

## **Distribution of Organochlorine Pesticides in a Sediment Profile of the Pearl River Estuary**

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Due to the extensive use in agriculture and industry in the past, organic environmental contaminants such as HCHs (hexachlorocyclohexanes), DDTs (dichloro-diphenyl-trichloroethanes) and other organochlorine pesticides are distributed globally by transport through air and water (Jones and de Voogt 1999). Marine sediment, particularly the sediment in an estuary, is one of the major sinks for these contaminants in the environment (Strandberg et al. 1998; Hong et al. 1999; Khim et al. 1999). These compounds are ubiquitous and persistent in various environmental media and biota. Their long term impacts on the estuarine ecosystem remain a cause of concern.

HCH and DDT were widely used from 1950 – 1983 in China. The production of HCH and DDT in this country accounted for 33% and 20% of the total world production, respectively (Hua and Shan 1996). Therefore, the application and distribution of the organochlorine pesticides (OPs) in environment have been at a great scale in China (Hong et al. 1995; Hua and Shan 1996, Zhang et al. 1999).

The Pearl River estuary is located in southern China, covering an area of about 8,000 km<sup>2</sup> (see Fig. 1). Recent environmental monitoring results showed that there was a trend towards water and sediment quality deterioration in the Pearl River estuary (Wen and He 1985; Wong et al. 1995). The heavy metal concentrations in the sediments of the Pearl River Estuary had increased over the last 20 years (Li et al. 2000). In a previous study, the elevated concentrations of organochlorine pesticides in surface sediments were recorded in some major river mouths and the Shenzhen Bay (Hong et al. 1999).

The study of sediment cores can provide historical records of various influences on the aquatic system by indicating both the natural background levels and the man-induced accumulation of elements and compounds over extended period of time (Latimer and Quinn 1996; Van Metre et al. 1997; Li et al. 2000). In the present study, organochlorine pesticides (e.g. HCHs, DDTs and other organochlorine pesticides) was analysed in a sediment profile of the Pearl River estuary to study the distribution and accumulation history of these contaminants.

## MATERIALS AND METHODS

The Pearl River is the largest river system flowing into the South China Sea. The main Pearl River estuary (also called Lingdingyang) is a north-south bell-shape area, with a N-S distance averaging about 49 km and the E-W width varying from 4 - 58 km (see Fig.1). The whole study area is within the sub-tidal zone with strong fresh water and marine water inter-reactions and circulation currents along the west coast (Zheng 1992; Wong et al. 1995). The rapid industrial development and urbanisation in the Pearl River Delta region in the last two decades has put great pressure in the estuarine environment. The main sources of heavy metal and organic contaminants in the river system have been reported to be industrial waste water discharge, domestic sewage effluent, atmospheric input, marine traffic and runoff from upstream mining sites and agricultural land (Wen and He 1985; Zheng 1992).

In the present study, sediment cores were collected in the Pearl River estuary in 1997 (see Fig. 1). Core samples were taken with a gravity corer with automatic clutch and reverse catcher. Sediment cores collected at each sampling station were stored at 4 - 6 °C immediately after collection until the laboratory analysis. About 15 samples (at 10 cm intervals between 0 - 1 m and at 20 cm intervals between 1 - 2 m) were taken from each core for further physical and chemical analysis. The details of the sampling locations and physical and chemical analysis were described by Li et al. (2000). The sediment samples at the sampling site D in the west side of the Pearl River estuary were analysed for organochlorine pesticides to study the distribution and historical accumulation of these contaminants in sediments.

The  $^{210}\text{Pb}$  analysis was carried out to study the deposition time of sediments in the profile. About 2 g of dried sediment was digested in a mixture of nitric and hydrofluoric acids in Teflon vessels, and then dissolved in 0.5M hydrochloric acid.  $^{210}\text{Po}$  and  $^{208}\text{Po}$  (added as a tracer) in the solutions were then electro-deposited onto nickel discs. The discs were then placed in an alpha-particle spectrometer and the activity of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  (which is equal to the  $^{210}\text{Po}$  activity in sediments) was determined using surface barrier detectors (Smith and Walton 1980). A constant flux/sedimentation rate (CFS) was used to calculate the average sedimentation rate.

