

PCDD/Fs IN SEDIMENTS FROM THE MAI PO MARSHES NATURE RESERVE IN HONG KONG

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Introduction

Hong Kong is one of the most densely populated cities in the world. On the other hand some areas in Hong Kong are of great natural heritage. For example the Mai Po and Inner Deep Bay wetland was listed as a Wetland of International Importance under the Ramsar Convention due to its importance for biodiversity. Besides the areas that are covered by mangroves and a section that is occupied by traditional and modified tidal shrimp ponds and fish ponds the Mai Po Marshes Nature Reserve includes a substantial area of intertidal mudflat. This mudflat, situated at the Delta of the Shenzhen River and exposed during low tide, is an important feeding ground for birds including a large population of wintering waterfowl. However recent studies have indicated that the ecosystem may be stressed as for example a decrease in the polychaete populations was observable³. While the cause for the observed decline is not clear relatively high levels of pesticides in the marine sediments around the Deep Bay area, including compounds that have been banned in Hong Kong (e.g. DDT) have been observed and were attributed largely to contamination sources in the Chinese mainland^{8,12}.

The aim of this study was to assess the levels of PCDD/Fs in sediments from the Mai Po mudflats to obtain baseline data of environmental levels in this area and assess potential sources for these chemicals in the respective environment.

Materials and Methods

Sampling sites

Core samples of surficial sediments (approximately 8 cm in depth) were removed from four sampling locations all of which were located on the mudflats (Figure 1). In addition to the surficial sediment samples at site A2 subsurface samples were collected from 9-16 cm (A2-2) 17-24 cm (A2-3), 25-32 (A2-4) and 33-40 cm (A2-5). Samples were collected in duplicates, and each sample was collected into a pre-cleaned container and stored at -10 °C for subsequent analyses.

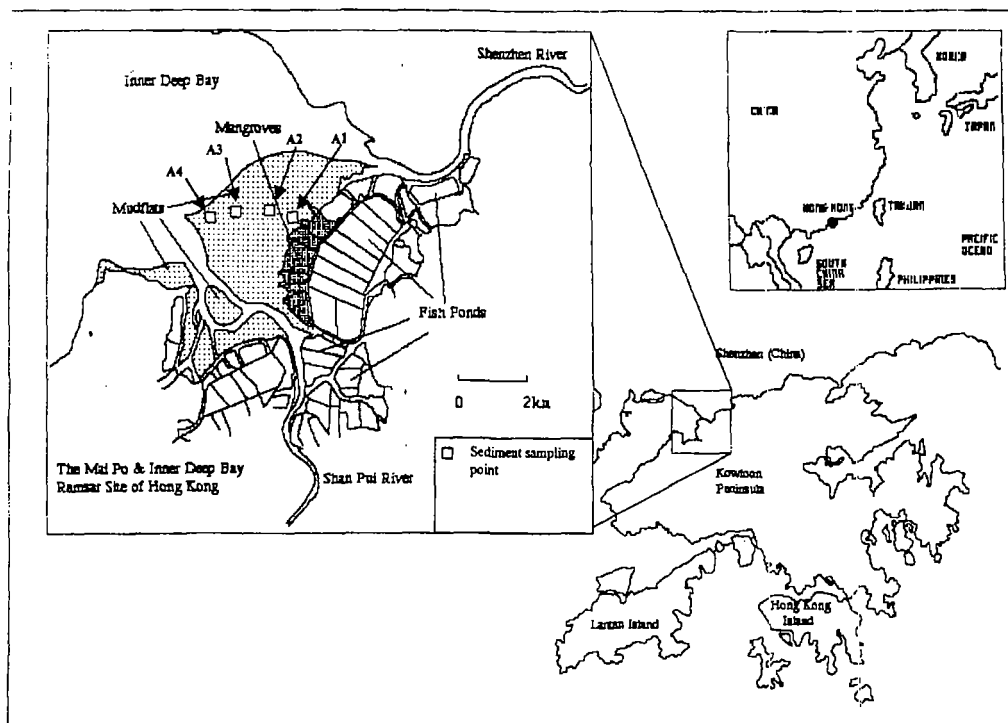


Figure 1 Map of the sampling sites in the Mai Po Marshes Nature Reserve.

