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Contamination of Organotin Compounds in Coastal Water of Southern Thailand

Abdul Naser Hajisamoh[1,*], Mohd Nur E Alam Siddique[2], Pawan Raj Shakya[3]

[1]Department of Chemistry, Yala Rajabhat University, Yala, Thailand
[2]Department of Chemistry, Dhaka Women's College under National University, Dhaka, Bangladesh
[3]Department of Chemistry, Padma Kanya multiple Campus, Tribhuvan University, Bagbazar, Kathmandu, Nepal
*Corresponding author: nasir_2002@yahoo.com

Abstract In this study, the determination of concentration of butyltin compounds (BTs), namely tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) were determined in surface sediment samples collected from 9 major fishery ports along the coastal area of Songkla, Pattani and Narathiwat province, southernmost of Thailand. Sampling was carried out during the year 2011-2012 and analyzed the above compounds for their possible sources and distribution in this area. The analytical results showed that TBT was commonly detected as a major pollutant at higher concentration levels than either DBT or MBT. Overall, sediment samples collected from Pattani and Songkla sampling locations were more polluted with TBT at higher concentrations than other locations. Pattani sampling locations were found to have the highest pollution level of total BTs, especially TBT detected as the major pollutant ranging from 56.92 % to 64.63 %. These findings showed that the degradation rate of TBT to the breakdown product of DBT and MBT was going on at very slow, which may associate with several parameters in the study area.

Keywords: *Butyltin, coastal water, GC-FPD, Southern Thailand*

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1. Introduction

Organotin compounds have been developed into important commodities for several industrial activities worldwide since the 1960s [1]. Tributyltin (TBT) was used an antifouling agents in paints applied on boats, lumber preservatives and slimicides in cooling system. Dibutyltin (DBT) was used as stabilizer for polyvinylchloride (PVC) production and catalyser in some industrial process [2]. The deleterious effects of TBT released by antifouling paints were first documented in Arcachon Bay (France) at the end of the 1970s [3]. Coastal water pollution by BTs from antifouling paints has been of great concern in many countries including South-East Asia region due to their deleterious effects on marine animals, especially imposex (the phenomenon whereby male sex characteristics are induced and leading to sterility in female), even at trace concentration level of ng/L TBT [4,5]. TBT is degraded to DBT, followed by MBT and finally to inorganic tin, through biotic and abiotic reaction. While inorganic form of Sn is considered to be nontoxic, toxicological pattern of organotin compounds is complex depending on the nature of organic groups reacted to the Sn cation [6]. Several studies reported that contamination of TBT in seawater at very low concentration of 1-2 ng/L, can pose serious effects to wide number of non-target marine animals, such as imposex in gastropods, shell- thickening and spat failure in oyster and other known toxic effects induced by this toxic pollutant occurred at trace concentration [7,8]. A study to assess effect of TBT contamination with mussel growth rate in sediment revealed that a possible effect on mussel growth rate occurred as TBT contamination in sediment was higher than 2.5 µg/g dry wet [9].

Base on these adverse effects on aquatic organisms and coastal ecosystem, the use of TBT antifouling paint has been restricted and partial regulated in many developed countries, e.g. France, United Kingdom, Switzerland, New Zealand and Japan [10]. However, the Asian countries, such as Thailand, Malaysia, Singapore and Indonesia, have carried out study surveys to assess environmental impacts of these toxic pollutants [11]. Meanwhile, an increase in the demand for antifouling paint is predicted in this region, as their aquatic environment may be exposed to these toxic pollution. Several studies have reported the TBT contaminations in various environmental compartments such as sea water, sediment and bivalves from Malaysia [12], Indonesia [13] and coastal water of upper gulf of Thailand [14,15]. These observations indicate that Butyltin compounds were widespread contaminated in the coastal water of south-east Asian region. To our knowledge, an extensive survey has not been conducted to elucidate BTs contamination levels in coastal water of southernmost of Thailand, covering coastal area of Songkla, Pattani and Narathiwat province. Due to comprehensive data on organic pollutant contaminations, especially BTs pollutions are very scarce and the widespread presence of BTs in natural coastal water,

particularly in southernmost of Thailand, is of significant concerns as they can pose adverse effects to natural environments. Hence, this study would be the first effort to determine current status of butyltin contaminations in coastal water of the southernmost of Thailand, which is very important to the local communities and sustainability of aquatic environment.

