

DIOXIN PRECURSORS IN AUSTRALIAN SOIL CHARACTERISED BY 1,4-PCDD/F SIGNATURES

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Introduction

A number of previous studies have identified elevated concentrations of PCDDs in sediments and soil from Queensland, Australia^{1,2}. Distribution data to date indicates the contamination to be restricted to the fertile coastal plains (approximately 100-300 km wide), but widespread along the 2000 km Queensland coastline and beyond. Major land-use in this area includes primary industries such as agriculture and cattle grazing, however, contaminated zones are not restricted to a particular type of land-use. Soil and sediment samples from this eastern Australian coastal plain are characterized by identical PCDD/F congener profiles and isomer patterns, suggesting a similar origin for these compounds³. The source of this contamination, however, remains unidentified, and the characteristic chemical fingerprints have not been reported from sources described to date. The unique congener profiles of these samples are characterized by the dominance of OCDD, decreasing concentrations towards the lower chlorinated PCDDs, together with low levels of furans and the dominance of 1,2,3,7,8,9-HxCDD among the laterally substituted HxCDDs. Similar congener profiles have been reported from elsewhere (e.g. Japan, China, USA), and the source could not be associated to known anthropogenic sources. Hence, previous studies have suggested that contaminations with such characteristics may be the result of natural processes¹⁻⁴. The PCDD/F isomer patterns of Queensland samples in particular, are distinctively dominated by 1,4,6,9-substituted compounds among their homologue groups³. Recent studies have demonstrated that this 1,4-pattern (i.e. the dominance of 1,4,6,9-substituted isomers as well as the congener profile described above) may result from environmental transformation processes, specifically a continuous lateral dechlorination from OCDD after source emission³. These findings indicated that the original source fingerprint may be obscured, but would be dominated by OCDD, which lead to the suggestion that anthropogenic pesticides with known OCDD impurities, or dioxin precursors, may be accountable for the observed contamination³. Such compounds include the fungicide pentachlorophenol (PCP) and high chlorinated phenoxyphenols (PCPPs). High chlorinated PCPPs have been identified as common contaminants of pentachlorophenol (PCP and Na-PCP) at levels of up to 5-6.2% in technical formulations^{5,6}. PCP and PCPPs are known as precursors and "pre-dioxins" due to their potential to form PCDD, in particular OCDD. The present study aimed to investigate whether such precursors can be identified in Queensland in PCDD/F contaminated samples that are characterised by the distinct 1,4-pattern. In addition, samples were screened for other co-contaminants of known origin to identify whether anthropogenic impacts could be detected.

Materials and Methods

Two topsoil samples that were previously analysed for PCDD/Fs at ERGO Forschungsgesellschaft mbH in Germany, and confirmed to contain elevated concentrations of PCDDs with a 1,4-pattern distribution were utilized for this study. Archived material from samples collected in 2002 was utilised initially to screen for the presence of high chlorinated phenoxyphenols. Subsequently, soil samples were re-collected in 2004 from the same sites and re-analysed to ensure no contamination has occurred during storage and/or processing of archived material. All samples were collected from the top 5-10 cm using solvent cleaned stainless steel equipment or glassware, and consisted of 5-10 homogenised subsamples. Samples were stored frozen (for 2004 samples), or after freeze drying (for 2002 samples) in Teflon sealed and solvent cleaned glassware in the dark. Topsoil EFS was collected from a forest area (43 hectares) in South East Queensland, which was gazetted a National Park in 1918. Additional topsoil (PS) was sampled approximately 300 m from the forest site EFS just outside the borders of the National Park, within an area that was assessed to have previously been used for pineapple farming, however, the period or intensity of farming activity is unknown.

