ORGANOCHLORINATED PESTICIDES IN THE AQUATIC ENVIRONMENT AT THE ESTUARIES AND IN TAM GIANG – CAU HAI LAGOON OF THUA THIEN HUE PROVINCE FROM 2005 TO 2007

I. STATUS OF ORGANOCHLORINATED PESTICIDES IN THE WATER AND SEDIMENT

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Abstract

09 water samples, 55 sediment samples and 20 biosamples (bivalve and fish) were collected from 11 locations of Tam Giang - Cau Hai lagoon during dry seasons of 2005, 2006 and 2007. The samples were treated under EPA methods and analysed by GC-MS for organochlorinated pesticides (OCs). The result showed that concentrations of pesticides of all water samples were at lower level than TCVN-5942-1995 (Vietnamese Standard) for organochlorine compounds (OCs) of surface water. Conversely, these chemicals were determined in sediment samples. Despite of decreasing from 2005 to 2007, the concentrations of them in sediment is still high. The samples from O Lau estuary next to Tam Giang lagoon were higher in DDT and HCH concentrations while the ones from Truoi estuary next to Cau Hai lagoon were higher in dieldrin and endrin. Analytical data indicated that the topography strongly affected to the distribution of organochlorinated pesticides.

Key words: estuaries, organochlorine compounds, Thua Thien Hue

1. Introduction

Similar to other areas in Vietnam, the economy of Thua Thien Hue is mostly based on agriculture. Many agrochemicals, epescially organochlorinated pesticides, are used intensively to improve crop yields. Every year, Thua Thien Hue utilise 150 - 200 tones of agrochemicals (Thua Thien Hue Crop Protection Agency, 2005). From 1991 to May 1994, 24 tones of DDT was used against malaria for the control of disease vectors and public health in the mountain areas of A Luoi, Nam Dong, Phu Loc (The Center against Malaria, Parasites and Insects of Thua Thien Hue, 2005). After that, although there has been increasing efforts to control the use of these persistent organoclorine pesticides in the country, they are still being used illegally. The paddy rice fields of Thua Thien Hue are located mainly along O Lau, Huong, Dai Giang and Truoi rivers. The annual rainfall here is high, (averaging 3200 mm, sometime 5800 mm), causes frequent floods, erosion of soil and transport of sediment (and residues of pesticides in sediment) from the river valleys and mountains into estuarine areas and Tam Giang - Cau Hai lagoon. Tam Giang – Cau Hai lagoon system, with the area of 22,000 ha and about 70 km length along the seaside, is one of the largest lagoon of South-East Asia, it plays an important role with socio-economical development of Thua Thien Hue province. At present, over 300,000 residents (appr. 30% population of the province) are living on aquaculture in the lagoon (Thua Thien Hue Fishery Dept., 2003). The objectively of this study is to evaluate the status of organochlorine pesticides in water and in sediment from several estuaries and Tam Giang - Cau Hai lagoon.

2. Materials and experimental

2.1. Sampling and sample pre-treament

Nine water samples, fifty-five sediment samples and twenty biosamples (bivalve and fish) from 11 locations of O Lau, Huong, Truoi and Dai Giang estuaries and Tam Giang - Cau Hai lagoon (Fig.1) were collected from 15th April to 15th May in dry seasons of 2005, 2006 and 2007. At each of 11 sites, several samples were collected and pooled in order to obtain a representative sample. The analysis method was according to US EPA-methods: 3540C, 3620 B, 3660, 3665A, 508 for soxhlet extraction, Florisil clean- up, sulphur clean-up, sulphuric acid clean-up and determination for organochlorine compounds, respectively.

Water sample extraction was carried out by mixing with n-hexan (10:1 in v/v). After 3 times of extraction, the extracts were collected and treated.

Sediment samples were wet sieved through a metallic screen and the fraction with particle size <0.1 mm was used. Samples were kept in a deep freezer at -20 0C until analysis. 2 g of sediment was taken and mixed with 2 g of anhydrous Na2SO4. Sample extraction was carried out by mixing with 100 ml n-hexane in a soxhlet extractor for 12 hours.

