

# FORMATION AND SOURCES: FIELD CASES

## AN ALTERNATIVE HYPOTHESIS TO NATURAL PCDD FORMATION

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### Introduction

In recent years, a number of environmental samples from pre-1900 deposits and/or rural areas have been reported with unusual congener profiles of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which could not be attributed to any known anthropogenic source. These samples were characterised by elevated levels of PCDDs dominated by the octachlorinated dibenzodioxin (OCDD), the dominance of the 1,2,3,7,8,9-substituted hexachlorinated dibenzodioxin (HxCDD) among the three laterally substituted HxCDDs, and a general lack, or relatively low concentrations, of PCDFs. Such characteristic signatures have been found mostly in sediments, but also in soil/clay samples collected from Australia<sup>1-3</sup>, U.S.A.<sup>4,5</sup>, Germany<sup>5</sup>, Japan<sup>6,7</sup>, China<sup>6</sup>, Philippines<sup>6</sup> and Hong Kong<sup>8</sup>. The unusual PCDD/F signatures and the apparent lack of possible anthropogenic influences and/or the depositional age of the sediments obtained from core analysis, suggested a non-anthropogenic formation process as a possible cause for the observed contaminations. Recent investigations of available PCDD/F data in the literature from these “natural formation samples” revealed that not only the congener profiles and laterally substituted HxCDDs, but the distribution of all individual PCDD isomers show similarities in most cases<sup>9</sup>. These are characterised by a striking dominance of isomers chlorinated in the 1,4,6,9-positions. This distinct fingerprint, referred to as “1,4-pattern”, has been shown to result from transformation processes occurring predominantly in the sink environments<sup>9</sup>. Preferred lateral, anaerobic dechlorination of OCDD represents a likely pathway resulting in the typical signatures observed. 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 possible PCDD/F sources. To identify possible source inputs, we compared the 1,4-patterns published from various locations to the isomer distributions caused by known contamination sources. Based on our results and these literature comparisons, we propose an alternative hypothesis to natural formation that, in our opinion, warrants further investigations as a possible source input in areas where PCDD 1,4-patterns have been observed.

### Materials and Methods

This study represents a reassessment of samples collected for previous studies on spatial and temporal PCDD/F concentrations in the coastal zone of Queensland<sup>1,2</sup>. For the present study, these data have been used to perform isomer specific analysis for sediment, soil and sediment core samples and were compared to data provided by the literature.

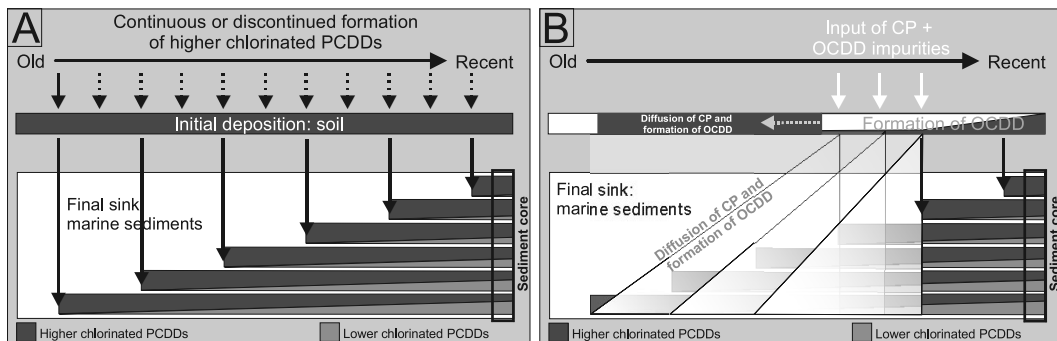
### Results and Discussion

Based on the results obtained by numerous studies showing elevated concentrations of predominantly OCDD and the distinct 1,4-pattern in pre-1900 sediment deposits and/or areas of little tertiary industry activities (see Figure 2A), two source scenarios present a possible explanation for the observed contaminations: (i) a natural, continuous or historical event OCDD source, or (ii) the involvement of vertical migration processes of a ubiquitous OCDD dominated anthropogenic source. A

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widespread, non-anthropogenic, historical event or continuous (since at least 3 centuries) land-based source of higher chlorinated PCDDs (predominantly OCDD) has been proposed previously to account for the PCDDs found in sediments deposited during the last 350 years<sup>10</sup> (see Figure 1A). Further investigations indicated that subsequent dechlorination of OCDD, occurring predominantly in the sediment environment, can result in the formation of lower chlorinated, 1,4,6,9-dominated PCDDs with depositional age<sup>9</sup> (Figure 1A). However, the processes resulting in a non-anthropogenic formation of PCDDs remain unknown.

