INVESTIGATIONS INTO AN UNKNOWN OCDD SOURCE IN QUEENSLAND, AUSTRAILA

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are known contaminants associated with byproducts from various industrial processes and the synthetic production of chemicals. While investigations have generally focused on such anthropogenic sources, a number of recent studies have highlighted elevated levels of higher chlorinated PCDDs in regions with no apparent anthropogenic PCDD/F sources. In Queensland (Australia), industrial activities are mainly confined to the southeast corner of the state with a few small additional pockets along the coast. The rest of the state is rural and large areas are dominated by agriculture. PCDD/Fs in sediment and soil samples collected from sites along the Queensland coast have indicated the existence of a widespread, unknown source of higher chlorinated PCDDs[1,2]. The PCDD/F congener profiles of these samples show strong similarities to kaolinite clay samples from Germany[3] and sediment samples from lakes in Southern Mississippi[4]. A lack of known anthropogenic PCDD/F sources in all three cases has led to suggestions that the contamination may be the result of natural formation processes[1,3,4]. The current study is part of an ongoing project, which aims to identify sources and processes which have resulted in the widespread contamination of PCDDs in Queensland.

Materials and Method

Sampling

For the purpose of this study irrigation drain/channel sediments (S1-3), river sediments (R1-8), as well as topsoil samples (W1, B1-3, I1-2), were collected from agricultural, rural and industrial sites in Queensland (Figure 1). Irrigation sediment samples were collected from either water supply channels (S1, S3) or drains (S2) within sugarcane irrigation systems. River sediment samples R1-4 were collected from sites located in regions dominated by sugar cane cultivation. River sediment samples R5-6 and R7-8 originated from sites where rivers passed through wetland and cattle/bushland areas, respectively. Soil samples were collected from a wetland area (W1), from cattle/bushland (B1-B3) and from sites adjacent to an aluminium refinery (I1) and a cement kiln (I2). River sediments were collected using a modified Van Veen sampling grab, while irrigation systems and topsoil samples (1-5cm) were collected after the removal of surface debris, using stainless steel sampling equipment. A series of sub-samples were collected from each site and aliquots from each sub-sample were combined in the field to form one composite sample.

Analysis

Samples were analysed at Queensland Health and Scientific Services (QHSS) laboratories using a modified screening method for OCDD concentrations[5]. In brief, 10g of freeze-dried, homogenised sample were soxhlet extracted for 20 hours using toluene. A blank was included in each batch of samples. Prior to extraction, samples were spiked with 1,2,3,4,7,8,9-HpCDF as an internal standard of known quantity. The extracts were concentrated to dryness and subject to cleanup using acid-base (H_2SO_4/NaOH) and alumina (Alox B-super, ICN) columns in series. The samples were eluted with hexane/dichloromethane (1:1). After concentration of the eluent, samples were transferred to vials and filled with 20µl of toluene containing a known concentration of recovery standard (dibutylchlorindate). Samples were analysed on a dual column Shimadzu GC (DB5, 30m, 0.32mm i.d., 0.25µm film thickness; DB1701, 30m, 0.32mm i.d., 0.25µm film thickness) equipped with electron capture detectors. Quantification of OCDD was performed using the internal standard.

Results and Discussion

In this study elevated OCDD concentrations were found in river and irrigation sediments as well as topsoil samples collected from a wide variety of environments and land-use types (Figure 1A). Highest OCDD concentrations were present in sediments collected from irrigation systems which supply/drain areas used for sugarcane cultivation (Figure 1B). OCDD concentrations ranged from 1 700 pg g^{-1} dw in irrigation sediments from the northern parts of Queensland (S1) to 31 000 pg g^{-1} dw in irrigation sediments collected approximately 700 km further south (S3). These results are consistent with earlier findings of relatively high OCDD concentrations in sugar cane irrigation drains from North Queensland[1]. Present results highlight that the OCDD source(s) in Queensland also extent to the southern parts of the state.

Similarly, elevated OCDD concentrations (40 pg g^{-1} dw to 520 pg g^{-1}) were present in river sediments from areas dominated by sugar cane cultivation (R1-R4) (figure 1C). However, relatively high OCDD levels were found at sites not influenced by agricultural activities but a variety of other land-use types. Highest OCDD concentrations in river sediments were found at sites dominated by bushland, often used as grazing grounds for cattle (R7, 800 pg $^{g-1}$ dw; R8, 1 700 pg g^{-1} dw). Elevated OCDD concentrations (400 pg g^{-1} dw to 750 pg g-^{1} dw) were also present in river sediments from wetland areas that are believed to be relatively pristine (R5, R6). In addition, low concentration of OCDD could be detected in river sediments collected at site R4 (40 pg g^{-1} dw), collected downstream of a mountainous National Park. In consideration to a classification by Holoubek *et al.,*[6] (for total PCDD/F), OCDD concentrations in most river sediments analysed during this study can be considered slightly polluted to polluted. However elevated concentrations are not attributable to one specific type of land-use.

