

Utilization of *es*-BANK of Ehime University for Monitoring Environmental Pollutants in Indonesia: A Case Study for Brominated Flame Retardants in Biota, Human and Environmental Samples

Agus SUDARYANTO^{1,2,3}, Iwan Eka SETIAWAN², Adi Slamet RIYADI²,
Muhammad ILYAS², Yudi ANANTASENA², Ridwan DJAMALUDDIN²,
Tomohiko ISOBE¹, Shin TAKAHASHI³ and Shinsuke TANABE³

¹*Senior Research Fellow Center (SRFC), Ehime University,
Bunkyo-cho 2-5, Matsuyama 790-8577, Japan*

²*Technology Center for Marine Survey, Agency for the Assessment and Application of
Technology (BPPT), JL. MH. Thamrin 8, Jakarta, Indonesia*

³*Center for Marine Environmental Studies (CMES), Ehime University,
Bunkyo-cho 2-5, Matsuyama 790-8577, Japan*

(Received 8 March 2010; accepted 23 April 2010)

Abstract—The concept of environmental specimen bank for archiving and retrospective analysis of biological and environmental samples has been recognized as an important component of systematic environmental monitoring and research programs. For example, well documented specimens that are preserved over long periods of time are valuable resources that can be used for future retrospective investigations and verification of previous studies that were carried out using such specimens. During the last decade, in collaboration with Ehime University, Technology Center for Marine Survey, Agency for the Assessment and Application of Technology (BPPT), Indonesia have conducted several sampling campaigns to collect various biotic and environmental samples for environmental monitoring in Indonesia, particularly for assessing the levels and risks of persistent toxic substances such as classical persistent organic pollutants (POPs) as well as emerging new contaminants such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). Due to limited sample storage and analytical capability in the country, the samples have been preserved and archived in environmental specimen bank (*es*-BANK) of Ehime University for further studies including analysis of various toxic pollutants. The present report aims at overviewing the findings made through those studies on the emerging new contaminants, the brominated flame retardants (BFRs) such as PBDEs and HBCDs in the environment of Indonesia by utilizing samples that have been stored in *es*-BANK of Ehime University.

Keywords: Environmental Specimen Bank, PBDEs, HBCDs, distribution and source, human exposure, fate and behavior, temporal variation, Indonesia

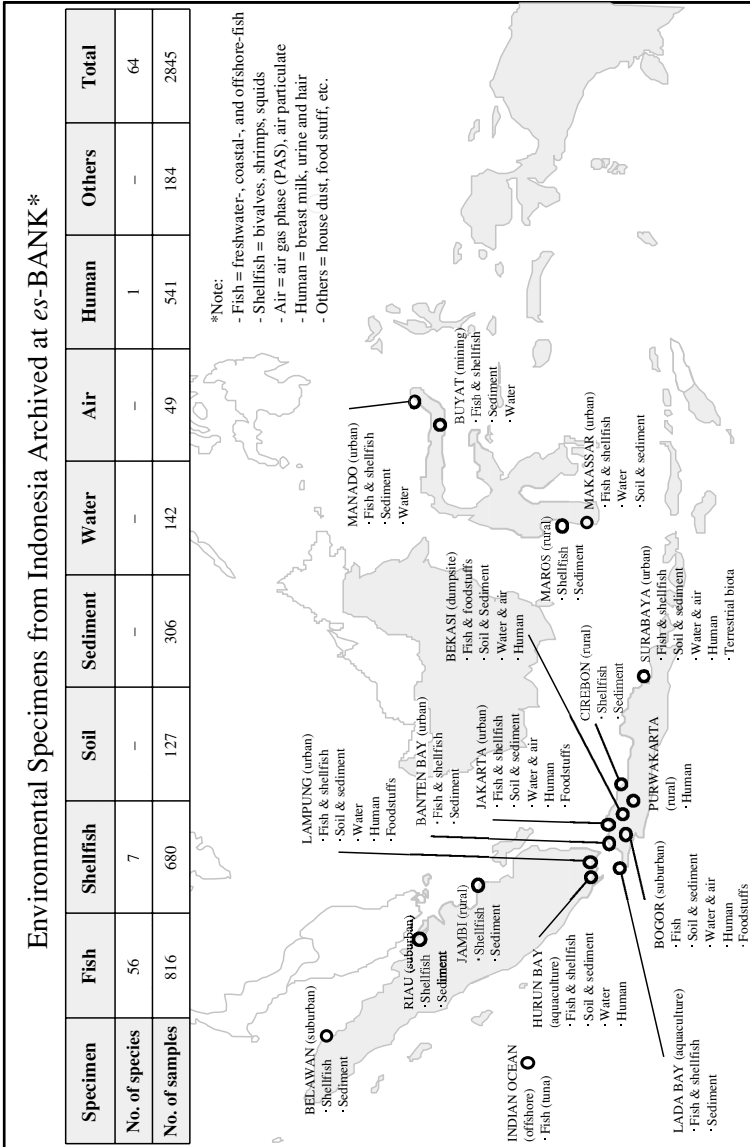


Fig. 1. Map showing sampling locations and environmental specimens from Indonesia archived at *es*-BANK of Ehime University.