Prior to extraction, sediment samples were freeze-dried and sieved with a 0.18 mm mesh. Each sample (~15 g) was placed in a Soxhlet thimble and spiked with organochlorine pesticide surrogate standard (4,4'-dichlorobiphenyl). About 2 g of activated copper granules was added to the flask to collect the extract. The sample was extracted three times (24 h each extraction) with 200 mL of methylene chloride at 50 °C. The thimble was cooled with circulating water maintained at 10°C. The combined extract was concentrated to 2-3 mL using a rotary evaporator at 30 °C and about 10 mL of hexane was added to the extract. The extract volume was continuously reduced to 2-3 mL (solvent exchanged to hexane). The hexane extract was further concentrated to 1 mL under a gentle  $\text{N}_2$  stream and subjected to an alumina/silica (1:2) gel glass column for clean-up and fractionation. The first

fraction containing aliphatic hydrocarbons was eluted with 15 mL of hexane. The second fraction containing OPs was eluted with 5 mL of hexane and 70 mL of methylene chloride/hexane (30:70). The extract containing OPs was concentrated to 0.4 mL under a gentle N<sub>2</sub> stream. An appropriate amount of internal standards (2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl) was added to the final extract prior to instrumental analysis.

Organochlorine pesticides were measured using an Hewlett-Packard (HP) 5890 series II gas chromatograph (GC) equipped with an electron capture detector (ECD) and an HP-5 silica fused capillary column (50 m × 0.32 mm i.d. with 0.17 μm film thickness). Splitless injection of 1 μL of sample was conducted manually

with 1 min solvent split time. The carrier gas was ultra high purity N<sub>2</sub> with a flow rate of 2.5 mL/min and linear velocity of 35 cm/s at 250 °C. The column temperature was initiated at 100 °C and ramped with a rate of 4 °C/min to 290 °C and was held for 10 min. A DDT degradation check solution was analyzed daily to examine the extent of degradation of DDT, which had to be less than 15% before sample analysis could be initiated. Data acquisition and processing were conducted using a HP ChemStation data system. Quantitation was performed using the internal calibration method based on 5-point calibration curve for individual components. 2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl were used as internal standards for organochlorine pesticides analysis. Identification of the OPs was confirmed using the GC/MSD system on SIM model with GC conditions identical to those used for GC/ECD analysis. Detection limits were 0.2-0.5 ng/g (dry weight) for OPs based on 1 g of sample.

Hexane, methylene chloride, acetone, and methanol in the sample analysis processes were of analytical grade and bi-distilled using a glass distillation system before use. Neutral silica gel (80-100 mesh) and alumina (100-200 mesh) were extracted with a mixture of 1:1 methylene chloride and methanol for 36 h using a Soxhlet extractor. Upon drying under room temperature, silica gel and alumina were baked at 180 °C and 250 °C for 12 h, respectively. Commercially acquired anhydrous sodium sulfate were baked at 420 °C and stored in sealed containers. Certified concentration of organochlorine pesticides (OPs) standard mixture (17 compounds, US-1128), surrogate standard and internal standards were purchased from the Ultra Scientific, Inc. (North Kingstown, RI, USA). Each instrument was calibrated daily with calibration standards and the relative percent difference between the five-point calibration and daily calibration was less than 20% for all target analytes. Method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spikes/matrix spike duplicates, sample duplicates, and a National Institute of Standards and Technology standard reference material (SRM 1941, NIST, Gaithersburg, MD, USA) were analyzed routinely with field samples. In addition, surrogate standard were added to all the samples (including QA samples) to monitor matrix effects. The recovery of surrogate standard (decachlorobiphenyl) ranged from 93.7-114% (n=15). Measured concentrations of target analytes in the NIST SRM 1941 were within 80-120% of the certified values.

