CONGENER-SPECIFIC INVESTIGATION OF SOURCES AND POST-DEPOSITIONAL FATE OF DIOXINS IN A DEEP SOIL CORE

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Introduction:
Post-depositional processes are known to affect the long-term fate of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in soils. For example, despite having low water solubility, a strong affinity with mobile facilitators in soil water can result in migration of PCDD/Fs in field soils[1]. Similarly, although PCDD/Fs are highly persistent they are not completely inert, and degradation can occur in the environment[2-4]. As many persistent contaminants and some of their degradation products represent hazardous pollutants, such processes can result in temporal and spatial changes to environmental and human health risks. For example, facilitated transport of otherwise immobile pollutants through the vadose zone may result in contamination of sensitive groundwater resources and associated off-site migration.

In addition to environmental conditions, transport and fate processes are governed by contaminant physico-chemical properties, and thus their effects can be compound-specific. It is well understood, for example, that post-depositional processes can change the relative, congener-specific concentrations of PCDD/Fs in the environment[1-5]. Where such effects are known or predictable, field-observed changes to PCDD/F profiles may be used as a tool to identify the processes that occurred[2,5].

The aim of this study was to investigate the distributions of PCDD/Fs in a deep soil core from an agricultural site with a history of pesticide usage. Homologue and isomer distributions were used to elucidate the possible sources and subsequent transport and fate processes influencing these compounds after release to surface soils.

Materials and methods:
Sites and sampling details: An intact soil core was collected adjacent to a sugarcane field, in a cane-growing region in north Queensland, Australia (SC core; 8.4 metres depth). This site has a long history of agriculture, growing pineapples and fruit trees since the late 1800s and predominantly sugarcane since the mid-1900s.

Sample analysis: The core was collected using a hydraulically powered Geoprobe model 6610DT with macro core sampling system and multiple sections of clean PVC sample tubes (1500 x 38 mm i.d.). The PVC coring tubes were cut into sections which were individually frozen and stored. The 500 g soil samples were defrosted, dried in a clean oven at 70°C, then sieved to remove particles >2 mm and ground in a sterile grinder to 0.5 mm.

Sample extraction, clean-up, instrument analysis and identification/quantification of tetra- to octa-chlorinated dibenzo-*p*-dioxin and dibenzofuran congeners were carried out at an accredited laboratory (National Measurement Institute, Sydney) and followed U.S.EPA method 1613 (isotope dilution method using HRGC/HRMS). The analytical procedure, the QA/QC process for this study, and the methods for identifying non-2,3,7,8-isomers followed those previously reported[1]. Recoveries were within 28-99% (average 71%) for individual PCDD/F congeners in most samples.

Combined facilitated transport and dechlorination model: A time and space discretised model was developed to predict the impact of integrated facilitated transport and lateral dechlorination on PCDD isomer profiles. Facilitated migration was approximated by assuming that during each time step a percentage of the total mass of each congener at all soil depths migrate at an average facilitated velocity. A relative velocity for each homologue group was assigned, increasing with increasing degree of dechlorination. There are 150 potential dechlorination pathways for tetra- to octa-chlorinated PCDDs, and each PCDD has a unique dechlorination rate, k_{ij} [T^{-1}], for congener i dechlorinating to a daughter congener j. PCDD dechlorination kinetics were defined based on a first order kinetic decay model reported by Kim et al[6]. Dechlorination rates which give rise to the

dechlorination observed in the present study (and in soils and sediments from Queensland and elsewhere) have not previously been reported. The rate constants k_{ij} were therefore derived via calibration to PCDD profile changes observed in sediment core field data for which a similar lateral dechlorination was reported[3]. A mass release of PCDDs at the soil surface was defined each year with an isomer profile similar to the sugarcane surface soil; mass was assumed to decrease over time in line with reported trends on PCDD impurities in pesticides. At each time step (1 yr) and at each prescribed soil depth (15 cm intervals) the relative mass of each isomer was calculated by 1) transporting each PCDD, followed by 2) the dechlorination process. These masses were used to define an estimated isomer profile over time and soil depth. Since many driving parameters, such as migration rates and the duration and quantity of PCDDs released, are not known at the site, plausible values were assigned and then adjusted as necessary to achieve a simulation of the combined processes that reasonably reflected the profile changes at the site (based on minimising least squares between actual and simulated homologue and 1,4,6,9-congener profiles).

