

CONNECTING THE HIGH FIELD LEVELS OF OCDD WITH HISTORICAL PESTICIDE USE IN A RURAL TROPICAL REGION

Camenzuli L^{1*}, Scheringer M¹, Gaus C², Grant S², Hungerbühler K¹

¹ETH Zurich, Institute for Chemical and Bioengineering, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland;

²National Research Centre for Environmental Toxicology, The University of Queensland, 39 Kessels Road, Coopers Plains 4108, Queensland, Australia

Introduction

Polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) have been detected in several environmental media worldwide¹, and PCDD/F emissions are generally attributed to industrial activity and large human settlements. Similarly, a widespread PCDD/F contamination has been measured along the coast of Queensland in Australia²⁻⁴. However, no clear source for this contamination is apparent, since no large industry is present in this area and the largest metropolitan area along this approximately 2000 km coastline is the city of Brisbane, in the south of Queensland.

In Queensland, Müller et al. in 1999 first reported high levels of PCDD/Fs in marine sediments². High PCDD/F levels were also observed in different types of land use by Gaus et al.³ and Prange et al.⁴. A similar congener pattern was reported amongst all these measurements with octachlorodibenzo-*p*-dioxin (OCDD) contributing 70–95% of the total PCDD/F concentration, indicating a similar PCDD/F source for all media sampled. While no north-south gradient along the coast was apparent, an east-west gradient was observed, where PCDD/F concentrations beyond the Great Dividing Range approached background concentrations. It was therefore concluded that this PCDD/F contamination originated from the coast of Queensland, where intense agriculture has been practised for several decades. Importantly, no clear source of this PCDD/F contamination is evident from the Australian dioxin emission inventory⁵; however, heavy pesticide use has previously been linked to high PCDD/F contaminations⁶.

PCDD/F impurities have been detected in several past- and current-use pesticides⁷⁻¹¹. However, due to the limited number of pesticide use data for Queensland, it is difficult to quantify whether the current land contamination has in fact originated from pesticide use. Furthermore, most impurity data available are from pentachlorophenol (PCP) and 2,4,5-T, but for PCP no evidence for use in Queensland is available¹².

In our work, we have developed a multi-compartment mass balance model for chemicals in the Tully River catchment¹³ in order to estimate the historical and current levels of OCDD emissions. We here use our model to test the hypothesis that pesticide use is the dominant source of OCDD within this catchment. Because the contamination is not restricted to agricultural land, we also aim at estimating the short-range transport from agricultural land to non-agricultural land, and the load of OCDD transferred to the near-coastal sediment.

Materials and methods

Study catchment. The Tully River catchment is located within the Wet Tropics of Queensland, and its main river, the Tully River, discharges directly into the Great Barrier Reef (GBR) Lagoon. This catchment covers an area of approximately 1685 km², with roughly 13% of the catchment under sugarcane production¹⁴. Sugarcane has been cultivated in this catchment for several decades, with a history of pre-harvest sugarcane trash burning until the mid-90s¹⁵.

Model setup. In this work, a similar model as presented by Camenzuli et al.¹³ was used, which is a dynamic seven-compartment multimedia chemical fate model. In order to better estimate the redistribution of OCDD between the two land compartments, two further processes were included, namely soil resuspension based on work by Qureshi et al.¹⁶ and OCDD volatilisation through pre-harvest sugarcane trash burning, based on field experiments within Queensland^{17,18}. A full uncertainty analysis was performed on all input parameters, based on error propagation¹⁹.

Field data. OCDD soil concentrations were taken from three separate studies between the years 1996–2004^{3, 20, 21} in three different catchments within the Wet Tropics of Queensland, in both agricultural and non-agricultural land. OCDD concentrations in sediment were taken from a sampling campaign in 2001³.

Emissions. Under the hypothesis that emission of OCDD took place in conjunction with pesticide use, we use OCDD concentrations in agricultural soil to back-calculate the emission of OCDD within the Tully River catchment that lead to the currently measured concentrations in this compartment. Once the emission time trend is defined, the model calculates temporally resolved OCDD concentrations in all seven compartments. Given the lack of historical information on pesticide application, we use a temporal trend for PCDD/F emissions which has been field-calibrated within Queensland²². This is emission trend A in Figure 1. Furthermore, in order to investigate the plausibility of other emission trends, we use the model to test two further temporal trends, also by back-calculating from the measured levels in agricultural soil. Emission trend B assumes an exponential increase and decrease peaking in 1969, and emission trend C assumes constant emissions until 1990 and then drops to 2010 levels (as defined by emission trend A). Finally, for comparison, a fourth emission trend, D, was also set up. Unlike emission trends A–C, this was not defined by back-calculating from field measurements but assumes constant emissions at 2010 levels (as defined by trend A). All emission trends and emission rates are shown in Figure 1.

