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Isomer-specific investigation of PCDD/F mobility and other fate processes in deep soil cores

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HIGHLIGHTS

- Deep soil cores (to 20 m) were analysed to assess field mobility and fate of PCDD/Fs.
- Isomer profiles could differentiate sources and elucidate subsurface fate processes.
- Facilitated transport of PCDDs in agricultural and other soils was extensive.
- PCDD profile changes with depth reflected aged-related lateral dechlorination.
- Substantial unrecognised subsurface PCDD loads may be stored in Queensland soils.

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are highly hydrophobic compounds with low migration potential in soil–water. Nevertheless, they have been occasionally reported in subsurface soils hypothesised as the result of facilitated transport processes with colloids or surfactants, or yet unidentified *in-situ* formation processes. To date, however, the prevalence of deep soil contamination, involved processes and their kinetics remain poorly understood. This study investigated PCDD/F concentrations and isomer profiles through deep soil cores (to 20 m) from agricultural, industrial and urban sites in Queensland, Australia. Based on isomer profiles, a unique source common to all core soils (regardless of depth) was identified, dominated by octachlorodibenzo-*p*-dioxin (OCDD). The source was consistent with contamination resulting from pesticide impurities. Elevated PCDD concentrations (μg/kg range) to depths up to ~4–17 m and a continuous increase of peri-chlorinated (1,4,6,9-substituted) isomers through the cores suggested that vertical transport and lateral dechlorination were key post-depositional processes at these sites. The mobility of PCDDs in the present study is far greater than previously reported in soils in general. High estimated mass transport rates for OCDD in four agricultural cores (3.0–6.2% year^{-1}) likely reflect significant levels of facilitating species, including surfactants, and intensive rainfall at these sites. The implications of such extensive subsurface transport of PCDD/Fs for groundwater contamination and load estimates may be significant. If the cores of the present study are assumed representative of the region, a total PCDD/F load in the order of 800 tonnes (1.6 tonnes TEQ) could be present in subsurface Queensland coastal soils.

1. Introduction

Many toxic and persistent hydrophobic organic contaminants (HOCs), including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), are sequestered in surface soils over time. Nevertheless, post-depositional processes can result in the release of such compounds from soils. Thus, soils can act as an important secondary source of PCDD/F and other HOCs to the environment and humans. Vertical migration of HOCs in association with mobile waterborne colloids, such as dissolved organic carbon (DOC) and surfactants, has been demonstrated in controlled laboratory experiments (Schramm et al., 1995; Kim et al., 2002). Extrapolation to complex field conditions, however, is not always viable and the extent of this process occurring in the field remains poorly understood (de Jonge et al., 2004; Bergknut et al., 2010). Besides

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physico-chemical properties, numerous site-specific factors control HOC mobility with facilitating species. These include hydrology, climate, soil properties, as well as the type and ubiquity of facilitators present (de Jonge et al., 2004; Paria, 2008). The majority of field evidence from remote (Brzuzy and Hites, 1995; Krauss et al., 2000; Moeckel et al., 2008; Bergknut et al., 2010, 2011), agricultural (Prange, 2003; Wang et al., 2004; Cheng et al., 2014) or contaminated (Persson, 2007; Yang et al., 2010; Grant et al., 2011) soils report HOC migration typically to depths only up to 0.5–1 m. At most sites, DOC or particulate organic matter (POM) has been proposed as the responsible facilitators. Although scarce, more extensive migration has also been attributed to facilitated processes with surfactants (Grant et al., 2011). Surfactants are commonly present in pesticide formulations, as well as biosolids and irrigation water applied to agricultural soils (Pennell et al., 2003). Their amphiphilic nature allows enhanced solubility and associated migration potential of HOCs. Despite this, the capacity for surfactants to mobilise HOCs at agricultural and other field sites where surfactants are frequently released has rarely been investigated.

Coastal Queensland, Australia, has a widespread surface dioxin contamination dominated by octachlorodibenzo-*p*-dioxin (OCDD) (Gaus et al., 2001). Due to the absence of major industrial activities and established contamination of many historical as well as currently used pesticides, this contamination has been linked to pesticide usage in this predominantly agricultural region (Holt et al., 2010; Holt et al., 2012; Camenzuli et al., 2014). Unusually high levels of PCDD/Fs have also been observed at depths of several metres at a Queensland forest site (Prange, 2003). Based on 2,3,7,8-congener and homologue profiles, however, the source and mobility of PCDD/Fs at this site could not be elucidated (Prange, 2003). Similarities in profiles between Queensland soils and deep soils dominated by kaolinitic and lignitic clays in the USA and Europe have further led to suggestions of a common PCDD/F source (Ferrario et al., 2000; Gadomski et al., 2004; Schmitz et al., 2011). Elevated PCDD levels in these clays up to 27 m depth were considered unlikely to result from vertical transport processes and an *in-situ*, non-anthropogenic formation process was hypothesised for these areas (Ferrario et al., 2000). This seemingly contradicts the work on source identification for the Queensland PCDD/F contamination, where an anthropogenic source to surface soils as well as a yet unidentified *in-situ* non-anthropogenic formation in deep soils appears less likely compared to known facilitated migration processes.