Analysis for PCDD/Fs was previously undertaken for samples collected in 2002 at ERGO Forschungsgesellschaft. Analytical methods and detailed results were reported previously⁷. All samples were transferred to Stuttgart were further processing (freeze drying and homogenization for samples collected in 2004) and analysis was undertaken for high chlorinated phenoxyphenols (PCPPs), PCDD/Fs and a range of other analytes, including various pesticides. Samples were freeze dried, weighed and soxhlet extracted for 24 hours using methanol:diethylether:HCL (100:10:0.01). An internal standard (mixture of eight ¹³C₁₂ labeled PCBs and PCP) was spiked prior to extraction. After soxhlet extraction, samples were subject to liquid-liquid partitioning using heptane and KOH. The organic (heptane) phase was processed for PCDD/F and pesticide analysis, while the water phase was processed for phenolic compounds including PCPPs. In brief, the organic phase was treated with H₂SO₄, followed by cleanup using Aluminum oxide and H₂SO₄ treated SiO₂, which was eluted with DCM:n-heptane (1:1). The water phase was methylated using dimethylsulphate (pH 10) and subject to liquid-liquid partitioning using n-heptane. Cleanup was performed on a silica column, which was eluted using DCM:n-heptane (1:1). The elutes from both fractions were concentrated and PCB 209 added to each fraction prior to instrument analysis. Samples were analysed on a HRGC-LRMS (HP 6890 GC, Agilent 5973 MS, splitless injection) on a non-polar column (DB-5MS; 0.25 mm i.d., length: 30 m, film thickness: 0.25 µm; Agilent, Waldbronn, Germany) using electron impact ionisation (EI). GC/MS SCAN mode was used to identify the presence of chlorinated organic compounds and for quantification of PCPPs. Due to their tendency for fragmentation in the MS (relatively small M⁺ compared to PCB 209), the integrated major mass fragments were used for quantification. For compounds where internal standards were available, the SIM mode was used for quantification

Results and Discussion

The concentrations of PCDD/Fs at both sites were reported previously (11,900 and 20,100 pg g⁻¹ dw in PS and EFS samples, respectively)⁷. The PCDD/F congener profile was dominated to 83-97% by OCDD in PS and EFS, respectively, with rapidly decreasing contributions according to chlorination state towards TCDDs (Figure 1). Concentrations of most PCDF congeners were relatively low compared to PCDDs (sum PCDFs = 1030 pg g⁻¹ dw, dominated by 1,2,3,4,6,8,9-HpCDF and 1,2,4,6,8,9-HxCDF) in PS, and below the limit of detection in EFS for all PCDFs. PCDD/F isomer patterns in all samples displayed a 1,4-pattern, which is characterized (in conjunction with the described congener profile) by the dominance of 1,4,6,9-substituted isomers among their respective homologue groups.

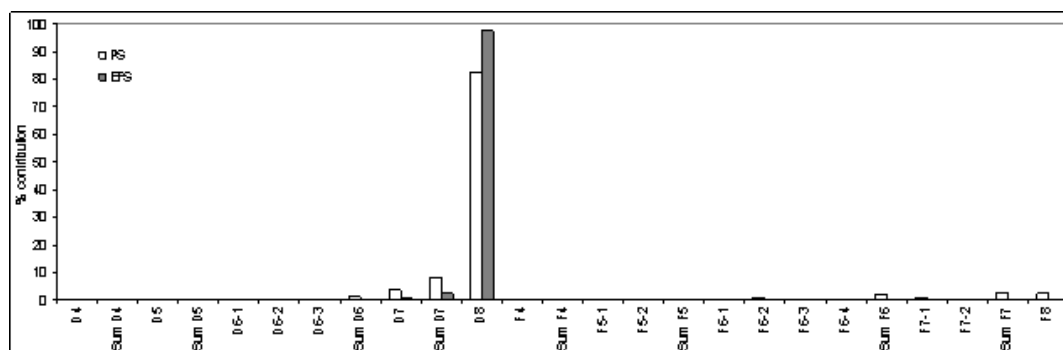


Figure 1. 2,3,7,8-PCDD/F congener and homologue profile in soil samples characterized by the 1,4-pattern.

