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Residue of organochlorinated pesticides (OCPs) in some organisms of the tidal flats in the northern part of Vietnam

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Abstract
Organochlorinated pesticides (OCPs) had been used widely in agriculture for protecting crop, eliminating insects. However, OCPs are banned in most countries because of their toxicity, long persistence and bio-accumulation. They are listed in carcinogen group and POP group (Persistent organic pollutants). In Vietnam, OCPs were banned in 1990s, but their residues are still found in the environments, including seawater, sediment and organisms. This paper presents the survey data of residues of OCPs in some organisms living in tidal flats in the northern part of Vietnam during the year 2013–2014. The results show that the total residue of OCPs in shellfish ranged from 5.57 µg/kg to 116.04 µg/kg dry weight. Compared with the American Guide for mollusk shellfish (2007), it is found that the organisms living in the tidal flats were not polluted by OCPs. However, these compounds can be accumulated in fat tissue even in very low concentration. Therefore, their presence in organism is alarming.

Keywords: Organochlorinated pesticides (OCPs), tidal flat, organisms.

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INTRODUCTION

The estuarine tidal flats are interaction areas between the river and the sea, so the environment there is influenced by fresh water from the rivers and inlands, on the other hand, they are also affected by the tidal regime from the sea. Based on the composition of the substrate, salinity, tidal regime as well as typical organisms, it is possible to classify the tidal flat in the north of Vietnam into the following types: Estuarine tidal flats, mainly concentrated in estuarine areas where mangrove forests developed; rock tidal flat, often found in Quang Ninh coast, Central coastal area and around big islands; karst tidal flat, often found in the islands in Ha Long, Bai Tu Long bays; dead coral tidal flat, often found on coastal islands. The role of the tidal ecosystem for environment protection is very significant, including prevention from salt intrusion, erosion, storms, prevention from dispersing pollutants of mangrove forest... (according to Do Cong Thung, 2016, the project "Study on the environment status, resources change, biodiversity of tidal ecosystems in the northern coast of Vietnam (from Quang Binh backwards), and proposal of sustainable models for exploitation, aquaculture, conservation and management".

The tidal flat area in the northern part of Vietnam extending from Quang Ninh to Quang Binh is very rich in biological resources. There are intertidal ecosystems with mangrove vegetation, sandy tidal flats, rocky tidal flats... These ecosystems are home to many species of shrimps, fish, crabs, snails, clams...; many of which are economically valuable species. However, this area is also greatly impacted by the socio-economic development of the northern coastal area such as being narrowed by sea encroachment and pollution due to waste from inlands. These factors affect the species that live in this area.

This paper provides data on residues of organochlorinated pesticides in some organisms living in tidal flats of the northern part during the period 2013–2014. Organochlorinated pesticide compounds are studied in the article including lindane; aldrin; endrin; dieldrin; 4.4-DDD; 4.4-DDE and 4.4-DDT. Detecting the existence of these compounds in tidal organisms demonstrates that their habitat (water, sediment) is still contaminated by OCP compounds. Therefore, it is necessary to strengthen monitoring and management of these compounds to minimize the residue in the environment.

MATERIALS AND METHOD

Sampling area and sampling points

Organism samples were collected at 8 tidal flat areas, including Tra Co, Tien Yen, Cat Ba, Thai Binh, Ba Lat, Lach Ghep, Lach Van and Cua Gianh (fig. 1) in April and August 2013, supplemented in April and September 2014. Collected organism samples were clams, oysters, shells (*Glaucomya chinensis* and *Aloidis laevis*). The samples were collected by scraping in situ, then put into plastic bags and stored in a cooler and transferred to the laboratory for analysis. These samples were collected under framework of the National Project, Code KC 09-07/11–15, "Study on the environment status, resources change, biodiversity of tidal ecosystems in the northern coast of Vietnam (from Quang Binh backwards) and proposal of sustainable models for exploitation, aquaculture, conservation and management", implemented since 2013.

