

## LEVELS AND DISTRIBUTION OF HEXACHLOROCYCLOHEXANE (HCH) AND DDT IN SEDIMENTS FROM EAST CHINA SEA

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### Introduction

Organochlorine pesticides (OCPs), typically HCH and DDT are known for their environmental persistence and toxicity effect. Monitoring work would provide knowledge for the distribution and temporal trends of OCPs<sup>1</sup>. In aquatic environment, OCPs have high affinity for particulate matters, thus sediments can serve as reservoirs or “sinks” for the pollutants. The present work is to investigate the contamination status and spatial distribution of the selected OCPs (OCPs= p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD,  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HCH) in sediments from a special area of East China Sea, where the inpouring of two large rivers (Changjiang River and Qiantang River) into the East China Sea formed two large estuaries, Changjiang Estuary and Hangzhou Bay. Along the coast of the East China Sea, there are some developed cities including Shanghai and Ningbo et al. Furthermore, a large fishery, Zhoushan Archipelago, is near to Hangzhou Bay. The newly data is indispensable for the risk assessment of OCPs in these sites.

### Materials and method

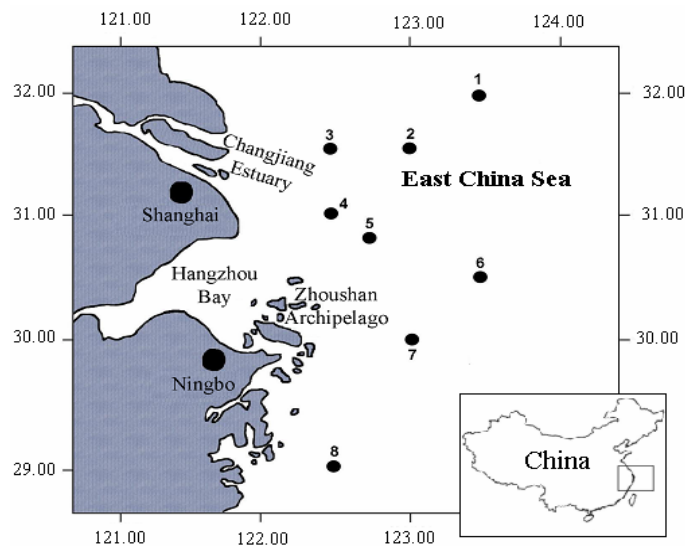
#### *Sampling*

Sediment samples were collected in November, 2002, from eight sites from East China sea (Fig.1). The sediments were immediately sectioned into subsamples using stainless plates with different depth. Approximately 2 cm deepness sediments were taken at each layer. The samples were sealed in PTFE bags and frozen immediately and transferred to the laboratory. Details of sampling locations, numbers and selected properties are listed in table 1.

#### *Chemical Analyses*

The analyses procedure was the modification of the method described by Lee, et al.<sup>2</sup>, briefly, 10-g of freeze-dried samples were extracted with the mixture of hexane and acetone (1:1 V/V) by sonicate wave method. Activated Cu was used to remove sulfur. The extracts were purified with concentrated sulfate and further separated by Silica-Florisil column, the effluents was exchanged with hexane and final volume was adjusted to 0.5 mL for GC analyses.

The concentrations of OCPs in the extracts were monitored with a HP-6890A GC- $\mu$ ECD (Agilent, USA). A HP-1 fused-silica column (30m length  $\times$ 0.25mm inner diameter) with 100% dimethylsiloxane (film thickness 0.25 $\mu$ m) was used. GC peaks were identified with the accurate assignment of retention times of each standard ( $\pm$ 1%) and further confirmed by GC-MS (Agilent 6890N). The concentrations of OCPs were quantitatively determined by the calibration curves of the standards using peak areas. The correlation coefficients ( $r^2$ ) of calibration curves of OCPs were all greater than 0.998. The limits of detection (LODs) of OCPs ranged from 0.02ng/g for  $\alpha$ -HCH to



**Figure 1.** Sampling locations of the sediments from East China Sea.

0.23ng/g for p, p'-DDT. The recoveries of OCPs with spiked samples were in the range of 88-103% and the RSD (n=5) values ranged from 4 to 9, which confirmed the feasibility of the analytical protocols herein in the determination of OCPs residues in the sediments.