Results and discussion:

PCDD/Fs were present in the soil core at depths far beyond their expected mobility based on physico-chemical properties (typically <10 cm). While upper soil layers contained the highest ΣPCDD/F concentrations (25 ng/g) which generally decreased with depth, concentrations remained elevated at ppb levels up to ~6 m (Figure 1). Overall, PCDD/F isomer, congener and homologue profiles were similar in all core and surface soil samples (Figure 1), indicating a common source origin. The PCDD profile in all samples was dominated by OCDD (range 68-99% of ΣPCDD) with decreasing concentrations towards lower chlorinated homologues (HpCDD>HxCDD>PeCDD≈TCDD), and characterised by dominant 1,4,6,9-isomers (1,4-pattern) (Figure 1). PCDFs contributed only a low proportion (<1.1%) to the ΣPCDD/F concentrations, and most congeners (with the notable exception of 2,4,6,8-TCDF) were near or below the limit of quantification. This PCDD/F profile is typical for soils and sediments from agricultural but also other land-use areas in Queensland (reviewed in ref[7]), and identical isomer patterns were recently described at a contaminated site where high volumes of current pesticide formulations were released[1]. Similar profiles have additionally been described from lake and bay sediments in Japan impacted by contaminated pesticides (mainly PCP and CNP)[2]. Consistent with this, it has been demonstrated that several historical and current use pesticides can contain PCDD/F impurities dominated by OCDD (e.g. PCP, γ-HCH, chlordane, PCNB, MCPA, triclopyr/picloram, imazamox, mecoprop, fenamiphos[8]), and 2,4,6,8-TCDF impurities are characteristic for 2,4-D[9] and chloronitrophen[10]. The observed PCDD/F profiles and history of rural agricultural land-use for the past century at the site thus suggest a source origin from pesticide use.

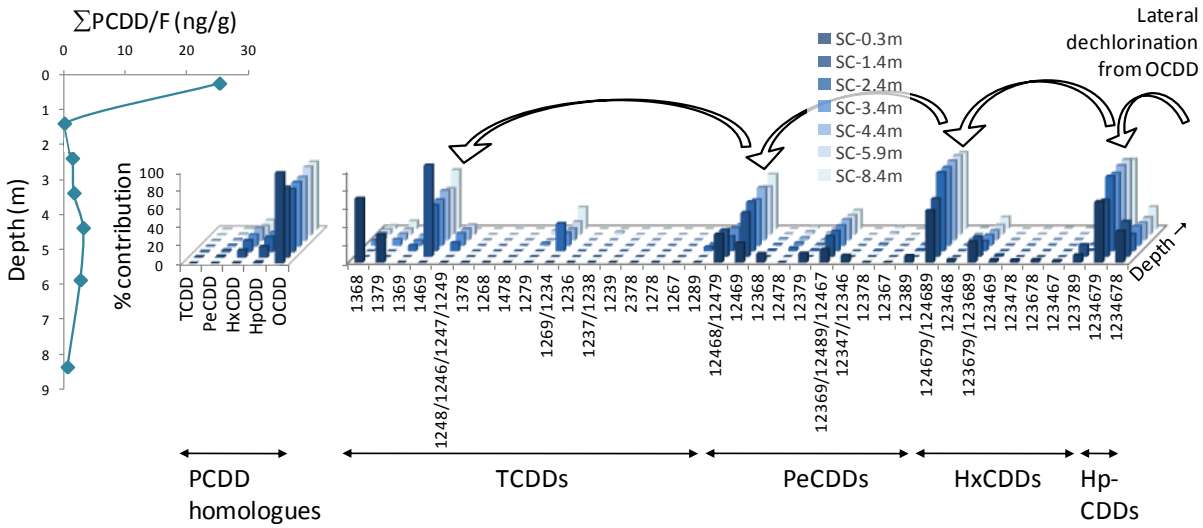

Figure 1. ΣPCDD/F concentrations with soil depth (left hand graph) at the sugarcane (SC) site; and PCDD homologue (left inset) and isomer (right inset) distributions with soil depth. White arrows represent the lateral dechlorination pathway from OCDD to 1,4,6,9-TCDD.