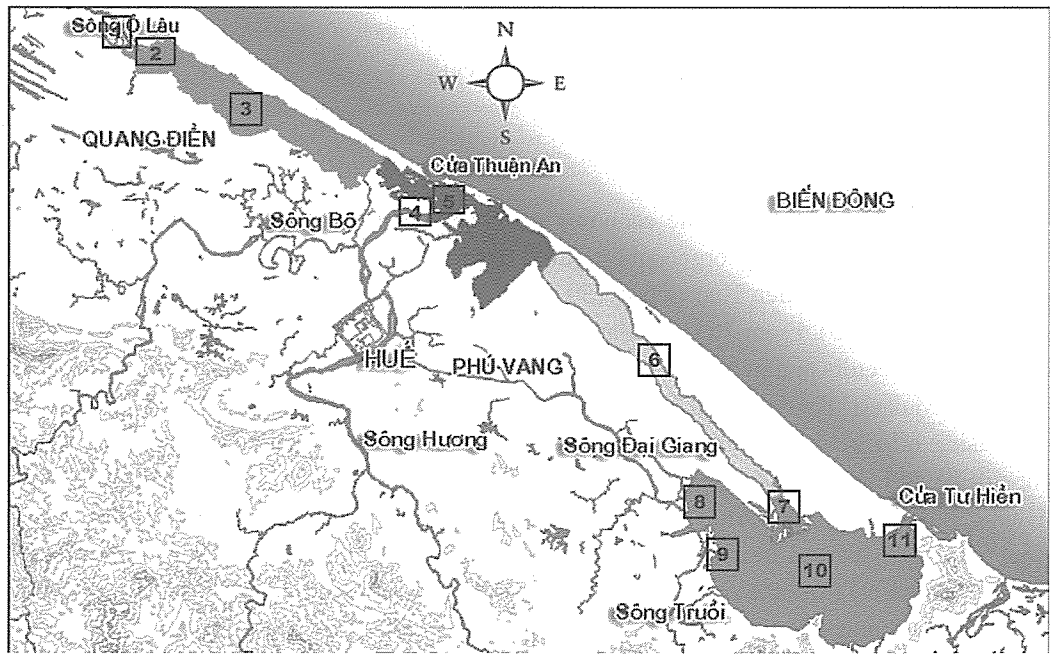

Figure 1. Map of sampling stations at estuaries and in Tam Giang - Cau Hai lagoon, Thua Thien Hue

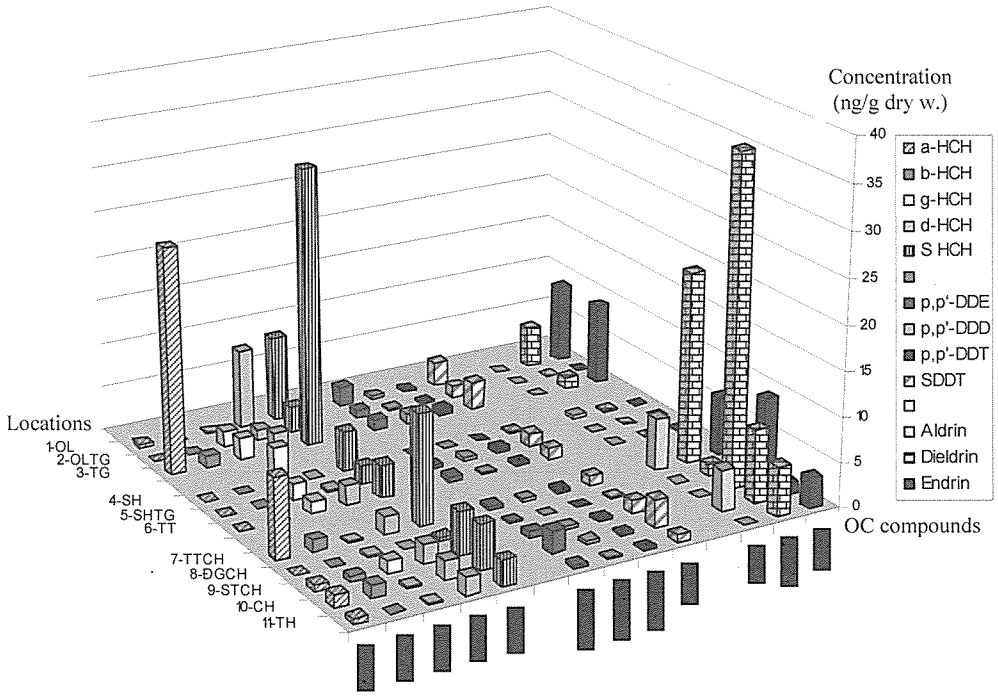

Figure 2. Concentrations of DDTs, HCHs, aldrin, dieldrin and endrin in the sediment from the estuaries and Tam Giang - Cau Hai lagoon

The extract from water or sediment samples were concentrated on a rotary evaporator and then reduced the volume of approximately 2-5 ml. The extract were treated with activated Cu powder to remove sulphur compounds, then by florisil column and follow with fumic H_2SO_4 before performing chromatography.

