LEVELS AND MASS INVENTORY OF DDTS IN SEDIMENTS FROM FISHING HARBORS:THE IMPORTANCE OF DDT-CONTAINING ANTIFOULING PAINT TO THE COASTAL ENVIRONMENT OF CHINA

Lin T[1], Zhang G[1,2], Li J[1], Liu X[1], Xu W H[3], Li X D[4]

[1]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China; [2]Yantai Institute of Coastal Zone for Sustainable Development, Chinese Academy of Sciences, Yantai, 264003, China; [3]South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou, 510250, China; [4]Department of Civil and Structural Engineering, Hong Kong Polytechnic University, Hong Kong, China

Abstract

Sixty sediment samples were collected from the nine fishing harbors in Southeast China and were analyzed for DDTs and HCHs. The DDT concentrations ranged from 9 to 7350 ng/g dry weight, which were generally one to two orders of magnitude higher than those from adjacent estuarine/marine systems. Higher DDT concentrations compared with lower HCH concentrations (<0.10-12 ng/g) and TOC contents (0.12%-2.6%) clearly denotes a significant input of DDTs within the fishing harbors. The most possible fresh DDT source in the fishing harbors is the release of DDT from fishing ships with DDT-containing antifouling paint. The sediment (0-10 cm) mass inventories were estimated 1.0-5.7 metic tons for DDTs in fishing harbors in the Pearl River Delta, which was several times higher than the DDT accumulation in the surface sediment of the Pearl River estuary. It may be a potential source to ajacent coastal water environment.

Introduction

DDT remains an important persistent organic pollutant (POP) in the environment of China[1,2]. Although banned by China from agricultural uses in 1983, high levels of DDT were still found in the environment. The long-term Mussel Watch Programme in Asia found that DDT residue concentrations in mussel samples from China presented the highest level in Asia[3]. A recent monitoring campaign of POPs in the atmosphere across Asia, using passive sampling techniques, also reported that the DDT concentrations in the atmosphere over the eastern coastal zone of China, in particular in the Pearl River Delta (PRD) of South China, were of the highest in East Asia[4]. DDT residue levels in the human breast milk from coastal China, especially in Hong Kong and Guangzhou, were also higher than those in other countries in the region[5].

China is still allowed to be used DDT for hygiene purpose, such as malaria control, upon the 5-year exemption of the Stockholm Convention. Currently, DDT released from dicofol serves as a continuing source of DDT in China. Qiu et al[6] revealed that dicofol contains high DDT residue at an average percentage of 20% in the Chinese formula and estimated that about 8,770 MT of DDT is released through dicofol usage from 1988 to 2002 in China. However, this seems not adequate to explain why such high DDT concentrations mostly occurred in the atmosphere of the coastal regions, given DDT for hygiene purpose and dicofol are used both in inland and coastal regions of the country

Recently, high DDT levels were found in the atmosphere of the Pearl River Delta (PRD), concurring the fishing suspension season (June-August) in the northern South China Sea, and, for the first time, the seasonal use of DDT-containing antifouling paint was identified to be an important source of DDTs in the coastal environment[7-9]. Today China is the only country that continues using DDT-based anti-fouling paint on its ships. It is estimated that about 150-300 MT of DDT per year is emitted through antifouling paint usage in China. And most of the product is used in small to medium size fishing ships. In this regard, sediments in fishing harbours in coastal China are expected to be heavily contaminated by DDTs from the use of the antifouling paint.

Here we report the levels, inventory and ecological risk of DDTs in the sediments of fishing harbors along the coastal line of China. The results prove that a large burden of DDTs exits in the fishing harbor sediments, denoting that the phasing out of DDT-containing antifouling paint is of urgent need for the protection of the coastal environment and human health.

