Octachlorodibenzodioxin in sediments from coastal areas and irrigation drains of Queensland - an indication for an unknown PCDD source

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Introduction

Sediments provide important sinks for persistent lipophilic environmental chemicals. Recent research in Australia's north east has detected high concentrations of PCDDs and in particular OCDD in coastal sediments[1]. In addition, high OCDD concentrations were also found in blubber samples collected from dugongs (*Dugong dugon*) which were found stranded within Australia's Great Barrier Reef Marine Park[2].

Elevated PCDD levels were not only associated with marine sediments collected near urban areas but were also found in relatively high concentrations in marine sediments from rural regions dominated by intensive agriculture. High OCDD levels were also present in topsoils from a sugar cane farm and it has been suggested that the cultivation of sugar cane may be associated with the occurrence of PCDDs[3]. The aim of this ongoing study is to screen sediment samples from coastal and agricultural regions for OCDD. This should allow determining the extent of the PCDD pollution and assessing potential sources.

Materials and Methods

The study consists of two components. The first focuses on marine sediments along Queensland's east coast and the second examines sediments collected from irrigation drains in sugar cane and cotton growing areas of Queensland (Figure 1). Marine sediments (M1-M15 numbered from north to south) were collected along the Queensland coast. M1 represents a control site distant to major agricultural or urban centres. M2-M7, M9 and M11 are marine sediments collected adjacent to an agricultural region dominated by sugar cane cultivation. Sediment samples M8, M10 and M12 represent coastal sediments collected from river plumes which do not pass through areas used for sugar cane cultivation. M13-M15 were samples collected in Moreton Bay, which is located in the vicinity of Brisbane and surrounding south east Queenslands metropolitan area. About two thirds of Queenslands population is concentrated in this area. In addition, sediments from irrigation drains in sugar cane growing areas (S1-S6) and cotton growing areas (S7-S12) were collected.

Marine sediments were collected from the top 5 cm using a modified Van Veen sampler. At each marine sampling site two locations were chosen and three samples were collected at each location. Within irrigation drains, eight subsamples were collected from each location. All subsamples from a given site were homogenised and combined to form one composite sample. A subset of the

marine samples was analysed at the University of Bayreuth, Germany for all 2,3,7,8-PCDD/F congeners as well as PCBs and the detailed results are reported elsewhere[1]. In QHSS laboratories, samples were freeze dried, ground, sieved and the fraction consisting of particles smaller than 2.3 mm was analysed. For OCDD analysis, 10 g of sample was homogenised with 15 g Na_2SO_4, transferred into soxhlets and extracted for 10 hours using acetone/hexane (1:1). A blank consisting of Na_2SO_4 and a blank spiked with OCDD were included with each batch of about 12 samples.

