

ORGANOCHLORINE PESTICIDE RESIDUES IN THE MAJOR RIVERS OF SOUTHERN THAILAND

Abd Naser Haji Samoh^{1*} and Md Sani Ibrahim²

¹Faculty of Science and Technology
Yala Rajabhat University, Yala 95000, Thailand

²School of Chemical Sciences
University Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia.

*Corresponding author: nasir_2002@yahoo.com

Abstract

Environmental contaminations by organochlorine pesticides (OCPs) of inland water have been a global issue, since most of these compounds are very persistent, bioaccumulative and toxic compounds. Due to the widespread use of DDT for malaria vector eradication programs in the past and no comprehensive works have been conducted to assess trace organic pollutants in river waters, this work is the first effort to assess the contamination levels of OCPs in the major rivers of Southern Thailand. The objectives of this study were to determine the concentration levels of OCPs and oil and grease in the 3 major rivers and to compare the present results with surrounding regions for further assessment of OCPs contamination status in inland waters of Southern Thailand. The water samples were collected along the 3 major rivers (Saiburi, Patani and Tiba River) during July 2006-February 2007. Water samples were solid phase extracted with Supelco C-18 cartridge (1g/6 mL) and quantified by gas chromatograph (GC-ECD). The concentration of oil and grease was determined by gravimetric method and reported as hexane extractable material (HEM) and silica gel treated hexane extractable material (SGT-HEM). Several parameters of waters such as total suspended solid, pH, turbidity, and conductivity were measured. The commonly found OCP residues in these rivers were β -HCH, γ -HCH, heptachlor epoxide, endosulfan 1, p,p'-DDE and endrin aldehyde. The overall results showed that Saiburi River was more polluted with OCPs than Patani and Tiba River, especially p, p'-DDE which was detected in the wide range concentration of 9.6 to 203.1 ng/mL. For oil and grease contamination, Tiba River waters were found to be more polluted than either Patani or Saiburi River. The experimental procedures and analytical results together with the possible sources of OCPs and its environmental impacts are presented.

Keywords: OCPs, SPE, oil and grease, river water, Southern Thailand.

Introduction

Organochlorine pesticides (OCPs) are categorized as a group of persistent organic pollutants (POPs), which most of these compounds have been prohibited from use due to their toxic effects [1]. Environmental contamination by OCPs in natural inland water have been a great concern, since most of these pesticide compounds are very persistent, bioaccumulative and their toxicity can pose harmful effects to human and natural environment [2]. The studies regarding endocrine disrupting chemicals revealed that various types of cancer such as breast, testicular, and prostate cancer may partially be induced by several OCPs, which of most well known are DDT and its degradation products of DDE and DDD [3].

Even though most of the Southeast Asian countries as well as Malaysia, Thailand, Indonesia, and Viet Nam have banned the use of these pesticide compounds since 1990s, but the residues of OCPs are still detected in waters and soil or sediments at the significant levels due to their highly resistant degradation compounds in natural environment [4].

In 1994, Thailand imported about 100 tons of DDT for the purpose of malaria vector control under the Ministry of Public Health [5]. In Southernmost of Thailand, several reports have indicated that wide range levels of OCPs were found in various compartments collected from the Patani bay and surrounding areas [6, 7]. Records by the Ministry of Public Health of Thailand showed that the amount of DDT used for malaria vector control program in the 3 southernmost provinces (Yala, Patani, and Narathewat) between 1987-1997 was 129,849 kg [8]. However, this figure did not cover the amount of DDT used for agricultural activities as large areas of land in the southernmost of Thailand are devoted to agriculture. It is anticipated that large amount of DDT used in the past may affect the quality of natural inland water, especially in 3 major rivers, namely Patani, Saiburi and Tiba River.

Our research study involved determining the concentration levels of 18 OCPs in river waters of the 3 major rivers, as these river waters were routinely used by local villagers for various purposes such as washing, bath and agricultural activities. Although some study have reported the quality of these river waters in terms of physical and inorganic parameters [9], but the comprehensive data on organic pollutant contaminations, especially OCPs are very scarce. This study would be the first effort to determine current status of OCPs contaminations in the 3 major rivers of southernmost of Thailand which is very important to the local communities settled along these rivers.

In our laboratory, extraction of OCP residues in water samples were performed by solid phase extraction (SPE) technique that has recently been modified and successfully applied for determining OCP residues in the Patani bay area [10]. This technique offers several advantages over normal liquid-liquid extraction such as efficient isolation, pre-concentration and solvent usage.