The main objective of the present study was to assess the contamination levels of butyltin residues (TBT, DBT and MBT) in surface sediment samples from major fishery ports along coastal area of Songkla, Pattani and Narathiwat province. In order to specify the pollution sources of these toxic substances, TBT and its degradation products, DBT and MBT were determined in sediment samples from respective sampling cites.

2. Materials and Methods

2.1. Chemicals and Glassware Preparation

Glassware and chemicals used for experimental purpose were prepared and maintained properly as stated in the US-EPA protocol [16]. Organic solvents and chemicals used in our laboratory analysis were of AR grade and used without further purification. Organometallic butyltin chloride standard was purchased from AccuStandard, Inc (USA). Organic solvents and other chemicals used throughout this study were from J.T. Backer and Merck, Inc. The standard solution of butyltin compounds was prepared and diluted into several concentration levels of working solutions for performing method validations, instrumental calibrations and quantification.

2.2. Study Area and Sampling

Sampling was carried out during a period of August, 2011 to June, 2012. Sediment samples were collected from 9 fishing boat piers or ports along coastal area of 3 southern provinces of Songkla (3 locations; SK1, SK2 and SK3), Pattani (4 locations; PN1, PN2, PN3 and PN4) and Narathiwat (2 locations; NT1 and NT2) as shown in Figure 1. The exact position of each sampling station was recorded using global position system device (GPS). Surface sediment samples were collected in triplicates with Eckman-Barge grab sampler. The samples from each location were pooled, mixed, stones and pebbles removed and collected to 500 g. Then, approximately 50 mL of 37 % formaldehyde solution was added to avoid biological degradation of BTs during storage. The samples were then put in polyethylene bags, stored in ice chest. After returning to the analytical chemistry laboratory, Science and Applied Science center, Yala Rajabhat University (YRU), they were kept in a freezer at -20 ^{0}C until analysis.

