

NATURAL FORMATION OF DIOXINS

HISTORICAL PCDD/F RECORDS IN DATED MARINE SEDIMENT CORES FROM QUEENSLAND, AUSTRALIA

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Introduction

Dated sediment cores can provide valuable information on temporal pollutant trends and have been used to evaluate the significance and origin of historical as well as more recent inputs of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Various studies on temporal trends of PCDD/F contamination have shown the presence of PCDD/Fs prior to the production of organochlorine chemicals, albeit in very low concentrations (e.g.¹⁻⁴). These historically low ambient concentrations are then typically proceeded by significant increases in PCDD/F levels and concurrent changes in congener profiles as a result of industrialisation from the 1940s onward. Recent studies have demonstrated a significant and widespread source of higher chlorinated PCDDs in the coastal environment of Queensland, Australia^{5, 6}. In particular, relatively high concentrations of octachlorodibenzo-*p*-dioxin (OCDD) have been found in marine surface sediments collected near urban, rural and at remote sites as well as in topsoil and irrigation drain samples. These samples were collected over a distance of approximately 2000 km, yet exhibited almost identical congener and isomer profiles that could not be related to known technical or industrial PCDD/F sources⁶. Similar PCDD/F profiles have been reported in sediments and kaolinite clay samples from Southern Mississippi⁷ and Germany⁸, respectively. The similarities suggest the possibility of a similar, yet unidentified PCDD source. In this study, dated marine sediment cores from Queensland were analysed to determine whether PCDD contamination in this coastal environment is the result of recent PCDD/F inputs or historical actions/processes. Temporal trends of PCDD/F concentration and congener profiles are presented in two marine sediment cores dated from pre 1900 to 1995.

Materials and Methods

Marine sediment cores were obtained from North Queensland, Australia collected from intertidal mangrove mudbanks (core 1262) and an estuarine embayment site (core 1260) (Figure 1). Both sites receive sediments from rivers that drain large, predominantly rural catchments. Dominant land-use within both regions include sugar cane agricultural crops (<5% of catchment area and cattle grazing (~80% of catchment area).

Sediment cores were collected using open and deep water Kasten cores⁹. Samples were handled with clean stainless steel tools and cores were sliced at intervals of 2-4 cm. Subsamples were taken for radiochemical measurements and various chemical analyses. Dating of sediments involved gamma spectrometric measurements Pb-210, Ra-226 and thermonuclear bomb fallout nuclide Cs-137 (for details see¹⁰). Counting errors of the sample measurements were less than 10%, except for some low activity Cs-137 samples with estimated errors up to 30%. Radiochemical tracer sedimentation history was interpreted using several submodels and diffusion coefficients for Pb-210 and Cs-137 in marine sediments^{10,11}. Estimates of the annual atmospheric flux of Pb-210 and the Cs-137 inventory have been obtained from soil profiles in north Queensland. Physical sediment core data are shown in Table 1.

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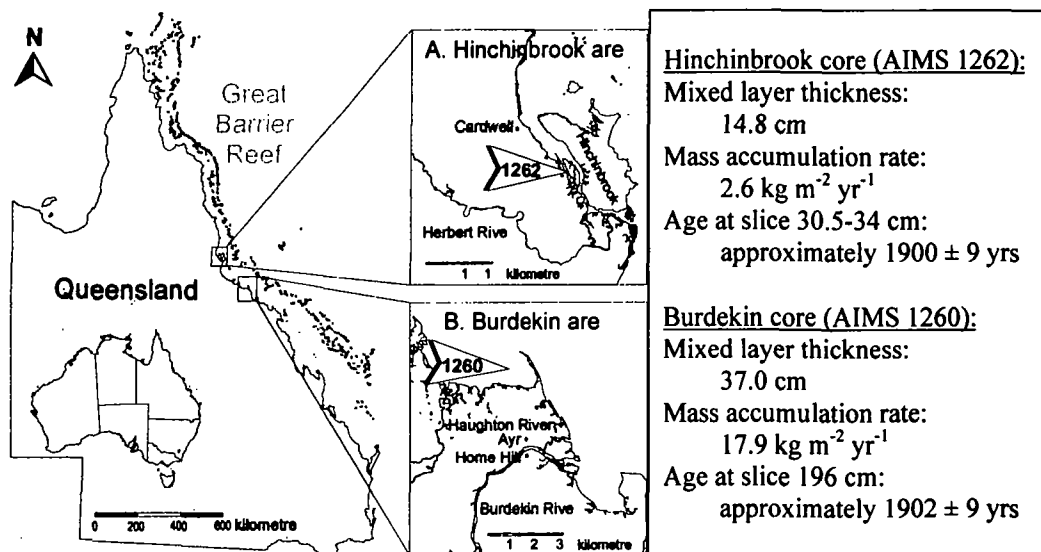


Figure 1. Sampling locations in Queensland, Australia.

