Science on Natural Resources and Environment
Journal homepage: hunre.edu.vn/hre/d16216

ASSESSMENT OF RESIDUAL OF OGANOCHLORINE INSECTICIDES IN THE COASTAL RIVER AREA AT KIM SON DISTRICT - NINH BINH PROVINCE

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Received 12 October 2018; Accepted 30 November 2018

Abstract

Sediment samples in coastal estuary of Kim Son district, Ninh Binh province were collected continuously at 3 sites for 3 years from 2016 to 2018 in June of each year. After taken, organochlorine insecticides content in sediment samples was determined by an electron trap detector using Agilent 7697A Headspace Sampler, model: 7890B/7697A/7000C. Analyzed result showed that total DDT content in the study area was in ranged from 0,0115 to 0,0415 ppm, HCH content was in range of 0,0326 to 0,0889 ppm, total aldrin and dieldrin in range of 0.012 to 0.046 ppm and endrin in range of 0 to 0,0015ppm. Organochlorine insecticides content tended to decrease over time, the slope of the linear equation for DDT varied from - 0.0002 to - 0.0011 smaller than the coefficient of HCH and total cyanosis showed that the rate of HCH and total cyanosis decreased more rapidly than DDT over time. No γ-HCH was detected in all analyzes, ratios of DDT/DDE, DDT/DDD, DDT/total DDT and DDD in 2017 and 2018 were 0,0 indicating that the study area was no longer receiving pesticides from other places. It is realized that topographic factors play a decisive role in the accumulation of pesticides residues. This is evidenced by the higher pesticide content in sediment in mangroves than in sediments in aquaculture and mudflats due to less susceptibility to erosion and frequent embossed sedimentation.

Keyword: Organochlorine insecticides; Ratios of DDT/DDE, DDT/DDD, DDT/total DDT; Residual of organochlorine insecticides.

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1. Introduction

Organochlorine insecticides are synthetic pesticides belong to the group of chlorinated hydrocarbon derivatives, which have vast applications in the chemical industry and in agriculture. These compounds used successfully in controlling a number of diseases but have adverse influence on ecosystem and environment. Organochlorine insecticides could pollute the tissues of virtually every life form on the earth, the air, the lakes and the oceans, the fishes that live in them and the birds that feed on the fishes [5]. Due to their high toxicity, slow degradation and bioaccumulation, they are involved in the binding of organic matter in the soil or accumulation in the organism's lipids and

cause biological amplification in the food chain [7].

According to the Vietnam Environment Administration, by 2015 Vietnam had about 1,562 pesticide residue spots, scattered across 46 provinces and cities. Compared with 2009, the number of contaminated sites increased by 500 points, but there are only 200 pesticide residues that are considered as high risk, causing severe environmental pollution and serious impacts on community health [4].

Since 2003, the investigation and assessment of the accumulation of pesticides in the environment has been paid attention by Vietnamese government in order to effectively participate in the Stockholm Convention. However, up to now, there has been no official report on the consequences of pest infestation on human health and ecosystems.Therefore, most of people in polluted areas are still unaware of its long-term harmful effects and they keep living farming, aquaculture,etc. daily in contaminated areas [4].

With a 15 kilometer long coastline, Kim Son is the only coastal district of Ninh Binh province. Located between Day River in the East and Can River in the West, most of the land in the coastal area of Kim Son is formed by the accretion of these two rivers. By December 2016, the Kim Son alluvial area was about 6,660 ha (occupying 32.1% of the natural area of the district) with 2,164 ha of brackish water aquaculture. Everyday, Kim Son mudflats ecosystem receive directly waste water source from all livelihoods, farming, and so on from Ninh Binh province and part of Nga Son district, Thanh Hoa province. Residual of organochlorine insecticides from the inland to the environment and the ecosystem of Kim Son district is of concern because local people use direct water from the coast for aquaculture and forestation.

This article studies and evaluates residual and accumulation of chlorinated pesticides in sediment in coastal mudflats of Kim Son district, contributing to assess the risks of organochlorine insecticides that can bring to the environment and the community.

2. Materials and methods

Sediment samples in the coastal estuary of Kim Son district, Ninh Binh province were collected continuously at 3 points for 3 years from 2016 to 2018 in June of each year. Three sampling sites were selected on the basis of field surveys. Mapinfo 15.0 and Coreldraw 10 software were used to represent the sampling map based on the actual sampling location coordinates. Fig. 1. shows the map of sampling location at coastal estuary of Kim Son district.