Method for analysis of OCPs in organisms

Shellfish samples (clams, oysters, mussel,...) are separated into tissue and shells, and then tissue part is put into a special mill to grind. A part of the tissue is weighed, dried at 105^{o}C to calculate the water content in the sample. Weigh about 20 g of tissue and dry naturally at room temperature, using anhydrous Na_2SO_4 to remove the water in the sample. The sample is then extracted 3 times in an ultrasonic extraction device with 60 ml of petroleum ether. The extraction solvent is collected and concentrated, then transferred to the Florisil column for cleaning. Elute with 70 ml of petroleum ether and then elution is collected. Continue evaporation of elution to about 1 ml. If the sample contains a lot of fat, remove the fat from the elution with H_2SO_4 acid. The final eluent is quantified to 0.1 ml and injected on the HP 6890 gas chromatographic system with the ECD electron

capture detector. These analysis steps are described in the documents of APHA (1995) [1], UNEP/FAO (1982) [2]; UNEP/IAEA (1982) [3]; UNEP/IAEA (1982) [4]; UNEP/IOC, IAEA (1988) [5].

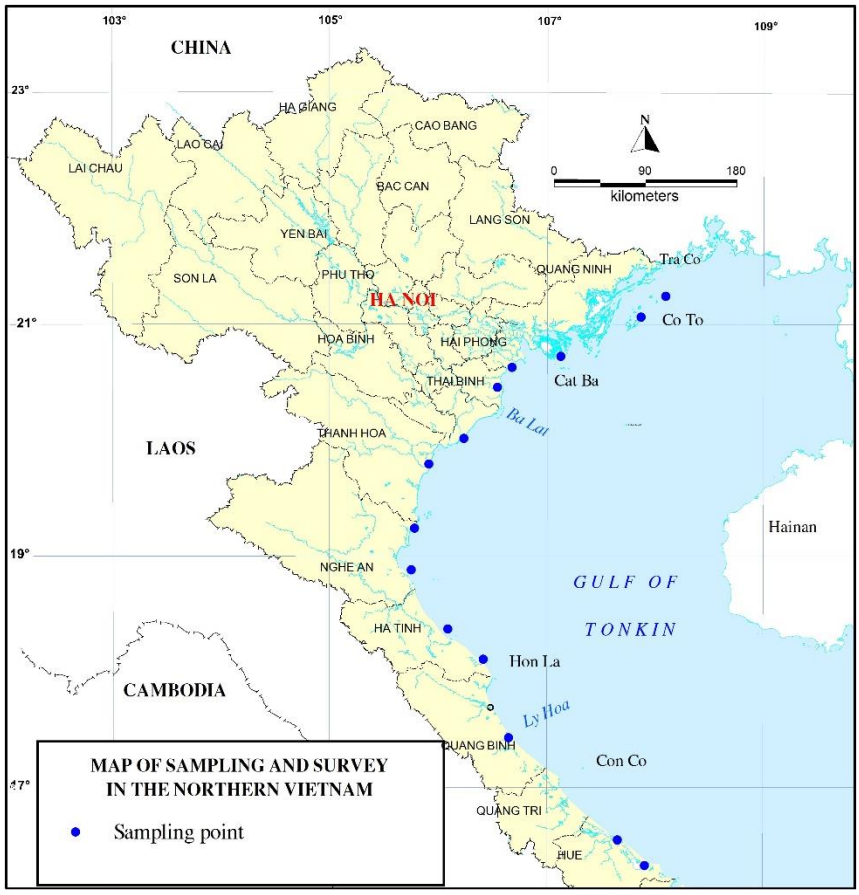

Fig. 1. Sampling points of shellfish at tidal flat areas

The parameters of gas chromatography system (GC/ECD HP 6890) include: The HP-5 capillary column with length 32 m, inner diameter 0.32 mm, coating thickness 0.25 μm, pressure 4.7 bar, flow through column 0.9 ml/minute, average velocity of flow 18 ml/min; the temperature program of the oven: start at 80^{o}C, keep at 80^{o}C for 1 minute, then increase to 290^{o}C at rate 20^{o}C/min, keep at 290^{o}C for 10 minutes; the start point temperature for injection 250^{o}C with split mode, the split rate 19.2:20.0, total flow 17.3 ml/min; detector temperature 300^{o}C, the anode flow 6.0 ml/min, the auxiliary nitrogen flow 60 ml/min.

