THE EVALUATION OF ORGANOCHLORINE PESTICIDES IN TISSUE AND SEDIMENT IN ESTUARY OF TAIWAN

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Introduction

Persistent Organic Pollutants (POPs) are those compounds that persist in the environment. They can transport across a long distance and tend to bioaccumulate in human or animal tissue through the food chains. Consequently, residual POPs have great chance to cause significant impacts on human health and the environment. The health hazard effect of POPs has been thoroughly debated in recent years resulting in a consensus agreement of the Stockholm Convention on Persistent Organic Pollutants in 2001, which prohibit the production and use of these chemicals. Some POPs have been widely used as pesticides for long. Organochlorine pesticides such as DDT, BHC, Lindane have been banned in Taiwan since 1977. In the same time, EPA Taiwan has been carrying out a systematic tracking on the residual concentration of organochlorine pesticides in environment with analytical tools such as GC/ECD for the past thirty years. Recently, we start to use the isotope dilution method by HRGC/HRMS to analyze organochlorine in environmental samples so as to determine the residual POPs in a more accurate way. We have collected 54 sediment samples and 54 tissue samples from some representative estuaries of Taiwan. The average POPs concentration in sediment and tissue samples are 709 ng/kg d.w and 4255 pg/g w.w. separately. The concentrations ranged 57.5~3970 ng/kg d.w. and 149~75300 pg/g w.w. in sediment and tissue. The highest POPs level is found in the sample of western estuary though still well below the official risk threshold limit. Hexachlorobenzene, DDE and DDT are detected in more than 90% of the sediment samples, while Hexachlorobenzene, DDE, DDT, Cis-Chlordane, Trans-Nonachlor, Dieldrin and Mirex are detected in more than 90% of the tissue samples. The ratio of DDT and its metabolites can be served as indicators for possible liable sources as well as the degree of degradation. The ratio of p,p'-DDT/(p,p'-DDT+p,p'-DDE) of all samples are found to be lower than 0.60 which imply that these DDT contamination in estuary of Taiwan might originate from aged pollutants in the long past.

Materials and methods

(1) Sample collection, extraction and clean-up

Samples were collected from 9 selected representative estuaries of Taiwan. 6 sampling sites were chosen for each estuary as shown in Fig.1. Sampling were carried out in spring and autumn season. The 9 rivers cover almost all essential agricultural area of Taiwan. Therefore the level of organochlorine of estuary will reflect the use of pesticides. All samples were dried, ground and homogenized before being spiked with 13C-isotopes of the analyzed compounds and extracted by Soxtherm with (1+1)Acetone/n-Hexane solvent mixture. Target compound standards and isotope labeled spiking solution were purchased from Chembridge Corporation. The extracts were concentrated to about 1 mL by turbo evaporation and then replaced their solvent with 1 mL hexane for the need of subsequent pretreatment process. Proceed the clean up step with Florisil SPE column. Gel permeation chromatography can be used to remove high molecular weight interference (such as polymeric materials, humic acids, lipids and so on).

(2) HRGC/HRMS analysis

23 organochlorine pesticides were analyzed by isotope dilution in according to EPA method 1699 with a high resolution mass spectrometer (HRMS) (AutoSpec Premier^{TM}) coupled with a gas chromatograph equipped with cold injection system. Pesticides were separated with J&W (Agilent Technologies) DB-1701 column (30m×0.25mm×0.25μm).

Results and discussion

The concentrations of 23 organochlorine pesticides in estuary samples ranged between 57.5~3970 ng/kg d.w. in sediment and 149~75300 pg/g w.w. in tissue. The average concentration are 709 ng/kg d.w and 4255 pg/g w.w. in sediment and tissue separately. Organochlorine pesticides concentrations in most sediment samples are below