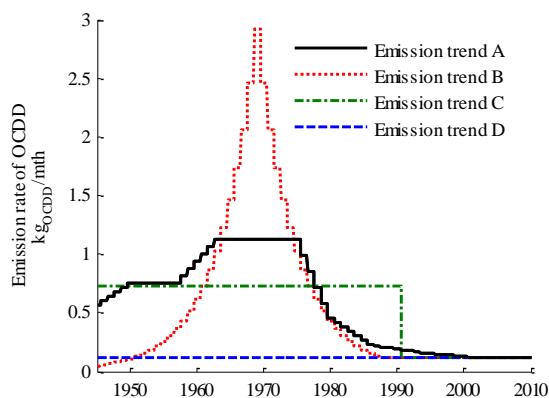


Figure 1. Time trends of OCDD emission rates in kg/month in the Tully River catchment from 1945 to 2010.

Results and discussion

Figure 2 shows monthly OCDD concentrations in agricultural soil, in non-agricultural soil, in sediment and in the air above both land compartments within the Tully River catchment, dating from 1945 until 2010. Results for the OCDD emission trend A are given by the black line. The model results show an increase in the OCDD soil concentration peaking around 1980, following the maximum emissions in trend A (1962–1978). As OCDD emissions decrease, a decrease can also be observed in the OCDD soil concentrations, however at a slower rate than for the emissions. OCDD concentration in the sediment compartment increases at a slower rate than in the soil and peaks approximately in 2000. A different trend takes place in the air compartment with large fluctuations occurring until the mid-90s, and with peak air OCDD concentrations in months of pre-harvest sugarcane trash burning. Once this practise of pre-harvest trash burning was phased out, OCDD atmospheric concentrations stabled at levels ranging between 50–200 fg/m³, which is within the range of measurements made in Queensland²³ with a yearly average of 62 ± 45 fg/m³ (data not shown here).

The limits of uncertainty of our model results are plotted in Figure 2 as grey bands, and are based on emission trend A. For agricultural soil, the geometric mean (indicated by ●) of the two field measurements was used to calibrate the OCDD model results. The model results therefore expectedly lie in-between these measurements; however the individual field measurements are outside the uncertainty limits of our model. In order to better estimate the current-day OCDD levels in soil, further measurements are required. Preliminary results from more soil samples from Tully indicate OCDD levels similar to those used in this work. In non-agricultural soil, two out the three measurements are within the uncertainty limits of our model results. The model OCDD results for the sediment compartment have the highest uncertainty in our results, and reach a maximum uncertainty of a

factor of 2. However, measured OCDD concentrations in the sediment are generally in good agreement with the model results (most of the field measurements are within the model uncertainty limits).

Soil concentrations peak after emissions start to decrease, since OCDD has a soil degradation half-life of several decades²⁴. OCDD sorbs strongly to soil organic matter²⁵, hence it is transferred to the sediment sorbed to soil solid particles during soil runoff. These two factors of high soil degradation half-life and high log K_{ow} also contribute to the continuous increase in OCDD concentration in the sediment, which makes the soil a secondary source of OCDD to the sediment, even long after emissions have been reduced.

