

# ENVIRONMENTAL LEVELS I

## PCDD/Fs IN THE QUEENSLAND COASTAL ENVIRONMENT - A MASS BALANCE INVESTIGATION -

Joelle A. Prange<sup>1,2</sup> and Jochen F. Müller<sup>1</sup>

<sup>1</sup> National Research Centre for Environmental Toxicology, 39 Kessels Road, Coopers Plains 4108, Queensland, Australia.

<sup>2</sup> School of Public Health, Griffith University, Nathan 4111 Queensland, Australia.

### Introduction

Mass balance studies, based on emission and deposition data have become a tool to evaluate sources and distribution of persistent pollutants such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Such studies have been conducted for individual countries, cities as well as for the global distribution of PCDD/Fs. To the knowledge of the authors, all PCDD/F mass balance studies have observed that the estimated deposition (from known emission data) for certain PCDD/Fs is much lower than the measured deposition data (often calculated from soil, sediment or atmospheric concentrations). Mass balance studies can therefore be used as a tool to evaluate the existence of potentially unidentified sources of PCDD/Fs.

Recent investigations in Queensland, Australia have identified elevated concentrations of PCDDs in topsoil collected from sites throughout Queensland and results suggest that the contamination is confined to the coastal region<sup>1</sup>. The PCDD/F congener profile is found to be similar in all samples analysed from Queensland, being consistently dominated by the higher chlorinated PCDDs, in particular OCDD, whereas concentrations of PCDFs are low or below the limit of detection. The PCDD/F profile is unlike known anthropogenic profiles and the source of elevated PCDD/Fs in the Queensland coastal environment is currently unknown. This study aims to examine the balance between atmospheric PCDD/F emissions and deposition estimates, in an attempt to identify possible sources to account for the unknown PCDD/F source in Queensland.

### Materials and Method

To perform a mass balance study, an inventory of PCDD/F emissions and a deposition estimate is required. Combustion processes were considered as the most relevant PCDD/F sources in Queensland since there are no chemical production facilities that knowingly emit significant quantities of PCDD/Fs, nor is there a registration of chemical use in Australia, therefore chemical

# ENVIRONMENTAL LEVELS I

sources could not be included in this inventory. Major contributors to combustion derived PCDD/Fs include medical and biomedical/quarantine waste incineration, cement and lime kilns, non-ferrous industries, various coal combustion activities (eg. power station, and industrial use), vehicle exhausts and forest fires. Emission estimates were calculated from PCDD/F emission per tonne of product combusted, multiplied by yearly production rates. Emission estimates were calculated on both a TEq (WHO) and congener basis. For the congener based PCDD/F inventory, select 2,3,7,8 PCDD and PCDF congeners were used to assess the PCDD/F emission sources in Queensland. These congeners were chosen on the basis that they are frequently detected in emission sources.

No experimental atmospheric deposition data are available from the region of interest, thus the deposition of PCDD/Fs in Queensland was estimated from soil concentrations using a method described by Brzuzy and Hites<sup>2</sup>. The soil data used in this study have been collected in dry sclerophyll forests during a study that focused on the distribution of PCDD/Fs in Queensland, (note that some of the results have been presented elsewhere<sup>1</sup>). The soil samples (top 0-5 cm) consisted of homogenised sub-samples collected within a 10 m<sup>2</sup> area, at 19 sites in the coastal and 4 sites in the inland regions. The data used for the mass balance does not focus on sites that are in the proximity of known point sources rather, the sites chosen are suggested to be representative of the ambient environment.

PCDD/F analysis of the soil samples was performed at ERGO Forschungsgesellschaft in Germany using a standardised method<sup>3</sup>. The depositional flux (F) was calculated from  $F = (C \times (\rho \times D)) \div T$ , where C is the concentration in the soil (ng g<sup>-1</sup>dwt),  $\rho$  is the average soil density in 5 representative soil samples (1 200 000 g m<sup>-3</sup>), D is the sampling depth (0.05 m) and T is the time (y). In this study, it was assumed that the PCDD/F quantity in the top 5 cm of soil represents a 30-year deposition history, thus T was set at 30 years. A total deposition was calculated for the coastal (636 000 km<sup>2</sup>) and the inland areas (1 100 000 km<sup>2</sup>).