## Results and discussion

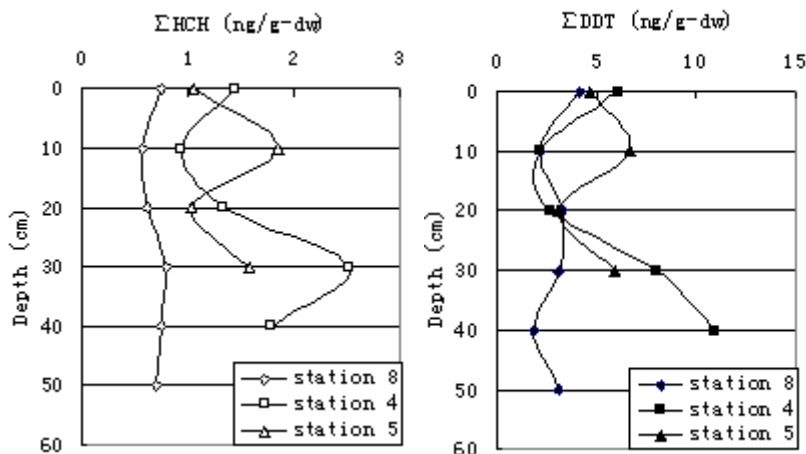
### *Levels and distribution of HCH and DDT in the sediments*

The identified sediments include 8 surface samples and 16 vertical samples with different depth. For surface sediments, the levels of HCH and DDT were in the range of <0.05 to 1.45ng/g (mean 0.76ng/g), <0.06 to 6.08ng/g (mean 3.05ng/g), respectively (shown in Table 1). The highest concentration of HCH and DDT were both found in station 4. There were no isomers detected in station 2, where the sediments were silt type and had lower organic matter.  $\Sigma$ DDT concentration in the surface sediments correlated with TOC content ( $r^2=0.71$ ,  $p<0.05$ ). However, distribution of  $\Sigma$  HCH didn't show any correlation with TOC contents possibly due to less lipophilic and more volatile nature of HCHs relative to the DDTs.

For the vertical concentration distribution, the levels of the sediments from three typical sediments cores were depicted in Figure 2. Station 4 and 5 were close to Changjiang Estuary and Hangzhou Bay, sample 4 collected from lower water (water depth: 16.5m), while sample 5 collected from deeper situation (water depth: 65.8m), sample 8 was collected at a farther distance site away from Changjiang estuary and Hangzhou bay. Figure 2 shows that in station 4 cores, concentrations of OCPs vary significantly with different sediments depth especially for DDT. The maximum of HCH (2.52ng/g) and DDT (10.94ng/g) were both found in station 4 cores at 30cm and 40cm depth,