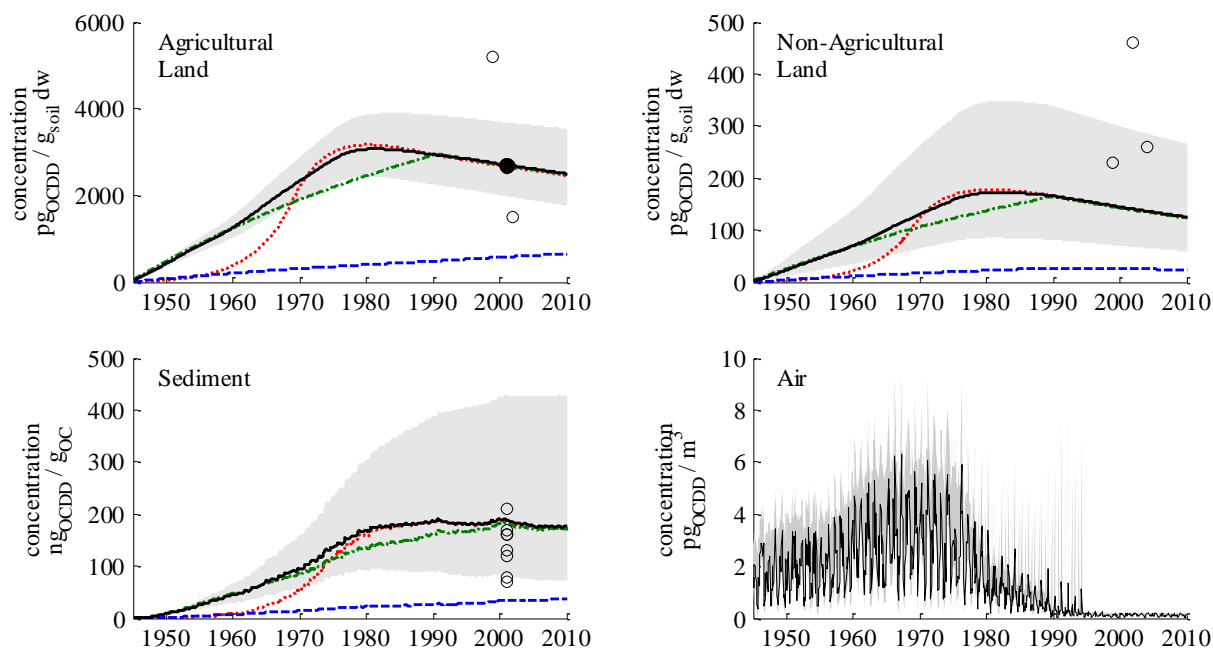


Figure 2. Modelled monthly OCDD concentrations and uncertainty limits in agricultural soil, in non-agricultural soil, in sediment and in air between 1945 and 2010. Modelled concentrations under emission trend A in black, emission trend B in red, emission trend C in green and emission trend D in blue. Field data from each compartment are shown as (○) and were obtained from ^{3, 20} for (I), from ^{3, 20, 21} for (II), and from ³ for (III). Starting point for emission estimation is shown as (●).

From Figure 2, it can be observed that under emission trends A–C, OCDD concentrations in soil converge to the same concentration already around 1990, irrespective of the emission trend. This convergence shows that there is no memory in soil for pre-1990 emission trends, such that the current OCDD concentrations are not sensitive to the past emission trend, but rather to the total amount of OCDD applied to the soil, which is similar for emission trends A–C. This is not the case for emission trend D, in which only 20% of the emissions of OCDD take place. The resulting concentrations for this trend clearly are below the limits of uncertainty of the model and field data, making this emission trend unlikely.

Through our model we therefore can estimate that approximately 400–450 kg of OCDD was emitted within the Tully River catchment between 1945 and 2010 in the three emission trends A–C. The 2010 emissions for this catchment are estimated to be 65 mg/ha per annum, with an equivalent 0.43 g TEQ/annum. Emissions within the Tully River alone (0.02% of land area of Australia), solely through the release of OCDD, equate to 0.02% of the total estimated Australian dioxin release through all identifiable routes (which currently does not include release with pesticide application)⁵.

Our model results indicate that the OCDD in non-agricultural soil may originate from direct emissions of OCDD to the air over the agricultural soil. In the period between 1945 and 2010, a total of 130 kg of OCDD was directly

emitted to air. A further 4.6 kg of OCDD were re-emitted to the air from soil during pre-harvest sugarcane trash burning. From the mass of OCDD in the air above the agricultural soil, approximately 68% was advected to the neighbouring air compartment above non-agricultural soil. From this 68%, roughly 47% was deposited to the soil, resulting in a total transfer of roughly 45 kg of OCDD to non-agricultural soil.

