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Historical emissions of octachlorodibenzodioxin in a watershed in Queensland, Australia: Estimation from field data and an environmental fate model

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HIGHLIGHTS

- OCDD emissions back-calculated with an environmental fate model.
- Estimated OCDD release of 2,500 kg to agricultural soil over the last 60 years.
- Facilitated downward transport is important for fate of OCDD in agricultural soil.

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ABSTRACT

An octachlorodibenzodioxin (OCDD)-dominated contamination is present along the coast of Queensland, Australia. Several findings indicate that this contamination originates from pesticide use, although due to limited information on OCDD levels in the pesticides used, estimating past and current emissions of OCDD solely from pesticide use data is unfeasible. We used all the qualitative and quantitative information available on OCDD in pesticides together with a previously validated chemical fate model for a catchment in the Queensland Wet Tropics to back-calculate the emissions of OCDD from measured soil concentrations. We estimate that under different emission scenarios an average of 2,500 kg of OCDD was emitted within the modelled 1,685 km^2 (Tully river) catchment between 1950 and 2010. Because this catchment represents only approximately 0.85% of the whole coast of Queensland under a similar contamination, the total amount of OCDD released in this region is considerably larger. For all emission scenarios, we could show that the OCDD currently present in agricultural soil is a result of historical emissions, and current-day emissions are less important in comparison to past emissions. Overall 18% was lost by degradation and 62% was buried below the agricultural surface soil, as a result of facilitated transport.

1. Introduction

Elevated levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have been measured in soil samples along the 2000 km coast of Queensland in Australia (Gaus et al., 2001b; Holt et al., 2008; Müller et al., 1996; Prange et al., 2002). All samples show a dominance of the octachlorinated dibenzodioxin, OCDD, with OCDD concentrations ranging from 1500 to 11,000 pg/g dw in agricultural soil and from 230 to 933 pg/g dw in non-agricultural soil. In contrast, soil measurements beyond the Great Dividing Range are several orders of magnitude lower than coastal soil measurements, with a median concentration of 20 pg/g dw (Prange, 2003). The source of OCDD in the soil of Queensland has been subject to debate since the first measurements of elevated levels of OCDD in 1996 (Müller et al., 1996).

Elevated levels of PCDD/F have also been measured in ocean sediment of the Great Barrier Reef (GBR) Lagoon (Gaus et al., 2001b; McLachlan et al., 2001). The measurements show that OCDD concentrations in the sediment decrease with increasing distance from river

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mouths (Gaus, 2003), and therefore the source of this contamination is assumed to be land based. Furthermore, given that a higher contamination in agricultural soil and in the irrigation drains from agricultural fields has been measured in comparison to non-agricultural soils (Gaus et al., 2001b), agricultural activity is most likely the source of this contamination. The two sources of OCDD in agricultural activity are biomass burning and pesticide use. Several studies (Black et al., 2012; Gullett et al., 2006; Prange et al., 2003) show that only small amounts of OCDD are formed during the biomass burn process, however, sugarcane burning can potentially result in redistribution of OCDD from agricultural fields. On the other hand, pesticide use has been linked to soil and sediment PCDD/F contamination in Japan (Masunaga et al., 2001b), and according to work by Holt et al. (2010), OCDD has been detected in both phased out and current-use pesticides in Queensland.

Pesticide use in Queensland is ongoing and has increased over the last few decades (Johnson and Ebert, 2000). OCDD contamination in the pesticide mixtures, however, follows a different trend. The highest levels, up to 5.8 $mg_{OCDD}/g_{Active\ Ingredient\ (AI)}$, were measured in pesticides, namely pentachlorophenol (PCP), produced in the 1960s–70s in Japan (Masunaga et al., 2001a). Varying levels of OCDD have also been measured in 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) — 88 ng/g_{AI} (Holt et al., 2010), 2,4-dichlorophenoxyacetic acid (2,4-D) — 10 ng/g_{AI} (Holt et al., 2010), 0.02 ng/g_{AI} (Masunaga et al., 2001a), chloranil — 44 ng/g_{AI} (Liu et al., 2012), pentachloronitrobenzene (PCNB) — 1.5 $\mu g/g_{AI}$ (Holt et al., 2010) and several others. Furthermore, the USEPA lists a further 150 pesticides with potential of containing PCDD/F (USEPA, 2005). Additionally, a range of PCDD/F precursors such as chlorinated phenols, phenoxyphenols and diphenylethers present in the pesticide mixture can result in substantial in-situ PCDD/F formation, even after the pesticides have been applied (Holt et al., 2012; Liu et al., 2013). The OCDD-dominant PCDD/F contamination in the agricultural soil of Queensland will most likely have resulted from a combination of the different routes associated with pesticide use.

