Project Report

Status of persistent organic pollutants (POPs) in mangrove sediment from Bintan Island, Kepulauan Riau – Indonesia: contamination levels, spatial distribution, and ecological risk

Deny Yogaswara[1*], Ita Wulandari[1], Dede Falahudin[1,2], Shin Takahashi[2,3*]

[1]Research Center for Oceanography, Indonesian Institute of Sciences, Jalan Pasir Putih 1, Ancol Timur, Jakarta Utara, Indonesia

[2]Center for Marine Environmental Studies (CMES), Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

[3]Center of Advanced Technology for the Environment (CATE), Graduate School of Agriculture, 7 Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan

**Member of project stated in the proposal*

1. Introduction

Mangrove wetlands, located in intertidal and the tropical and subtropical regions, play a momentous role in the biogeochemical cycles of carbon, nitrogen, phosphorus, sulfur and other elements in coastal environment (Otero et al., 2014). Although mangrove ecosystems can provide important socio-economic value and ecological services for diverse fauna and flora (Nagelkerken et al., 2008), they are one of the most threatened tropical environment because often receive large amounts of heavy metals and organic pollutants from human activities on account of rapid urbanization and industrialization in coastal regions (Bayen, 2012). The recent paper reviews the occurrence, bioavailability and toxic effects of trace contaminants in mangrove ecosystem (Lewis et al., 2011). It has been reported that mangrove sediment act as important sinks/receivers for varieties of persistent organic pollutants (POPs) due their unique properties such as organic carbon content, poor oxygen and plentiful detritus (Bodin et al., 2011; Hu et al., 2019; Wu et al., 2017).

POPs are among the most well known as environmental organic contaminants and have been listed in under The Stockholm Convention due to their persistent, long-range transport, bioaccumulation and toxicity which along a few recent decades were made them as concern pollutants worldwide (UNEP, 2001). In addition, POPs able to be forms un-deliberately as by-products in some thermal industry and chemical manufacturing processes (Takahashi et al., 2020). POPs have been detected in many types of environmental compartments e.g. in sediment, soil, organism, air, and aquatic in every point of worldwide, even in remote areas such as deep ocean and polar areas (Takahashi et al., 2014). Bintan Island is small island in the Riau Archipelago and has large of mangrove ecosystem (Mujahidawati, 2018). The mangrove ecosystem is threatened by sinks of organic contaminants (POPs) from anthropogenic waste and oil spill from the coastal water because this island is crossed by international shipping lines (Yogaswara et al., 2019). However, POPs contaminants status in this ecosystem has not been investigated in the bottom sediment sink.

2. Aim of Study

The project in this proposal will determine the concentration, spatial distribution, and potential ecological risk of persistent organic pollutants (POPs) including PCB in mangrove sediment collected from Bintan Island, Kepulauan Riau - Indonesia.

3. Analytical Procedures

Study area and sediment sampling. *Mangrove sediments* were collected from selected mangrove forest in Bintan Island, Kepulauan Riau-Indonesia based on variation of location and potential anthropogenic contamination. In general, anthropogenic activities in both locations are dominated by tourism, shipping, and cargo line activities crossing the Malacca Strait. Thus, the coastal waters of North Bintan led to serious environmental pollution due to oil spilled, which occurs annually when north monsoon regime (Yogaswara et al., 2019). Sediment samples were collected using PVC coring (d:2.5 inches, l: 50cm) without disturbing the sediment–water interface and perpendicular to the waterline (landward, middle zone, and seaward) at mangrove sediments of Sprung Prei and Pengudang, Bintan Island, Riau Archipelago on 11 March 2018. Each station was selected based on the dominant species including *Rhizophora apiculata*, *Xylocarpus granatum*, and *Ceriops tagal* (Table 1). From each station, core samples were collected, vertically transported to the laboratory, sectioned into 5-cm layers up to 0–30 cm of depth, and stored at 4°C in ice box for further analysis in laboratory.

