DIOXINS IN THE MARINE ENVIRONMENT

Sources, pathways and fate of polychlorinated dibenzo-p-dioxins and dibenzofurans in Queensland, Australia

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A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy by

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July 2002

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The photograph shows a dugong feeding on seagrass.]

STATEMENT

The work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text, and the material has not been submitted, either in whole or in part, for a degree at this or any other University.

Signed .....

ACKNOWLEDGEMENTS

It is often said that it is the journey that counts, not the destination. The people I met and worked with during the last three years made this journey special. They pointed the direction, helped to clear the road of obstacles or provided the necessary equipment and food for thought.

Dr. Jochen Müller and **Prof. Des Connell** gave me the map to undertake this journey and provided the right gear, advice and some great opportunities to present and discuss my work at international meetings. **Olaf Päpke** provided access to his vast knowledge and experience in the world of dioxins, and to the ERGO laboratories, where I undertook most of the analysis. **Dr. Roland Weber** played a key role in developing my ideas on formation processes during many hours of enthusiastic phone discussions. **Dr. Gregg Brunskill** enabled the work on dated sediment cores by sharing his work and knowledge. **Dr. David Haynes**, **Dr. Wendy Blanshard** and **Dr. Bruce Hill** provided most of the dugong samples, as well as many and much appreciated hours of discussions and insight into the biology and ecology of the animals. **Mary Hodge** provided access to the laboratory at Queensland Health Scientific Services, where I adopted methodology and techniques from ERGO, which allowed the analysis of many more samples than would have been otherwise possible. Financial support, provided by the **Australian Research Council**, **Ergo Forschungsgesellschaft** and the **Great Barrier Reef Marine Park Authority**, and my scholarship, granted by the **Australian Postgraduate Award (Industry)** is greatly appreciated.

The most important person in my life not only provided constant personal but also professional support. Thanks **Mark O'Donohue** for all your genuine interest in dioxins, for sharing your scientific talent, your ideas and enthusiasm for my work and valuable inputs into every single paper, presentation, grant application, hypothesis number 1 to 34-C, and this thesis. Thanks for teaching me how to get around obstacles without too much damage and for listening to any damage reports. THIS THESIS IS FOR YOU.

Without **Joelle Prange** my days would have been a lot less enjoyable. Thanks for the great discussions, for all the help from analysis to last minute proof readings, and for your happiness, bounciness and tonnes of coffee shared.

Thanks to **Roland Weber** for getting me through university organic chemistry and – more than a decade later – for another fantastic teaching job on the formation and fingerprinting of dioxins. Thanks for your continuous friendship, your support and motivation.

Thanks to **Nigel Dennison** for answering all my questions any time with incredible patience and for showing me all the tricks of a chemist. But most of all, thanks for your friendship and your support in absolutely everything that I did or planned to do.

Thanks to **Olaf Päpke** for his hospitality, open door policy during my stays at ERGO, open phone policy on all the "quick questions", and for the opportunity to learn at his laboratory.

Thanks to **Peter Ebsen** for teaching me the mysteries of HR MS and peak identifications, and for making this interesting and fun.

Thanks to the **pesticides** section of QHSS for making me feel part of your fantastic team. I'm afraid that any labs that I will come across in the future will not be comparable.

For help with the analysis or laboratory work I thank Joelle Prange, Stefan Hartkopp, Peter Ebsen, Katja Kusch, Holger Jürgenson, Mano Krishnamannii, Katie Bundred, Melinda Cook, and the QHSS Mining section. For assistance in the field I thank David Haynes, Joelle Prange, Jochen Müller and Mark O'Donohue. Thanks also to Steve Benn, the Moreton Bay Marine Parks, Donna Kwan and the Quandamooka community for providing access to stranded animals in Moreton Bay and Torres Strait, and to Queensland Parks and Wildlife Services in Maryborough for collecting the "missing data points". Thanks for last minute and late night proof reading over the last few weeks to Mark, Joelle and Jochen. Last but not least a big thankyou to my family for providing their long-distance support.

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two groups of lipophilic, persistent organic pollutants that are produced as by-products of various anthropogenic and industrial processes. Due to their relatively high toxic potencies and potential to bioaccumulate and biomagnify in organisms and through the food chain, the contemporary widespread distribution of these compounds is a concern to the health of the environment, wildlife and humans. This study determined the distribution, pathways and fate of PCDD/Fs in the coastal zone of Queensland, Australia, including the inshore marine environment of the World Heritage Great Barrier Reef Marine Park. This ecosystem supports unique fauna and flora such as the marine herbivorous mammal dugong (*Dugong dugon*) and its food source, seagrass.

Elevated PCDD/Fs were present in soils and sediments along the entire Queensland coastline. Highest concentrations were found in soil from agricultural irrigation drains and in sediments near the mouths of major rivers. Elevated concentrations were associated with rural and urban types of land-use, and PCDD/Fs were present even in locations remote from anthropogenic activities. PCDD/F congener-specific analysis revealed an unusual profile in all samples, dominated by OCDD, with PCDFs present in low concentrations or below the limit of detection. Distinct HxCDD isomer patterns were observed, with the 1,2,3,7,8,9-HxCDD/1,2,3,4,6,7-HxCDD isomer pair dominating the 2,3,7,8-substituted HxCDDs. Similar congener and isomer characteristics were reported in sediments, soil and clay samples from other continents, but could not be attributed to any known source.

