

TRANSFORMATION OF DIOXINS IN ENVIRONMENTAL SINKS – FORMATION OF THE DISTINCTIVE “NATURAL PCDD SIGNATURE”

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Introduction

In recent years, samples collected from rural areas and/or pre-1900 deposits in Australia^{1,2}, U.S.A.³, Germany⁵, Japan, China, Philippines^{6,7} and Hong Kong⁸ have shown distinctive, yet unusual dioxin congener distributions. These samples were all characterised by elevated levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) and a strong dominance of the octachlorinated dibenzodioxin (OCDD), as well as a general lack of dibenzofurans (PCDFs). Such characteristics could not be attributed to any known anthropogenic PCDD/F sources and the processes involved in their formation remained unclear. A natural formation of PCDDs in the environment was suggested in all cases. Little is known about natural PCDD/F formation processes and their significance in the environment. On the other hand, various abiotic and biotic transformation processes along the environmental pathways of PCDD/Fs have been found to result in considerable alterations of the original PCDD/F source emission signatures⁹. Previously, we reported indications of such alterations of PCDD/F congener profiles with depositional age in dated sediment cores from Queensland, Australia¹⁰. A first step for understanding the possible processes involved in the formation of the distinctive “natural PCDD signatures” therefore is, to determine whether these represent the actual source output pattern or are the result of post-depositional transformation processes, obscuring the original patterns. The present study aimed to identify the specific processes and their pathways involved, providing new information on the original source signatures responsible for the PCDD contaminations of a range of samples with distinct PCDD congener and isomer distributions.

Materials and Methods

Previously published results on spatial and temporal (Hinchinbrook Channel and Burdekin estuary core sediments) PCDD/F concentrations in the coastal zone of Queensland were reassessed and compared to similar PCDD/F profiles reported from elsewhere^{1,2}. These data have been used to perform isomer specific analysis, including non 2,3,7,8-isomers, for sediment, soil and sediment core samples. Materials and methods for sample collection, locations, PCDD/F analysis and quality control during sampling, storage and analysis of samples are presented elsewhere^{1,2}.

Results and Discussion

Isomer specific analysis of dated estuarine sediment cores collected in Queensland, Australia revealed that all core slices, ranging from sediments deposited recently up to approximately 350 years

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ago, show similar isomer distributions. These are characterised by a striking dominance of isomers fully chlorinated in the 1,4,6,9-positions (see Fig. 1A). In the following we will refer to this isomer distribution as a "1,4-pattern" which, to our knowledge, is unlike any known anthropogenic source pattern and has not been described previously. A similar 1,4-pattern was also found in most surface sediment samples analysed to date from Queensland, including those collected from riverine (Fig. 1A), estuarine and marine locations along the 2000 km coastline. Comparing these characteristics to data published from other "natural formation samples", interesting similarities become apparent. Isomers from pre-1900 deposits and/or surface sediments in a Japan estuary (Osaka Bay (Fig. 1B) and Harima Nada)⁶, as well as from the Yellow and East China Sea and the Philippine Basin⁷ also show the distinctive 1,4-pattern. The 1,4-patterns are also apparent from PCDD isomer patterns published by Rappe et al.^{3,4} from Southern Mississippi, U.S.A., in particular from river sediment (Fig. 1B), dried oxbow samples, as well as rural lake sediments. Further, estuarine sediments from Mai Po Marshland near Hong Kong (Figure 1B)⁸ and kaolinite clay from Germany (Fig. 1B)¹¹ and Australia¹² are dominated by the 1,4,6,9-substituted isomers. Apart from these unique isomer characteristics, all these samples have in common a strong dominance of OCDD and relatively low or non-detectable concentrations of PCDFs. These striking similarities strongly suggest that specific formation and/or transformation processes occur (or have occurred) not only in Queensland, but possibly globally. These processes result in the formation of PCDDs, in particular OCDD and the 1,4-pattern from a yet unidentified PCDD/F source.