## Results and Discussion

### *Emission estimates*

Based on available data the total emission of PCDD/Fs (WHO-TEq) from combustion processes in Queensland is in the range of 12.5 to 350 g TEq yr<sup>-1</sup> (Table 1). Forest fire emissions exhibit the highest contribution (78 – 90%) to the total TEq, while combustion based industries and motor vehicles make up the surplus 10 – 22%, with potentially the greatest contributions from the combustion of coal and non-ferrous industries.

# ENVIRONMENTAL LEVELS I

**Table 1 – Emission estimates from combustion PCDD/F sources**

PCDD/F source	Emission (g TEq y <sup>-1</sup> )
Cement kilns	0.012 – 0.023
Lime kiln	0.014
Waste Incineration	0.13
Non-ferrous Industry*	2.3 – 16.3
Coal combustion (power generation)*	1.07 – 5.68
Coal combustion (industry)*	0.09 – 11.08
Motor Vehicles*	0.014 – 1.68
Forest fires (natural+prescribed)*	12.5 – 350
<b>TOTAL</b>	<b>16.1 – 385</b>

\*No data was available for the potential PCDD/F emission for these industries in Queensland estimates were calculated from the available literature data

Fire is a significant component of the Queensland environment due to land management practices and approximately 5 000 km<sup>2</sup> (~12.5 million tonnes of biomass) are burnt each year. In contrast, there are few industrial PCDD/F sources in Queensland and the majority are confined to the southeast corner of the state and a few small pockets along the coast. The rest of the state is mainly rural and large areas are dominated by agriculture. The specific congeners OCDD, 1,2,3,4,6,7,8 HpCDF and OCDF are the most abundant congeners in the total emission estimates from combustion sources (Table 2). Similar results have been found in a congener specific source inventory calculated for the UK<sup>4</sup>.

### *Deposition estimates*

In Queensland there is no available deposition data for PCDD/Fs thus, deposition was estimated from soil PCDD/F concentrations using the model described above. Based on the soil concentrations in the respective regions, the total deposition estimates for the Queensland coastal and the inland regions are in the range of 0.2 to 9.8 kg TEq y<sup>-1</sup> and 0.03 to 0.97 kg TEq y<sup>-1</sup> (respectively). The  $\Sigma$ PCDD/F investigated are estimated to be in the range of 510 to 28 270 kg y<sup>-1</sup> and 0.04 to 72 kg y<sup>-1</sup>, for coastal and inland regions (respectively) (Table 2). The soil data used in the model calculations suggest that deposition is strongly dominated by OCDD, and that deposition of OCDD in the coastal region is approx. 500 – 20 000 fold greater than in inland areas. Despite the limitations associated with using soil concentrations to estimate deposition, the treatment of the data in this way allows the comparison between the individual PCDD/F congeners investigated.

### *Mass balance*

The comparison of emission (from known combustion sources) and deposition data (derived from soil concentrations) indicates that emission estimates are orders of magnitudes lower than the deposition estimates for the  $\Sigma$ PCDD/Fs investigated, particularly in the coastal region. In Queensland the majority of the population and industry are distributed in the coastal region and

# ENVIRONMENTAL LEVELS I

therefore we assumed that all PCDD/Fs are emitted and deposited in the coastal area and including this assumption the imbalance remains. Interestingly, for the PCDF congeners the range of emission estimates are within the range of the deposition estimates and therefore the soil PCDF concentrations can be explained by the emission data. The imbalance in this study is solely due to discrepancies between the deposition and emission estimates for the PCDD congeners and in particular for OCDD and HpCDD. The deposition estimate for OCDD for example is 700 – 15 000 fold greater than emission estimates, assuming all PCDD/F sources are deposited in the coastal region. The data therefore suggests that unaccounted sources of PCDDs have contributed to more than 99 % or an equivalent of between 0.5 and 28 tonnes of OCDD per year in the coastal region of Queensland.

**Table 2 – PCDD/F deposition and combustion emission estimates for Queensland**

	Coastal deposition (kg y <sup>-1</sup> )		Inland deposition (kg y <sup>-1</sup> )		Total combustion emission estimates (kg y <sup>-1</sup> )	
	Min	max	min	max	Min	Max
1.2.3.7.8-PeCDD	0	2.3	0	0.208	0.01	0.02
1.2.3.7.8.9-HxCDD	0.28	8.4	0	4.4	0.03	0.05
1.2.3.4.6.7.8-HpCDD	4.2	240	0.04	2.13	0.24	0.29
OCDD	508	28 000	0	63	0.70	1.90
2.3.7.8-TCDF	0	2.4	0	0.6	0.09	0.19
1.2.3.7.8-PeCDF	0	0.52	0	0	0.09	0.24
1.2.3.7.8.9-HxCDF	0	0.8	0	0.63	0.10	0.21
1.2.3.4.6.7.8-HpCDF	0.033	2.4	0	0.57	0.67	1.00
OCDF	0.38	10.9	0	1.1	0.38	0.70
*ΣPCDD/F	510	28 270	0.04	72	2.3	4.6
Σ WHO TEq	0.207	9.8	0.029	0.97	0.016	0.38