Methodology

Reagents and Glassware

All glasswares and chemicals were prepared and maintained properly as stated in the US-EPA protocol [11]. Organic solvents and chemicals used were of AR grades and used without further purification. The 1000 mg/L TLC standard mixture of 18 OCPs and C-18 endcapped SPE cartridges (1g/6mL size) were purchased from local deliver of Supelco. 200 ng/mL stock solutions were prepared and diluted into several concentration levels of working solutions for the purpose of method validations and instrument calibrations.

Sampling and Parameter Measurements

Sampling was carried out during July 2006–February 2007. Water samples were taken from different locations of the 3 major rivers (Saiburi, Patani and Tiba River). Sub-surface waters (about 1 m below surface) were collected using a 4.0 liters amber bottle and kept in ice chest before being transported into analytical laboratory for further analyses. Several physical parameters of water such as temperature and pH were measured on sites. For turbidity, conductivity and total suspended solid (TSS) were determined using instruments in analytical laboratory. Total suspended solid content was determined by filtering water samples using 0.22 μm membrane filter with the help of vacuum suction. The concentration of oil and grease was determined by gravimetric method and reported as hexane extractable material (HEM) and silica gel treated hexane extractable material (SGT-HEM).

Sample Preparation and Extraction

Prior to extract, endcapped C-18 SPE cartridge was cleaned by eluting with 10 mL hexane and acetone (in 1:1 ratio) and conditioned with 10 mL methanol. 1.0 L water sample was filtered using 0.22 μm membrane filter and then acidified with 5 N HNO_3 to $\text{pH} < 2$. Simultaneous extraction of OCP residues from water samples were carried out at the flow rate of 10 mL/min and manifold pressure of -15 inHg. After extraction, SPE cartridges were dried by nitrogen flow at the pressure of 5 Psi for 30 minutes. The dried cartridges were eluted with 3 mL solvent mixture of hexane: acetone (1:1ratio). The eluent was then adjusted into exactly 1 mL by blowing down with a gentle stream of nitrogen gas and kept at 4 $^{\circ}\text{C}$ for further GC-ECD analyses.

GC analysis

A Varian 3600 Cx gas chromatograph (GC) equipped with electron captured detector (ECD) was used for the analysis of 18 OCPs. 1 μL sample was injected (splitless for 2 minutes) with the help of 8200 Cx autosampler (sandwich injection technique). The analytes were separated on SPB-5 capillary column (30 m x 0.25 mm i.d. x 0.25 μm film thickness). The column oven was programmed from 120 $^{\circ}\text{C}$ (maintained for 1 min) increased to 195 $^{\circ}\text{C}$ at 15.0 $^{\circ}\text{C}/\text{min}$ (maintained for 0.5 min), from 195 $^{\circ}\text{C}$ to 240 $^{\circ}\text{C}$ at the rate of 4.7 $^{\circ}\text{C}/\text{min}$ and held at the final temperature for 4.82 minutes. The temperature of injection port and ECD detector were set at 250 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. All data were processed and quantified by external standard of five point calibrations with correlation coefficients of all calibration curves were greater than 0.99. The instrument limit of detection (LOD) and limit of quantification (LOQ) for 18 OCPs were ranging from 0.005 to 0.035 ng/mL and 0.015 to 0.106 ng/mL, respectively.

In most cases, the recovery results for this multicomponents mixture were within the acceptable range of 70% to 130 % [12]. Method blanks were analysed with each set of real samples to verify the absence of interferences from either sorbent material or eluting solvent used. The standard mixtures of 18 OCPs used for calibration

purposes were routinely checked for area counts in order to maintain a proper concentration during quantifications.

RESULTS AND DISCUSSION

Physical parameters

The parameters of waters measured during this study are summarised in Table 1. In general, the analytical results of water parameters in the respective rivers are still within the acceptable values according to the standard water quality criteria for natural inland water of Thailand [13]. pH values, for example, all water samples measured during this study were within the Water Quality range of pH 5.0-9.0. As for other parameters such as TSS and temperature were also not exceed the maximum level as stated in the standard quality criteria.

Table 1. Some physical parameters of water samples collected from the 3 major rivers

parameters Rivers	Temperature (°C)	pH	turbidity (NTU)	TSS (mg/L)	conductivity (uS/cm)	HEM (mg/L)	SGT-HEM (mg/L)
1. Saiburi River (5 locations)	27.7-28.5 (27.9±0.5)	7.2-7.5 (7.3±0.1)	8.1-21.8 (16.3±6.5)	13.4-22.9 (18.3±4.3)	38-132 (65.3±44.7)	0.1-1.2 (0.6±0.5)	0.1-0.5 (0.2±0.2)
2. Pattani River (5 locations)	28.3-29.4 (28.9±0.5)	6.6-6.8 (6.7±0.1)	16.0-26.4 (19.9±4.3)	27.0-63.0 (39.5±14.9)	73-85 (78±4.5)	0.1-0.9 (0.5±0.4)	<0.1 (-)
3. Tiba River (4 locations)	29.4-30.2 (29.8±0.4)	6.8-9.1 (7.5±1.1)	7.4-46.9 (25.7±18.7)	13.2-31.8 (19.6±8.3)	22-157 (98±56.6)	0.7-2.2 (1.6±0.7)	0.7-2.2 (1.3±0.6)

