Project Title: Occurrence, levels and sources of PAHs, PCBs, PBDEs and Dioxins in Malaysian mangrove sediments and their possible ecotoxicological implications

Report Title: An assessment on the pollution levels of PCBs and PBDEs in mangrove sediments in Peninsular Malaysia

Principle Investigator (Malaysia): **Prof. Dr. Narayanan Kannan**

Affiliation: Postgraduate Research and Innovation and Strategic Development, Taylor's University (Lakeside Campus), No.1, Jalan Taylor's, 47500, Subang Jaya, Selangor Darul Ehsan, Malaysia.

Research Fellow: **Han Yeong Kaw**

Affiliation: Key Laboratory of Natural Resource of the Changbai Mountain and Functional Molecular (Yanbian University), Ministry of Education, Park Road 977, Yanji City, Jilin Province, 133002, China.

Introduction

Mangrove forests are regarded as one of the most unique ecosystem in the world. Mangroves play a significant role in protecting coastlines against erosive waves, remove toxic compounds through natural filtering processes, provide abundant natural resources and act as an important breeding ground for a variety of marine animals (WWF-Malaysia, 2016). There is approximately 641,886 hectare of mangrove forest in Malaysia, which is the second largest mangrove forest coverage in South-East Asia. Peninsular Malaysia accounts for about 17% of the total mangroves in Malaysia (Abd. Shukor, 2004), and 70% of it are categorised as permanent reserve forest (Kamaruzaman and Dahlan, 2009) (Figure 1). Unfortunately, the mangrove ecosystem in Peninsular Malaysia, particularly in the west coast along the Strait of Malacca with high anthropogenic activity succumb to pollution. Such pollution arising from urbanisation and development affect mangrove forests severely, at rates faster than their regeneration capacity (Bosire et al., 2003). According to a recent ecotoxicological study conducted by Krishnan et al. (2016) on mangrove sediments collected from various locations in Peninsular Malaysia using tetrazolium salt reduction (MTT) assays, mangrove ecosystem is under heavy toxic pressure.