In addition to elevated PCDD/F levels, a range of other anthropogenic contaminants were identified in these samples. The most striking co-contaminants represented high chlorinated phenoxyphenols (PCPPs) (Figure 2). PCPPs are typical impurities (up to 5-6.2%) of pentachlorophenol (PCP)⁵, a fungicide that has found widespread and worldwide application in the timber industry, agriculture and domestic use since the late 1930s⁸. The import, production or use of PCP and its sodium salt (NaPCP) has been banned in numerous developed countries during the 1980s and 90s, however, import and use in Australia remains registered (with some restrictions under the Rotterdam Convention) to date^{9,10}. Only limited information exists on PCPPs other than with respect to their contamination of PCP, and it is unknown whether these compounds may be produced during other organochlorine

production processes. Elevated concentrations of hepta- (H7CPP), octa- (O8CPP) and nona- (N9CPP) chlorinated phenoxyphenols were found in particular in the soil PS (4, 40 and 40 ng g⁻¹ dw, respectively). The concentrations of PCPPs in this sample represented approximately 9-fold compared to the OCDD concentration. In contrast, while hepta- to nonachlorinated PCPPs were present in the forest soil EFS, they represented only ~5% of the OCDD concentration in these samples (1 ng g⁻¹ dw). The presence of these compounds were confirmed in both archived and samples collected immediately prior to analysis for this study, thereby excluding a contamination of the sample during sampling or processing. In addition, other contaminants were identified in both soils, albeit in relatively low concentrations compared to PCDD/Fs and PCPPs. These include triclosan, high chlorinated diphenylethers, 2-hydroxybiphenyl, 4-chloro-2-methylphenol and hexachlorobenzene.

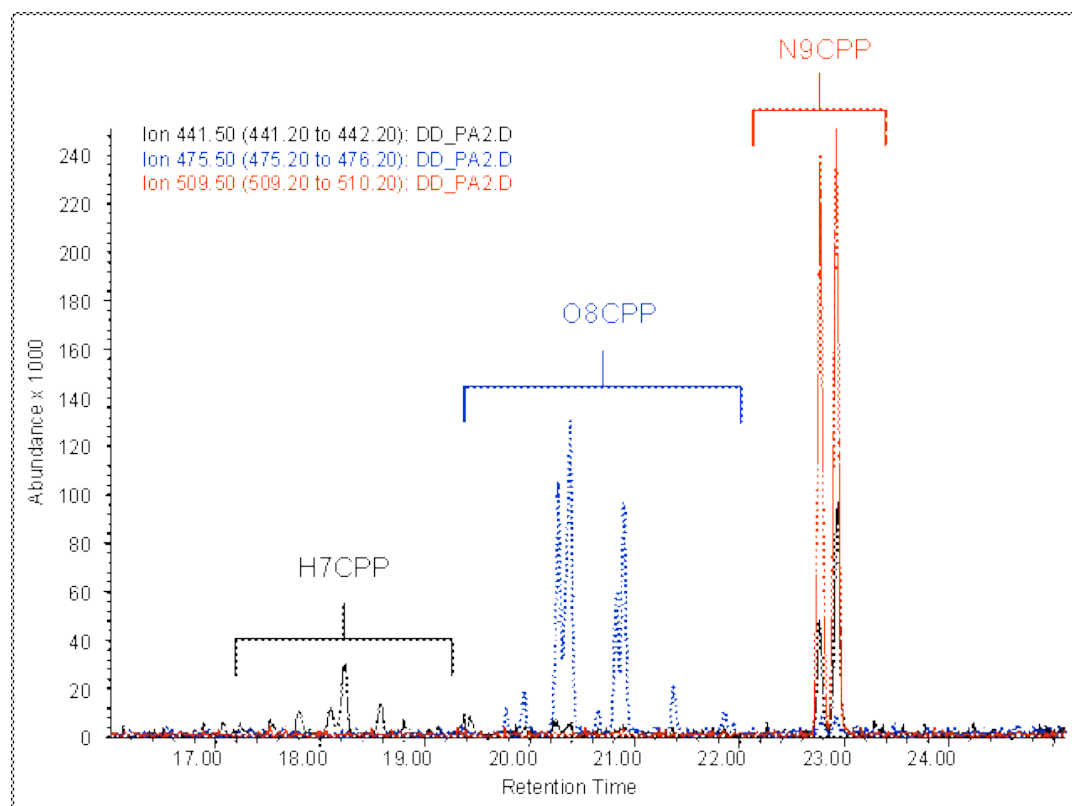


Figure 2. GC/MS chromatogram showing hepta-, octa- and nona- chlorinated phenoxyphenols identified in soil sample PS from South East Queensland.