External calibration was used to calculate OCPs compound concentration with standards lindane, aldrin, endrin, dieldrin, 4,4'-DDE, 4,4'-DDD and 4,4'-DDT. The recovery of the method for individual standard is about 70.6–97.8%. The detection limit of the method at 99% confidence is 0.03 μg/kg for lindane, 0.02 μg/kg for 4,4'-DDT and 0.01 μg/kg for remaining compounds.

RESULTS AND DISCUSSIONS

The survey results on OCPs residues in some organisms (clams, shells (*Glaucomya chinensis* and *Aloidis laevis*)) collected in the April 2013 in the western tidal flats area of the Tonkin Gulf (TG) showed that total 7 OCPs compounds (lindane, aldrin, endrin, dieldrin, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT) ranged from

12.62 μg/kg to 116.04 μg/kg dry weight, most of them are compounds of 4.4'-DDE, 4,4'-DDD and 4,4'-DDT (fig. 2).

Clams in Tra Co area (Quang Ninh) contain the highest total pesticide residue, followed by clam samples in Dien Chau (Nghe An) and in Thai Thuy (Thai Binh). It is worth noting that shell samples (*Glaucomya chinensis* and *Aloidis laevis*) also have the accumulation of these compounds in their tissue in which the cumulative level of *Aloidis laevis* is much lower than *Glaucomya chinensis* and clam.

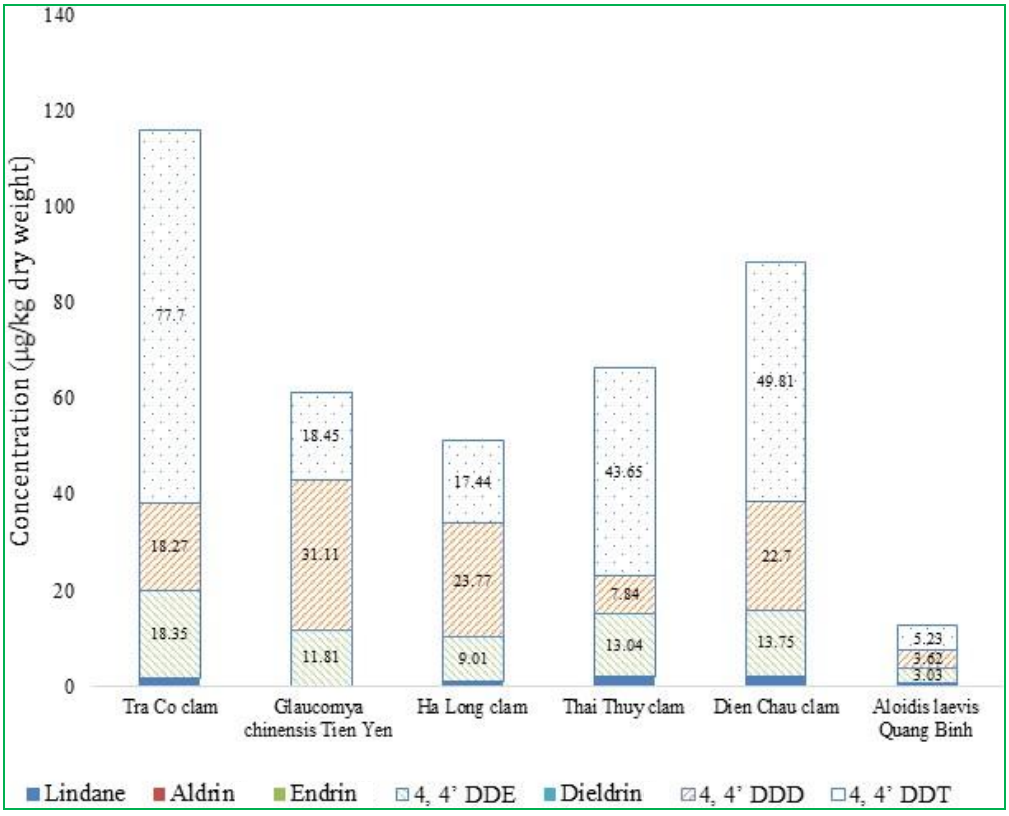

Fig. 2. OCPs residue in clam and shells of the western tidal flats area of the Tonkin Gulf in April 2013