Table 1. Physical sediment core data.

Samples were analysed for full profile of all 2,3,7,8-substituted PCDD/Fs at Ergo Forschungsgesellschaft mbH as previously described¹². In brief, sediment samples were spiked with ¹³C-labeled PCDD/F standard and soxhlet extracted for 20 hours using toluene. A blank was included with each batch of 6 samples. The extracts were concentrated and sample clean-up performed on a combined acid/base activated silica gel ($\text{H}_2\text{SO}_4/\text{CsOH}$) and alumina column (Alox B-super, ICN). After concentration of the eluent, samples were transferred to vials and ¹³C-labelled 1,2,3,4-TCDD recovery standard was added. Analysis of tetra- to octa-CDD/Fs was performed on a GC (DB-5 fused silica column, 60 m, 0.25 mm i.d., 0.1 μm film thickness) interfaced to a VG Autospec mass spectrometer operating on a resolution of approximately 10,000. Identification of 2,3,7,8-substituted PCDD/Fs was performed using retention times of the labeled standards and isotope ratios at M^+ and $\text{M}+2^+$. For quality control the retention times of the analyte in a sample had to be within 2 s of the retention times of the internal standards. The limit of quantification for PCDD/Fs in a given sample was defined by a signal to noise ratio greater than 3 times the average baseline variation and a substance quantity in the sample greater than 3 times the quantity in the respective blank.

Total organic carbon (TOC) was determined after acid catalysed digestion (10% HCl, 1% FeCl_2 at 70 °C) of subsamples. The remaining material was dried and combusted in a LECO induction furnace with subsequent detection of CO_2 (LECO WR12 CO_2 detector).

Results and Discussion

Concentrations of 2,3,7,8-substituted PCDD/F homologues ranged from 1,000 to 1,900 pg g^{-1} dry weight (dw) in core 1262 (Hinchinbrook) and 750 to 980 pg g^{-1} dw in core 1260 (Burdekin). Congener profiles were dominated by OCDD (65% to 86% of $\Sigma\text{PCDD/F}$) with concentrations ranging from 660 to 1,300 pg g^{-1} dw in core 1262 (Hinchinbrook) and 520 to 810 pg g^{-1} dw in core 1260 (Burdekin) (Figure 2). OCDD concentrations from the surface slices of both cores are comparable to OCDD concentrations in surface sediments collected from the same or nearby sites in 1999. Due to higher total organic carbon content (TOC) in core sediments from the Hinchinbrook area (3.8% average TOC) compared to the Burdekin area (0.82% average TOC) OCDD concentration on a TOC basis were higher in core sediments from the Burdekin compared

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to the Hinchinbrook area. Irrespectively of that, vertical trends of OCDD concentration were similar, expressed on either TOC or dry weight basis.