Possible PCDD/F sources in Queensland were assessed using segmented estuarine sediment cores, for which radiochemical chronologies were established for each depth. Variations of PCDD/F concentrations in the sediment cores over several centuries of depositional history were relatively small. Elevated PCDD levels were still present in sediment slices from the early 17th century. PCDD/F homologue profiles in sediments deposited during the last 350 years were almost identical and correlated well to the characteristic profiles observed in surface sediments and soils from the entire Queensland coastline. These results suggested the presence of an unidentified PCDD source prior to the production of commercial organochlorine products.

To investigate the formation of the unusual PCDD/F profiles, congener and isomer specific analyses were undertaken in soils, sediments and dated sediment cores. The results demonstrated that specific transformation processes in the environment have resulted in the observed PCDD profile characteristics. Dechlorination of OCDD was proposed to result in distinct 1,4-pattern characteristics (i.e. formation of isomers chlorinated in the 1,4,6,9-positions). Consequently, the environmental samples do not reflect the signatures of the original source. An alternative hypothesis to natural formation is discussed evaluating these processes and their implications for possible source contributions. This hypothesis explores the potential for the influence of anthropogenic PCDD precursors (e.g. pentachlorophenol) during the 1940s to 1990s.

Transport of PCDD/Fs from the land-based source via impacted tributary river systems, and subsequent deposition processes are proposed to result in PCDD/F accumulation in the inshore marine ecosystem. The extent of the sediment PCDD/F contamination governs the concentrations in the extensive inshore marine seagrass meadows of Queensland. Partitioning processes in the sediment-seagrass system lead to increased toxic equivalency (TEQ) in the seagrass, compared to sediment.

The relationship between contaminated inshore sediments, seagrass and dugongs were evaluated using six dugong habitat regions along the coastline. PCDD/F body burdens in dugongs are governed by sediment (and seagrass) PCDD/F concentrations in their habitat. High seagrass (and incidental sediment) ingestion rates, selective retention of toxicologically potent congeners and relatively low PCDD/F elimination capacities in dugongs are proposed to result in elevated PCDD/F concentrations and TEQ levels in

adult animals. Transfer efficiencies of 4 and 27% of maternal TEQ levels to foetuses and calves (respectively) during gestation and lactation result in relatively high exposure potentials to offspring.

Compared to no-observed-adverse-effect-levels in other mammals, and based on the results of this study, a tolerable daily intake (TDI) of 10-24 pg TEQ kg^{-1} day^{-1} was estimated for dugongs. The results of the present study found that dugongs from some regions along the coastline of Queensland exceed this TDI by up to 20 fold, suggesting that these populations may be at risk from PCDD/F contamination in their habitat.

These results have important implications for the health of the environment, wildlife and humans and were used to develop a conceptual understanding of the sources, pathways and fate of dioxins in Queensland, Australia.

TABLE OF CONTENTS

DIOXINS IN THE MARINE ENVIRONMENT - SOURCES, PATHWAYS AND FATE OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN QUEENSLAND, AUSTRALIA

FIGURES

TABLES

ABBREVIATIONS AND DEFINITIONS

POP	Persistent organic pollutant; e.g. PCDD/Fs, PCBs, DDT, Hexachlorobenzene, Mirex, Toxaphene, Aldrin, Dieldrin, Endrin, Chlordane, Heptachlor
Dioxins	General term used here to include PCDDs and PCDFs
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
TCDD/F	Tetrachlorodibenzodioxin/furan
PnCDD/F	Pentachlorodibenzodioxin/furan
HxCDD/F	Hexachlorodibenzodioxin/furan
HpCDD/F	Heptachlorodibenzodioxin/furan
OCDD/F	Octachlorodibenzodioxin/furan
Congener	Compound member of the same chemical family; e.g. there are 75 PCDD congeners
Homologue	Group of structurally related chemicals that have the same degree of chlorination; e.g. there are 8 PCDD homologues
Isomer	Substance that belong to the same homologue class; e.g. there are 22 isomers in the homologue group TCDD
2,3,7,8-substituted PCDD/Fs	PCDD/F congeners with chlorine substituents in the 2, 3, 7, and 8 position
K_{ow}	Octanol-water partition coefficient
TEF	WHO Toxic equivalency factor, toxicity of a compound relative to that of 2,3,7,8-TCDD (Van den Berg et al. 1998)
TEQ	Toxic equivalency defined as the concentration of a compound multiplied by its toxic equivalency factor (TEF) (Van den Berg et al. 1998)
ADI	Average daily intake
TDI	Tolerable daily intake
NOAEL	No observed adverse effect level
LOAEL	Lowest observed adverse effect level