Table 1. Description of the sampling stations in this study

Station	Mangrove species	Location	Station description
SPRM-1	*R. apiculata*	Sprung Prei, Bintan	Near coastal of North Bintan
SPRM-2	*X. granatum*	Sprung Prei, Bintan	Middle layer of mangrove forest
SPRM-3	*C. tagals*	Sprung Prei, Bintan	Near mainland of urban area
PGDM-1	*R. apiculata*	Pengudang, Bintan	Near coastal of North Bintan
PGDM-2	*X. granatum*	Pengudang, Bintan	Middle layer of mangrove forest

Chemical analysis. Analysis of the samples followed method applied by Takahashi et al. (2020). In this report, surface layer (0-5 cm) of sediment was determined for PCBs contamination. Each freeze-dried sediment sample (about 2 g) was thoroughly mixed and ground with about 12 g of anhydrous sodium sulfate and then directly Soxhlet extracted with toluene for 8 h at an extraction rate of 6 min per cycle. The crude extract was evaporated until

10 mL and kept in the test tube. A portion of extract about 5 mL which corresponding to 1 g of sample in toluene was transferred into Syncore tube, spiked with $^{13}C_{12}$-PCB surrogate standards of PCBs (PCB-LCS-H; Wellington Laboratories, Inc., Japan), evaporated and solvent-exchanged into hexane. Before clean-up, extract in 5 mL hexane was treated with reduced copper granules to remove elemental sulfur for 1 hours, concentrated until 0.3 mL, and clean-up with semi-automated clean-up system (RAPiANA®, Miura Co., Ltd., Japan). The elute was concentrated under a gentle stream of nitrogen, and spiked with internal standards of PCB-ISS-H from Wellington Laboratories, Inc., Japan ($^{13}C_{12}$-PCB-9, -37, -79, -111, -162, -194, and -206) before GC/MS quantification. Chemicals and solvents used in this study were reagent grade for the determination of PCBs and purchased from Wako Pure Chemical Industries, Ltd.

Instrumental analysis for PCBs. PCBs (209 mono- to deca-chlorinated congeners) were quantified using a 6890N gas chromatograph (Agilent Technologies) connected to a JMS-800D high resolution mass spectrometer (JEOL). The separation was performed on a HT8-PCB capillary column (60 m length × 0.25 mm internal diameter × 0.25 μm film thickness, Kanto Chemical). Helium was used as carrier gas at a constant flow of 1 mL min^{-1}. Inlet temperature was 280 ^{o}C. A sample volume of 1 μL was injected in splitless injection mode. Column oven temperature was programmed from 120 ^{o}C, increased to 180 ^{o}C (20 ^{o}C min^{-1}), to 260 ^{o}C (2 ^{o}C min^{-1}), and ramped to 300 ^{o}C (5 ^{o}C min^{-1}, hold 4 min). Mass spectrometer was operated in positive electron ionization (EI) mode at a resolution of ≥ 10,000 at 10% valley. Ionization energy was 38 eV and acceleration voltage was 10 kV. Temperature of interface and ion source was 280 ^{o}C. Data were acquired in selected ion monitoring (SIM) mode using two molecular ions for each native and $^{13}C_{12}$-PCB congener.

Sample quality assurance and quality control measures were conducted by analysis procedural blank in each batch of sample analysis, replicate standard and samples analysis, and analysis of sediment SRM. Recovery of SRM 1944 (NIST, USA) was between 59 to 102 % with RSD < 20%. Reported concentrations in this report were corrected by levels of detected compound in the blank samples.

4. Results and discussion

Concentration of PCBs in surface sediments

The concentration of the total 209 PCB in mangrove sediment from five sampling site in the Northern part of Bintan Island ranged from 2.1 to 4.7 ng g^{-1} dry weight (dw), with a mean value of 3.2 ng g^{-1} dw (Table 2). Representative PCBs including seven indicator PCBs were detected in all sediment samples, indicating widespread contamination by these compounds in the mangrove forest of Northern part of Bintan Island.