(X±SD): mean and standard deviation values

For the concentrations of oil and grease in terms of HEM and SGT-HEM, Tiba River waters were found to be more contaminated than either Saiburi or Patani River. Oil and grease detected in Tiba River were classified as non-polar hydrocarbons or SGT-HEM. However, the contamination levels of oil and grease found in this study were not exceed the maximum level of 10 mg/L as recommended by Department of Pollution Control, the Ministry of Science Technology and Environment of Thailand. On the other hand, the pollution levels of oil and grease in Saiburi and Patani River were found to be at trace concentration levels.

OCP residues

The individual concentrations of 18 OCP residues in river waters from Saiburi, Patani and Tiba River are summarised in Table 2. Overall, water samples collected from Saiburi River were found to be highly polluted with OCPs compared to other two rivers. Surprisingly, p, p'-DDE which is a breakdown product of p, p'-DDT was detected in all analysed samples at the range concentrations of up to 9.60-203.10 ng/mL. As for p, p'-DDT and p,p'-DDD were detected in one sample at the concentration of 0.40 and 3.90 ng/mL, respectively. High levels of p, p'-DDE detected in this river suggested that p, p'-DDT, a parent compound of p, p'-DDE, was widely applied in this area. Other agricultural pesticide residues detected in almost all water samples from Saiburi River were β-HCH, γ-HCH, endosulfan I, heptachlor epoxide, endrin aldehyde and methoxychlor at the wide range concentrations.

Table 2. Summary of OCP residues detected in river water samples collecting from different sampling locations of the respective rivers.

OCP residues (ng/mL)	Saiburi River (5 sampling locations)	Patani River (5 sampling locations)	Tiba River (4 sampling locations)
α -HCH	ND	0.65-2.09 (1.36)	1.81-2.85 (2.33)
β -HCH + γ -HCH	0.20-0.36 (0.27)	0.82-7.52 (3.72)	0.60*
δ -HCH	0.43*	0.27-0.30 (0.29)	1.85*
Heptachlor	1.31*	0.50-2.96 (1.44)	ND
Heptachlor epoxide	0.31-1.12 (1.11)	0.74-3.61 (1.70)	0.50-0.97 (0.74)
Aldrin	ND	1.85*	3.30*
Dieldrin	ND	0.28*	ND
Endrin	0.06-1.10 (0.44)	0.89-1.74 (1.19)	2.50*
Endrin aldehyde	1.01-1.34 (1.22)	0.14-0.40 (0.32)	0.33-0.90 (0.62)
Endrin ketone	0.07-2.90 (1.49)	0.14*	ND
Endosulfan I	0.22-3.02 (1.24)	0.38-1.62 (0.94)	ND
Endosulfan II	ND	ND	ND
Endosulfan sulfate	0.02*	ND	ND
P,p'-DDT	0.40*	ND	1.40-2.62 (2.01)
P,p'-DDD	3.90*	0.09-0.12 (0.11)	ND
P,p'-DDE	9.60-203.10 (67.18)	11.29*	12.81*
Methoxychlor	7.3-36.1 (22.16)	ND	ND
Total OCPs	468.94	52.19	33.17

ND: not detected, (x): mean concentration value, *: OCPs concentration detected in 1 sample.

The Patani River, the longest river in the southernmost of Thailand, was polluted with various agricultural OCP residues at wide variety concentration values. Among OCPs detected in almost all water samples were α -HCH, β -HCH, γ -HCH, endosulfan I, heptachlor, heptachlor epoxide and endrin aldehyde. The highest average concentration level (detected in 3 locations) of agricultural OCPs found in the Patani River water was β , γ -HCH, which was detected at the concentration between 0.82-7.52 ng/mL. The breakdown product p,p'-DDE was found in a sample from Sateng sampling location (in the area of Yala city) at the concentration of 11.29 ng/mL.

The concentration of total OCP residues detected in the Tiba River samples were lower as compared to those detected in either Patani or Saiburi River waters. The OCPs detected were mostly agricultural pesticide residues which widely used in surrounding areas. However, p, p'-DDT and its degradation products p, p'-DDD and p, p'-DDE were also detected in a few samples. The highest concentration level of OCP residues found in Tiba River waters was p, p'-DDE (at Lamplai bridge sampling location) at the concentration of 11.29 ng/mL.