500 ng/kg d.w.. However in the case of tissue samples, the concentrations scattered in a wide range for samples from different organism species and ages. The lowest average concentration in sediment is the one from Hualien(82.0 ng/kg d.w.). Sediment samples from Sihcao and Wuwei both have much higher OCP concentrations than those from other locations. Sample from one site of Sihcao estury reached up to nearly 4000 ng/kg d.w.. It is quite different than other sites of that estuary. On the other hand, sediment samples from four sites of the Wuwei estuary are over 2000 ng/kg d.w.. Analyzed results of tissue samples collected from Sihcao and Wuwei are about the same. Wuwei estuary has been disconnected from the sea since the two typhoon calamities in 1942 and 1968. There is no tidal dilution since then and it explains the relatively higher concentrations over the whole estuary area (6 sample sites). Organic pollutants tend to adsorb on sediment particles and be carried down along the water bodies. Particles of different characteristics will migrate to different locations depending on their sizes and densities. Tidal and currently flushing will also move the sediment according to the geographical features in the tidal flat. Therefore, concentrations are widely varied for different sampling sites where tidal frictions present. Take the case of Sihcao estuary for example, among the 8 sampling sites as shown in Fig. 2, we found that the sediment sample of A4 site has a significant higher OCPs content than other 7 sites. A4 site is a typical river delta that accumulates the sediment from the upstream pollution sources. Tidal dilution is also less than those sites near the seawater such as A5 or A8. As the highest concentration of Sihcao and Wuwei are about in the same level, we can estimate the concentration of organochlorine pesticides in the estuaries of Taiwan have been reduced to approximately 20% of their original levels during the past forty years. Average concentration distributions of each congener for the 23 organochlorine pesticides in sediment and tissue samples are illustrated as shown in Fig.3 and Fig.4. Some of previous research works revealed that the half-lifes of DDTs are about two years or more in soil. However, they will last longer even more than eight years in tissue before being metabolized to DDDs and DDEs. The largest portion of OCPs is p,p'-DDE (30% in sediment and 35.7% in tissue). p,p'-DDT and p,p'-DDD also accounted for more than 10% each. Residual data of these congeners reflects the widely usage of DDTs in the past. Nevertheless, the concentrations of DDTs in sediment (125 ng/kg d.w.) and tissue (884 pg/g w.w.) found in the estuaries of this investigation are far below the regulated level for sediment (0.01 mg/kg d.w.). FDDTe is a frequently used indicator for the degree of DDT degradation as show below:

FDDTe = p,p'-DDT/(p,p'-DDT + p,p'-DDE)

For the fresh DDT, the FDDTe will generally fall within the range of 0.95-0.99. On the other hand, aged DDT contamination usually exhibits lower values. As illustrated in Fig.5, all FDDTe indices are lower than 0.60 which implied that no fresh DDT input into the environment is found. The concentration distribution of four BHCs in sediment and tissue are about of the same level. Lindane accounted for about 40% , possibly due to that the banning of Lindane was late than other BHCs for about ten years in Taiwan. The levels of chlordane are much lower and are in consistent with the levels of nonachlor in sediment. However, the levels of chlordane in tissue (348 pg/g w.w.) are much higher than those of nonachlor(38 pg/g w.w.). It might be reasonably attributed to the slower metabolism of chlordane in the tissue of organisms.

Acknowledgements
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Table 1 Summary of Total OPPs concentration in estuary sediment ~~of estuary~~

Location	Sampling sites	Sample	Concentration range (ng /kg d.w.)	Average (ng /kg d.w.)
Sihcao	8	8	342~3970	1231
Beigang	6	6	195~545	396
Puzi	6	6	109~1199	427
Bajhang	6	6	98.2~756	366
Zengwun	4	4	139~457	258
Chiku	6	6	81.7~460	263
Lanyang	6	6	148~544	344
Wuwei	6	6	883~3959	2691
Hualien	6	6	57.5~162	82.0

Table 2 Summary of concentration in tissue of estuary.

Location	Sampling sites	Sample	Concentration range (pg /g w.w.)	Average (pg /g w.w.)
Sihcao	8	10	1080~75300	9243
Beigang	6	10	97.3~13340	396
Puzi	6	8	103~23855	3681
Bajhang	6	8	149~2538	875
Lanyang	6	6	877~5055	2217
Wuwei	6	6	2608~8941	5776
Hualien	6	6	1427~2927	2159

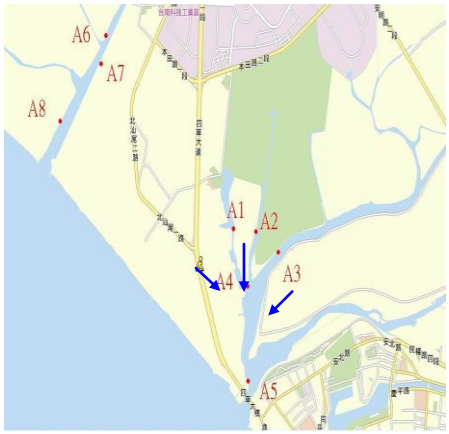

Figure 1 Location of the 9 sampling estuaries. Figure 2 Location of the 8 sample sites of Sihcao.