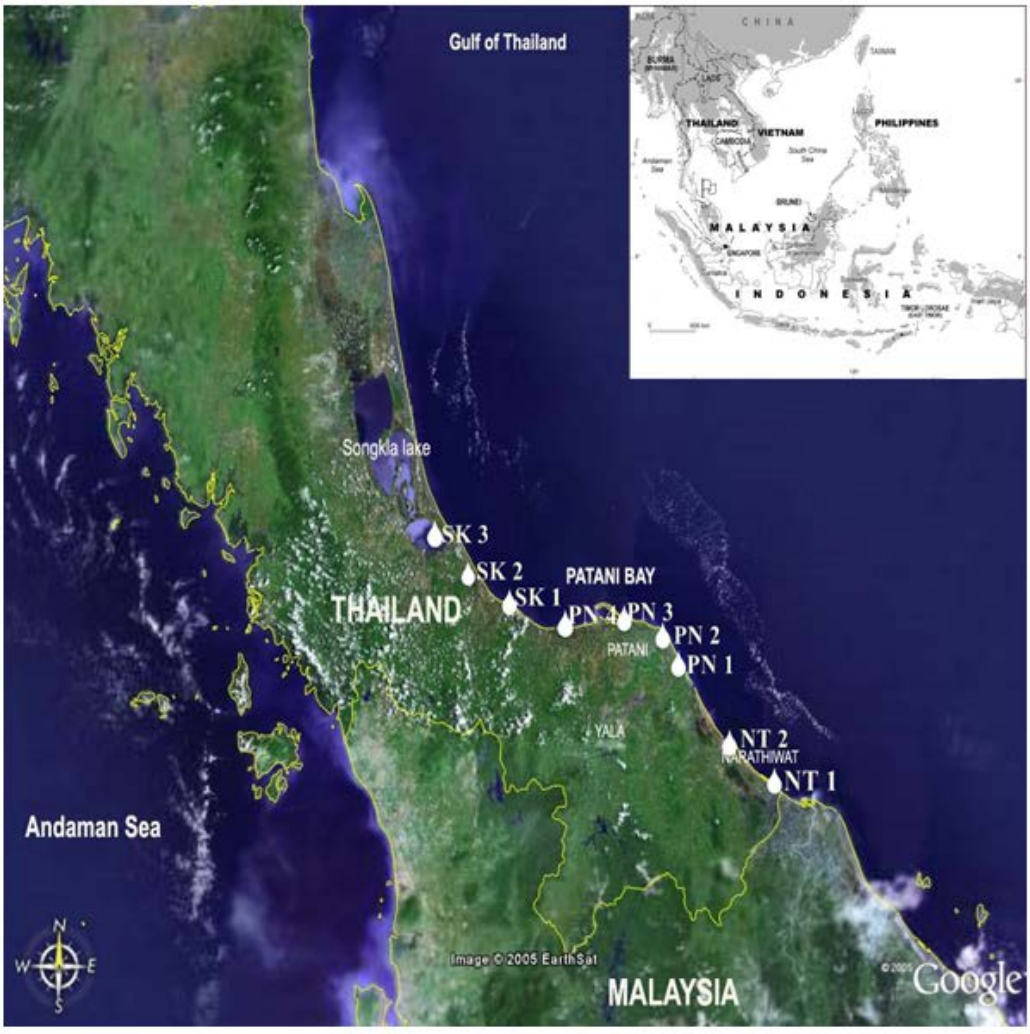

Figure 1. Map showing 9 sampling locations on the eastern coast of southernmost of Thailand

2.3. Sample Preparation and Extraction

The chemical analysis of BTs was carried out following the method of Iwata *et al.* [17] with slight modification to suit conditions in our laboratory. Briefly, extraction of BTs from 10.0 g of wet sediment was carried out with 30 mL of 1 % tropolone-acetone and 5 mL of 2 N HCl followed by shaking for 15 minutes. The extracts were centrifuged at 2500 rpm and supernatants were transferred to 0.1 % tropolone-benzene. Moisture in extract was eliminated by adding 30 g of Na_2SO_4, concentrated to dryness by rotary evaporator (45°C) under reduced pressure and taken up in approximately 5 mL of benzene. BTs in extract were propylated by addition of 5 mL n-propylmagnesium bromide (2 M in THF solution) and shaken at 40°C for 30 minutes. Unreacted Grignard reagent was removed by adding 20 mL of 1M H_2SO_4. The extracts were then cleaned up through hot florisil column by eluting with hexane. The final eluent of hexane extracts were concentrated to exactly 5 mL. The moisture content of sediment samples was determined to express the analytical results on a dry weight basis.

2.4. Instrumental Analysis

A Varian 3600 Cx gas chromatograph (GC-FPD) with 610 nm tin mode filter was used for BTs quantification. Sample was injected (splitless for 2 minutes) with the help of 8200 Cx autosampler (sandwich injection technique). The analytes were separated on DB-1 capillary column (J&W Scientific Co., Ltd, 30 m x 0.25 mm i.d. x 0.25 µm film thickness). The column oven temperature was programmed from 80°C (maintained for 1 min) increased to 170°C at 15.0°C/min and then increased at the rate of 5°C/min to 210°C (1 min hold) and increased to the final temperature of 260°C at the rate of 15°C/min with final holding time of 7 minutes. The injection port and detector temperature were kept at 250°C and 300°C, respectively. Helium was used as the carrier gas at the flow rate of 2.0 mL/min. The analytical results of BTs concentration were reported as ng cation per gram dry weight of sample.

2.5. Quality Control

All data were subjected to strict quality control procedures. Method blanks were analyzed with each set of real samples to verify the absence of interferences during experimental. The concentration of working solutions was routinely checked for area counts in order to maintain a proper concentration during quantifications. To examine data quality obtained from the analytical procedure, 0.2 µg/mL of butyltin chloride compounds (TBT, DBT and MBT) was spiked in cleaned sediments and performed recovery experiments through the existing analytical procedures. Recoveries of TBT, DBT and MBT from spiked sediments (n=4) were within the acceptable range of 94±7 %, 85±22 % and 62±14 %, respectively. The calculated limit of detections (LOD) for TBT, DBT and MBT were 1 ng/g, 1.6 ng/g and 2 ng/g, respectively.

