individual 2,3,7,8-PCDD/F congeners ranged from 34% to 90%. Duplicate analysis was also undertaken at Queensland Health Scientific Services (QHSS) laboratories using an established PCDD/F screening method (quantification of OCDD) described previously[13]. The variation in OCDD levels between the two laboratories ranged between 1% and 17%.

Results and discussion

PCDD/Fs were detected in all Hawaiian soils samples (Table 1). Total PCDD/F concentrations and respective TEQ levels in all agricultural soils were elevated (5,800-60,000 ng/kg dw ∑PCDD/F; 11-110 ng TEQ /kg dw) compared to those found in soil from the remote site (22 ng/kg dw ∑PCDD/F; 2.2 ng TEQ /kg dw).

Table 1*. PCDD/F, OCDD/F and TEQ concentrations (ng/kg dw) and ratio of PCDD to PCDF (D/F) for Hawaiian soil samples*

	Pineapple, Oahu	Sugarcane, Maui	Sugarcane, Maui	Sugarcane, Hawaii	Remote, Hawaii
∑PCDD/Fs	11,000	6,500	60,000	5,800	22
∑PCDDs	8,500	5,200	48,000	4,600	14
OCDD	7,100	4,500	43,000	4,000	8.8
∑PCDFs	2,600	1,300	12,000	1,200	7.5
OCDF	1,000	480	4,500	510	2.9
WHO-TEQ_{DF}	22	11	110	18	2.2
D/F ratio	3.3	4.0	4.1	3.8	1.8

Dioxin contamination has been reported at pesticide mixing and loading sites, landfills and wood treatment plants in Hawaii, with dioxin levels in two soil samples at a sugar company pesticide mixing plant reported to be above the acceptable preliminary remedial goals for industrial use[14]. However, to the authors' knowledge there is no published information on the concentrations of dioxins in Hawaii. The concentrations of total PCDD/Fs in Hawaiian agricultural soils in this study are comparable to those reported for sugarcane and pineapple soils from Queensland (1700-19000 ng/kg dw; n=7)[7-11]. However, PCDD/F concentrations of both Hawaiian and Queensland soils are elevated compared to those reported for cultivated soils elsewhere in the world. For example, Chinese cotton and rice fields (18-200 ng/kg dw; n=4)[15], German plowland (33-250 ng/kg dw; n=14)[16] and a Polish agricultural region (680 ng/kg dw; n=n.d.)[17] contain PCDD/F levels approximately 10 to 1000 fold lower compared to those observed in Hawaiian agricultural soils. Similarly, TEQ levels in most agricultural soils from Hawaii were comparable to those reported from Queensland pineapple soil (21-32 ng TEQ/kg n=2) [9], whereas TEQ in Queensland sugarcane soils were generally lower (1.4-6.0 ng TEQ/kg; n=5)[7,8,10,11]. These TEQ levels are elevated compared to those reported for Chinese cotton and rice fields (0.11-2.5 ng I-TEQ/kg; n=4)[15], German plowland (0.3-3.7 ng I-TEQ/kg; n=14)[16]and Polish agricultural region (2.0 ng I-TEQ/kg; n=n.d.)[17]. These results indicate that an anthropogenic source exist(ed) for sugarcane and pineapple agricultural land which result(ed) in elevated PCDD/F and TEQ levels in associated soil.

In order to elucidate the source of this contamination, the PCDD/F congener profiles and isomer patterns were investigated. The 2,3,7,8-substituted congener and homologue profiles for Hawaiian soils were almost identical among all agricultural soil samples. Congener and homologue profiles were characterized by a dominance of PCDDs compared to PCDFs (D/F ratio 3.3 to 4.1) (Table 1). OCDD contributed the major proportion to ∑PCDD/F concentrations (77-82%). The concentrations of remaining 2,3,7,8-substituted PCDD/Fs (as well as homologue groups) were found to decrease with decreasing degree of chlorination for most agricultural soils (2,3,7,8-substituted HpCDD 19-33%, HxCDD 14-23%, PnCDD 6.6-33%, TCDD 1.1-7.2%). 2,3,7,8-substituted PCDFs were present at relatively low concentrations, dominated by 1,2,3,4,6,7,8-HpCDF (1.8-2.2% of ∑PCDD/F) and OCDF (7.4-9.4%). In contrast, soil from the remote area was characterized by low concentrations of 2,3,7,8-substituted congeners, many below or close to the limit of detection, with OCDD (40% of ∑PCDD/F) and OCDF (13%) dominating the profile.