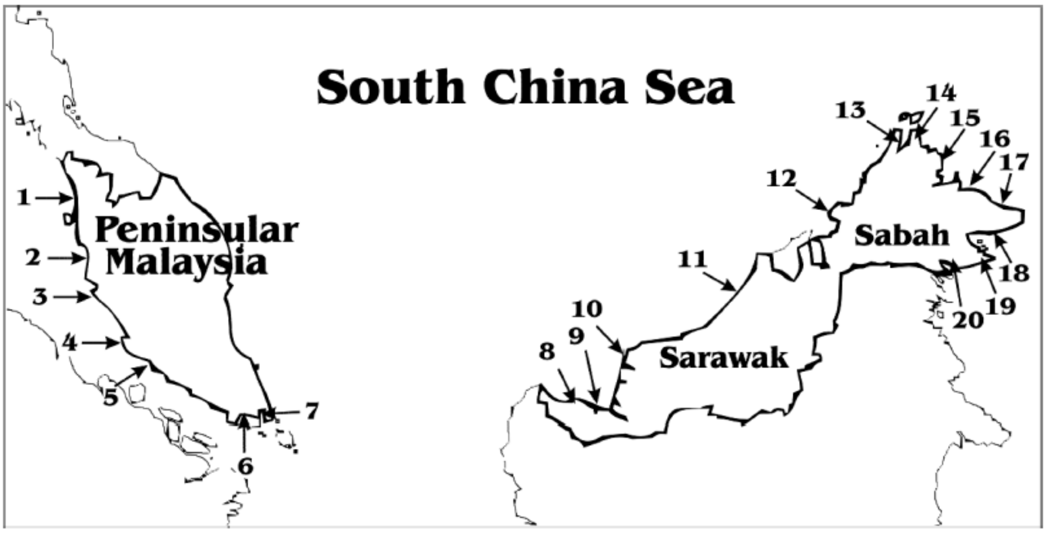

Figure 1. Map showing some of the major mangrove forest reserves in Malaysia. 1:Merbok; 2:Matang; 3:Rungkup and Bernam; 4:Klang; 5:Sepang and Lukut; 6:Pulai; 7:Sungai Johor; 8:Sungai Sarawak; 9:Kampung Tian; 10:Rajang; 11:Kuala Sibuti; 12:Menumbok; 13:Kudat and Marudu Bay; 14:Bengkoka; 15:Sungai Sugut and Sungai Paitan; 16:Trusan Kinabatangan; 17:Kuala Segama and Kuala Maruap; 18:Lahat Datu; 19:Segarong and Semporna; 20:Umas-umas, Tawau and Batumapun (Chong, 2006).

Methodology

Study Area

Nine mangrove areas in Peninsular Malaysia that located at the coastline facing the Strait of Malacca in the west and facing the South China Sea in the east were selected for investigation. The sediment sampling was carried out during May 2015 until July 2015 under low tide. At each location three sub-samples were taken at a distance of 15 to 40 meters. Figure 2 and Table 1 shows the latitude and the longitude of the sampling locations.

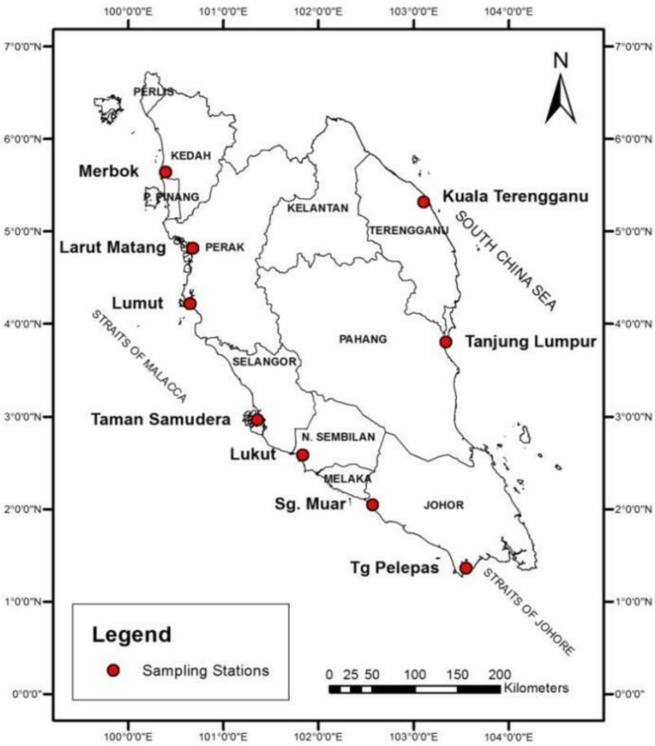

Figure 2. Location of the mangrove forests selected in this study.

Table 1. Details of the sampling sites

Site	Location	State	Longitude	Latitude	Surrounding activities
1	Larut Matang	Perak	4.84358	100.63317	Eco-tourism
2	Lumut	Perak	4.21846	100.64486	Residential area
3	Merbok	Kedah	5.68183	100.46875	Fisheries
4	Tanjung Pelepas	Johor	1.34829	103.56989	Domestic dumping site
5	Tanjung Agas	Johor	2.05510	102.56932	Industrial, commercial
6	Lukut	Negeri Sembilan	2.58571	101.82659	Industrial, fisheries
7	Pulau Indah	Selangor	2.94469	101.35795	Residential, industrial
8	Tanjung Lumpur	Pahang	3.80583	103.33459	Commercial, dumping site
9	Kuala Terengganu	Terengganu	5.32084	103.10193	Fisheries, boating

Sample Collection

Triplicate top surface sediment samples (1-5cm) were collected using stainless steel spoon at each of the nine mangrove forests in Peninsular Malaysia. The scrapped surface sediment samples were immediately transferred into amber glass container and stored at -20^{o}C until further analysis. All the sampling tools and apparatus were soaked in acid for at least 24 hours and rinsed with distilled water before use to avoid contamination. All sediment samples were freeze dried before chemical analysis.