3. Results and Discussion

Table 1 shows the concentration ranges of butyltin compounds (ng/g dry wt) in sediment samples collected from coastal area of southern Thailand. The results showed that the pollution levels of BT compounds (TBT, DBT and MBT) in coastal sediments of southern Thailand were found to vary widely from locations to locations. High concentration levels of BT pollutants were found in the intensive boating activities of Pattani city (PN 3) and Songkla lake sampling cites (SK 3). The remaining 7 out of 9 locations were found to be lower levels of BT concentrations ranging from 2 to 74 ng/g dry wt. Overall, BT compounds detected in all sediment samples of this study were in the range of 2-593 ng/g dry wt. The Pattani city location (PN), the busiest fishing boats port in the southernmost of Thailand, was polluted with BT pollutants at variable concentration levels The highest mean concentration of total BTs detected in Pattani city location (PN 3) was 239.20 ng/g dry wt. Individual concentration of TBT, DBT and MBT analysed in this study survey were in the range of 3-280 ng/g, 1-110 ng/g and 1-203 ng/g, respectively. However, possible effect on mussel growth rate occurred as TBT concentration in sediment was higher than 2.5 µg/g dry wet, as reported earlier. Based on this information, our findings (TBT concentration ranges 3-280 ng/g dry wt.) are assumed to be unlikely to affect mussel growth rate.

Table 1. Concentration ranges of butyltin compounds (ng/g dry wt) in sediment samples collected from coastal area of southern Thailand in 2011/2012

Sampling locations	TBT	DBT	MBT	∑BTs
1. Narathiwat province; 2 locations				
NT 1: Takbai River Mouth (n=3)	4-12 (7.67±2.89)	1-9 (4.33±3.11)	2-7 (4.67±1.78)	7-28 (16.67±7.56)
NT 2: Bangnara River Mouth (n=3)	3-6 (4.67±1.11)	ND	1-3 (1.33±1.11)	3-9 (6.00±2.00)
2. Pattani province; 4 locations				
PN 1: Saiburi River Mouth (n=3)	10-21 (14.67±4.22)	ND-10 (5.67±3.78)	4-18 (10.33±5.11)	14-49 (30.67±12.22)
PN 2: Kuala Beruas (n=3)	ND-7 (3.00±2.67)	ND	ND-6 (2.00±2.67)	2-13 (5.00±5.50)
PN 3: Pattani City (n=5)	50-280 (118.40±70.48)	13-110 (45.60±29.12)	25-203 (75.20±51.12)	88-593 (239.20±149.48)
PN 4: Nong Chik (n=3)	3-10 (5.67±2.89)	ND	ND-5 (2.33±1.78)	3-12 (8.00±3.33)
3.Songkla province; 3 locations				
SK 1: Thepha River Mouth (n=2)	10-31 (20.50±10.50)	ND-24* (12.00±12.00)	7-19 (13.00±6.00)	17-74 (45.50±28.50)
SK 2: Pak-Bang (n=3)	3-27 (11.33±10.44)	ND-2 (1.00±0.67)	ND-16 (5.33±7.11)	5-43 (17.67±16.89)
SK 3: Songkla Lake (n=5)	17-90 (52.40±22.48)	9-32 (20.20±5.84)	12-43 (26.00±11.20)	38-131 (98.40±24.16)

ND: not detected; below detection limit, (x): mean concentration value,
∑BTs: total concentration of TBT, DBT and MBT
*: DBT concentration detected in 1 sample