Once in the soil, OCDD was transferred to the sediment compartment through surface soil runoff. Through our model, we could estimate that a total of 34 kg of OCDD was transferred to the sediment from land, predominantly from the more contaminated agricultural soil. Following the high rate of sedimentation, and the long degradation half-life of OCDD within the sediment²⁴, roughly 68% was buried below the top sediment layer, resulting in approximately 6 kg of OCDD in the top 5 cm of sediment, which corresponds to 1.8 g TEQ.

Through our model we estimated the total OCDD emissions within the Tully River catchment, and show that historical OCDD emissions were greater than current-day emissions. However, more OCDD measurements in soil are needed to improve the emission estimates derived with the model. Furthermore, within the uncertainty of our model, we could show that pesticide use on agricultural soil may be the source of OCDD in non-agricultural soil. Also, we could show that both land compartments act as a continuous secondary source of OCDD to the sediment, and could estimate the flux of OCDD to the sediment.

References

1. Alcock RE, Jones KC. (1996) *Environ Sci Technol.* 30(11): 3133-43
2. Müller JF, Haynes D, McLachlan M, Böhme F, Will S, Shaw GR, Mortimer M, Sadler R, Connell DW. (1999) *Chemosphere.* 39(10): 1707-21
3. Gaus C, Pöpke O, Dennison N, Haynes D, Shaw GR, Connell DW, Müller JF. (2001) *Chemosphere.* 43(4-7): 549-58
4. Prange J. (2003) Griffith University, Brisbane
5. Bawden K, Ormerod R, Starke G, Zeise K. (2004) Canberra, Australia
6. Masunaga S, Yao Y, Ogura I, Nakai S, Kanai Y, Yamamuro M, Nakanishi J. (2001) *Environ Sci Technol.* 35(10): 1967-73
7. Masunaga S, Takasuga T, Nakanishi J. (2001) *Chemosphere.* 44(4): 873-85
8. Hagenmaier H, Brunner H. (1987) *Chemosphere.* 16(8-9): 1759-64
9. Holt E, Weber R, Stevenson G, Gaus C. (2010) *Environ Sci Technol.* 44(14): 5409-15
10. Schecter A, Pöpke O, Isaac J, Hrimat NS, Neiroukh F, Safi J, El-Nahhal Y. (1997) *Organohalogen Compd.* 32: 4
11. Liu W, Tao F, Zhang W, Li S, Zheng M. (2012) *Chemosphere.* 86(3): 248-51
12. Holt E, von der Recke R, Vetter W, Hawker D, Alberts V, Kuch B, Weber R, Gaus C. (2008) *Environ Sci Technol.* 42(5): 1472-78
13. Camenzuli L, Scheringer M, Gaus C, Ng CA, Hungerbühler K. (2012) *Sci Total Environ.* 440: 178-85
14. Pitt G, Grounds S, van den Berg D, Denham R. (2007) Queensland, Australia
15. Schroeder B, Panitz J, Linedale T, Whiteing C, Callow B, Samson P, Hurney A, Calcino D, Allsopp P. (2009) Queensland, Australia
16. Qureshi A, MacLeod M, Hungerbühler K. (2009) *Chemosphere.* 77(4): 495-500
17. Prange JA, Gaus C, Weber R, Pöpke O, Müller JF. (2003) *Environ Sci Technol.* 37(19): 4325-29
18. Black RR, Meyer CP, Yates A, Van Zwieten L, Chittim BG, Gaus C, Müller JF. (2012) *Environ Pollut.* 166(0): 10-16
19. MacLeod M, Fraser AJ, Mackay D. (2002) *Environ Toxicol Chem.* 21(4): 700-9
20. Müller JF, Sutton M, Wermuth UD, Hawker D, Connell DW. (1996) Brisbane, Australia
21. Müller JF, Muller R, Goudkamp K, Shaw M, Mortimer M, Haynes D, Burniston D, Symons RK, Moore M. (2004) Canberra, Australia
22. Grant S, Stevenson G, Malcolm D, Gaus C. (2011) *Organohalogen Compd.* 73: 1908-11
23. Kennedy K, Bentley C, Heffernan A, Paxman C, Stevenson G, Müller JF. (2009) The University of Queensland
24. Sinkkonen S, Paasivirta J. (2000) *Chemosphere.* 40(9-11): 943-49
25. Aberg A, MacLeod M, Wiberg K. (2008) *J Phys Chem Ref Data.* 37(4): 1997-2008