Table 2. Concentration of homolog PCBs in mangrove sediment from different sampling site

	SPRM-1	SPRM-2	SPRM-3	PGDM-1	PGDM-2
Mono-CBs	0.06	0.04	0.03	0.01	0.02
Di-CBs	0.99	0.42	0.39	0.33	0.46
Tri-CBs	0.94	0.46	0.30	0.21	0.26
Tetra-CBs	1.29	1.10	1.30	0.88	1.11
Penta-CBs	0.76	0.46	0.51	0.36	0.49
Hexa-CBs	0.53	0.46	0.51	0.32	0.49
Hepta-CBs	0.07	0.08	0.06	0.02	0.10
Octa-CBs	ND	ND	ND	ND	ND
Nona-CBs	ND	ND	ND	ND	ND
Deca-CBs	ND	ND	ND	ND	ND
Total 209 PCBs	**4.7**	**3.0**	**3.1**	**2.1**	**2.9**

Note: ND=Not detected

Accordingly, concentrations of indicator PCBs in the mangrove sediments ranged from 0.56 to 0.82 ng g^{-1} dw in Sprung Prei and 0.43 to 0.59 ng g^{-1} dw in Pengudang area (Table 3). The sites with the lowest level of contamination were found in mangrove forest area, near mainland of urban area in Sprung Prei. Whilst, the sites with the highest contamination were found in the mud flats in Sprung Prei mangrove forest area near estuary of North Bintan. It reveals that the contaminants predominantly source from riverine input and coastal waters that affected by tidal regime. Previous study reported that intertidal area plays important rule on distribution of organic contaminants in estuary (Zhao et al., 2012).

Table 3. Concentration of indicator PCB in mangrove sediments of Sprung Prei and Pengudang (ng.g^{1-} dw)

	SPRM 1	**SPRM 2**	**SPRM 3**	**PGDM 1**	**PGDM 2**	**Average**
CB-28	0.18	0.09	0.05	0.05	0.05	0.08
CB-52	0.18	0.12	0.12	0.08	0.13	0.13
CB-101	0.13	0.08	0.08	0.06	0.08	0.09
CB-118	0.07	0.05	0.04	0.04	0.04	0.05
CB-138	0.09	0.07	0.09	0.06	0.10	0.08
CB-153	0.16	0.14	0.16	0.11	0.16	0.15
CB-180	0.02	0.02	0.01	0.02	0.02	0.02
$\sum_7$PCBs	0.82	0.57	0.56	0.43	0.59	0.59

Comparison with other mangrove sediment from other study site worldwide, total 209 PCBs in this study were relatively low, such as in mangrove forest in Jobos Bay, Puerto Rico (0.42 to 1232 ng.g^{1-} dw) (Alegria et al., 2016) and Songhua River (0.59 to 12.38 ng.g^{1-} dw)

(Cui et al., 2016). On the other hand, the PCBs levels in this study relative high compared with the values reported in marine systems such as in coastline of Bahrain (0.004 to 0.881 ng.g^{1-} dw), as well in Beibu Gulf of China (ND to 0.22 ng.g^{1-} dw) (Kaiser et al., 2016). Ordinarily in sediment, previous study reported that characteristic of PCBs contamination could reflect the industrial and economic development processes, the control and regulation levels for organic contaminants, and the marks of anthropogenic activities (Cui et al., 2016). However, in mangrove forest of Sprung Prei and Pengudang area, industrial activities are less influence on PCBs contaminations. Therefore, the potential source of PCB contamination in mangrove forest in Bintan Island is long range transport of PCBs as reflect in profile of PCBs from current study.