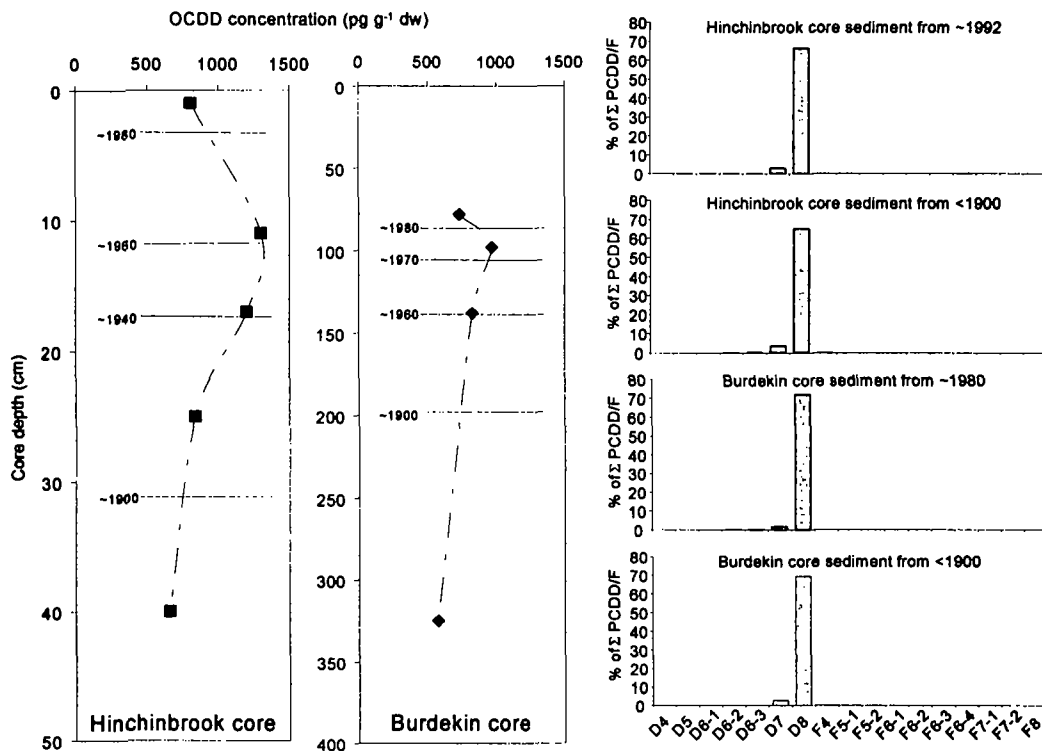


Figure 2. Vertical OCDD concentration and PCDD/F congener profiles in dated sediment cores from Queensland, Australia

Temporal trends from these initial data show little change in PCDD/F or OCDD concentrations throughout the depth of both cores, although a trend of slightly increased levels seem to be present in sediments estimated to originate from the second half of the 20th century. These results are in contrast to the majority of historical PCDD/F trends studied to date which typically reflect several fold increases in PCDD/F concentrations from onset of organochlorine use around the 1940s compared to pre industrial time-periods (e.g.^{4, 13}). In the present study, OCDD concentrations in Queensland sediments derived from prior the 1900s are considerably higher than in the majority of similar aged sediments analysed from elsewhere (e.g.^{1, 2}). PCDD/F concentrations in sediments from pre 1900 in the present study are comparable to elevated ΣPCDD/F levels recorded during concentration peaks in sediment cores from the Baltic Proper³.

PCDD/F congener profiles from the two sediment cores are characterised by a) PCDD/F concentrations near or below the limit of detection (LOD), b) TCDD concentrations below the LOD, c) increasing PCDD concentrations with increasing chlorination and d) a strong dominance of OCDD (Figure 2). PCDD/F congener profiles were similar in sediments from both the Hinchinbrook and Burdekin area and have been found in most surface sediment and topsoil samples from Queensland collected up to 2000 km apart^{5, 6}. Remarkably, sediments in core slices dating from pre 1900 to 1995 show almost identical PCDD/F congener profiles. The majority of temporal PCDD/F records studied from elsewhere show vertical shifts in congener profiles that concur with the onset of industrialisation reflecting a change of PCDD/F input significance to the

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environment (e.g.^{4,14}). These first results from Queensland highlight the possibility of a continuous and uniform PCDD/F source from pre 1900 to present. Similar results have been reported in Japanese coastal sediments¹⁵ and offshore sediments in the Pacific, the Yellow and East China Seas¹⁶. The authors of these studies suggest the relatively high concentrations of OCDD and similar congener profiles in deep core relative to surface sediments may be the result of non-anthropogenic formation of PCDDs in the marine environment^{15,16}. Sediments from Southern Mississippi⁷ as well as kaolinite clay samples from Germany⁸ also show strong similarities to the Queensland soil and sediment PCDD/F profiles. The source(s) and processes involved in the formation of PCDD/Fs resulting in such an unusual profile on three continents is not yet known. However, first results from this study may indicate a possible non-anthropogenic PCDD/F formation in coastal Queensland. More work is presently undertaken using additional core sediments from Queensland cores to further assess temporal trends and the more ancient history of contamination, providing necessary information on possible sources and formation processes.

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