The samples were taken according to TCVN 7538-2: 2005 - Soil quality - Sampling Part 2: Technical guidance on sampling. At each site identified on the map, sediment samples were collected as combinated sample of 20 nearby sites by grid method to characterize the location. After taken samples were processed in accordance with TCVN 6647 : 2007 (ISO 11464 : 2006) - Soil quality - Preliminary treatment of samples for physical and chemical analysis. After preliminary treatment, the content of plant protection agents in sediment samples was determined with the procedure of TCVN 8061 : 2009 (ISO 10382 : 2002) - Soil quality - Determination of organic chlorine plant protection chemicals and polyclorin biphennyl - Gas chromatography with an electron trap detector. Qualitative and quantitative determination of chlorinated pesticides was carried out in the laboratory of Vietnam Academy of Science and Technology using Agilent 7697A Headspace Sampler, model: 7890B/7697A/7000C.

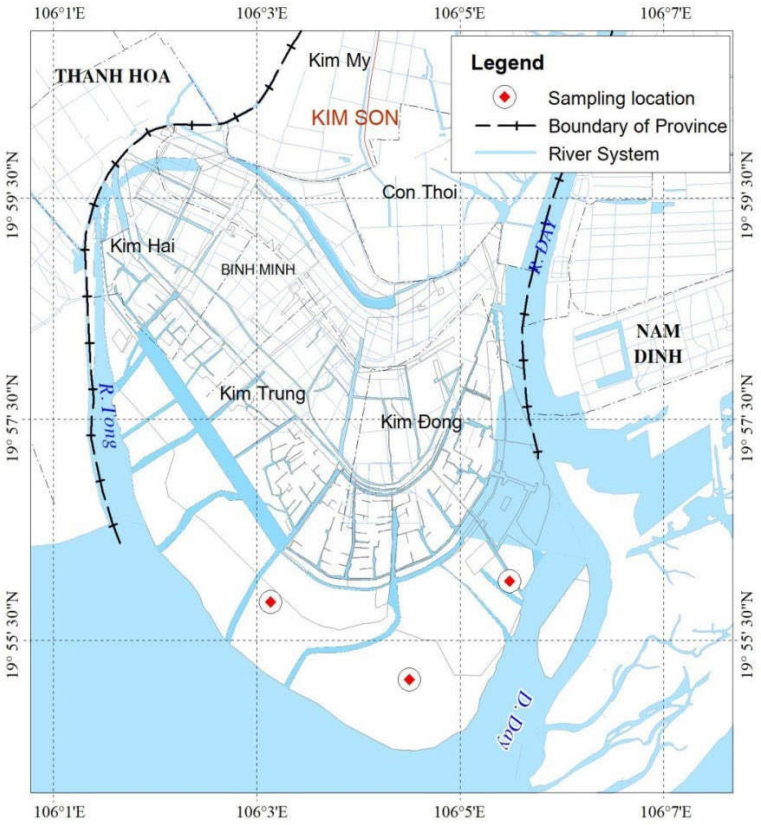

Figure 1: Sampling location at coastal estuary of Kim Son district

Tab. 1 presents water sampling sites and sampling purposes.

Table 1. Sediment sampling sites and sampling purposes

No	Study sites	Coordinates		Sampling purposes
		Latitude	Longitude	
1	NB1	19° 55' 49"	106° 37' 44"	Assessment of plant protection agents content at Kim Son mudflat site - where contiguous estuary of Day River, receiving agricultural waste water from inland.
2	NB2	19° 54' 57"	106° 44' 59"	Assessment of plant protection agents content at clam culture site.
3	NB3	19° 55' 59"	106° 50' 28"	Assessment of plant protection agents content at Kim Sơn mangrove site.

3. Results and discussion

3.1. The distribution of organochlorine insecticides in the studied area

The distribution of organochlorine insecticides in the studied locations of coastal estuary of Kim Son district is presented in Tab. 2. The analyzed result indicated that the content of organochlorine insecticides at mangrove area was higher than other areas several times. At mangrove site, NB03 = 0,1366 ppm while at mudflat site NB01 = 0,0452 ppm and at clam culture site NB02 = 0,066 ppm. This can be explained that organochlorine insecticides remaining in soil from agricultural areas in upstream of Day River were washed out and the amount of material deposited in the mangrove forest area was higher many times than in the areas without mangroves.