## RESULTS AND DISCUSSION

Concentrations of HCHs, DDTs and other organochlorine pesticides in the sediment profile at Site D of the Pearl River Estuary are presented in Table 1. The sedimentation rate of Site D was calculated to be 1.52 cm/a based on the <sup>210</sup>Pb analysis (Wang et al. 2001). The approximate deposition time of the sediment layers in the profiles is listed in Table 1. The distribution of HCHs, DDTs and other OPs in the sediment profile is shown in Fig. 2.

The concentrations of HCHs (sum  $\alpha$ -,  $\beta$ -,  $\delta$ -, and  $\gamma$ -isomers) ranged from 0.43 – 5.56 ng/g (see Table 1). The HCHs detected in the sediment cores were mainly  $\delta$ -HCH (>60% of HCHs), followed by  $\alpha$ - and  $\beta$ -HCHs. The concentrations were

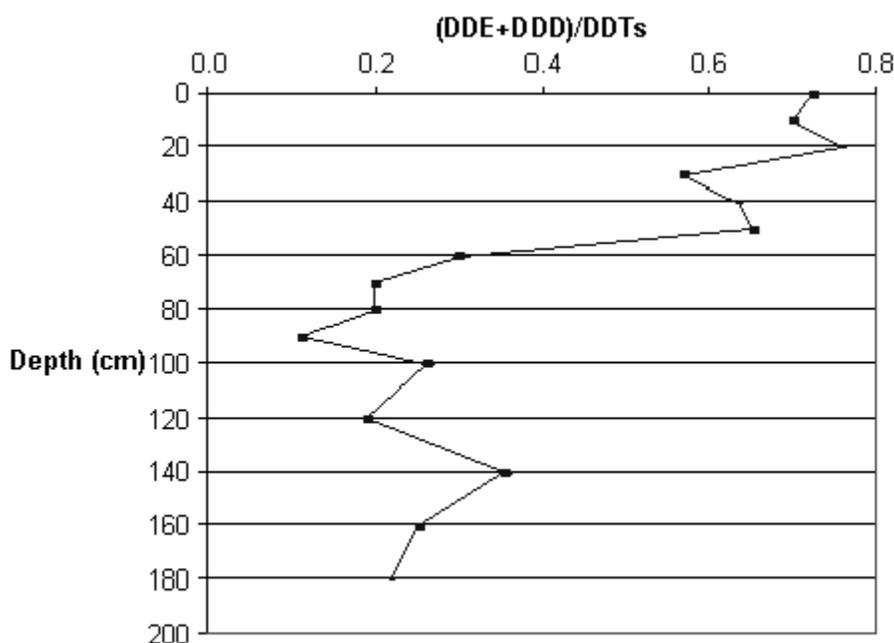
generally higher than the mean level (0.68 ng/g) of surface sediments of the Pearl River Estuary reported in a previous study (Hong et al. 1999). The top sediments (0 - 21 cm layer) had higher concentration of HCHs, with the maximum level of 5.56 ng/g at 20-21 cm layer, corresponding to the deposition time around 1984 estimated from the  $^{210}\text{Pb}$  dating results (see Table 1). The ban on the production and use of HCHs and DDTs in China commenced in 1983 (Hua and Shan 1996). The concentration of HCHs in the sediment profile reached its peak immediately after the ban in 1983. The more recent sediments showed a declined concentration of HCHs. The concentration of HCHs in deeper sediment layers was generally lower than 2 ng/g. It is also interesting to note that the relatively higher concentration of HCHs in the bottom layers of the sediment core (see Fig. 2). It may indicate possible migration of HCHs in sediment profiles. The water solubility of HCHs is usually higher than DDTs and other OPs, especially  $\delta$ -HCH (Verschueren 1983; Chu and Chan 2000)