Evaluating facilitated transport processes in field soils is, however, exceedingly challenging, particularly retrospectively (i.e. for historical contamination). Characterising complex natural soil systems and subsurface hydrology is costly and often unfeasible, and responsible facilitators can seldom be identified in retrospect (Grant et al., 2011). However, previous field studies have demonstrated the utility of assessing congener-specific subsurface distributions of HOCs to further understanding of various post-depositional fate and mobility processes (Guggenburger et al., 1996; Krauss et al., 2000; Moeckel et al., 2008; Bergknut et al., 2010). Fate and transport processes are generally governed by contaminant physico-chemical properties and thus result in compound-selective changes. For example, preferential partitioning and associated transport of more hydrophobic HOC congeners with facilitators has been shown to increase their relative abundance with soil depth (Schramm et al., 1995; Kim et al., 2002; Grant et al., 2011). For PCDD/Fs, reported profiles are typically limited to 2,3,7,8-chlorinated congeners. Similarities in physico-chemical properties between isomers within a homologue group, however, preserve the relative distribution of isomers in the environment to a greater extent than the congener patterns (Masunaga et al., 2003). This aspect is commonly used as the basis for using isomer distributions as the most robust information for source identification (Masunaga et al., 2003), and equally can be applied to evaluation of post-depositional processes.

The present study aimed to provide information on the extent of deep (up to 20 m) soil contamination in Queensland, and undertake an isomer-specific investigation of PCDD/Fs. A total of nine intact cores from agricultural, industrial and urban sites were analysed for PCDD/Fs, and two cores were further examined in detail to (1) investigate PCDD/F isomer, congener and homologue profiles compared to other soils with a suspected common PCDD/F source; and (2) assess whether profile patterns could assist elucidating the particular processes that lead to this subsurface contamination.

2. Materials and methods

2.1. Site and sampling details

Nine intact soil cores were collected from three different regions in Queensland (Fig. 1). Cores A1 and A2 (8.4 m deep) were located 6 km apart adjacent to sugarcane fields within the Cairns cane-growing region in north Queensland, Australia. This site has a long history of agriculture, growing pineapples and fruit trees since the late 1800s and predominantly sugarcane since the mid-1900s. Cores B1 to B4 were collected along a 2 km transect adjacent to sugarcane fields in the Tully sugarcane region, approximately 140 km south of Cairns (B1: 4.5 m; B2, B3: 3.5 m; B4: 3.4 m). This agricultural region is also dominated by sugarcane, dating back to 1865. Core Q1 (5.3 m) was located in south-east Queensland at a suspected chemical and pesticide waste disposal site near an industrial estate dominated by pesticide

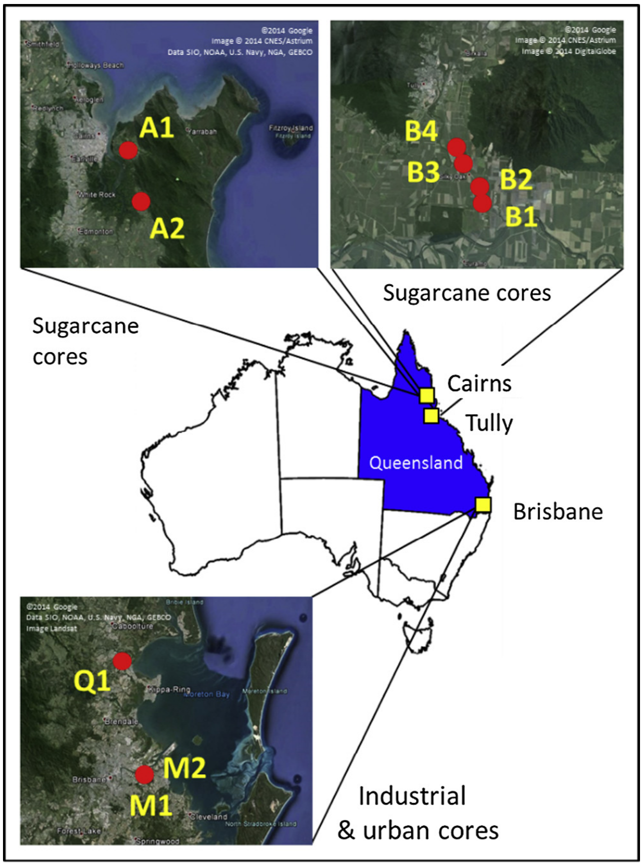

Fig. 1. Map of sampling sites for the sugarcane (A1, A2, B1–B4), industrial (Q1) and urban (M1, M2) cores in Queensland, Australia. Images ©2014 Google.