Previously, we reported a relative increase of tetra- to heptachlorinated homologues, and decrease of OCDD with increasing sedimentation age within the Queensland sediment cores¹⁰. The rate of appearance of lower chlorinated PCDDs with age of deposition was found to decrease with decreasing degree of chlorination. Further investigations of surface samples collected from rivers and soils show higher contributions of OCDD and lower contributions of lower chlorinated PCDDs to SPCDDs compared to the estuarine core samples. This suggests that the trends of increasing tetra- to heptachlorinated PCDDs with core depth are indeed a function of age after deposition in the marine system, and indicate that dechlorination processes may have altered the original PCDD/F source signature.

The distinct 1,4-patterns in Queensland samples indicate the predominant lateral chlorine elimination from OCDD, resulting in higher concentrations of 1,2,3,4,6,7,9-HpCDD compared to 1,2,3,4,6,7,8-HpCDD (see Fig. 1A). In subsequent lateral chlorine eliminations the 1,4,6,9-substituted HxCDDs, PnCDDs and TCDDs can be formed as the main isomers in the respective homologue groups with increasing time of transformation (Fig. 1A). This would result in an increase of 1,4,6,9-substituted isomer contributions to the respective homologue groups with increasing age after deposition, which was observed in the present study (Figure 1A illustrates this for the top and bottom sediment slices of both Queensland cores). Further, the ratio of HpCDD isomers obtained through lateral dechlorination (L) to those obtained through elimination of chlorine from the peri-positions (P) (i.e. 1,2,3,4,6,7,9- to 1,2,3,4,6,7,8-HpCDD) was found to influence the L:LP:P ratio obtained for HxCDDs (i.e. 1,2,4,6,7,9/1,2,4,6,8,9- to 1,2,3,6,7,9/1,2,3,6,8,9- to 1,2,3,6,7,8/1,2,3,7,8,9-HxCDD) and the % contribution of lower chlorinated L isomers to the respective Shomologues (i.e. 1,2,4,6,9-PnCDD and 1,4,6,9-TCDD). The most distinct 1,4-pattern, present in the deepest core slice of the Hinchinbrook Channel sediments core (i.e. longest sedimentation history) (Fig. 1A) showed the highest L:P HpCDD ratio (8:1), highest L:LP:P HxCDD ratio (45:5:1) and highest contributions of L PnCDD (56%) and L TCDD (66%). Lower L:P HpCDD ratios in surface sediments of the Hinchinbrook core (L:P HpCDD = 4:1) and sediment slices from the Burdekin core (L:P HpCDD = 5:1 in deep- and 4:1 in surface sediments) as well as Hinchinbrook river sediments (L:P HpCDD = 2:1) resulted in less distinct 1,4-patterns (i.e. lower L:LP:P HxCDD ratios and lower % contribution of L PnCDD and L TCDD). These trends indicate that the formation of 1,4,6,9-isomers, and therefore the overall isomer distribution of tetra- to hexa-chlorinated PCDDs, is time dependant and that the specific isomer pattern is already determined

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from the ratio of the two HpCDD isomers. Hence, the appearance of 1,4,6,9-substituted isomers is governed mainly by the dechlorination preference from OCDD and resulting PCDDs. Estuarine and marine sediments from other 1,4-pattern samples (e.g. Osaka Bay, Harima Nada⁶, Philippine Basin, Yellow Sea⁷ Hong Kong⁸) show similar ratios compared to the estuarine sediments from Queensland. Lake sediments on the other hand (Mississippi^{3, 4}) generally show less distinct 1,4-patterns and are mostly comparable to the river sediments collected from Queensland's Hinchinbrook area. Considering the results of this and other studies, the differences in the extent of 1,4,6,9-substituted isomer dominance and the resulting differences in isomer distributions can be explained by the initial dechlorination preference and the time of deposition.