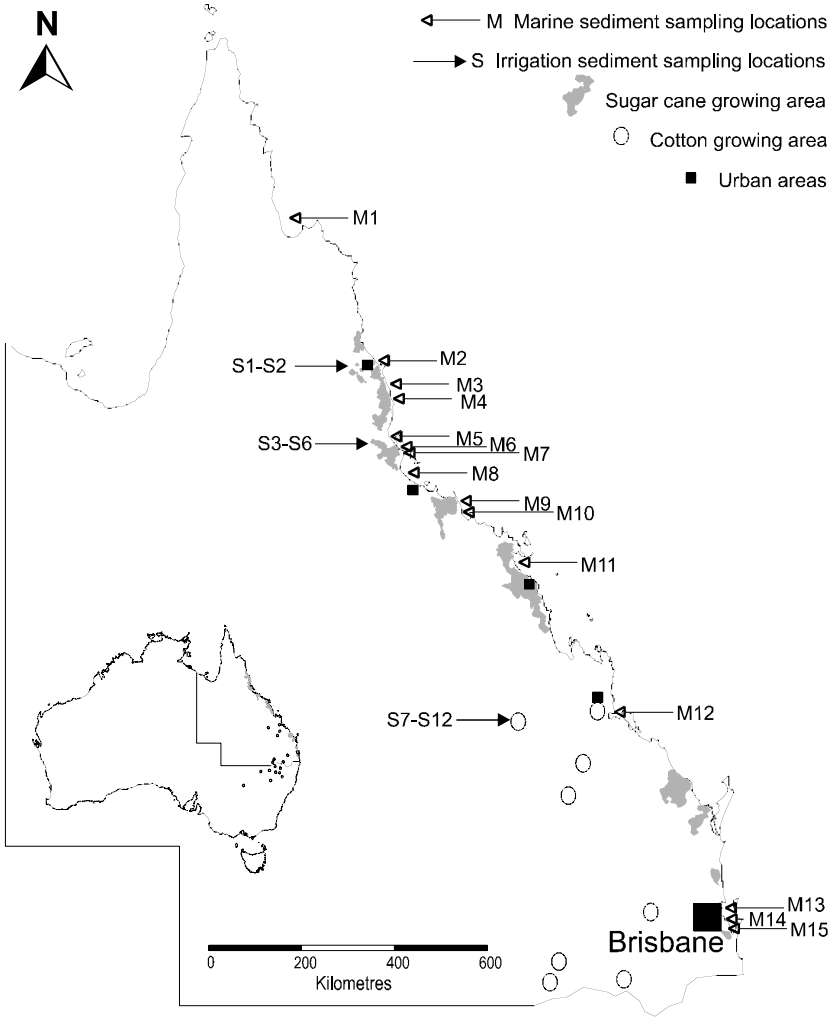

Figure 1 Map of Queensland indicating the locations of the sampling sites

The extract was concentrated and subject to a clean-up using acid/base activated silica. Separation of the PCDD/Fs from PCBs and other co-contaminants was performed on an aluminum column (Alox B-super). After the clean-up samples were concentrated almost to dryness and filled with 20 μL of toluene containing a known amount of dibutylchlorindate, the latter being used to assess

the performance of the instrument and/or volume differences in the vial. Samples were analysed on a GC (DB5) equipped with an electron capture detector. Quantification was performed using external calibration with known concentrations of a range of OCDD standards. Confirmation of peaks was carried out using GC-MS, where the MS was operated in full ion scan. For quality control the GC retention times of the analyte in a sample had to conform to the retention times of the standards. The limit of quantification for OCDD in a given sample was defined by a signal to noise ratio greater than 3 times the average baseline variation and a substance quantity in the sample greater than 3 times the quantity in the respective blank. The recoveries of OCDD ranged from 69 to 97 %.

Results and Discussion

The concentration of OCDD in marine sediments ranged from less than 50 pg g^{-1} dry weight (dw) in sediments M10 and M15 to 6,700 pg g^{-1} dw in sediment M7 (Figure 2). The four highest sediment concentrations (M2, M4, M5 and M7) were collected in northern Queensland. The OCDD concentrations in these sediments were found to exceed those in sediment M13 collected from the most industrialised area of Queensland, which is located in the south east of the state. Lowest OCDD concentrations were found in sediments M1, M8, M10, M12 and M15. These samples were collected from areas that are unlikely to be impacted by sediments originated from areas associated with sugar cane cultivation.

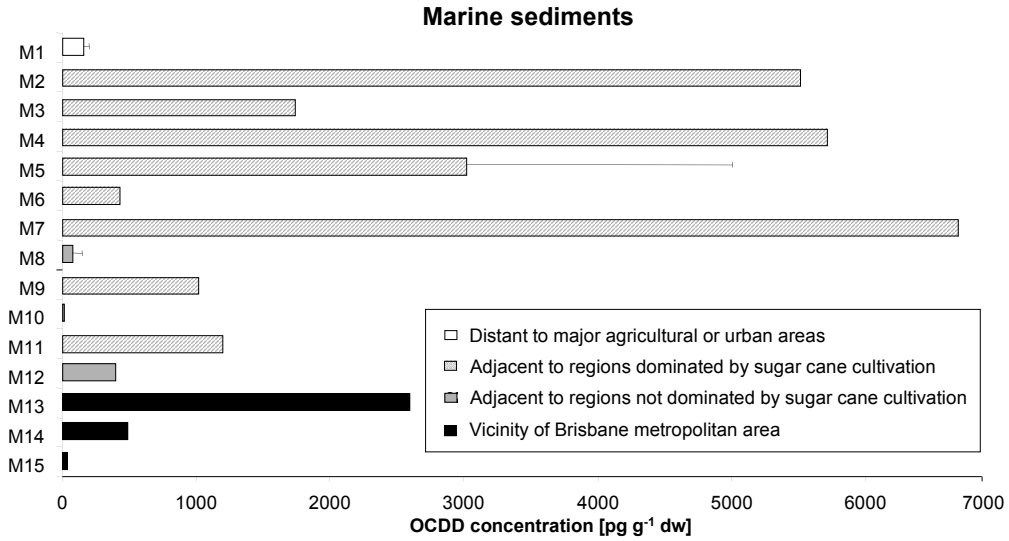

Figure 2 Concentrations of OCDD in marine sediments from the Queensland coastal areas. Sample M1, M5 and M8 were analysed in replicate and the mean and standard deviation of the analytical results are presented here.