Similar to the congener profiles, the Hawaii agricultural soil samples had comparable isomer distributions for both PCDDs (Figure 1A) and PCDFs (Figure 1B), indicating that the origin of the contamination is due to the same source or formation process at all sites. In contrast to agricultural soil, the soil distant from agricultural activities differed considerably in isomer distribution, showing a pattern dominated by the 2,3,7,8-substituted isomers, with only one non-2,3,7,8-substituted isomer at levels above the limit of detection (LOD) (1,2,3,4,6,7,9-HpCDD).

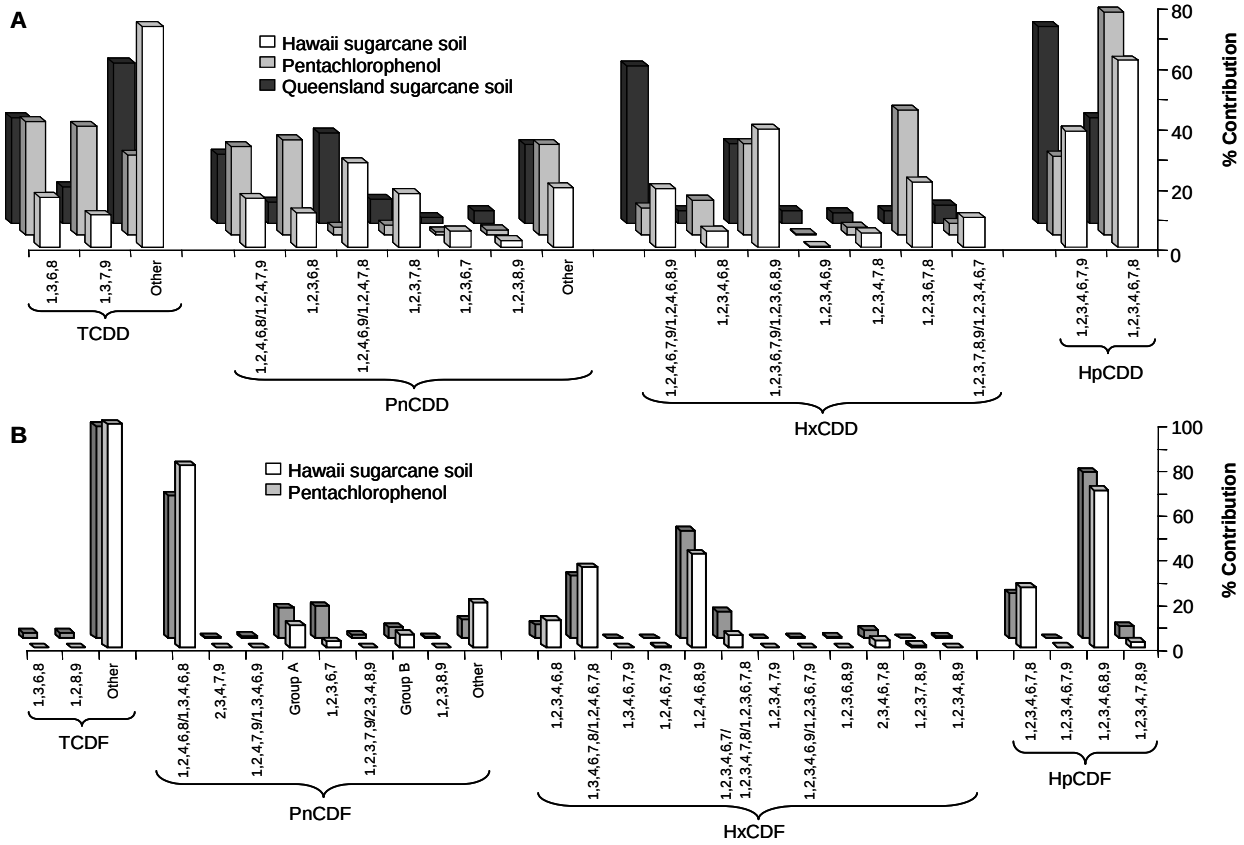

Figure 1. *Isomer distribution for PCDDs (A) and PCDFs (B) in representative soil for Hawaiian sugarcane, Queensland sugarcane[9] (A), and a sample of PCP[6] (1971, 13.4% active ingredient). Note: samples shown were analysed on different GC columns and some PCDD/F isomers were grouped to allow comparison between samples: Group A: 12347/13468/12346/12378/12348/12469; Group B: 12347/23468/12346/12378/12348/12469-PnCDF.*

Of the organochlorine pesticides known to be commonly contaminated with PCDD/F, pentachlorophenol (PCP), 2,4-D and 2,4,5-T are documented as previously being used in Hawaii; for termite control[1], weed control in sugarcane and pineapple production[2], and to eliminate invasive plant species[18], respectively. Comparison of isomer patterns revealed that the profile for the PCDD/Fs in soil from the remote site had few similarities with any of these pesticide source profiles. In contrast, striking similarities between the Hawaiian agricultural soils and PCP were observed (Figures 1A and 1B). In particular, the PCDD/Fs in the Hawaii agricultural soils were dominated by OCDD, OCDF, 1,2,3,4,6,8,9-HpCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,4,6,8,9-HxCDF, which are considered markers for PCP contamination[19]. Also, the ratio of PCDDs to PCDFs has been reported in the range of 1.6 to 82 in PCP[6,19], which is comparable to that found in Hawaiian agricultural soils (range 3.3 to 4.1). These results imply that PCP was a contributing source to the PCDD/Fs in the Hawaiian