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DEPOSITIONAL PROCESSES AND THEIR SOURCE IMPLICATIONS FROM TEMPORAL PCDD DISTRIBUTIONS IN QUEENSLAND (AUSTRALIA)

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are ubiquitous contaminants in the environment. The majority of the contemporary global PCDD/F burden undoubtedly arises from anthropogenic and industrial sources. However, during the last decade an increasing number of evidence in the scientific literature suggest that PCDD/F can also be formed from natural processes in specific environments and conditions¹⁻⁷. Some of the media where such non-anthropogenic formation processes are thought to occur or have occurred show characteristic 2,3,7,8-congener profiles: in particular, the dominance of OCDD, decreasing PCDD concentrations with decreasing degree of chlorination and low or non detectable concentrations of PCDFs⁴⁻⁷. Despite the evidence that PCDDs can be formed naturally, the specific processes, their history, possible precursors and mediators as well as influencing factors leading to the observed signatures remain unknown and difficult to identify. Without this knowledge, it is difficult to attribute observed PCDD contaminations to natural formation processes and to evaluate their significance to the environmental PCDD/F burden. In Queensland (Australia), the presence of elevated PCDD concentrations, in particular OCDD, along the entire coastline as well as in dated sediments accumulated up to 350 years ago have been observed⁶⁻⁸. This, in combination with almost identical 2,3,7,8-congener profiles and isomer patterns in recent and historical samples that could not be attributed to known anthropogenic sources provides evidence for the formation of PCDDs from naturally occurring processes. The widespread nature of this contamination emphasises the need to identify the sources and processes involved. Temporal contaminant patterns in historical materials may provide more information on these issues. Therefore, such patterns have been evaluated in dated sediment cores from Queensland and are discussed with respect to depositional processes that may be involved in the formation of the specific signatures and their implications on the possible PCDD sources.

Materials and Methods

Two estuarine sediment cores were collected from two separate sites located in coastal embayments of the Great Barrier Reef Lagoon of North Queensland, Australia. Cores were collected using a custom made Kasten corer, and samples were handled with clean stainless steel tools. Methods for estimation of radiochemical chronology of sediment depositional history are presented elsewhere⁶. Samples were analysed for full profile of all 2,3,7,8-substituted PCDD/Fs

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and Σ homologues at Ergo Forschungsgesellschaft mbH as previously described⁷. Several criteria had to be fulfilled for quality control: a) the retention times (RT) of the analyte in a sample had to be within 2 s of the RT of the internal standards b) isotope ratios for each congener of the M^+ and $M+2^+$ ions had to be within 20% of the respective individual value c) PCDD/F limit of quantification 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. Precautions have been taken to ensure samples were not contaminated and sampling/storage and analytical blanks as well as replicate analysis were used to assess the possibilities of contamination during the respective steps.

Results and Discussion

Sediments from the deepest slices of the two cores were estimated to have deposited in 1850 ± 20 years (Burdekin core, BC) and 1627 ± 54 years (Hinchinbrook core, HC). The surface sediment mixed layer thickness at these coring sites averages seasonal and yearly inputs over approximately 18 and 35 years, for BC and HC, respectively. Below the surface sediment mixed layer, the sediments are no longer mixed, and the sediment slices represent increasing age with depth in the core. Preliminary results from PCDD/F analysis on these two cores have been presented earlier⁶, although additional analysis has been carried out for the present study. Summarizing the results to date, concentrations of Σ PCDD/Fs ranged from 1000 to 2500 pg g^{-1} dry weight (dw) in HC and 760 to 1300 pg g^{-1} dw in BC. The temporal distribution of Σ PCDD/F concentrations showed little changes throughout the depths of both cores and were still elevated in the deepest core slices analysed (870 pg g^{-1} dw in BC and 2500 pg g^{-1} dw in HC) suggesting the presence of PCDDs in sediments deposited up to ~350 years ago. 2,3,7,8-PCDD/F congener profiles from core sediments were consistently characterised by a) PCDF concentrations near or below the limit of detection ($\text{LOD}_{(\text{PCDF})} = 0.1\text{-}1.2 \text{ pg g}^{-1}$), b) increasing PCDD concentrations with increasing chlorination and c) a strong dominance of OCDD (OCDD 43% to 85% of Σ PCDD/Fs). Isomer distribution in both cores did not show any trends with depth and was almost identical in sediments from all deposition years from the Hinchinbrook and Burdekin area. In addition, the PCDD/F signatures from sediment cores were almost identical to those observed in surface sediments from the entire coastline of Queensland. This suggests the presence of a widespread non-anthropogenic PCDD source and a qualitative similar source input of PCDDs.