Comparison to the US FDA guideline, 2007 [6] for each compound, the shellfish samples collected in April 2013 in the western tidal flats area of Tonkin Gulf are not polluted by OCP compounds.

Fig. 2 shows the results of OCPs residues in shellfish samples collected in April 2013. It is clear that DDT compound are detected at higher concentrations than other compounds.

In August 2013, shellfish samples collected in the tidal flat area of the Tonkin Gulft were mainly clams and oysters. There are 17 samples of clams and oysters collected throughout the northern tidal flat area. Water content in clams and oysters ranges from 86.86% to 94.82%, an average of 91.11%. Except for the clam sample collected in Lach Ghep (Thanh Hoa province) with the size much larger than other samples (height 40.7 mm, length 88.3 mm, width 69.7 mm), all the remaining samples are quite similar in size. Specifically, the height is from 15–33 mm; length from 32–45 mm, width from 28–35 mm. At this size, clams and oysters are mature and can be sold in the market.

Analysis results of OCPs in clam and oyster samples in August 2013 showed that OCPs residues were in the range of 10.47–37.59 μg/kg dry weight, lower than the sampling in April 2013. In which, endrin, 4,4'-DDE and 4,4'-DDD were found in higher

frequency. Most of the samples had the total OCPs content in the range of 10–20 μg/kg of dry weight, however clams and oysters in Diem Dien area had the content greater than 20 μg/kg dry weight (fig. 3).

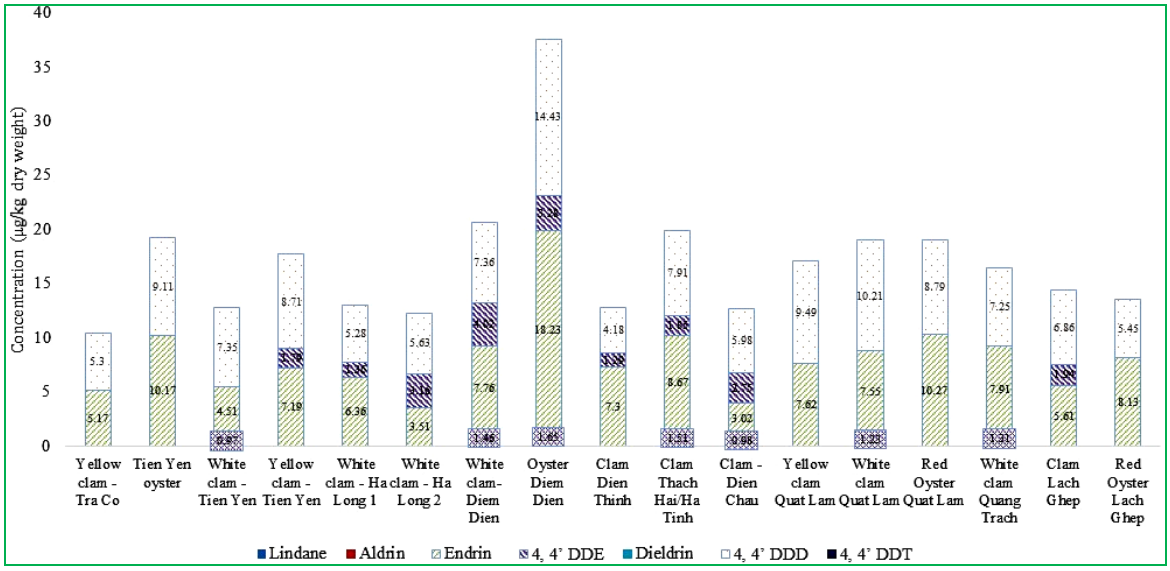

Fig. 3. OCPs residues in clams and oysters in the western tidal flats of Tonkin Gulf, August 2013

In the sampling in August 2013, 4.4'-DDT was not found in all samples. However, 4.4'-DDD was still detected from 4.18 μg/kg to 14.43 μg/kg dry weight. In particular, the content of OCPs compounds in oyster samples in Diem Dien is quite high, 1.5–3 times higher than other samples (fig. 3).