The total DDTs in sediments ranged from 1.56 – 26.5 ng/g in the sediment profile (Table 1). The concentrations were usually higher than the mean value (2.84 ng/g) in surface sediments of the Pearl River Estuary (Hong et al. 1999), particularly in the top layers of the profile (see Fig. 2). This result was in agreement with the observation of high concentrations of heavy metal contaminants in sediments in the west side of the estuary due to hydraulic conditions and direct inputs from western tributaries (Li et al. 2000). The DDTs identified in the core were p,p'-DDT, o,p'-DDT and their derivatives, DDE and DDD. The concentration of DDTs in sediments declined from surface sediments to the depth of 30 cm, corresponding to the year of 1977, and further declined to the depth of 60 cm at around 1957. The "ISQV-low" (interim sediment quality value below which adverse biological effects are unlikely) proposed for Hong Kong marine sediments are 2.2 and 1.58 ng/g for p,p' DDE and DDT, respectively (Chapman et al. 1999). Compared with these values, most of the sediment layers had higher DDT concentration than the ISQV-low and the p,p' DDE levels in the top three layers of the sediment core were also elevated. Some low concentrations of DDTs were detected in the deeper layers (>80 cm) of the core, particularly p,p' DDT, which may indicate possible leaching or migration of these compounds along the profile.

The composition of organochlorines and its metabolites can provide a tool for better understanding of the origin and transport pathways of these contaminants in the environment. DDT is degraded under aerobic conditions by microorganisms to DDE and under anaerobic conditions to DDD. The DDTs residue in soil can be mobilized by land transformation and transported by surface run-off to the river bed sediment (Hitch and Day 1992). The (DDE+DDD)/DDTs ratios can be used to evaluate if the DDT emission occurred recently or in the past. Lower (DDE+DDD)/DDTs ratios indicate direct input of DDT and higher ratios reflect past usage. As shown in Fig. 3, (DDE+DDD)/DDTs ratios were between 0.58 – 0.77 in top sediment layers (< 50 cm) of the profile. The result shows that the degraded derivatives (DDE + DDD) formed significant proportion of the total DDTs, indicating more inputs of DDE and DDD to sediment from the weathered DDT in soils in the last 30 years. There was also an increasing trend of the

DDE/DDD ratios in recent sediment, which might reflect the aerobic conditions of the weathering process of DDTs in soils and sediment in recent years.

The other organochlorine pesticides analysed in this study (e.g. 11 different compounds) are listed in Table 1. The major species in the sediments included endosulfan sulphate, kepone and heptachlorepoide. Most of these pesticides were concentrated in the top sediments (< 60 cm ) (see Fig. 2). There is a declined trend of these pesticides along the sediment profile. The two peaks of concentrations occurred in 10 and 40 cm of the core, corresponding to the deposition time 1990 and 1970, respectively. The compounds with higher solubility (e.g. kepone) were also present in the deeper layers of the sediment core, which confirmed the observation of possible migration and leaching of HCHs and DDTs from the upper layers.



**Figure 3.** The (DDE+DDD)/DDTs in the sediment profile

Organochlorine pesticides were analysed in samples of a sediment core of the Pearl River Estuary. The results showed that the sediments, particularly the top sediments had higher concentrations of HCHs, DDTs and other organochlorine pesticides. The maximum concentrations recorded in the profile were 5.56 ng/g for HCHs, 26.5 ng/g for DDTs and 45.8 ng/g for endosulfan sulfate. The vertical variations of (DDD + DDE)/DDT ratios indicated that DDTs in recent sediments had more on-land weathering process. The elevated concentrations of HCHs, DDTs and other organochlorine pesticides in recent sediments indicated that these contaminants had long residual time in soils after the ban of production and usage in 1983. The presence of the organochlorine pesticides, particularly HCHs in deeper sediment layers may indicate possible migration of these contaminants along the profile after deposition.

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