A large variety of pesticides have been used in Queensland (Johnson and Ebert, 2000). Additional to these pesticides, there is some evidence of PCP use in Queensland (Gordon, 1956). However, Johnson and Ebert (2000) only give the application rate for ten pesticides and in the publication by Gordon (1956), there is no information on the application rate of PCP. The remaining source for pesticide application rates is from the Agricultural chemical usage database (Australian Department of the Energy), however these records (for a limited number of pesticides) only date back to 1995.

Therefore, all the information available on pesticide application rates and PCDD/F impurities in the pesticide mixtures is insufficient to quantify the past and current-day release of PCDD/F, or even, for simplication, solely of OCDD, in Queensland on the basis of pesticide use data. Furthermore, sediment core measurements off the coast of Queensland have been unsuccessful in quantifying the historical amounts of OCDD used (Gaus et al., 2001a) due to an unexpected and substantial vertical movement through the sediment.

However, it is still an important question as to how the substantial OCDD contamination in the agricultural soils in Queensland has come about. With our modelling approach, we use the existing information, namely the current-day OCDD concentrations in soil and the knowledge that OCDD impurities in the pesticide mixtures peaked between 1960 and the 1970s, to back-calculate the historical OCDD emissions (we have restricted our emission estimation to OCDD, since it is by far the dominant congener present in all samples measured). We use the available information to constrain the historical OCDD emissions and to determine possible OCDD emission scenarios that are consistent with the available empirical information.

We have limited our study to a small catchment in the tropics of Queensland, a catchment for which a validated multimedia fate model is available (Camenzuli et al., 2012) and elevated levels of OCDD in agricultural soil have been measured. The Tully river catchment is ideal for this study since it is roughly 1000 km north of the closest heavy industry and long-range transport is considered negligible for this congener. In a second step, we aim to quantify the environmental fate of OCDD and to identify any possible sinks of OCDD in this environmental system.

2. Methods

2.1. Study catchment

The Tully river catchment is located within the Wet Tropics of Queensland, situated between the GBR Lagoon to the east, and the Great Dividing Range to the west. The main river, the Tully river, flows through the length of the catchment and after about 90 km, discharges directly into the GBR Lagoon. This catchment covers an area of approximately 1,685 km^2, with roughly 13% (219 km^2) of the catchment under sugarcane production (Pitt et al., 2007). Brisbane is roughly 1600 km south of Tully and the closest heavy industry is 1000 km south in Gladstone. The town of Tully has 2436 inhabitants (Australian Bureau of Statistics, 2011), and the only industrial activity within this catchment is the Tully Sugar Mill. Sugarcane growth is the dominant agricultural activity, and has been present within this catchment for several decades (Johnson and Ebert, 2000). Up until the mid-1990s, pre-harvest sugarcane trash burning was common agricultural practice, which was eventually phased out, and green cane harvesting was adopted (Schroeder et al., 2009).

2.2. Field data

Seven surface soil samples, four in 2005 and three in 2008, were collected from sugarcane fields within the Tully river catchment. The soils collected in 2005 were soil core samples, and soil up to a depth of 4.5 m was collected and measurements made at four depths. The soils collected in 2008 were composite samples made up of five subsamples. The sampling sites are shown in Fig. 1. Full details of the sampling techniques and analysis are given in Section S2 of the Supplementary Material. For non-agricultural soils, OCDD concentrations were measured in neighbouring catchments, namely the Murray river catchment (Müller et al., 1996), the Herbert river catchment (Gaus et al., 2001b) and the Johnstone river catchment (Müller et al., 2004), all of which are within approximately 40 km from the Tully river catchment.

2.3. Modelling approach

2.3.1. Environmental description

Model setup. A similar model as presented by Camenzuli et al. (2012) was used, which is a dynamic (level IV) four-compartment multimedia mass-balance model (Fig. 2). Based on the hypothesis that the source of OCDD in the Tully river catchment is pesticide use, and only 13% of the catchment is used for agriculture, there are two surface-soil compartments in the model: non-agricultural land and agricultural land. The air compartment is subdivided into two compartments; one over each land compartment. Wind data provided by the Australian Bureau of Meteorology show that the predominant wind direction is from east to west.

Three new processes were added to this version of the model, namely soil resuspension from agricultural land, OCDD volatilisation through pre-harvest sugarcane trash burning, and facilitated transport from agricultural soil into deeper soil. Soil resuspension was based on work by Qureshi et al. (2009), and a mass-transfer coefficient (MTC) for soil resuspension of $2.8 \cdot 10^{-10}$ m/h was used. Release of OCDD from soil