BACKGROUNDS

During the last decade, through Center for Marine Environmental Studies (CMES), Ehime University—Agency for the Assessment and Application of Technology (known as BPPT in local abbreviation) research collaboration, we have conducted several sampling campaigns to collect various biotic and abiotic samples for environmental monitoring in Indonesia, particularly for assessing the levels and risks of persistent toxic substances. Due to limited sample storage and analytical capability in the country, the samples have been preserved and archived in environmental specimen bank (*es*-BANK) of Ehime University for global monitoring study of various toxic pollutants (Tanabe, 2006). The present report aims at overviewing the findings made through those studies on emerging new contaminants used in various consumer products (electrical and electronic equipments, polymer materials, textiles, etc.), the brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in the environment of Indonesia and compared with classical persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) by utilizing samples that have been stored in *es*-BANK to understand their distribution and source, human exposure, fate and behaviors and temporal trends. The data used in the present study was based on available information published in the literature.

ARCHIVING SPECIMENS FROM INDONESIA

Under several projects either from research collaboration between CMES and BPPT (Asia-Pacific Mussel Watch, Sustainable Environment for Fisheries, Marine Environmental Conservation, etc.) or national programs by BPPT, various samples including water, air, soil, sediment, dust, shellfish, fish, foodstuff and human matrices were collected during 1998–2009 at Indonesia representing areas such as urban, suburban, rural, aquaculture, dumpsite, mining area, terrestrial, coastal and offshore. Figure 1 is map showing sampling location of several environmental samples, biota and human matrices in Indonesia. In this figure, number of samples collected from Indonesia and achieved at *es*-BANK of Ehime University is also included.

CHEMICAL ANALYSIS

Analysis of BFRs and POPs were conducted in the Laboratory of Environmental Chemistry, CMES using GC-MS and LC-MS-MS following procedures described elsewhere (Sudaryanto *et al.*, 2008). For QA/QC, data from our laboratory were in good agreement with Standard Reference Materials.

RESULTS AND DISCUSSION

Distribution and sources

As those of organochlorine compounds (OCs) such as PCBs and DDTs (Monirith *et al.*, 2003; Ueno *et al.*, 2003; Sudaryanto *et al.*, 2005, 2007a),

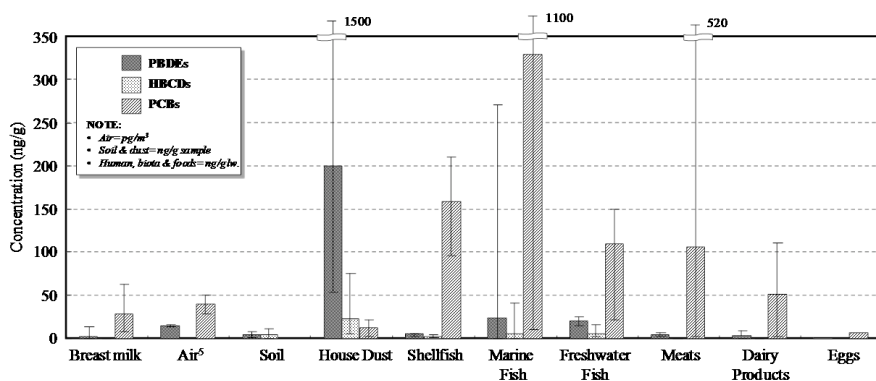


Fig. 3. Levels of BFRs and PCBs in various environmental media, fish and shellfish, food items and human breast milk.

their different usage patterns in Asia (Watanabe and Sakai, 2003). Higher concentrations of BFRs were found in the locations associated with high population, industry, and urban areas such as Jakarta Bay and Surabaya coastal areas (similar to PCBs but not for DDTs). Whereas, lower levels of PBDEs and HBCDs were found in the samples from rural/remote areas such as Lada Bay (Banten), Hurun Bay (Lampung), Maros (South Sulawesi) and offshore waters revealing from tuna data (Ueno *et al.*, 2004, 2006). In comparison with PCBs, the level of BFRs was lower.