On the other hand, various anthropogenic compounds, in particular chlorinated phenols (CPs) such as pentachlorophenol (PCP) and sodium pentachlorophenol (Na-PCP) (and their derivatives, such as chlorophenoxyphenols) have been shown in numerous studies to produce OCDD via both biological and abiotic processes<sup>11, 12</sup>. Moreover, these compounds can be relatively water-soluble, depending on their ionization states in the environment, which significantly impacts their aqueous solubility, sorption and transport. At pH >7 for example, PCP is 99 % disassociated, moving easily through soils<sup>13</sup>. Estimation of the diffusion coefficient of PCP in water ( $D_{BW} = 7.29 \cdot 10^{-6}$  cm<sup>2</sup>/s) confirms that disassociated PCP may have diffused to the deepest core sections of the sediment cores in Queensland. Hence, we cannot ignore the potential for anthropogenic influences as possible contamination sources, in particular CPs that had the potential to migrate through the sediment cores in the past 50-60 years of their application and represent precursors for the formation of OCDD in deep sediments.

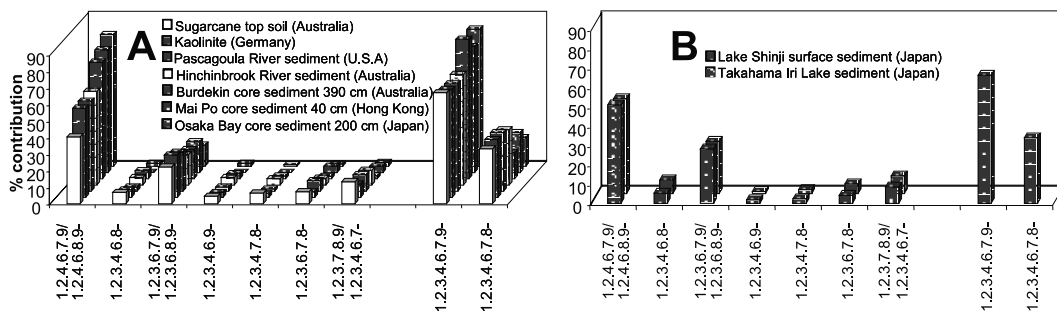


**Figure 1.** Conceptual schematic of two hypotheses on PCDD sources and processes that led to the contamination of environmental samples with OCDD and distinct 1,4-isomer patterns in pre-1900 sediment deposits from A. non-anthropogenic and B. anthropogenic input sources.

Based on recent results from our work in Queensland, in combination with the possibilities of a diffusion and transformation of anthropogenic OCDD precursors in deep sediments, we propose a second scenario (Figure 1B). This scenario hypothesises on a precursor source input of commercial chlorophenols (CPs), such as PCP, during the mid-end 20<sup>th</sup> century, and the subsequent condensation of predominantly OCDD from CPs (and their derivatives) in the environment. CPs and their predominant OCDD-impurity runoff to the marine system, together with an OCDD formation from this precursor within the sediment environment would result in the strong OCDD dominated profiles observed in the sediment layers from the mid-end 20<sup>th</sup> century. From these sediment sections however, diffusion of the deposited CPs into the deeper sediment layers may have occurred. A condensation of OCDD from diffused CPs in these sediment sections would again result in OCDD dominated PCDD profiles and may have contaminated deep sediment layers, deposited prior to the production of organochlorines. Subsequent dechlorination of OCDD after deposition may then result in the distinctive 1,4-pattern typical of Queensland samples.