Chemical Analysis

Approximately 7g of the freeze-dried sediments samples were extracted with a mixture of acetone/hexane (1:1 v/v) using a rapid solvent extractor (SE100, Mitsubishi Chemical Analytech) at a flow rate of 6ml min^{-1} at 35^{o}C for one hour. The extract was spiked with ^{13}C-labelled standards for PCBs and PBDEs. The spiked extract was treated with hexane-washed sulphuric acid (98%) and passed through a multi-layer silica gel column packed in a bottom-up order with deactivated silica (Wakogel® DX, Wako, 0.5g), KOH-impregnated silica (Wako, 3% KOH, 3g), deactivated silica (0.5g), and sulphuric acid-impregnated silica (Wako, 44% Sulphuric acid, 2g and 22% sulphuric acid, 6g), with hexane/DCM (3:1 v/v, 150ml) as eluant. The extract was then subjected to activated silica column clean up step using 5% DCM/Hexane (1:19 v/v, 80ml) as eluant. The extract was being treated with copper and then subjected to GC-MS quantification (Agilent 7890A GC; Agilent 5975C inert XL MSD).

Congener specific analysis of 31 PCBs (CB18, CB28, CB33, CB22, CB37, CB52, CB49, CB44, CB74, CB70, CB77, CB95, CB101, CB99, CB87, CB110, CB118, CB105, CB151, CB149, CB153, CB138, CB158, CB128, CB167, CB156, CB183, CB177, CB180, CB170, CB209) and 16 PBDEs (BDE28, BDE49, BDE47, BDE100, BDE99, BDE154, BDE153, BDE183, BDE201, BDE197, BDE203, BDE196, BDE208, BDE207, BDE206, BDE209) were carried out on sediment samples. Analysis of PAHs and Dioxins was not carried out on these samples as proposed in the original proposal due to time restriction, availability trainers, availability of research fellow's training schedule and finally on the availability instruments.

Result and discussion

The concentrations of

Levels (ng/g dry weight) of PCBs and PBDEs determined in mangrove sediments collected from Puninsular Malaysia are shown in figure 3. The highest value of PCBs concentration was recorded in sediments samples from site 6 (Lukut - 16.5 ng/g dry weight) and the lowest PCBs concentration was found at site 3 (Merbok). At site 8 (Tanjung Lumpur) and site 9 (Kuala Terengganu) no PCBs were detected. On the other hand, relatively higher concentration of PBDEs (169 ng/g dry weight) was found at site 5 (Tanjung Agas), followed by site 7 (Pulau Indah) and the lowest value was recorded at site 4 (Tanjung Pelepas). A map was generated to compare PCBs and PBDEs concentrations of mangrove sediments analysed in Malaysia. It is obvious that the concentration of PBDEs in all sites were higher than PCBs concentrations, particularly at Tanjung Agas, Lukut and Pulau Indah. The PBDEs were several magnitudes higher than PCBs. PCB-containing electrical equipment are not manufactured in Malaysia and the import has stopped on June 1998 (Hashim, 2003) Hence it is reasonable to observe low PCBs concentration than PBDEs. On the other hand, flame retardants (PBDEs) are used widely on electronic devices whose consumption increases constantly in Malaysia. In 2014, the electronic components sub-sector became the largest sub-sector with an approved investments of RM 5.8 billion (MIDA 2017). The most dominant PBDEs among the 16 PBDEs studies was PBDE 209, the deca PBDE. According to Kwan (2013) the sedimentary BDE-209 concentrations in Asia showed a trend toward higher concentrations in the more industrialized Asian countries, and were similar to or higher than those reported for highly urbanized and industrialized countries worldwide. Thailand, Cambodia, India, the Philippines and Malaysia are possible hot spot areas of PBDE pollution.