**Table1.** The total isomers of HCHs and DDTs in the surface sediments (ng/g dw)

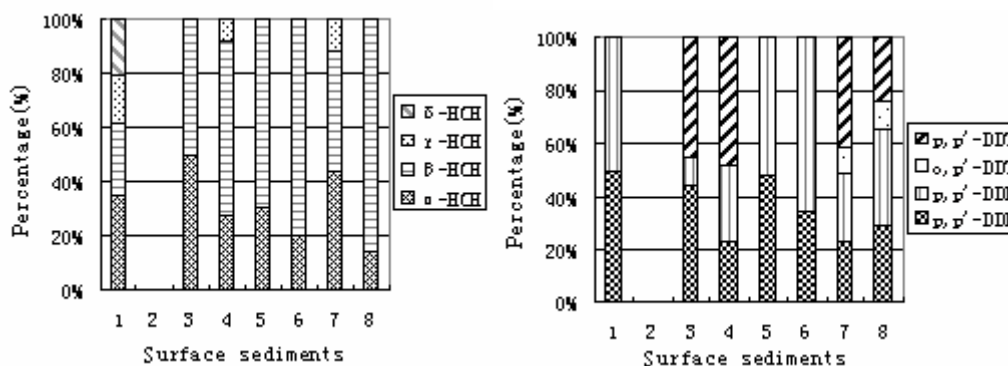
Sample code	Positions	Water depth(m)	TOC (mg/g)	Water content (%)	T-HCH	T-DDT
1	31°59.893'N 123°30.195'E	39.8	3.03	18	0.73	1.48
2	31°30.092'N 123°00.272'E	36.5	1.42	20	<0.05	<0.06
3	31°30.061'N 122°30.679'E	28.5	3.76	22	0.2	2.76
4	31°00.460'N 122°29.870'E	16.5	6.98	48	1.45	6.04
5	30°41.866'N 122°43.798'E	65.8	9.26	52	1.06	4.26
6	30°30.603'N 123°29.623'E	58.3	2.39	21	1.0	0.80
7	30°00.220'N 123°00.507'E	51	6.55	32	0.86	4.82
8	29°00.098'N 122°30.665'E	50.1	9.24	55	0.75	4.16

**Figure 2.** Vertical profiles of  $\Sigma$ HCH and  $\Sigma$ DDT in the sediments cores from East China Sea.

respectively. These sediments originate primarily from erosion of the land, municipal sewage from Changjiang River and Qiantangjiang River, which may be an important reason for the detected residues of OCPs in the sediments.

#### *Compositions of HCHs and DDTs*

The percentages of different isomers in surface sediments are shown in figure 3. In China, the commercial HCHs were produced mainly as a technical mixture containing  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -isomers of 55-80%, 5-14%, 8-15%, and 2-16%, respectively. Here isomers of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HCH were observed to contribute about 29.0%, 62.7%, 5.7% and 2.5%, respectively. These results can be explained by the lower vapor pressure and less degradable property of  $\beta$ -HCH compared to other HCHs. After long time aging,  $\alpha$ - and  $\gamma$ - HCH could be transformed into  $\beta$ - HCH<sup>3</sup>.



**Figure 3.** Compositions of HCHs and DDTs in the surface sediments from East China Sea.

DDT can be biodegraded to DDE under aerobic condition and to DDD under anaerobic condition, the relative concentration of the parent DDT compound and its biological metabolites, DDD and DDE, can be used as indicative indices for assessing the possible pollution sources. DDT compositions in this study varied between stations (Figure 3). The percentage of  $p, p'$ -DDT ranged from 0 to 48.1% with a mean 20.0%. The ratio of  $(DDE+DDD)/\sum DDT > 0.5$  can be thought to be subjected to a long-term weathering<sup>4</sup>. Here the mean ratio of  $(DDE+DDD)/\sum DDT$  in the surface sediments was 0.67, which indicated that the degradation occurred significantly after the official ban of HCH and DDT since 1983. However, a point pollution source could not be excluded, the proportion of  $p, p'$ -DDT was higher in station 4, 7, 8 (in Figure 3), which indicates a possible recent use of DDT at some sites.

#### Acknowledgements

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#### References

1. Wu, Y., Zhang, J., Zhou, Q. (1999). Environmental Pollution. 105, 143-150.
2. Lee, K.T., Tanabe, S. Koh, C.H. (2001). Environmental Pollution. 114, 207-213.
3. Willett, K.L., Ulrich, E.M., Hites, R.A. (1998). Environ. Sci. Technol. 32, 2197-2207.
4. Hong, H., Chen, W., Wang, X., Zhang, L. (1999). Marine Pollution Bulletin. 39, 376-382