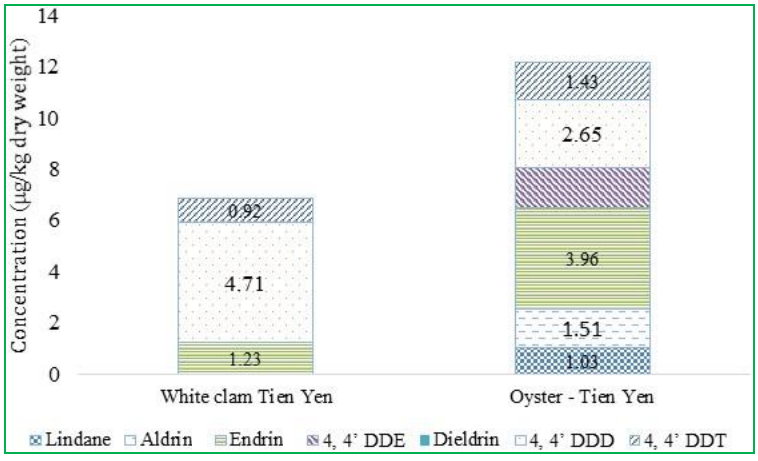

Fig. 4. OCPs residue in clam and oyster at Tien Yen tidal flat in April 2014

Additional samplings in 2014 focused only on one tidal flat area or one experimental subject. Sample collection in April 2014 focused on clam and oyster samples in Tien Yen (Quang Ninh province) - 2 samples. The analytical results show that 4,4'-DDD compound is still detected frequently. Notably, there were 6/7 compounds found in the oyster, but at low concentrations (fig. 4).

In the sampling phase in September 2014, cultured clam samples in Nam Dinh tidal flat at different sizes were collected and analyzed for OCPs residues in tissue. Characteristics of experimental clam are as follows (table 1).

Table 1. Characteristics of the cultured clam sample at Nam Dinh tidal flat in September 2014

No.	Sample index	Height (mm)	Length (mm)	Width (mm)	Water content (%)
1	Natural Clam	13.7	28.3	20.3	92.14
2	Experimental clam (150 individuals/m^2)	18.3	38.7	31.1	92.25
3	Experimental clam (250 individuals/m^2)	16.7	32.9	26.7	89.07
4	Experimental clam (350 individuals/m^2)	15.7	31.3	25.4	86.93

The analytical results show that the clams with larger size had the higher accumulation level of OCPs in tissues (Figure 5). However, only 4, 4' - DDD was detected in experimental clams at Nam Dinh while the natural clam sample contained more compounds but in low concentration or below detection limit.