Congener profiles and potential sources of PCBs

In this study, the homolog pattern of PCBs were generally dominated with tetra-CBs (34%) and followed by di-CBs (18%), penta-CBs (16%), tri-CBs (15%), hexa-CBs (14%), hepta-CB (2%) and mono-CB (1%). Higher homolog PCBs such as octa- to deca-CBs was not detected in all mangrove sediment (Table 3). However, proportion of homolog PCB was varied in each sampling site in this study. For example, in mangrove sediment from Sprung Prei area, percentage of major homolog PCB is tetra-CBs (31%), followed by di- and tri-CBs (19%), penta-CBs (16%), and hexa-CBs (13%), while in Pengudang area, the highest homolog PCB was similar even their percentage is more higher than in Sprung Prei (40%). After that, the second highest homolog PCBs was penta-CBs (17%) and followed by hexa-CBs (16%) and di-CBs (16%). Tri-CBs in mangrove sediment from Pengudang area is only 9%. Generally, organic substances in the sediment are affected the behavior of hydrophobic organic contaminants, deposition of atmospheric particulate, and particulate suspended matter (Cui et al., 2016). Therefore, in our case study, detected lower chlorinated biphenyl could be as indicator for long range transport of PCbs through atmospheric deposition or ocean transport.

Ecological Risk Assessment

Ecological risk assessment for PCBs in the sediment was determined based on potential ecological risk index (RI) adapted from Hakanson (1980) and Cui et al. (2016) with equations as follows:

$$RI = \sum_{r}^{i} E \qquad (1)$$

$$E_r^i = T_r^i C_f^i \qquad (2)$$

$$C_f^i = C_o^i / C_n^i \qquad (3)$$

Where RI is sum of eight parameter including PCB and seven heavy metals; E_r^i is potential ecological risk factor, T_r^i is the toxic-response factor for a given substance (e.g. T_r^i $f$or PCBs is 40, C_f^i is the contamination factor, C_o^i is the concentration of PCBs in the sediment, and C_n^iCn i is a reference value for PCBs (10 ng/g dw). Therefore, based on calculation with equation (1), (2), and (3), the potential ecological risk factors for each mangrove site in Pengudang and Sprung Prei area were at low potential ecological risk, with value of E_r^i below 40 (Hakanson 1980) (Figure 1).

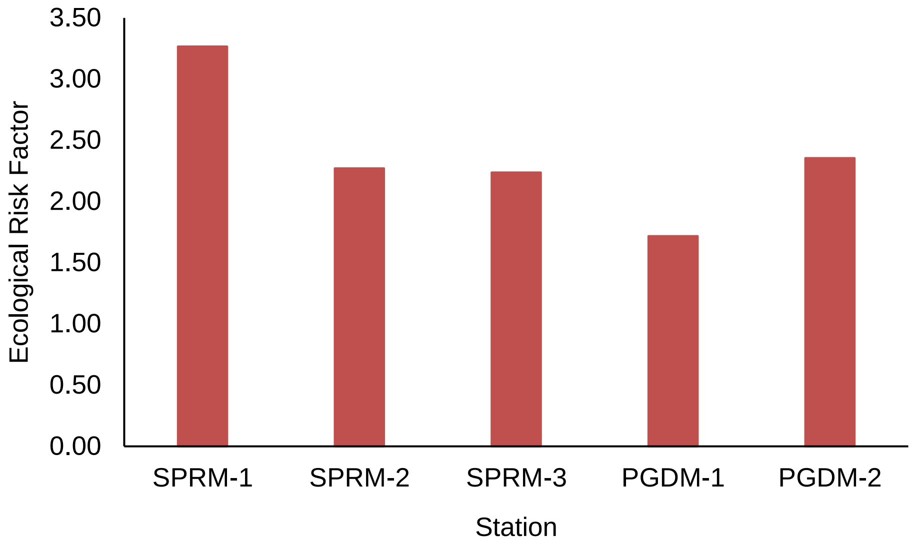

Figure 1. Potential ecological risk factor of PCBs in the mangrove sediment of Sprung Prei and Pengudang area

In addition, total PCB concentrations in present study were also lower if compare to threshold value of sediment quality guidelines (SQGs) from Canadian Council of Ministers of the Environment (CCME, 1999) with SQG for human health (SQG_{hh}) was 500 ng g^{1-} and SQG for environmental health (SQG_e) was 1300 ng g^{1-}. The assessment of ecological risk of PCB in the sediment is important way on estimation of a potential adverse effect of PCBs on the environment.

5. Perspectives in future

Chemical analysis is continued to determine PCBs and other potential emerging organic contaminants in the other surface sediment and core sediment from Bintan Island.

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