agricultural soil samples in this study. The main documented use of PCP in Hawaii is as a termiticide[1], and widespread termite pressure in Hawaii has led to wood treatment chemicals, which include PCP, having one of highest per capita uses in the US[20]. In addition, PCP has been reported at concentrations above regulatory action levels at pesticide mixing/loading and seed cane fumigant dipping sites at a sugar mill on Oahu[14] and it has a known history of usage elsewhere in the world as an agricultural fungicide, an insecticide and a herbicide in rice paddy fields[21].

Similar PCDD/F profiles compared to Hawaii agricultural soils have been reported for sediments located in areas of known PCP usage in Japan[22] and for Queensland pineapple soils[9], as well as to some degree Queensland sugarcane soil and areas surrounding these agricultural lands (including forest and urban areas)[7,8,11]. However, compared to agricultural soil from Queensland, samples analysed for this study showed on average slightly lower contributions of OCDD and correspondingly higher contributions of the remaining PCDD congeners. In addition, PCDFs were typically near or below the LOD in most samples from Queensland; however, where PCDFs are detectable their homologue and 2,3,7,8-congener distributions are similar to those observed in the present study. It has been suggested that PCP may be a contributing source to the PCDD/Fs identified in the Queensland agricultural soils, and that environmental transformation processes have resulted in an alteration of the PCDD/F profile to result in the dominance of 1,4,6,9-substituted isomers due to lateral dechlorination[12]. The results from this study highlight that application of PCP can result in PCDD/F contamination in agricultural soils, which, despite a ban on PCP production and usage, remain at elevated levels after application has ceased. Further, the contamination of PCP with OCDD precursors is well documented[23] and may provide further pathways for the formation of PCDDs after PCP emission to the environment.

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