The presence of these co-contaminants, and in particular PCPPs in PCDD/F contaminated soils of Queensland has implications for whether the characteristic PCDD/F contamination observed in Queensland, Australia, as well as elsewhere, is of natural or anthropogenic origin. Overall, the present results demonstrate that not only former agricultural soil, but also forest soil collected from a National Park, that has presumably been undisturbed since the early 1900s, have been impacted considerably by human activities. In particular the presence of PCPPs indicates a potential contamination with PCP (or other pesticides that may be contaminated with PCPPs through similar production processes). PCP (and PCP contaminated soil) is typically characterized by elevated OCDD levels¹¹. In addition, a number of studies have demonstrated that PCPPs and PCP readily form dioxins, in particular OCDD under heat or photolysis, as well as in the environment and in biota¹²⁻¹⁴. Due to these characteristics, PCPPs and PxCPs are often referred to generally as pre-dioxins and dioxin precursors. The formation of OCDD from PCPPs (and PCP) after their deposition may hence represent a possible source (in addition to OCDD impurities in agrochemical formulations) for the contamination observed in Queensland. It has previously been hypothesized that the formation of OCDD from precursors may provide an explanation for the observed PCDD/F contamination in Queensland³. This is particularly relevant since key similarities are apparent in the chemical signatures between pentachlorophenol (and hence PCPP) contaminated soil and Queensland soils and sediments. These include the relatively low concentrations of PCDFs compared to PCDDs (see text below), as well as the predominance of

OCDD among PCDDs. In addition, where PCDFs are detectable in Queensland samples, in particular in higher contaminated soils (e.g. sample PS of the present study) and sediments, as well as biota (i.e. with PCDFs above the LOD due to biomagnification processes), a dominance of OCDF, followed by 1,2,3,4,6,8,9-HpCDF and 1,2,4,6,8,9-HxCDF among PCDFs is observed. These isomers are considered markers for PCP contamination¹⁵. However, a relatively short half-life in soil (in the order of weeks to months) due to evaporation, microbial degradation and leaching^{5,16,17}, provides challenges to identifying PCP at contaminated sites, in particular if contamination has occurred years or even decades prior to analysis. In contrast, PCDD/Fs and PCPPs resist degradation for more extended periods.

In contrast, the dominance of 1,4,6,9-substituted isomers (1,4-pattern), in particular among HxCDDs, has not been described from PCP sources to date. A recent study has demonstrated, however, that specific lateral dechlorination processes from OCDD occurs in the Queensland environment (i.e. after deposition), resulting in the described 1,4-pattern after source deposition³. In addition, the ratio of PCDDs to PCDFs (D:F) has been reported in the range of ~10-100 in PCP^{11,15}, whereas most Queensland samples are characterized by higher ratios (D:F ~10-1000). It is unknown whether environmental transformation processes may have resulted in this shift. It is evident, however, that formation of OCDD from PCP and PCPP would result in an increased D:F ratio.

In conclusion, despite the current lack of understanding on the formation processes of the contamination observed in Queensland, the presence of known and potent OCDD precursors and other, known anthropogenic contaminants in samples characterised by the unique 1,4-PCDD/F pattern highlights that these sites have been impacted by anthropogenic activities. Hence, these samples cannot be considered "undisturbed" or "pristine" as may be presumed by their origin from a National Park established prior to the use of organochlorines. The contamination from agrochemical formulations and formation of OCDD from PCPPs represents a possible contamination process in these areas and a detailed investigation into the formation pathways and rate is currently underway to provide a better understanding on these chemicals' role in Queensland's PCDD contamination.

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