The OCDD concentrations in the sediment samples from irrigation areas (S1-S12) ranged from less than 20 pg g^{-1} dw to about 19,000 pg g^{-1} dw. The highest concentration in sediments collected from the area dominated by cotton cultivation was 290 pg g^{-1} dw (M12). In contrast, the OCDD concentration in sediments from irrigation drains in the sugar cane growing areas were all higher

than this value (Figure 3). It is noteworthy that results from a recent study on sediments from Queensland irrigation areas demonstrated that concentrations of most traditional organochlorine compounds are significantly higher in areas used for cotton cultivation when compared with areas dominated by sugar cultivation[4].

Both, the results from the analysis of marine and irrigation drain sediments of areas dominated by the cultivation of sugar cane and cotton indicate that a source for PCDDs (i.e. OCDD) exists in Queensland's sugar cane growing area. The process that has resulted in this widespread contamination with PCDDs remains unclear at this stage.

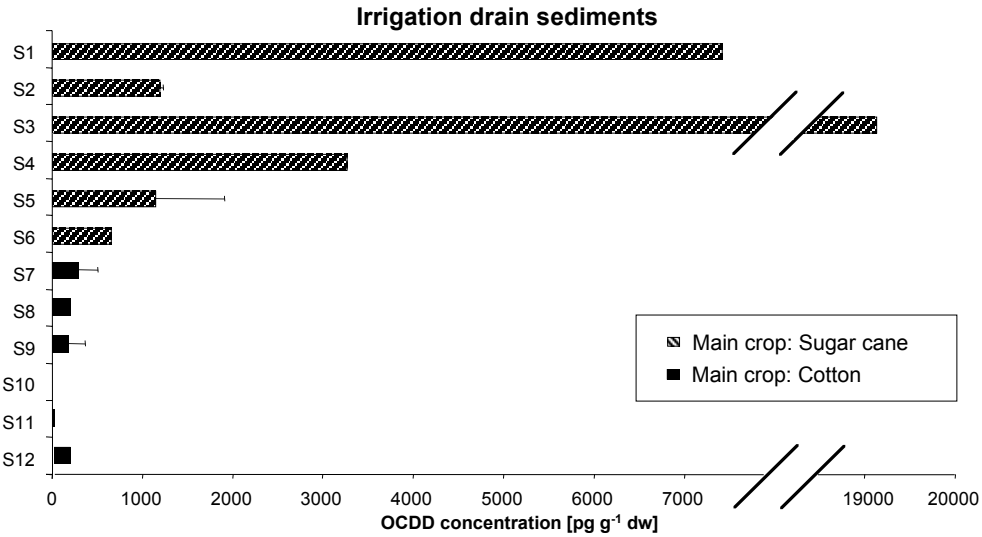

Figure 3 Concentration of OCDD in sediment samples from irrigation channels in areas dominated by either cultivation of sugar cane or cotton. For samples with error bars the results represents the mean and standard deviation of replicate analysis.

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References

1. Müller, J. F.; Haynes, D.; McLachlan, M.; Boehme, F.; Will, S.; Shaw, G. R.; Mortimer, M.; Sadler, R.; Connell, D. W. *Chemosphere*, **in print**.
2. Haynes, D.; Müller, J. F.; McLachlan, M. S. *Chemosphere* **1998**, 38, 2, 255-262.
3. Müller, J. F.; Sutton, M.; Wermuth, U. D.; Will, S.; Hawker, D. W.; McLachlan, M. S.; Connell, D. W. In: *Sugarcane: Research towards efficient and sustainable production*; Wilson, J., Campbell, J. & Garside, A. Ed.; CSIRO, Brisbane, Australia, **1996**, p 273-274.
4. Department of Natural Resources, *unpublished results* .