Figure 3 Total concentrations of 23 organochlorine pesticides in estuaries.

Figure 4 Average concentration distributions of 23 organochlorine pesticides in samples.

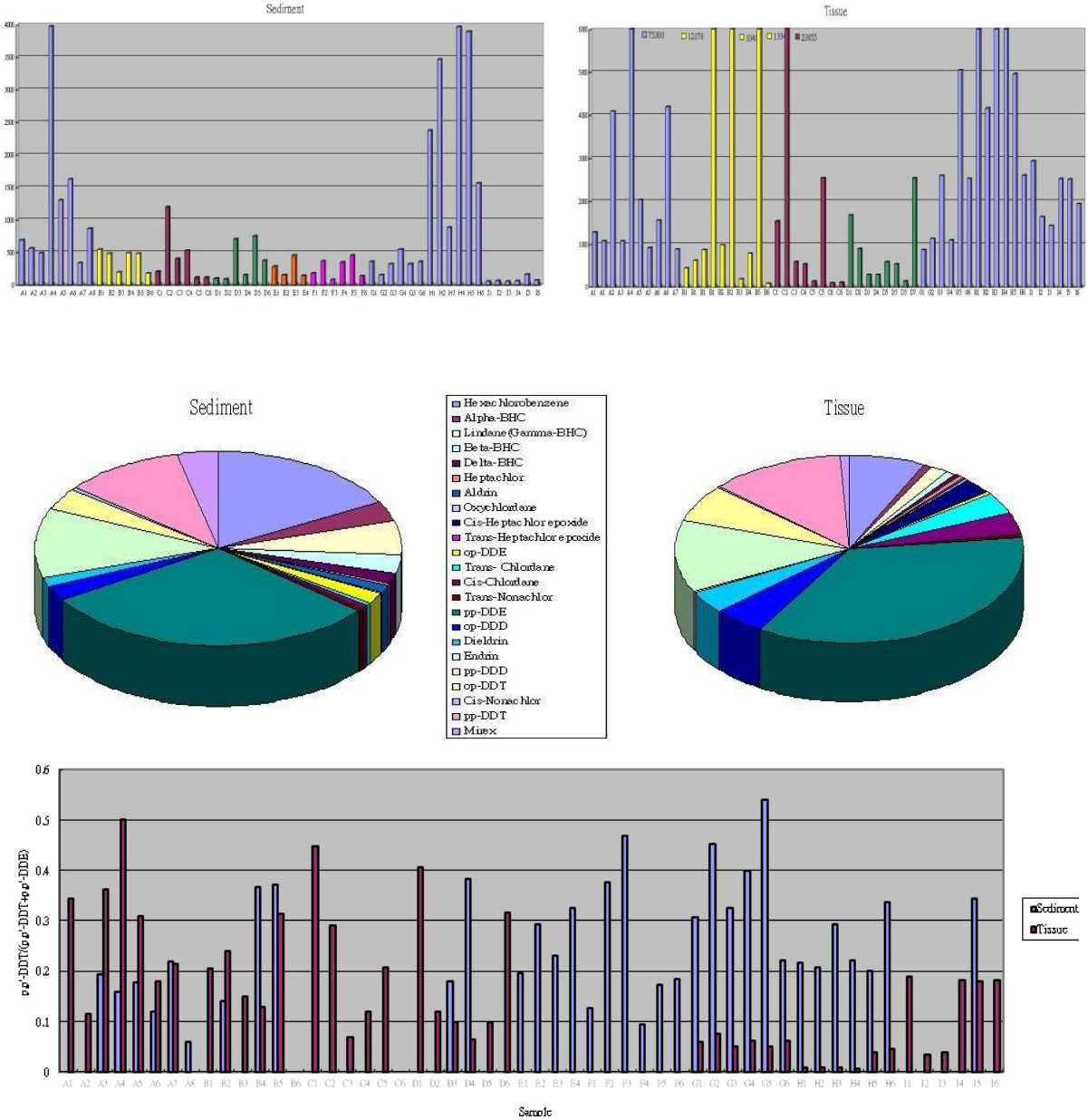

Figure 5 Index for evaluating the degradation of DDT in sediment and tissue.