Supporting evidence for Scenario B is found in literature reports of studies on Japan lake- and tributary river sediments with known PCP contamination from agricultural use. The HpCDD and HxCDD distribution in Lake Shinji core sediments<sup>17</sup> and some Lake Kasumigaura (Takahama Iri) surface sediments<sup>18</sup> show a distinctive 1,4-pattern (including the dominance of 1,2,3,7,8,9/(1,2,3,4,6,7)-

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**Figure 2.** HxCDD and HpCDD isomer patterns of environmental samples from A. “natural formation samples” from Australia<sup>9</sup>, Germany<sup>14</sup>, U.S.A.<sup>15</sup>, Hong Kong<sup>9</sup> and Japan<sup>7</sup> and B. areas with substantial PCP input in Japan<sup>16, 17</sup>.

HxCDD among the toxic HxCDDs) (Figure 2B) and are remarkably similar to those observed in “natural formation samples” (Figure 2A). Principal component analysis from Kasumigaura lake and river surface sediments revealed that one group of samples was characterised by these unusual HxCDD patterns, contributing 18 % to the total variation, but could not be attributed to a known source or transformation process<sup>18</sup>. Importantly, in particular the sediments from the lake environment showed the unusual HxCDD patterns, whereas its tributary river sediments correlated to principal components representing pentachlorophenol (PCP) and/or chloronitrophen (CNP) impurities, used in rice paddy cultivations of the area. The authors suggested that “either some input or lack of some loss/transformation” could have resulted in the signatures found in the lake environment. PCDD transformation studies on dated sediment cores<sup>9</sup> confirm this and further suggest that dechlorination of OCDD may have resulted in the alteration of lake Kasumigaura sediment PCDD signatures. Dated core sediments from Lake Shinji were also shown to contain high PCDD/F contributions (average 68 %) from PCP impurities, derived from its extensive use as rice paddy herbicide in the area during the 1960s and 1970s<sup>17</sup>. Apart from characteristic 1,4-patterns present in these core samples, it is particularly interesting that an increase in PCDD/F concentrations was found several years ahead of PCP use. Sediments deposited during the time of PCP application showed relatively high PCDF concentrations, and low PCDD : PCDF (D/F) ratios (11 to 14), corresponding well to the D/F ratios reported from PCP formulas<sup>19</sup>. Older sediments, deposited before the application of PCP, still showed relatively high PCDD concentrations (>2500 pg g<sup>-1</sup> dw); however, PCDF concentrations were considerably lower, resulting in a D/F ratio of up to 82. Considering the history of land-use in this area, it seems possible that this trend may be due to the formation of higher chlorinated PCDDs after migration of PCP into deeper sediment layers, whereas PCDD/F impurities originally present in PCP are relatively immobile, and sorbed strongly to the organic material in the original sediment layer of deposition. The (predominant) OCDD formation from diffused PCP could explain the low PCDF concentrations found in most Queensland’s sediments (PCP has been shown to produce predominantly OCDD and to a lesser extent HpCDDs, whereas low levels of PCDFs are typically present in PCP as impurities). Interestingly, recent studies on forest soil cores in Queensland have shown that almost exclusively OCDD and HpCDD are present in deep soil layers, while the surface sections show PCDD congeners typical for Queensland profiles and PCDFs that are comparable to those found from PCP contamination<sup>22</sup>.

PCP has found worldwide extensive application during the 1940s to 1990s as a fungicide, general biocide and herbicide. Our enquiries regarding past CP application quantities within the coastline of Queensland or even within Australia have been unsuccessful, and reliable data have been inaccessible to date. However, PCP has been produced in Australia (until the mid 1990s), imported into Queensland and found application for preservation of timber<sup>20, 21</sup>.

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Considering all present knowledge about the PCDD contamination in Queensland, a land-based source of primarily OCDD (and/or OCDD precursors) seems most probable. A subsequent transformation via dechlorination after OCDD formation (and/or migration and condensation) is likely to result in the accumulation of lower chlorinated PCDDs, in particular the peri-chlorinated isomers, producing the characteristic 1,4-patterns observed along the Queensland coastline. With respect to the source input, natural formation of PCDDs presents a possibility that may explain the presence of PCDDs in deep sediments. However, our recent results and the hypothesis presented herein warrant, in our opinion, further investigations into a possible anthropogenic contamination of areas where PCDD 1,4-patterns are observed.

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