Analyzed results also prove that topographic factors play an important role in material accumulation, specially organochlorine insecticides. Topographic factors determines the residuals and accumulation of pesticide residues in the regions. Clam culture site NB02 and mangrove site NB01 are shallow water (depth of tidal < 1m), less tidal influenced, so the accumulation of material together with organochlorine insecticides was greater than the erosion, surface sediment is often accreted, especially in the rainy season.

Table 2. Content of organochlorine insecticides in period 2016 - 2018

Study site	Content of organochlorine insecticides (ppm)		
	NB 01	NB 02	NB 03
Total HCH	0,0326 ± 0,0021	0,0444 ± 0,0067	0,0889 ± 0,0043
Total DDT	0,0115 ± 0,0013	0,0201 ± 0,0018	0,0415 ± 0,0011
Total aldrin - dieldrin	0,0012 ± 0,0002	0,0015 ± 0,0001	0,0046 ± 0,0023
Endrin	KPH	KPH	0,0015 ± 0,0009
Total organochlorine insecticides	0,0452 ± 0,0021	0,0660 ± 0,0082	0,1366 ± 0,0071

3.2. The variation of organochlorine insecticides in study area for time

The variation of organochlorine insecticides in the target area for time is presented in the Table 3. Up to the time of sampling 2018, HCH content was in range of 0,0308 - 0,0874 ppm, higher than DDT (in range of 0,0102 - 0,0411 ppm). This has shown that the study area has accumulated a relatively large amount of HCH compared to DDT from before. Total cyclodiene (aldrin, dieldrin and endrin) also decreased relatively slowly over time, in 2016 it was in range of 0,0012 - 0,0088 ppm, in 2018 it was in range of 0,0009 - 0,0050 ppm. This result is consistent with the previous studies and suggests that HCH is capable of diffusing in air greater than DDT [3, 2, 7].

Table 3. Organochlorine insecticides content in study area by time

N	Group of organochlorine insecticides	Content of Organochlorine insecticides (ppm)		
		2016	2017	2018
1	Total HCH	0,0316 - 0,0872	0,0311 - 0,0932	0,0308 - 0,0874
2	Total DDT	0,0114 - 0,0424	0,0112 - 0,0416	0,0102 - 0,0411
3	Total aldrin and dieldrin	0,0012 - 0,0069	0,0011 - 0,0042	0,0009 - 0,0039
4	Endrin	0,0017 - 0,0024	0,0018 - 0,0019	KPH - 0,0011
5	Total organochlorine insecticides	0,0442 - 0,1372	0,0436 - 0,1399	0,0427 - 0,1332

Table 4. Variable equation of organochlorine insecticides content in study area by time

Study sites	Total DDT	Total HCH	Total cyclodiene
NB01	y = -0,0002x + 0,4146 r^2 = 0,9812	Y = -0,001x + 2,051 r^2 = 0,9774	y= -0,001x + 0,3036 r^2 = 0,9643
NB02	y = -0,0011x + 2,2395 r^2 = 0,9973	y= -0,0025x + 3,0748 r^2 = 0,9829	y= -0,0024x + 0,9096 r^2 = 0,9322
NB03	y = -0,0008x + 1,5545 r^2 = 0,9643	y = -0,0023x + 4,7278 r^2 = 0,9163	y = -0,0019x + 3,8389 r^2 = 0,9304

The equation showed the variation in the amount of organochlorine insecticides over years has negative coefficients, correlation coefficient is high (r^2>90%). This proves that the trend of organochlorine insecticides decreases over time with linear relationship. Besides, the slope of the equation represents that DDT content is smaller than HCH and the total, meaning that DDT remained in the study area longer than other isomers and HCH and total cyclodiene decreased more rapidly than DDT over time.

3.3. Rate of isomers in each chlorinated muscle group

3.3.1. Rate of decomposition products in DDT

When released into the environment DDT is decomposed to form different isomers due to the impact of chemical and biological factors in the environment. Rate of DDT/DDE, DDT/DDD, DDT/ total DDT and DDD reflects the level of decomposition of DDT. This high rate indicates that DDT will be decomposed slowly, DDT continues to accumulate over time in sediment in the study area. Besides, this rate also reflects the influence of environmental conditions during decomposition and can be used in environmental assessment and management [6,8].