OCDD concentrations in topsoil samples ranged from 280 pg g^{-1} dw at site I1, adjacent to an alumina refinery to 6 300 pg g^{-1} dw at site I2, adjacent to a cement kiln (Figure 1B). However, concentrations of OCDD were also relatively high in some samples collected from cattle/bushland (500–5 000 pg g^{-1} dw) and topsoil collected in the wetland (2 900 pg g^{-1} dw). In comparison to soil samples from rural areas of western US, all Queensland soil samples show 10-100 fold elevated OCDD concentrations[7].

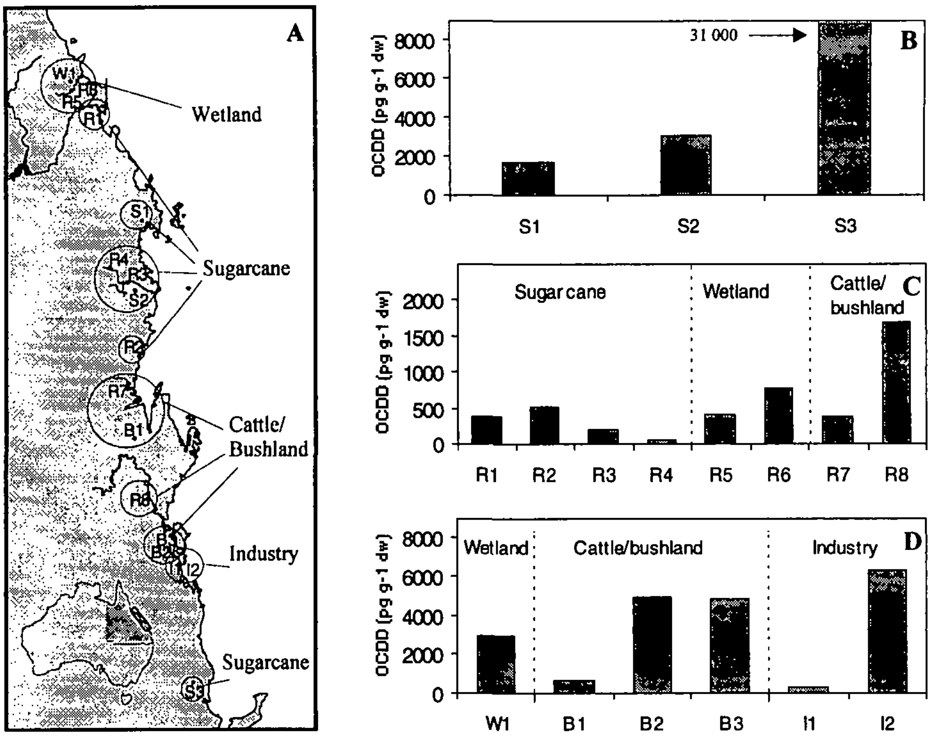

Figure 1: A – Sampling site locations along the Queensland coast from river, irrigation systems and topsoil collected from different land-use regions. B – OCDD concentrations in sugarcane irrigation drain/channel sediments. C – OCDD concentrations in river sediment samples. D – OCDD concentrations in topsoil samples.

The results to date highlight that the source of PCDDs in Queensland cannot be associated with a particular environment, or industry. Interestingly, elevated levels of PCDDs with an almost identical PCDD/F congener profiles compared to Queensland samples[1,2] have been reported in other studies[3,4,8,9], suggesting that the relevant process may not be endemic to Queensland. For example, elevated OCDD concentrations have been detected in river sediments downstream of a National Park in Southern Mississippi, an area characterised by several wetland and swamp regions[8]. Additionally in the same region, congener profiles similar to Queensland samples were detected in sediments from lakes[4]. Similar congener profiles have also been detected in kaolinite clay from Germany[3], as well as sediments collected from the Yellow Sea, the East China Sea and the Pacific Ocean[9]. Besides elevated PCDDs and strong similarities in the congener profiles the only other factor which connects all these studies, is the obvious lack of known anthropogenic sources. It has been suggested that a natural formation process, linked to aquatic environments may be occurring[9], however the data from Queensland studies indicate high OCDD concentrations in soil samples, suggesting that a similar formation process may (also) be occurring on the land.
Biogenic formation of PCDDs from precursors as well as formation of the relevant precursors has been demonstrated recently[10-12]. Also, geogenic formation involving for example volcanic activities are being investigated as a possible PCDD/F source[13]. The relevance of non-

activities are being investigated as a possible PCDD/F source[13]. The relevance of non-anthropogenic sources has been subject of intensive discussions in the past. If natural formation has resulted in the contamination in Queensland, the geographical extent and magnitude of the contamination would highlight the importance of this process. Irrespective of whether the PCDD contamination in Queensland is 'natural', it is important to understand the process(es) which have resulted in this contamination and to quantify the relevance of this unknown source to Queensland and elsewhere.

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