PCDD/Fs in the Great Barrier Reef Environment of Australia

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Introduction

The Great Barrier Reef stretches over more than 2000 km along Australia's relatively isolated north east coast. It is considered to be a largely pristine environment. It is an important habitat for a significant proportion of existing world stocks of the threatened dugong (*Dugong dugon*), the only living herbivorous mammal that is completely marine (1).

Polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) are ubiquitous environmental contaminants which have been detected in a variety of marine mammals from the Southern Hemisphere (2,3). However, little information on the occurrence of PCDD/Fs in tropical marine environments and no information as to whether these pollutants are present in marine herbivores is available. This paper presents a comparison of results from a recent study in which PCDD/F concentrations were determined in Great Barrier Reef marine sediment samples and dugong fat and from an earlier study in which agricultural soils from Northern Queensland were analysed for the same compounds.

Materials and Methods

Sampling

Dugong tissue samples used in this study were collected from carcasses of three dugongs which were drowned in nets and washed onto beaches between Mackay and Townsville, North Queensland, in 1996 (4). Fat tissue from the carcasses, (which were all in good condition at the time of sampling) were collected from the outermost layer of fat immediately below the dermis, just to one side of the mid-ventral line. Marine intertidal sediment samples were collected from sites that are known dugong habitats within the area where the dugong carcasses were stranded. Surface sediment samples were collected by scooping sediment

layers directly into solvent washed glass jars. The results for the soil samples presented here originate from an earlier study in which top soil samples (25 mm) were collected from a sugar cane farm in the Herbert Valley (approximately 200 km north of Townsville) (5). Soil and sediment samples were freeze dried while dugong samples were frozen and transported on dry ice to the analytical laboratory at Bayreuth, Germany.

Analysis

All samples were analysed for PCDD/Fs in Bayreuth, Germany. The analytical methods are described in detail elsewhere (6,7). Briefly, dugong fat was extracted after mixing it with anhydrous sodium sulfate and then pouring it into a glass column. All used utensils were rinsed with 35 ml of a 1:1 (v/v) mixture of n-hexane/dichloromethane which was also transferred to the glass column. A mixture of internal standards (12 $^{13}C_{12}$-labelled 2,3,7,8-substituted PCDDs and PCDFs) was applied to the top of the glass column. This was allowed to percolate into the sample, and elution with a further 35 mL of the 1:1 (v/v) mixture of n-hexane/dichloromethane completed extraction. Soil and sediment samples were soxhlet extracted for 20 h after addition of the internal standards to the extraction solvent (toluene). The extracts were concentrated to 1 ml and transferred to glass columns containing (from the bottom) NaOH/silica gel, silica gel and H_2SO_4/silica gel. The PCDD/Fs were eluted with n-hexane. All samples were further cleaned on Al_2O_3 (ICN B Super 1). Al_2O_3 was first eluted with 80 mL of n-hexane/dichloromethane 98:2 (v/v) which was discarded. The PCDDs and PCDFs were eluted from the Al_2O_3 column with n-hexane/dichloromethane 1:1 (v/v). A $^{37}Cl_4$ labelled 2,3,7,8-TCDD standard was added to estimate recovery. The extracts were transferred to vials, evaporated almost to dryness, and taken up in 30µL of toluene. The samples were analysed on a HP-5890 gas chromatograph (60 m x 0.25mm i.d. RTX 2330 (Restek) column, film thickness 0.10 µm) coupled to a VG-Autospec Ultima mass spectrometer operating in EI mode at 34 eV and a resolution of 10,000.

Results and Discussion

A range of 2,3,7,8-substituted PCDD/Fs could be quantified in soil, marine sediment and dugong samples. Only 2,3,7,8-substituted congeners were detectable in dugong fat. On a TE basis, the PCDD/F levels in the dugong samples from this study (13 - 22 pg TE g^{-1}) are similar to those determined in samples from Hectors dolphins stranded on the New Zealand coast (1), and slightly lower than present in many northern hemisphere marine mammals (3,8,9,10).