DDE levels increase over time and vice versa, DDD content decreases over time. The ratio of DDE/total DDT is higher than other isomers suggesting that most DDTs are decomposed into DDE - the most toxic isomers in DDT isomers. Is it right if low salinity in the study area has created favorable conditions for aerobic bacteria to decompose DDT into DDE? Many previous studies have shown that the decay rate of DDT in the soil is more than 10 years, depending on environmental conditions [7, 8]. However, in 2017 and 2018, the DDT / DDE, DDT/DDD, DDT/DDT and DDD ratios of 0.0, indicated that the study area received no or very little pesticides. It is due to the rapid decompositional rate and products are mainly DDE and DDD. This is shown in Fig. 2.

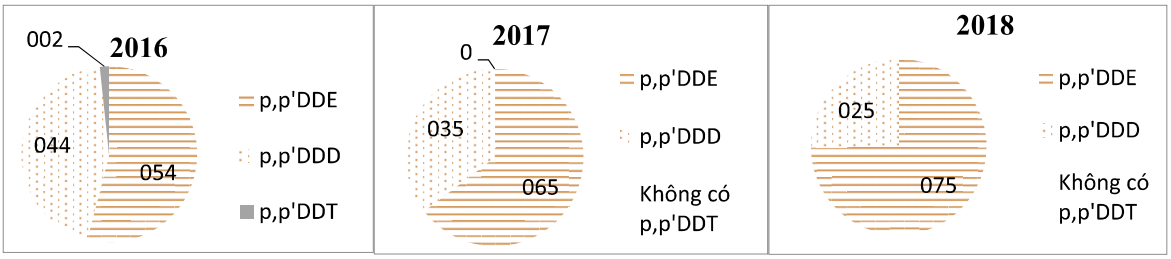

Figure 2: Rate of decomposition products in DDT

3.3.2. Rate of decomposition products in HCH

Vietnam has banned the use of DDT, HCH since 1994. The decompositional products of HCH are mainly included α-HCH, β-HCH,γ-HCH and δ-HCH, among which β-HCH is the most stable isomer and γ-HCH is the most biologically active isomer [4].

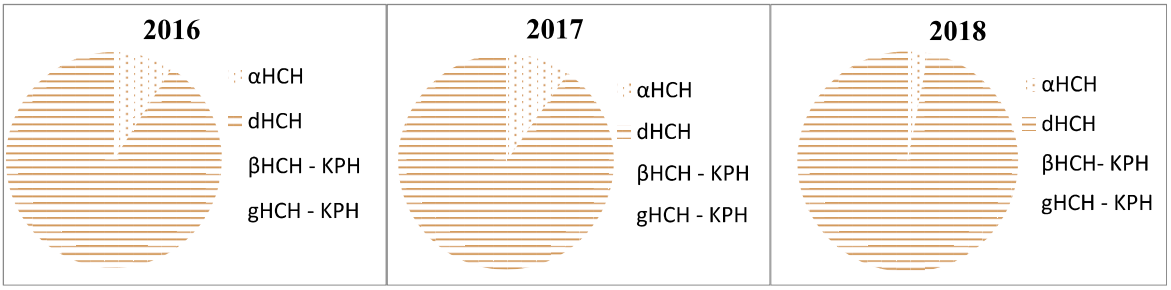

Figure 3: Rate of decomposition products in HCH

The majority of HCH in the study area were δ - HCH, in 2016 it was 91,02%; in 2017: 90,29%; in 2018: 97,01%; rate of isomers α - HCH is low and reduces by time. Analyzed result showed that no γ - HCH was detected in all of samples, proving that the study area received no longer or received very little. However, no β - HCH detected in all of samples means that other isomers of HCH group decomposed very slow and not yet reformatted the most sustainable β - HCH, only a small part of α - HCH move to form δ - HCH.

4. Conclusions

The analyzed result showed that total DDT content in the study area was in ranged from 0,0115 to 0,0415 ppm, HCH content was in range of 0,0326 to 0,0889 ppm, total aldrin and dieldrin in range of 0.012 to 0.046 ppm and endrin in range of 0 to 0,0015 ppm. Organochlorine insecticides content tended to decrease over time, the slope of the linear equation for DDT varied from - 0.0002 to - 0.0011 smaller than the coefficient of HCH and total cyanosis showed that the rate of HCH and total cyanosis decreased more rapidly than DDT over time.

No γ - HCH was detected in all analyses, ratios of DDT/DDE, DDT/DDD, DDT/total DDT and DDD in 2017 and 2018 were 0,0 indicating that the study area was no longer receiving pesticides from other places.

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