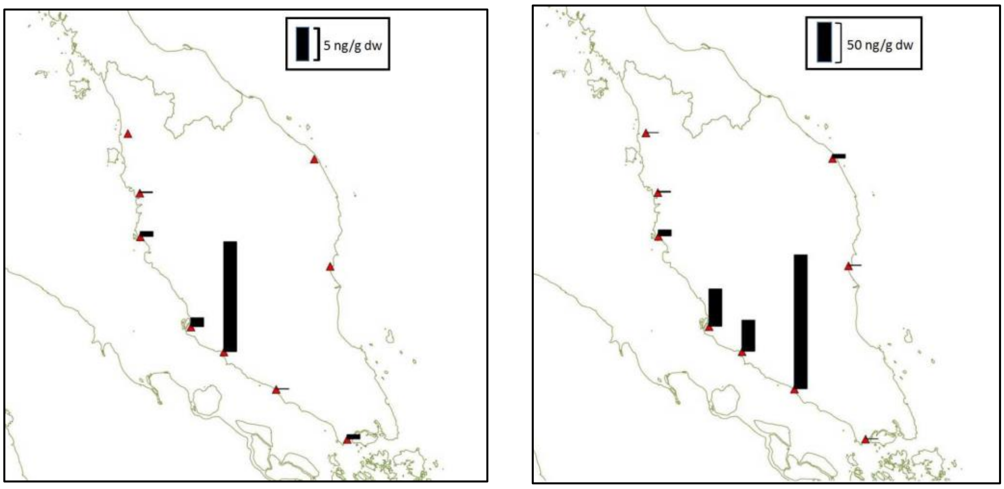

Figure 3. Maps showing PCBs concentration (left) and PBDEs concentrations (right) of mangrove sediment samples collected in Peninsular Malaysia.

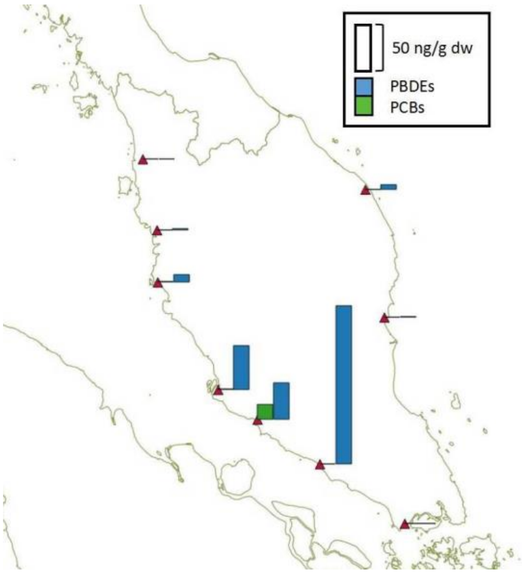

Figure 4. Comparison of the PCBs and PBDEs concentrations of mangrove sediment samples collected in Peninsular Malaysia.

The concentrations of PCBs and PBDEs in mangrove sediments collected from Peninsular Malaysia are compared with similar studies conducted elsewhere in Table 2. PCBs concentrations in Hong Kong and Singapore are comparable, however Indonesia shows several fold higher concentration. The PBDEs trend is similar to Malaysia. Kaw and Kannan (2016) observe that substantial studies on these chemicals in Malaysia need to be conducted to compare and assess the pollution level and impact.

Table 2. Comparison of the concentration of PCBs and PBDEs in surface sediments collected from mangroves in Peninsular Malaysia and other countries.

Site	Location	PCBs (ng/g dw)	PBDEs (ng/g dw)	Reference
1	Larut Matang	0.252	1.90	This study
2	Lumut	0.773	8.03	This study
3	Merbok	0	0.63	This study
4	Tanjung Pelepas	0.690	0.56	This study
5	Tanjung Agas	0.107	169	This study
6	Lukut	16.5	39.5	This study
7	Pulau Indah	1.433	47.3	This study
8	Tanjung Lumpur	0	0.877	This study
9	Kuala Terengganu	0	5.1	This study
	Singapore	0.59-1.86	<1	Bayen et al. (2005)
	Hong Kong	-	14.4/2.10*	Zhu et al. (2014)
	Indonesia	0.07-420	0.17-35	Ilyas et al. (2011)

*Concentration of PBDEs at two different mangrove areas in Hong Kong.