Although the information on BTs use in southern part of Thailand is unclear, the presence of TBT in sediments from this study suggested that these pollutants were widely contaminated in coastal water of southernmost region of Thailand. The spatial distribution of BTs in sediments was apparently associated with boating activities, especially Pattani city and Songkla lake sampling location. On the other hand, TBT pollutions in sediments from small fishing boat and small local boat ports or coastal marine culture areas were found to be low concentrations. However, It was reported that the high levels of TBT contamination in coastal environments have been associated with boating activities where TBT-based antifouling paints were applied on boat hulls, and found within marinas, small boat harbours and adjacent to vessel repair facilities [18]. Our study revealed that high contamination level of TBT was found in sediment samples from location where far sea vessels and intensive fishing boat activities, such as Pattani City, Songkla lake, Takbai and Thepha River Mouth. This finding suggests that the major TBT pollution in coastal water of southernmost region of Thailand might be originating from antifouling paints used mainly on the hull of far sea vessels and medium to large fishing boats. In addition, high level of TBT in several fishing boat ports detected in this study may be implicit evidences of the wide use of TBT-based antifouling paints on fishing boat hulls in the southernmost of Thailand.

Among BT breakdown products, TBT was the most commonly detected in all sampling locations at higher concentration than either DBT or MBT derivatives as shown in Figure 2. The percentage proportion of TBT in total BTs was ranging from 45.05 % to70.88 %, whereas DBT and MBT were in the percentage range of 5.23-26.71% and 22.43-40.65%, respectively. Figure 2 showed the composition of TBT, DBT and MBT concentrations detected in sediment samples from 9 targeted sampling locations of the present study. Overall, percentage composition of TBT, DBT and MBT was on the average of 57 %, 13% and 30 % of total TBT, respectively.

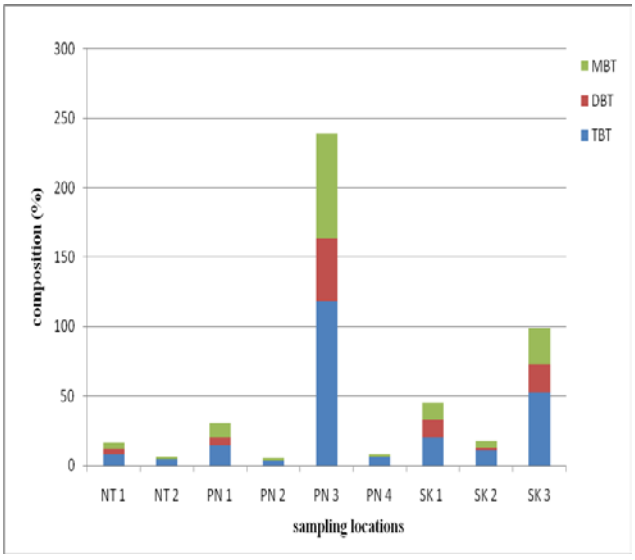

Figure 2. Composition of TBT, DBT and MBT concentrations detected in sediment samples

In most cases, the concentrations of BTs detected in the present study were comparable with several study surveys on pollution levels of BTs along coastal water of Thailand, especially a study conducted by Kan-Atireklap and his co-workers (1997) from several coastal areas in the upper gulf of Thailand. According to their study survey, Pattani sampling area at the Pattani river mouth was polluted highly with BTs at the concentration level of up to 1,630 ng/g dry wt. On the contrary, our present findings revealed that BTs pollution level in the same location was 593 ng/g dry wt, which is approximately three times lower than those reported from previous study survey. However, this study did not analyse BT pollution in water. A report presented by the Department of Pollution Control of Thailand (2004) revealed that coastal water in the area of Pattani river mouth was contaminated with TBT at the concentration of 14 ng/L, which exceeds the maximum level of 10 ng/L as recommended by Department of Pollution Control, the Ministry of Science Technology and Environment of Thailand.

4. Conclusion

It can be concluded from the present study that the coastal sediments in southernmost of Thailand were slightly polluted with TBT, DBT and MBT at variable concentration levels. TBT was found to be the most commonly detected in all sampling locations at higher concentration than either DBT or MBT derivatives. The higher pollution level of TBT in sediments from the Pattani and Songkla lake location did not exceed the critical level of 2.5 µg/g dry wet, which by this value of concentration can pose threat effect on the growth rate of living organisms in sediment and aquatic ecosystem. Further study on BTs pollution in coastal water is still required to determine current contamination status in order to avoid serious pollution problems in aquatic environment and to maintain environmental sustainability in this region.

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