Although – as indicated above – PCDD/F signatures were similar in all samples and no clear trend of Σ PCDD/F concentrations over time was apparent, the relative contributions of homologues to Σ PCDD/F concentrations were found to change with depth and an increase of lower chlorinated PCDDs with increasing core depth was indicated by the data. In order to assess possible trends we have normalised the concentration of Σ homologues to the Σ PCDD concentrations in each sediment slice. Figure 1A shows the Σ PCDD : OCDD ratio versus the estimated year of sediment deposition. The results from both cores indicate a trend of decreasing contribution of OCDD to the Σ PCDD concentration with increasing time of deposition (i.e “age”). Corresponding to this, a trend of increasing contribution of hepta- (Figure 1B) as well as hexa- to tetraCDDs (not presented here) to the Σ PCDDs with increasing time of deposition was apparent. The relationship of decreasing OCDD (or increasing lower chlorinated PCDDs) with age of deposition was found to be linear and replicable using sediments analysed in duplicate from several core slices.

The regression slopes obtained from the ratios calculated for each homologue group (Σ PCDD : Σ homologue) versus the time of deposition serve as an indication of the relative change of the contribution of tetra- to heptachlorinated homologues (and the relative decrease of OCDD) with

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time of deposition. Figure 1C illustrates these relative changes for tetra- to octaCDDs and indicates the presence of a decreasing trend with increasing chlorination (note that the regression slope of Σ PCDD : OCDD versus time of deposition is negative, reflecting the observed relative decrease of OCDD) with time of deposition.

The role of post-depositional, vertical diffusion processes, governed by the different physico-chemical properties of PCDD congeners, have been considered as a possible explanation for the shift toward lower chlorinated congeners in deeper sediment slices. However, based on diffusion coefficients for PCBs in lake sediments⁹ the time for a molecular diffusion of even PCBs would be insufficient to result in the observed trends within ~350 years and an even stronger sorption and reduced mobility compared to PCBs could be assumed for the PCDD/Fs due to their greater hydrophobicity. Further, it seems unlikely that these relatively small and linear changes in congener distributions were caused by changes of the formation process itself. Hence, the present results suggest that degradational processes have occurred to result in the observed trends. Two scenarios are considered: a) "weathering" (defined as degradation or volatilisation processes occurring during exposure to the environment) of the original source profile and b) dechlorination processes of a consistent source profile.