In most case, the concentration of OCPs detected in the present study were comparable with those detected in several major rivers in the west coast of the Peninsula Malaysia as reported by Tan and co-workers [14]. According to their report, Muda river waters were contaminated with various OCP residues such as endrin, endosulfan and HCHs at the concentration of 4.94, 6.86 and 2.02 ng/mL, respectively. As for DDTs (included p, p'-DDD and p, p'-DDE) was reported to be 1.76 ng/mL. Whereas our study showed that DDTs detected in the 3 major rivers, especially in Saiburi River waters were much higher concentration levels than those report for Muda River. However, the highly contaminated fresh water in Saiburi River with p, p'-DDE required more comprehensive informations in order to assess the current status of contamination explicitly.

CONCLUSION

The results of this study showed that major rivers in southernmost of Thailand were slightly polluted with various kinds of OCPs as well as agricultural pesticides and metabolite product of vector control chemicals such as p, p'-DDE. The level of total OCPs quantified in the Patani and Tiba River were not exceed the maximum

level of total OCPs in natural inland water of 50 ng/mL as recommended by the standard water quality criteria of Thailand. Overall, river waters in the major rivers of southern Thailand are classified as natural inland water Class II which required several treatments before being used.

Acknowledgement

The authors would like to acknowledge Faculty of Science and Technology, Yala Rajabhat University, Thailand for providing the research grant for this study. Acknowledgement is also to the School of Chemical Sciences, UNIVERSITI SAINS MALAYSIA, Pulau Pinang, Malaysia for supporting SPE drying manifold used in analytical experiment.

References

1. UNEP/GEF. 2002. *Regionally Based Assessment of Persistent Toxic Substances: South East Asia and South Pacific Regional Report*. United Nations, Geneva, Switzerland. p 1-53.
2. Supelco. 1996. Instructions for assembling and using Visiprep and Visiprep-DL solid phase extraction vacuum manifolds. Bellefonte, PA, USA.
3. Tanabe, S. 2002. Contamination and toxic effects of persistent endocrine disrupters in marine mammals and birds. *Marine Pollution bulletin*. 45: 69-77.
4. Ibrahim, M.S., Jacinto, G., Connell, D. and Leong, L.K. 2002. Regionally based assessment of persistent toxic substances region VIII – Southeast Asia & South Pacific. *Proceeding of Workshop on Environmental Monitoring of Persistent Organic Pollutants (POPs) in East Asian Countries*. 2nd – 4th December 2002. Tokyo. p 146-154.
5. Boon-Long, J. 1997. Managing POP in Thailand. *Proceeding of the Sub-regional Awareness Raising Workshop on Persistent Organic Pollutants*, Bangkok, Thailand. 25-28 November 1997.
6. Ruangwises, S., Ruangwisen, N. and Tabucanon, M. 1994. Persistent organochlorine pesticide residues in Green Mussels (*Perna viridis*) from gulf of Thailand. *Marine Pollution Bulletin*. 28 (6): 351-355.
7. Everaarts, J.M., Bano, N., Swennen, C and Hillebrand, T.J. 1991. Cyclic chlorinated hydrocarbons in benthic invertebrates from three coastal areas in Thailand and Malaysia. *Journal of Science Society of Thailand*. 17: 31-49.
8. Yala malaria centre. 1998. *Report on the use of DDT for malaria vector control in southern border provinces in 1997*. Department of Communicable Disease Control, Ministry of Public Health. Thailand. (in Thai).
9. The water quality of Saiburi River. 2006. [Online], [Accessed 17th April 2006]. Available from World Wide Web: <http://www.iwis.pcd.go.th>.
10. Hajisamoh, A. 2006. *Determination of Persistent Organic Pollutants (POPs) in the Patani Bay, Thailand*. Ph.D. thesis, UNIVERSITI SAINS MALAYSIA (USM).
11. US-EPA. 1995. Method 1664: *N-Hexane extractable material (HEM) and silica gel treated N-Hexane extractable material (SGT-HEM) by extraction and gravimetry (Oil and grease and total petroleum hydrocarbon)*. Washington: Engineering and Analysis Division. p 1-24.
12. US-EPA. 1996. Method number 3540A, SW-846: *Testing methods for evaluating solid waste*.
13. Department of Health Affairs. (1997). *Manual of Water Quality Analysis*. Ministry of Public Health, Bangkok, Thailand.
14. Tan, E.C. 2001. *Development of Analytical Method for Persistent Organic Pollutants in Fresh Water Using Solid Phase Extraction*. Ph.D. Dissertation, University Sains Malaysia.