\* ΣPCDD/F includes only the PCDD/Fs investigated in this study. Deposition was calculated from soil PCDD/F concentrations using the model described above, areas for the coastal and inland regions were 363 000 km<sup>2</sup> and 1 100 000 km<sup>2</sup> (respectively). Zero deposition arises from concentrations below the limit of detection in the soil samples.

### Missing Sources

The current PCDD/F emission estimates in this study comprises of combustion derived PCDD/Fs only and does not include chemical sources of PCDD/F, such as the contamination of agricultural and industrial chemicals. It seems unlikely that the imbalance of PCDDs can be attributed to agricultural chemicals, particularly since previous investigations in Queensland have found that PCDD concentrations are only elevated in the coastal sugarcane irrigation sediments, while very low PCDD levels were observed in irrigation drain sediments from inland cotton growing areas,<sup>5</sup> both of which are subject to intensive use of agricultural chemicals.

The results from this study suggest that of all known PCDD/F emissions from combustion sources, forest fire is potentially the most important source in Queensland. In this study forest fire emission

# ENVIRONMENTAL LEVELS I

estimates were calculated using emission data from wood stove combustion studies and similar profiles and concentrations were assumed to occur in natural fires. At this point it is not known whether the emission from the laboratory combustion studies provide good estimates for PCDD/F emission from forest fires in Queensland and it may be that emission from natural forest fires are much higher. However, PCDD/F profiles from combustion sources include a significant proportion of a range of PCDF congeners and in particular HpCDF, which are usually below the detection limit in soil and sediment samples analysed from Queensland. Despite this further investigations into the PCDD/F emission from forest fires are currently underway to clarify this issue.

The results from this mass balance investigation is concurrent with the global mass balance study which identified an imbalance of OCDD and HpCDD<sup>6</sup>. The discrepancy of OCDD and HpCDD between emission estimates and deposition estimated from soil data may be due to natural formation processes of these compounds. Elevated OCDD concentrations have been detected in sediments downstream of a National Park, characterised by wetland and swamp regions<sup>7</sup> and elevated PCDDs have been observed in geological samples including ball clay from the US<sup>8</sup> and kaolinite clay from Germany<sup>9</sup>. Due to the lack of apparent PCDD/F sources in each of these studies, natural formation mechanisms have been suggested as a possible PCDD source although at this stage the formation mechanisms remain unclear. The widespread PCDD contamination in the coastal Queensland environment may provide a unique opportunity to investigate the source and potential formation mechanisms responsible for the imbalance of higher chlorinated PCDDs observed in this and potentially other mass balance studies.

## References

1. Prange, J.A., Gaus, C., Paepke, O. and Müller, J.F. (accepted) *Chemosphere*.
2. Brzuzy, L.P. and Hites, R.A. (1995) *Environmental Science & Technology* 29, 2090.
3. Klärschlammverordnung, (AbfKlÄV), (1992) Abfallgesetz Stand 15, Germany.
4. Alcock, R.E., Sweetman, A.J. and Jones, K.C. (2001) *Chemosphere* 43, 183.
5. Müller, J.F., Duquesne, S., Ng, J., Shaw, G.R., Krishnamohan, K., Manonmanii, K., Hodge, M. and Eaglesham, G.K. (2000) *Marine Pollution Bulletin* 41, 294.
6. Brzuzy, L. and Hites, R. (1996) *Environmental Science and Technology* 30, 1797.
7. Rappe, C., Anderson, R., Bonner, M., Cooper, K., Fiedler, H., Howell, F., Kulp, W.E. and Lau, C. (1997) *Chemosphere* 34, 1297.
8. Ferrario, J.B., Byrne, C.J. and Cleverly, D.H. (2000) *Environmental Science and Technology* 34, 4524.
9. Jobst, H. and Aldag, R. (2000) *UWSF - Zeitschrift für Umweltchemie* 12, 2.