Conclusion

This project has initiated a research collaboration between Japan and Malaysia using LaMer, Ehime University, Matsuyama, Japan. Sediment samples were collected from Mangrove ecosystem and analyzed for PCBs and PBDEs. The analytical results indicated low PCBs levels but an increasing PBDEs, particularly Deca BDE. This trend needs to be established in the future, if samples of other matrices are collected and analyzed.

Reference

Abd. Shukor, A.H. (2004) The use of mangroves in Malaysia. In: Promotion of mangrove-friendly shrimp aquaculture in Southeast Asia. Aquaculture Department, Southeast Asian Fisheries Development Center, 2004, 136-144.

Bayen, S., Wurl, O., Karuppiah, S., Sivasothi, N., Lee, H.K., Obbard, J.P. (2005) Persistent organic pollutants in mangrove food webs in Singapore. Chemosphere, 61, 303-313.

Bosire, J.O., Dahdouh-Guebas, F., Kairo, J.G., Koedama, N. (2003) Colonization of non-planted mangrove species into restored mangrove stands in Gazi Bay, Kenya. Aquatic Botany, 76, 267-276.

Chong, V.C. (2006). Sustainable utilization and management of mangrove ecosystems of Malaysia. Aquatic Ecosystem Health & Management, 9(2), 249-260.

Hashim, R. (2003) PCBs situation in Malaysia. PCB Symposium 2003 in Malaysia. Retrieved from http://tabemono.info/report/former/pcd/2003/malaysia/e_1.html

Ilyas, M., Sudaryanto, A., Setiawan, I.E., Riyadi, A.S., Isobe, T., Takahashi, S., Tanabe, S. (2011) Characterisation of polychlorinated biphenyls and brominated flame retardants in sediments from riverine and coastal waters of Surabaya, Indonesia. Marine Pollution Bulletin, 62(1), 89-98.

Kaw, H.Y., Kannan, N. (2016) A review on polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in South Asia with a focus on Malaysia. Reviews of Environmental Contamination and Toxicology, 242, 153-181.

Kamaruzaman, J.; Dahlan, H.T., (2009). Managing sustainable mangrove forests in Peninsular Malaysia. Journal of Sustainable Development, 1, 88-96.

Kwan, C.S. (2013). Distribution and Debromination of Polybrominated Diphenyl Ethers (PBDEs) in Tropical Asian Countries. Retrieved from https://www.jsps.go.jp/english/e-ronpaku/data/data_fellows/FY2013/12_Philippines_KWAN,%20Charita%20Saloma.pdf on Feb. 28, 2017.

Krishnan, P., Kannan, N., Aris, A.Z., Arulselvan, P., Fakurazi, S. (2016) Possible application of bio-analytical assays in the biological impact assessment of persistent organic pollutants (POPs) in mangrove sediments in South East Asia with particular reference to Malaysia. American Chemical Society, 1244, 203-222.

MIDA (Malaysian Investment Development Authority) - Retrieved from http://www.mida.gov.my/home/electrical-and-electronic/posts/ on Feb.28, 2017

WWF-Malaysia (2016). Mangrove Forests. Retrieved from http://www.wwf.org.my/about_wwf/what_we_do/forests_main/the_malaysian_rainforest/types_of_forests/mangrove_forests/ on Feb.28, 2017

Zhu, H., Wang, Y., Wang, X., Luan, T., Tam, N.F. (2014) Distribution and accumulation of polybrominated diphenyl ethers (PBDEs) in Hong Kong mangrove sediments. Science of the Total Environment, 468-469, 130-139.