2.2. Contaminant quantitation

Analyses of the samples were carried out using a progammed temperature gas chromatograph equipped with mass spectroscopy QP-2010-GC-MS with DB-1 column. Quantification of the contaminants is based on the internal standard method using pyren -d10. Final results are expressed as ng/l for water samples, ng/g dry weigh basis for sediment samples and ng/g lipid for biosamples.

3. Results and discussions

3.1. Organochlorine pesticides in the water

Concentrations of pesticides in nine samples from three estuarine areas were below level of Vietnamese Standards TCVN-5942-1995 for organochlorine compounds (OCs) of surface water. This is in agreement with the previous obsevation from 1998 to 2001 (Nguyen Xuan Khoa, 2005). The OC concentrations were below the detection in most of water samples, indicating that the ban of usage of these chemicals from 1994 has been executed well. DDTs, aldrin and dieldrin could not be quantified in any of these samples. However, the reported environmental half-life of OCs is estimated as 10-30 years in the land, and these OC residues have still entered into the marine environment through different pathways. Estuary input is, in particular, the most important because estuaries are major interfaces between land and sea. It is not surprised that there was trace amounts of OCs in water samples from rivers and lagoon of Thua Thien Hue. Total DDT (only DDE and DDD, without DDT)

concentrations range from below detected limit to 5.0 ng/l, the minimum concentration of HCHs is below detected limit and maximum one is 413.4 ng/l. Their values decreased in samples from 2005 to 2007 and were below the detection in all samples in 2007.

3.2. Organochlorine pesticides in the sediment

- The concentration of OC residues at the estuaries and in the Tam Giang - Cau Hai lagoon

Table 1. Comparison of organochlorine residue levels (ng/g) in the sediment collected from some different estuaries, harbour and seas in the world

Area	Σ DDTs		Σ HCHs	
	Range	Mean	Range	Mean
T.T. Hue, Vietnam	0.2- 3.2	1.5	0.3 - 31.2	7.2
China [1]	2.5- 24.7	10.2	nd* - 1.2	0.7
India [2, 3]	0.1 - 1.2	0.6	0.0 - 0.3	0.1
Hongkong [4]	1.4 - 25.4	10.2	nd - 2.3	0.6
SriLanka [5]	0.1 - 1.6	–	0.1 - 0.3	–

nd: *not detected*

Organochlorine pesticides are rather high in the sediment of the estuaries and Tam Giang - Cau Hai lagoon, Thua Thien Hue (Fig.2). Many of the commonly detected OCs in other regions of the world, such as DDTs, HCHs, aldrin, dieldrin and endrin, are also present in these samples. In that, the DDT family is the lowest. HCH and its degraded products were detected very high in sediments at locations next to O Lau estuary: 1-OL, 2-OLTG and 3-TG. In the samples from Cau Hai estuary, the major OC that was detected are dieldrin and small amounts of endrin, aldrin and HCHs.

Concentrations of total DDT ranged from 0.15 ng/g (at 4-SH) to 3.17 ng/g (at 3-TG) in the sediment, with a mean of 1.50 ng/g. The minimum value of HCHs is 0.3 ng/g, the maximum one is 31.2 ng/g and the mean is 7.2 ng/g. The mean of aldrin, dieldrin and endrin is 1.0; 7.2 and 3.5 ng/g, respectively. Compared with concentrations reported for sediment from the several estuaries in other areas in the world (Table 1), the sediment from Thua Thien Hue estuaries appear to have lower contaminant concentrations of DDTs, but higher ones of HCHs, aldrin, dieldrin and endrin than China (Dongxing Yuan et al., 2001) and Hong kong (Hong H, et al., 1995). In general, the contaminant of OCs in Thua Thien Hue is rather more serious than India (Sarkar A. et al., 1994; Badal B., 2003), Sri Lanka (Guruge, K.S., 2001),...