The presence of dioxins throughout the soil core attributed to a common source suggests that the PCDD/Fs at depth resulted from migration through the vadose zone. The extremely low water solubility and high affinity to soil organic matter for even lower chlorinated PCDD/Fs (e.g., log K_{OW} = 6.5–6.9, S_W = 1.0–1.8×10^{-4} mol/m^3 for TCDDs[11]), limits the degree of transport expected in the dissolved state with soil water; although under preferential flow conditions, where a large proportion of water flows through channels and fissures by-passing the bulk soil matrix, sorption to soil is reduced and rapid transport of (low concentrations of) even highly hydrophobic compounds may be possible[12]. Due to reduced sorption, however, preferential flow is generally characterised by a multimodal concentration profile with no chromatographic separation of compounds of different hydrophobicities through the soil profile[12] which was not observed in the current cores. The relatively high concentrations of PCDD/Fs throughout the soil cores suggest that transport with preferential flow was not the dominant process and that migration therefore occurred with mobile carriers in the soil water. PCDD/Fs sorb (in)to facilitators such as surfactant micelles, soil humic acids or bacteria, and are co-transported in the aqueous phase. The land-use and PCDD/F source profile at the site indicates a history of pesticide use, and therefore surfactants (which typically constitute 5-10% v/v in pesticide formulations) represent potential facilitators. However, a range of carriers were likely present at the study site, and transport via other facilitators such as natural soil colloids may also have occurred.

The isomer distribution with depth indicated a progressive increase in the concentrations of isomers fully chlorinated in the 1,4,6,9-positions (Figure 1); for example, the percentage of 1,2,3,4,6,7,9-HpCDD to ΣHpCDDs increased from 66% near the surface (0.2 metres) to 76% at 8.4 metres, with a similar increase for the 1,4,6,9-substituted HxCDDs (59-83%), PeCDDs (21-60%) and TCDDs (0-64%) over the depth of the core. PCDD profiles dominated by 1,4,6,9-chlorinated PCDD isomers among higher chlorinated[2] or all homologue groups (i.e. '1,4-pattern')[3] have previously been described as the result of lateral dechlorination processes. Preferential removal of lateral (2,3,7,8-substituted) chlorines leads to a PCDD profile dominated by 1,4,6,9-congeners with increasing age. In the soil environment, dechlorination pathways depend on prevailing conditions and mixed peri and lateral pathways are often observed; however, preferred lateral dechlorination pathways have been demonstrated under laboratory and field conditions for both abiotic and biotic reductive environments[2,3,13]. In particular, lateral dechlorination of PCDDs has been reported in sediments from Queensland[3] and the dominant isomers formed during dechlorination were identical to those of the current study suggesting a common dechlorination process.

The key post-depositional processes affecting PCDDs at the sugarcane site are, thus, indicated to be facilitated transport and preferred lateral dechlorination. An increase in lateral dechlorination products with depth entails a homologue profile shift from higher to lower chlorinated PCDDs[3], as observed in the core of the present study; i.e., the contribution of OCDD to ΣPCDDs decreased from 98% at 0.2 metres to 74% at 8.4 metres for core SC, with a concomitant increase in tetra- (0.0059-0.71%), penta- (0.019-1.5%), hexa- (0.20-10%) and hepta-chlorinated (1.4-14%) homologues (Figure 1). In contrast to this observed homologue profile shift, facilitated transport via either natural colloids or surfactants is expected to have the reverse effect and result in preferential migration of more hydrophobic, less water soluble and correspondingly higher chlorinated congeners (e.g., OCDD)[1,14]. This reversal of mobility, compared to the expected aqueous mobility predicted by physico-chemical properties, has been shown under both laboratory and field conditions to result in a progressive shift of PCDD/Fs towards higher chlorinated congeners with depth[1,15]. However, the PCDD homologue changes governed by a specific increase of 1,4,6,9-substituted isomers may have masked the effect of facilitated transport processes on homologue distributions. To confirm this, the combined effect of facilitated transport and lateral dechlorination were simulated using a model capable of predicting the impact of each process on the PCDD isomer distribution over time and soil depth.