Materials and Methods

A total of 9 fishing harbors were selected in this survey, with 5 stations located in the PRD, e. g. Guangzhou (GZ), Zhuhai (ZH), Shenzhen (SZ), Macao (MC) and Hong Kong (HK). A total of 58 sediments samples were collected in August 2007 to November 2007, using a Kajak corer (KC Denmark Co., Denmark). At each site, the upper 10 cm sediment was collected, sealed in polytetrafluoroethylene (PTFE) bags, immediately transferred to the laboratory and freeze-stored until

analysis. The dry samples were Soxhlet extracted with dichloromethane, the extracts were fractionated and clean-up on a silica/aluminum oxide column. Quantification was done on an HP-6890 GC-ECD, with selected samples being confirmed by GC-MS. Field blanks, lab blanks, and surrogate recovery reported good data quality control.

Results and Discussions

Levels and source of DDTs in the harbor sediments. The concentration levels of total DDT ranged from 9 to 7350 ng/g, which were generally one to two orders of magnitude higher than those from adjacent estuarine/marine systems, and were much higher than those reported in other places in the world, except for several sediments also from harbors, e. g. the Inner Harbor of Macao[10] (1630 ng/g), Xiamen harbor[11] (4.5-311 ng/g) in southeast China, and Alexandria Harbor in Egypt[12] (<0.25 to 885 ng/g).

Both a local point source input and a sediment environment favors the retaining of hydrophobic organic compounds (HOCs). An accumulation of all available HOCs, rather than only DDTs, is expected to be observed in the sediment. To test this we have measured HCHs, another mostly widespread organochlorine pesticide, in the harbor sediments. The results showed that the total HCH concentrations (the summation of α-HCH, β-HCH, γ-HCH and σ-HCH) ranged from <0.10 to 12 ng/g, which were well within the range of the reported concentrations in sediments from the adjacent coastal area and river estuary, a sharp contrast to the outstanding DDT levels in the harbor sediments. The ratios of DDTs/HCHs in the fishing harbor sediments (2.5 to 8860, with a median value of 120) were much higher than those of the adjacent coastal/estuarine sediments. This clearly denotes a significant input of DDTs within the fishing harbors.

Sediments showing high DDT concentrations were generally located at sheltered locations and/or mooring area within each of the fishing harbors. And the DDT concentrations declined sharply, by one or two orders of magnitude, from the harbor centre to the outbound channel site. It was shown that local input of DDTs occurred at or near fishing harbors.

The TOC content of all the fishing harbor sediments ranged from 0.12-2.6%, well within the range for estuarine/marine sediments in the world. In the studied fishing harbors in the Pearl River Delta, as an example, the total TOC normalized concentrations of DDTs were 1.5-321 ng/g-TOC, with a mean of 58 ng/g-TOC, while a much lower concentrations of 0.11-13 ng/g-TOC were observed for the Pearl River estuary sediments[10,13]. The above evidence showed that TOC was not the key factor responsible for the accumulation of DDTs in the harbor sediment, further pointing to a local DDT source.

The most possible DDT source in the fishing harbors is the release of DDT from fishing ships with DDT-containing antifouling paint. In fact, a previous investigation of DDT in commercially available antifouling paints in the Pearl River Delta reported a high DDT residue of 525-2360 ng/g in the products, although much lower than the early estimation of 5% (Unsubmitted Manuscript). In addition, the heavy metal Cu which also defined as release from fishing ship with antifouling paint had good correlation with DDTs in fishing harbor sediments.

Mass inventory of DDTs. Based on the dataset generated from this study, we attempted to assess the mass inventory of DDTs in the fishing harbor sediments in the PRD region. The method assumed that the concentration and distance showed a good linear correlation due to mixing and dilution in fishing harbor area coverage. A total of 35 samples in the PRD region were used. The mass inventory was calculated according to the following formula, where C is the DDT concentrations.