However, ΣPCDD/F in dugong ranged between 260 and 390 pg g^{-1}, which is higher than concentrations determined in most marine mammal samples collected from both the northern and southern hemispheres (6,9). Also, an unusual pattern of increasing PCDD congener concentration with increasing degree of chlorine substitution and a lack of PCDFs in these samples (Figure 1) stands out when they are compared with other marine mammal samples. Especially the levels of OCDD are very high (Table 1) (2,3,6,8,9,10).

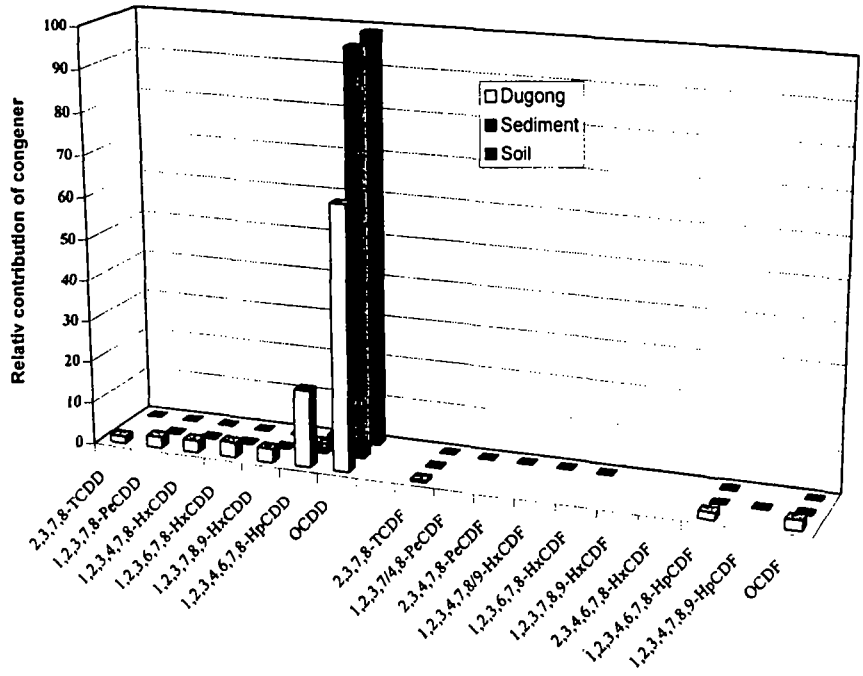

Figure 1 Congener profiles of PCDD/Fs in soil, marine sediments and dugongs of samples collected from Northern Queensland. (Soil data from (6) dugong data from (3); sediment data unpublished).

Table 1 Comparison of OCDD concentration in fat tissue (pg g^{-1} ww) from various marine mammals from the Southern and Northern Hemisphere

Species/location	Concentration range	Reference
Dugong Great Barrier Reef, Australia	170 – 250	This study
Hector's Dolphin, New Zealand	7.1 – 15.8	2
Fur Seal, Bird Island, South Georgia	3.6 – 71	3
Baikal Seal, L. Baikal, Russia	<2.3	6
Harbour Seals, North Sea, Germany	2.0 – 11	8
Cetaceans, W. Coast, North America	< 20	9
Ringed Seal, Baltic, Gulf of Finland	< 10	10

The domination of the PCDD/F congener profile by OCDD in dugong samples is similar to both marine sediment samples collected from this area, and the soil samples collected from a sugarcane farm located in a catchment draining into the Great Barrier Reef environment (Figure 1). At this point it seems reasonable to hypothesise that a common, as yet unidentified source of these higher chlorinated PCDDs is, or has existed in the region. There is a clear need for more research to clarify the nature, magnitude and current importance of this source.

Acknowledgements

The authors thank Tony Preen (James Cook University) and Locky Markwell (Queensland Department of Primary Industries) for assistance with tissue collection. Des Connell (Griffith University) and Bill Dennison (University of Queensland) are thanked for their ongoing support for this work. We also thank Sandra Zeitler, Stefan Will and Frieder Böhme for assistance with sample preparation and analysis.

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