The sites next to O Lau estuary (1-OL and 2-OLTG) and next to Truoi estuary (6-TT and 9- STCH) which are close to paddy rice fields, have the higher organochlorine concentration than the ones next to Huong estuary (4-SH and 5-SHTG). In general, at the estuaries (1-OL, 2-SH, 8-DGCH), OC concentrations in the sediment increased when to the center areas of lagoon (3-TG, 6-TT, 10-CH), but after that they are decreased (11-TH). The use of DDT and HCH was widespread in Thua Thien Hue last to early 1994, and was banned in June 1994. The different of concentrations of OCs in sediment samples indicate that the concentrations of OCs in the estuaries are lower due to the ban of using OCs, but the estuaries have received significant amount of OCs from river outflow and transported into the lagoon.

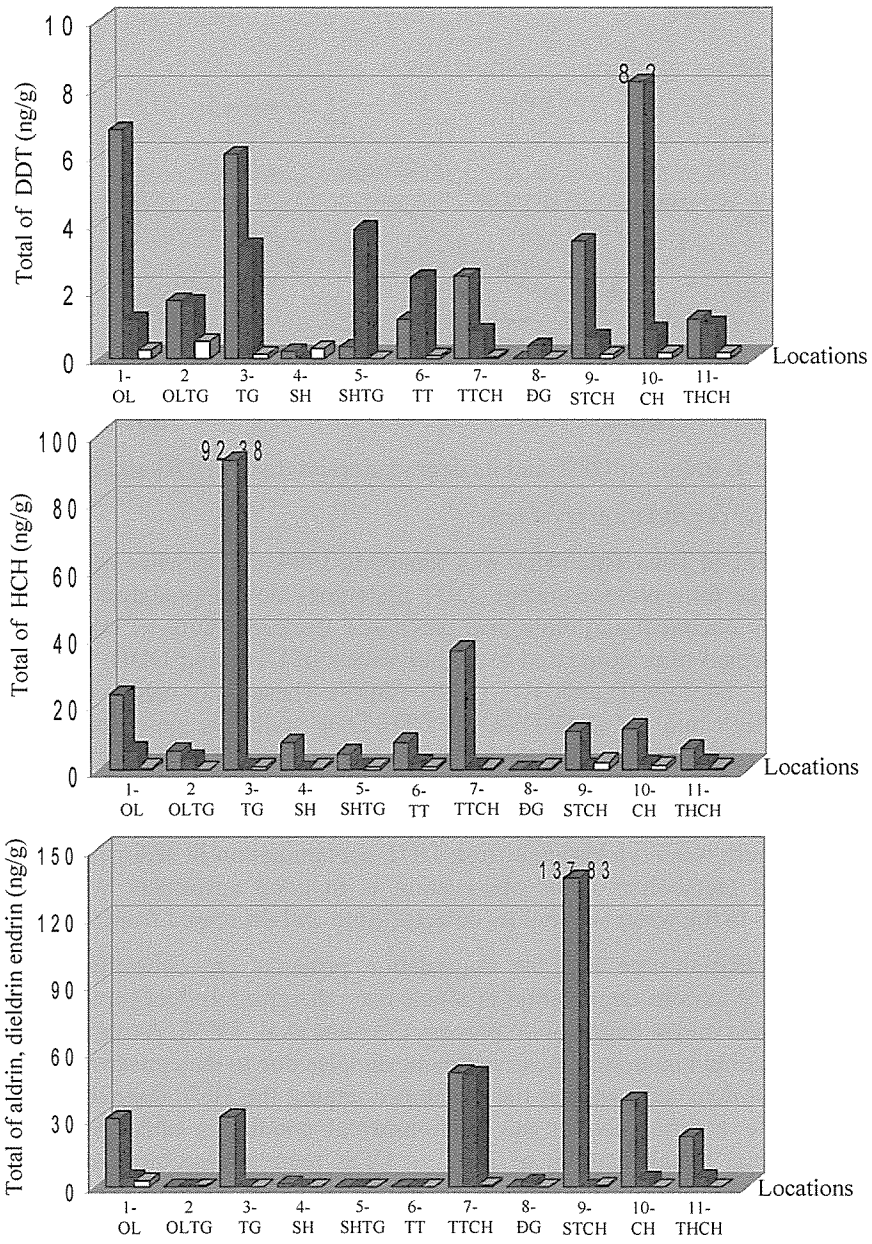

Figure 3. The variation of OC concentrations from 2005 to 2007 at sampling locations

- The concentrations of OC residues from 2005 to 2007

The concentrations of OCs in sediment are expected to be decreasing due to the ban of using DDTs and HCHs in 1994. This is represented on the Fig 3. These results are in agreement with decreasing of OC concentrations in water samples from 2005 to 2007.