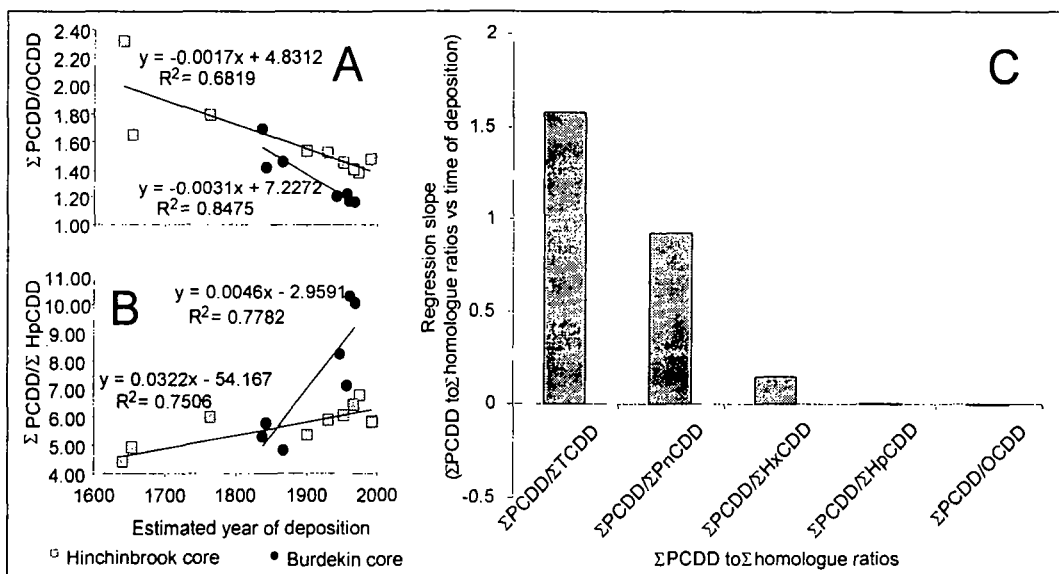


Figure 1A-C. A. Relative decrease of OCDD contribution to Σ PCDDs with time of deposition. B. Relative increase of Σ HpCDDs contribution to Σ PCDDs with time of deposition. C. Relative change of Σ homologue contribution to Σ PCDD with time of deposition in BC.

A "weathering" of an originally different source profile resulting in the OCDD dominated profiles observed today would imply - at least in Queensland - a discontinued, historically old source (e.g. volcanic PCDD/F emissions several ten-thousand to million years ago). OCDD is the least mobile and most persistent PCDD congener in the environment (i.e. lowest vapour pressure and water solubility)¹⁰. Hence, OCDD has the longest retention time in soil after deposition. Therefore, an OCDD dominated PCDD/F profile similar to that observed in Queensland soil and sediments could result from the loss of lower chlorinated PCDDs due to "weathering". In this scenario, once

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PCDD/F contaminated soil is deposited in the marine environment, degradational processes would have to be strongly reduced in order to explain the observed changes in core profiles with time of deposition. In addition, a mixing of soil (over different layers and degrees of degradation) would be expected to occur over the relatively long time period between formation and deposition, in particular during soil/sediment transport into the marine system, resulting in less distinguishable trends than the linear changes observed in the sediments from the present study.

On the other hand, Σ PCDD to individual homologue ratios obtained from topsoil and river sediments in the study area in Queensland correspond to those from surface slices of core sediments. This, in combination with the changes in homologue contribution to the Σ PCDD concentrations observed from sediments accumulated during the 350 years deposition period suggest that degradation processes occurred primarily after the deposition of sediments in the marine environment. The processes involved resulted in a shift toward higher concentrations of tetra- to heptachlorinated homologues with increasing "age" after deposition. These trends are in accordance with dechlorination processes of PCDD/Fs in sediments e.g.¹¹. Implications from this second scenario – in combination with the consistently elevated PCDD/F concentrations throughout the last ~350 years of sediment deposition – is the presence of a continuous source resulting in the consistent release/formation of higher chlorinated PCDDs (primarily OCDD) that are subsequently subject to progressive dechlorination processes.

Similar profiles compared to Queensland sediments and soils have been observed in both kaolin and ball clay material from the US and Germany^{4, 5, 12}. Compared to Queensland sediments, these clays show however higher contributions of lower chlorinated PCDDs to the Σ PCDD concentrations. This is reflected in an extremely low Σ PCDD to homologue ratio within the lower chlorinated homologues compared to Queensland core sediments. Since the results of the present study indicate an increase of lower chlorinated congeners with increasing age of deposition it is interesting that these clays have been deposited 40-45 million years ago (quoted in⁴). Extrapolations analogue to those of the present study may therefore present a tool to identify the deposition age of PCDDs. More work is presently underway to provide a better understanding on the formation- and post-formation processes involved.

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