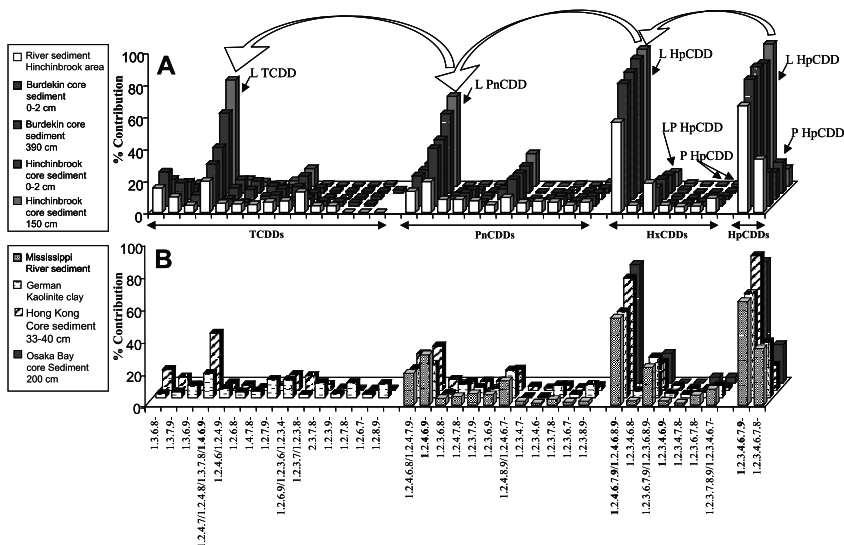


Figure 1. PCDD isomer distribution from A. Queensland samples and B. sediments from Mississippi River³, Osaka Bay core⁶ and Hong Kong core as well as German kaolinite¹¹ clay. (Note that some isomers could not be obtained from the literature). White arrows indicate the pathway of lateral dechlorination; black arrows indicate the isomers resulting from lateral (L), peri-lateral (LP) and peri (P) dechlorination from OCDD.

An unusual distribution of the 2,3,7,8-HxCDDs, with a dominance of 1,2,3,7,8,9-HxCDD (See Fig 1), has often been reported to be characteristic of the “natural formation samples”. This characteristic of the HxCDD isomer pattern was to date supporting the theory of natural PCDD formation in these samples, since it could not be attributed to a known anthropogenic source output. However, the heterogeneous catalysed, thermal dechlorination leads to such a 2,3,7,8-HxCDD pattern¹³. Further, a preferred lateral dechlorination was recently reported by Ohtsuka et al.¹⁴ from studies on photodegradation pathways using UV (254 nm) radiation, resulting in a 1,4,6,9-dominated isomer pattern, strikingly similar compared to the 1,4-patterns of natural formation samples. With respect to Queensland's and other deep core sediments however, UV radiation is unlikely the catalyst of the observed transformation of PCDD signatures. Since these sediments are predominantly anaerobic, reductive dechlorination seems a more likely pathway. Several microbial and/or abiotic driven reductive dechlorination pathways have been identified, depending on microorganisms present, the substitution patterns of the original source profile and a number of abiotic factors. Similar to results of the present study, an increase in 1,2,3,7,8,9-HxCDD was reported in anaerobic sediment cores from

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Lake Ketelmeer¹⁵. A subsequent study from Lake Ketelmeer indicated that specific microorganisms are capable of simultaneous lateral- and peri-dechlorination activities¹⁶. Recently, bacteria from Spittel Wasser sediment were found to selectively dechlorinate the lateral positions («SP-pathway»)¹⁷. These results indicate that a specific lateral dechlorination by microorganisms is possible and may therefore provide a potential mechanism for the transformation of PCDD source profiles into the 1,4-patterns observed. Differences in L:P HpCDD and L:LP:P HxCDD isomer ratios observed in the 1,4-patterns of estuarine/marine and river/lake samples may therefore depend, in addition to timeframes available for transformation, on the biotic (and abiotic) environment of the specific locations.

The results of the present study strongly suggest that not the PCDD/F source, but post-formation dechlorination processes in the environment result in the distinct 1,4-patterns (including the specific distribution of the 2,3,7,8-HxCDDs) characteristic for “natural formation samples”. Consequently, the environmental samples do not reflect the signatures of the original source and any formation process that results in the production of predominantly OCDD represents a possible source input. This provides new aspects with respect to the identification of possible PCDD/F sources and their formation processes.

Acknowledgements

This project was funded by ARC-SPIRT, GBRMPA, Ergo Forschungsgesellschaft, CSIRO Coastal Zone Project and CRC Reef. QHSS provides funding for NRCET.

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