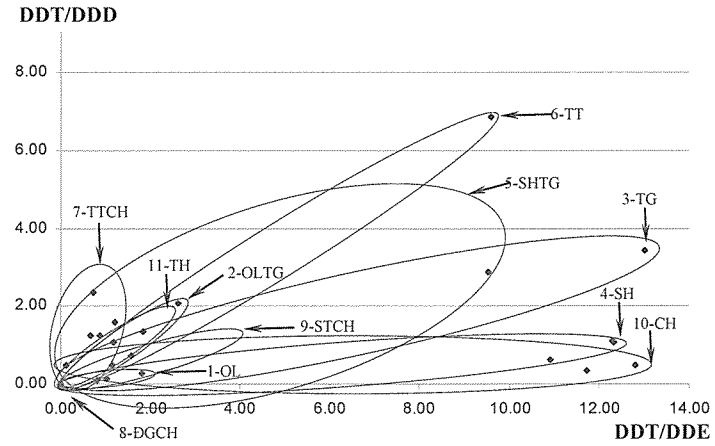

Figure 4. Ratios of DDT and its degradation products (DDD and DDE).

- The ratios DDT and its degradation products

Because the use of DDT in Thua Thien Hue was banned in 1994, the presence of DDT in the sediment is predominantly residue from previous usage. DDT undergoes slow degradation to DDD and DDE in natural environment by chemical and biological processes. Concentrations of DDT in 22/55 sediment samples are under detected limit compared to higher values of DDE and DDD. This also presents by the ratios of DDT/DDE, DDT/DDD and DDT/(DDE +DDT). These ratios can be used to evaluate DDT degradation degree. High ratio of DDT/DDD or DDT/DDE indicates slow degradation of DDT or addition of unaltered DDT contamination to the samples. The ratios of 22/55 samples are 0.00 and the ratios of others are below 1.5. It is very interesting that the DDT/(DDE +DDT) of all sediment samples collected in April - May, 2007 are 0.00. It suggests that DDT was not newly released into sampling locations, therefore, there was no additional fresh DDT contamination in sediment samples and DDTs are mainly present as metabolites. This observation is in good agreement with the fact that the concentration of DDTs in the water was below detected limit and decreased from 2005 to 2007.

In addition, the degradation rate and the degradation products are controlled by environmental conditions. The ratios of various degradation products may, therefore, reflect some of the effects of the environmental conditions on the degradation process (Tavares et al, 1999). Assuming that there was no additional fresh DDT contamination in these sediment samples due to the concentration of DDTs in the water there is low (not detected), so that the difference among the DDT degradation products in the sediment may indicate a difference in the environmental conditions under which DDT is being degraded. The microbial metabolization of DDT to DDE requests aerobic conditions of an active hydrodynamic open system with water often changed with the open sea (Anguliar, 1984). In contrast, the reductive dechlorination of DDT to DDD might be implied under anaerobic redox conditions with restricted water exchange with the open ocean (Baxtor, 1999). Our results suggest some other comments. The dominance of DDE over DDD in sediments from 1-OL (Fig. 3) might imply microbial metabolization of DDT to DDE; in contrast, the environmental conditions in 2-OLTG and 3-TG may favor the reductive dechlorination of DDT to DDD, which would result in the higher concentration of DDD and lower amount of DDE in this sample. It is the same for 4-SH (DDE is higher) and 5-SHTG (DDD is higher). 1-OL is fresh water area (salinity is only 0.10‰) compared to 2-OLTG (0.96‰) and 3-TG (8.67‰). The salt concentration of 4-SH is 0.70‰ wherea one of 5-SHTG is 8.50‰. So the lower salinity may favor the degradation of DDT to DDE, and the higher ones may favor DDT to DDD. The other locations (6-TT, 7-TTCH, 9-STCH, 10-CH) with salinity above 13‰ and next to open East

sea have the same DDE and DDD concentrations in the sediment. DDE is the breakdown product which has higher toxic property than DDD.