$I=CAdp$

Conservative estimate of total DDT concentrations of 87 and 480 ng/g dw were adopted for the lower limit and the upper limit, respectively. A is the total water area of fishing harbors in PRD region (80 km^2). With an assumed sediment density of 1.5 g/cm^3, and a high DDT concentration sediment thickness limited in 10 cm, the calculated inventories were 1.0-5.7 metric tons for total DDTs in fishing harbor sediment in the PRD. In a previous study using a similar approach, it was calculated that 0.4 and 1.4 metric tons of total OCPs were stored in the regional sediment (0-5 cm) in the Pearl River Estuary and the northern South China Sea[14]. Clearly, the mass inventories of DDTs in fishing harbor sediment greatly surpass those in the regional sediments, highlighting the importance of DDT-containing antifouling paint to the DDT contamination along the coastal length of China.

Implication to food chain transfer. A series of studies have shown DDT residue concentrations in samples including mussels, dermersal fishes and human breast milk from Pearl River Delta region presented the highest level in the world. The occurrence of high concentrations of *p,p'*-DDT and its metabolites in surface sediments of fishing harbors in the region may responsible, in part, for high level DDTs in biologic chain. As mentioned above that *p,p'*-DDD accounted for a large proportion of

p,p'-DDTs, an average of 64% in the fishing harbors was presented as *p,p'*-DDD. However, in all the fish samples and human breast samples, *p,p'*-DDE and *p,p'*-DDT were identified to dominate the DDT compositions[5,15]. It was widely reported that, in organisms located at the upper trophic levels of a food web, such as birds, whales and human being, *p,p'*-DDE was the most predominant isomer accounted for more than 90% of the total *p,p'*-DDTs[16]. Question arises that whether this could be attributed to the greater accumulation rates for *p,p'*-DDE in foodwebs, and to the metabolization of *p,p'*-DDT to *p,p'*-DDE by organisms, or organisms located at the upper trophic levels of a food web have high exposure levels of *p,p'*-DDT and *p,p'*-DDE in the living surrounding.

As is well known that significant proportion of *p,p'*-DDD to *p,p'*-DDTs were observed in littoral sediment[10] and even in benthic spices such as mussels and shellfish[17,18], but the absence or very low concentrations of *p,p'*-DDD in organisms located at the upper trophic levels of a food web. Little information is available about the bioaccumulation and metabolization of *p,p'*-DDD in foodweb. The season that either *p,p'*-DDD may not likely to be bioaccumulated by fishes and humans, or it is bio-transformed to other metabolites, such that it cannot be tracked down in the foodweb in its original form.

Acknowledgements

The study was funded by Natural Scientific Foundation of China (NSFC No. 40590391, 40802087, 40821003), a CAS Initiative Project (KZCX1-YW-06) and the Research Grants Council (RGC) of the Hong Kong SAR Government (N_PolyU535/05). The authors would like to thank Dr Jun Wang and Mr Jinglei Shi for their kind help in field sampling.

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Table1. Concentrations (ng/g dry weight) of DDTs in surface sediments of fishing harbors in China

Harbor	Num.	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDD	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	DDTs
Sanya	4	0.13-1.0	11-130	15-87	54-270	3.7-27	12-46	108-561
Maoming	3	0.30-1.3	20-98	50-210	190-830	34-140	67-180	361-1250
Macao	5	1.5-4.1	170-420	130-760	520-2900	29-530	65-1200	967-5810
Zhuhai	10	0.11-2.5	9.3-280	9.7-520	32-2000	0.53-130	2.2-310	55-3040
Hong Kong	4	0.20-3.0	20-300	8.7-650	34-2600	4.3-1500	9.4-2300	76-7350
Shenzhen	10	0.17-2.0	2.0-220	2.6-270	5.4-940	0.08-21	0.36-37	17-1460
Guangzhou	8	N.D.-0.13	3.2-13	2.4-6.7	9.5-27	3-12	3.6-10	21-68
Zhoushan	10	N.D.-0.36	1.6-91	1.3-40	3.5-140	0.58-110	2.2-200	9-563
Qingdao	6	N.D.-0.49	1.0-46	1.0-110	3.9-450	0.47-73	2-160	9-839

N.D.= Not-detectable