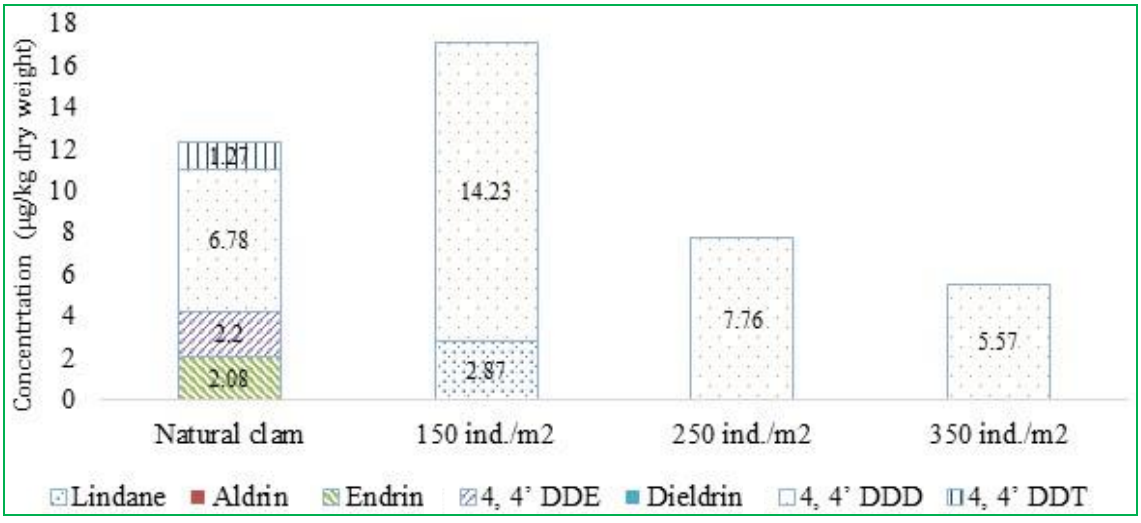

Fig. 5. OCPs residue in experimental clams in Nam Dinh tidal flat area in September 2014

The monitoring results of OCPs in clam samples collected in Tra Co and Cua Luc tidal flats (Quang Ninh province) and Ba Lat tidal flat (Thai Binh province) during 2013–2014 in the operation framework of the Northern Marine Environmental Monitoring Station showed the decrease in the concentration of OCPs residues with time (according to the Technical Report on the task of "Monitoring the marine environment in the North of Vietnam, 2014"). These results are quite similar to the results presented above, in which the concentrations of OCPs are high in the dry season of 2013 (April) and the 4.4'-DDD compound is found with high frequency.

In Thanh Hoa province, the monitoring results of OCPs residues in 2011–2012 showed that the total amount of OCPs ranged from 4.69 µg/kg to 173.35 µg/kg dry weight in bivalve; from 5.05 µg/kg to 13.22 µg/kg dry weight in crustaceans; and from 8.24 µg/kg to 31.35 µg/kg dry weight in fish (according to the research results of the project "Building a database for marine resource and environment of Thanh Hoa province" by Tran Dinh Lan, Nguyen Van Thao and Cao Thi Thu Trang in 2013).

According to the report "Current status of environmental pollution caused by pesticide residue belonging to the persistent organic

pollutant group in Vietnam" done by the National Environment Agency (2015), before 1995, DDT was still used in health and military to control and prevent malaria, in which about 1000 tons/year had been used in the years of 1962, 1963 and 1981. Also according to this report, currently, the amount of pesticide residue is being stored in very large warehouses, up to nearly thousands of storage places. On the other hand, the smuggling of pesticides through the northern borders is frequent and very difficult to control. Most of these chemicals are the old generation pesticides, highly toxic, banned from circulation, banned from use but still smuggled to Vietnam. For example, in early 2015, 41 bottles of endosulfan (OCPs type) in volume of 100 g/bottle had been detected and arrested in Me Linh district (Hanoi), showing that the source of OCPs into the environment is understandable.

CONCLUSION

All the shellfish samples such as clam, oyster, and shells (*Glaucomya chinensis* and *Aloidis laevis*) had been collected in the tidal flat areas in the northern part of Vietnam, showing the presence of OCPs, including endrin, 4.4'-DDE and 4.4'-DDT. The survey of experimental clam samples in Nam Dinh tidal flats showed that the bigger the clam, the greater the accumulation level of OCPs. The concentration of total OCPs in collected shellfish is mainly in the range of 10.47–116.04 μg/kg dry weight, which is lower than the permitted limit for food safety threshold in the US. These results show that OCPs residues are still found in organisms living in the tidal flats in the western part of the Tonkin Gulf and 4.4'-DDD is a common compound found in all samples. The detection of these compounds in clam and oyster indicates the potential for the level of accumulation, sustainability and persistence of these compounds in the environment. Although their concentration is still safe for health, we need to regularly monitor their residues in the environment.

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