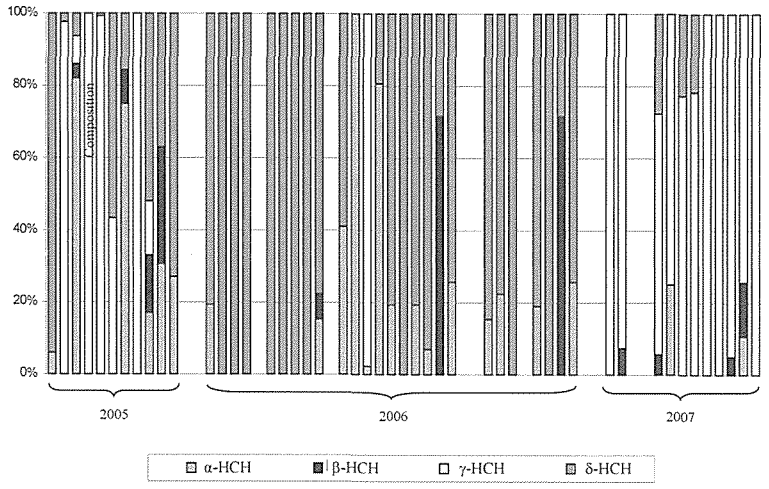

Figure 5. Compositions of HCH isomers in HCHs

- *Compositions of HCH isomers in HCHs*

There were some types of HCH which was used in agriculture. First is technical HCH consists of γ-HCH, α-HCH and β-HCH accounted in average for about 30, 50 and 20%, respectively; so that α-HCH and γ-HCH are the main components of technical grade HCH. Second is lindane is pure γ-HCH or 98-99% of γ-HCH and 1-2% of α-HCH.

Regarding the HCH isomers in sediment samples collected in 2005 and in 2006 (Fig.5), δ-HCH accounted for the majority of HCHs, follow by γ-HCH and α-HCH. Conversely, the level of β-HCH was below the detected limit in most of the samples excepting some cases. It could be said that δ-HCH is the feature of more stability and resistances to degradation from parent technical grade HCH in conditions at sampling locations.

However, it is worth noting that in samples collected in 2007, the percentage of γ-HCH found in the samples is too higher than its proportion in technical HCH mixture. As well as DDT, the usage of HCH was banned in 1994, so that the detection of α-HCH and γ-HCH in sediment samples collected in 2007 is unexpected. This may suggest that recently exposure input of lindane to environment.

- *Potential for biological effects*

Both concentrations of OCs in the sediment and observed biological effects were provided by an extensive review of articles (Long and Morgan, 1990). A 10th and 50th percentile were determined and were designated effects range low (ER-L) and effects range median (ER-M). The ER-L and ER-M values for total DDTs are 3 and 350ppb, for p,p'-DDT are 1 and 7ppb, for p,p'-DDE are 2 and 15ppb, for p,p'-DDD are 2 and 20 ppb, for dieldrin are 0.02 and 8 ppb, for endrin are 0.02 and 45ppb, respectively. Total DDT concentrations in the sediment are below the ER-M values and only 5/55 samples are above the ER-L value for the sediment. It is rather good for DDT. In contrast, dieldrin and endrin concentrations are much above its ER-M, suggesting that the concentration of dieldrin and endrin in the sediment are likely to pose detrimental biological effects on the benthic organisms. We will have quanitical assessements in detail for biological effects of organochlorine pesticides in sediment from Thua Thien Hue in next study.

4. Conclusions

4.1. Concentrations of pesticides in most of water samples from three estuarine areas were below detected limit and below the level of Vietnamese Standards TCVN-5942-1995 for organochlorine compounds (OCs) of surface water. DDT, aldrin and dieldrin could not be quantified in any of these samples.

4.2. Sediment samples from estuaries studied have high DDT, HCH, dieldrin and endrin concentrations. Especially, HCH concentrations at O Lau estuary and in Tam Giang lagoon; dieldrin, endrin concentrations at Truoi estuary and in Thuy Tu - Cau Hai lagoon are very high. Compared with coastal environmental in some Asian countries, estuaries and lagoon in Thua Thien Hue are contaminated at moderate degree by DDT, but at high degree by HCHs, dieldrin and endrin. The concentrations of organochlorine compounds in the estuaries are lower due to the ban of organochlorine compounds from 1994, but the estuaries have received significant amount of organochlorine compounds from river outflow and transported into the lagoon.

4.3. DDT was not newly released into sampling locations due to: the concentrations of total DDT in the water and in the sediment decreased from 2005 to 2007, there is no detection of DDT in water and in the sediment saples collected in 2007, the relatively high concentrations of DDE and DDD in the sediment indicate that DDT being degraded. In the low salinity water, DDE is dominant over DDD and vice-versa.

Acknowledgments

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