When the model was calibrated to the field data, simulation of the isomer profiles observed in the core could best be achieved when both the key post-depositional processes identified at the site were considered (Figure 2) (compared to modeling each process in isolation). Specifically, the predicted isomer profiles were characterized by the progressive shift towards both 1,4,6,9-congeners and lower chlorinated homologues with depth (Figure 2). The model was parameterised as follows: a long-term, continuous but decreasing release of PCDDs (up to 60 years), with an OCDD dominated source profile, a preferred lateral dechlorination pathway with homologue-averaged dechlorination half-lives in the range of 8-40 years for tetra- to octa-chlorinated congeners,

respectively, and facilitated migration of 0.6-1.2% of congener mass moving 15 cm per year with increasing rates towards higher chlorinated congeners.

These results suggest that extensive, and potentially relatively rapid (metres per decade), facilitated transport of highly hydrophobic chemicals can occur in agricultural soils. Thus, typical approaches for estimating contaminant loads (and risks) based on topsoil monitoring results would represent considerable underestimates, and would fail to identify the potential for unexpected groundwater contamination and (suspended) aqueous offsite transport. This suggests a need for careful evaluation of hydrophobic contaminant, including PCDD/F, and facilitator release sources and their risks to the environment and human health.

The current study highlights that particular processes (or source patterns) can be masked and be difficult to identify from field data due to concurrent transformation and migration processes. Hence, the possible sources and fate of PCDD/Fs cannot be directly obtained from field data and/or physico-chemical properties alone. Lack of information on contaminant source history, environmental conditions and other determining factors, as well as poor understanding of their interaction with post-depositional processes, often limits the option for mechanistic models to predict site-specific contaminant fate and risks. However, where congener-specific changes are known or predictable, the approach of the current study may facilitate understanding on possible source input and/or fate processes in field soils.

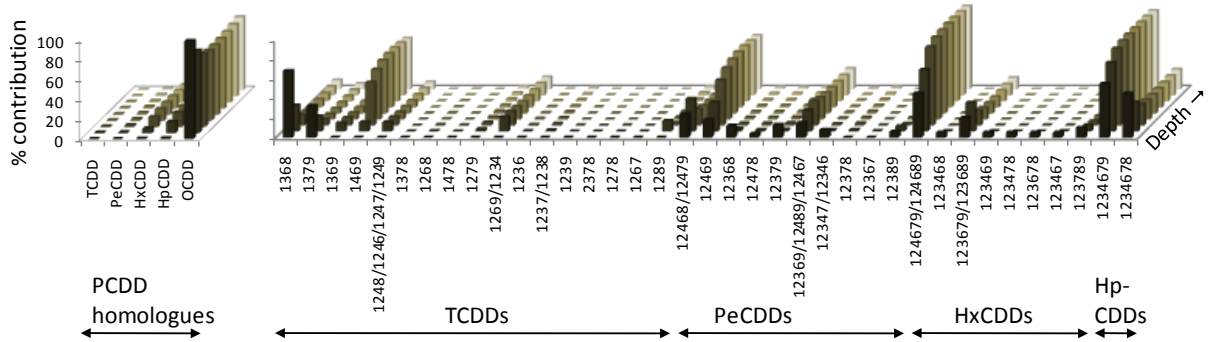

Figure 2. Combined facilitated transport and lateral dechlorination model output predicting PCDD isomer distributions with depth (to 8 metres) in the sugarcane core.

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