Analytical methods

Samples were analysed for full profile of all 2,3,7,8-substituted PCDD/Fs in a collaboration between the NRCET/QHSS and Ergo laboratories. In brief, the freeze-dried, homogenised sample were Soxhlet extracted for 20 hours using toluene. A blank was included in each batch of 7 samples. Prior to extraction samples were spiked with a ^{13}C -labelled PCDD/F standard of known quantity. The extracts were concentrated to dryness and subject to clean up using acid-base ($\text{H}_2\text{SO}_4/\text{CsSiO}$) and alumina (Alox B-super, ICN) columns in series. Samples were further subject to purification on activated carbon and an acid-base ($\text{H}_2\text{SO}_4/\text{CsSiO}$) cleanup, if required. Samples were concentrated to near dryness and transferred into vials with a known quantity of 1,2,3,4-TCDD, used as recovery standard. Analysis of tetra to octa-CDD/Fs was performed on a GC (DB-5 fused silica column, 60 m, 0.25 mm i.d., 0.1 μm film thickness) interfaced to a VG Autospec mass spectrometer operating on a resolution of approximately 10 000. Identification of 2,3,7,8-substituted PCDD/Fs was performed using retention times of the ^{13}C -labelled standard and isotope ratios M^+ and $\text{M}+2^+$. Several criteria had to be fulfilled for quality control: a) the retention times (RT) of the analyte in a sample had to be within 2 s of the RT of the internal standards b) isotope ratios for each congener of the M^+ and $\text{M}+2^+$ ions had to be within 20% of the respective individual value c) PCDD/F limit of quantification 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.

Results and Discussion

The mean normalized difference of detectable 2,3,7,8-PCDD/Fs and the calculated I-TEqs in replicate samples was 28 % and 14 % respectively. Considering that this includes sampling and relatively low concentrations of many of the PCDFs and 2,3,7,8-TCDD the reproducibility is relatively good.

In all samples analysed PCDD/Fs were detectable. If the concentrations are expressed on a toxicity equivalency basis, the concentrations range from 11 to 16 pg I-TE g⁻¹ dwt (Fig 2a). The sum of the 2,3,7,8-PCDD/Fs range between 5000 and 6900 pg g⁻¹ dwt. No significant differences in the concentrations in surficial sediments from the four different sampling location A1 – A4 in the Mai Po mudflat were observable. Furthermore no significant differences (and thus no trends) in the PCDD/F concentration with sediment depth at sampling Site A2 was found (i.e. mean concentrations were very similar in A2-1 – A2-5).

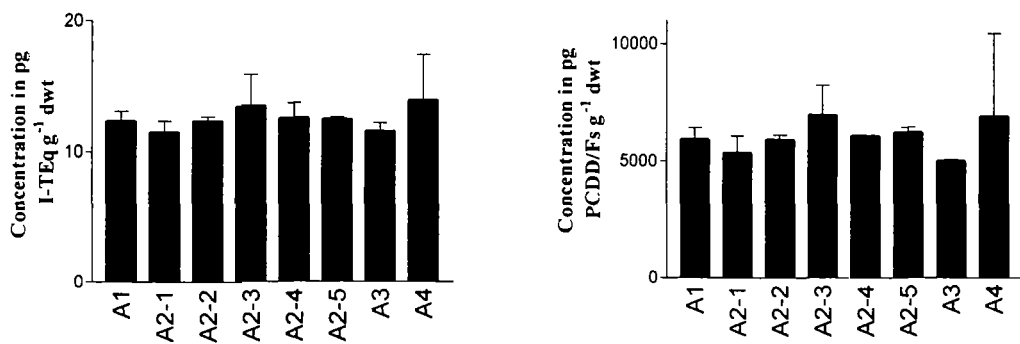


Figure 2: Mean and standard deviation (n=2) of PCDD/F concentration in sediments from the Mai Po Marshes expressed as international toxicity equivalencies (left graph) and as the sum of the 2,3,7,8-chlorine substituted PCDD/Fs (right graph)

A comparison of the results shows that the concentrations of PCDD/Fs in sediment samples from the Mai Po mudflat are relatively high considering that the mudflat is a nature reserve. For example the Σ PCDD/F concentrations in the samples from the Mai Po mudflat are orders of magnitude higher than those observed in sediment samples analysed from the Bass Strait (southern Australia)² and the Barent Sea⁴. They are also substantially higher than those observed in samples collected from the North Sea⁴, the Baltic¹¹, Japan⁵ and Casco Bay, USA⁹.

The homologue and congener profiles in the samples are dominated by the higher chlorinated PCDDs, with OCDD contributing on average 95.5 % of the total of the 2,3,7,8-Cl substituted PCDD/Fs. All samples have a peculiar HxCDD profiles where the 1,2,3,7,8,9-HxCDD/1,2,3,4,6,7-HxCDD pair was found to dominate among the 2,3,7,8-substituted HxCDDs.

In a recent study on PCDD/Fs in soil and bark samples, Wagrowski and Hites included three soil samples from the New Territories of Hong Kong and observed unusual high levels of OCDD and referred to "OCDD anomalies"¹⁰. Furthermore elevated levels of particular the higher chlorinated PCDDs have also been found in marine sediment samples covering the entire coast line of Queensland¹ plus soil samples from the coastal plains⁶ and samples from the Southern Mississippi in both river and lake sediments⁷.

In summary PCDD/Fs occur in relatively high concentrations in the Hong Kong marine environment. The data from this study indicate that a source of particularly higher chlorinated PCDDs exist that has lead to this contamination. Similarities in the profiles of the PCDD homologue profiles with those observed in samples from Queensland's coast indicate a similar source which is yet unidentified.

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