Human exposure to BFRs

Preliminary human exposure to BFRs has been conducted through multimedia analysis of the samples collected from four locations representing urban, suburban and rural/remote areas (Wurl *et al.*, 2006; Sudaryanto *et al.*, 2008). BFRs and PCBs were detected in various environmental media (air, soil, and house dust), fish and shellfish, eggs, meats, dairy products, and breastmilk (Fig. 3), suggesting wide environmental contamination and human exposure to these compounds in Indonesia. Except in house dust, PCBs (which have longer pollutant history and larger amount of usage than BFRs) were found to be higher than PBDEs and HBCDs in all the samples. This result indicates a significant source of BFRs in the home environment.

Estimation of total intake of BFRs by adults (52 ng/day for PBDEs and 9.8 ng/day for HBCDs) was lower than that of PCBs (560 ng/day), and agrees well with the body burdens estimated from breast milk concentrations (Sudaryanto *et al.*, 2008). Compared to PCBs (<0.20%), contribution by non-dietary intake of BFRs by adults was much larger (17% for PBDEs and 12% for HBCDs). For toddlers, the contribution by dust ingestion to total intake of BFRs was greater than for adults (41% for PBDEs and 36% for HBCDs).

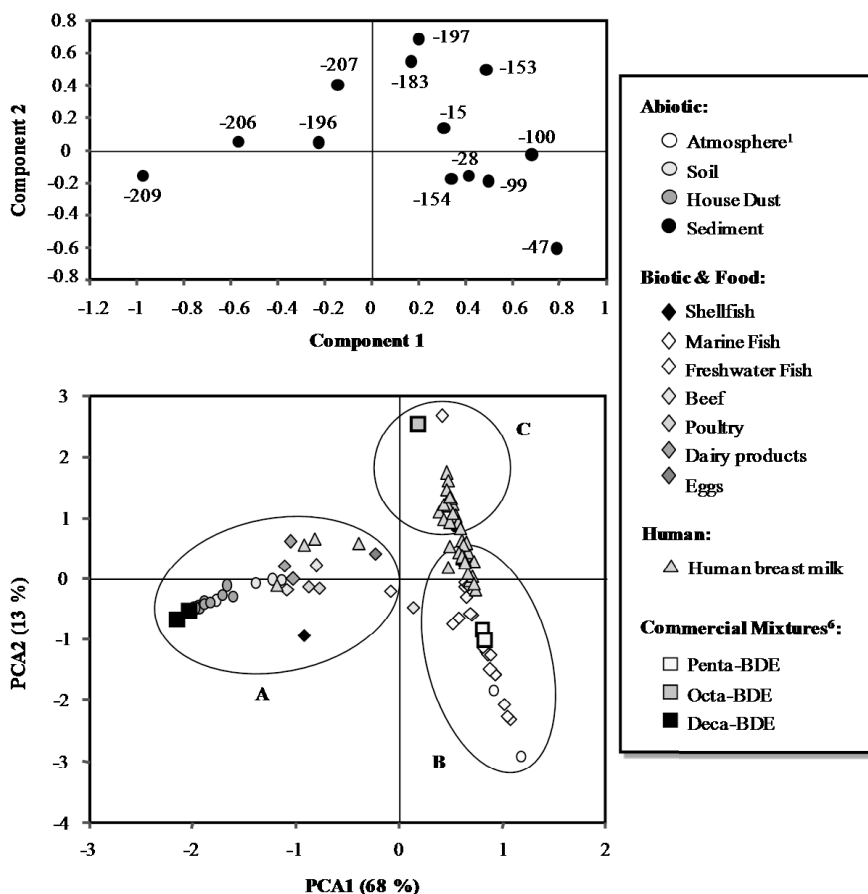


Fig. 4. PCA analysis of PBDE congener profiles in humans, environmental media, food products and commercial formulations.

Fate and behavior

Wide range of the sample matrices and PBDE congeners analyzed allow us to predict the fate and behavior of these contaminants in the environment. Figure 4 shows principle component analysis (PCA) on the similarities of fourteen PBDE congeners (BDE-3, -15, -28, -47, -99, -100, -153, -154, -183, -196, -197, -206, -207 and BDE-209) among sample matrices and available commercial formulations such as Penta-, Octa- and Deca-BDE mixtures (La Guardia *et al.*, 2006). Characterizing BFRs profiles in sediments, soils and dust indicates that BDE-209 was the most predominant (Fig. 4, cluster A), suggesting that Deca-BDE commercial mixtures could be the main formulation used in Indonesia and/or also due to the high binding affinity of this large molecule size congener to

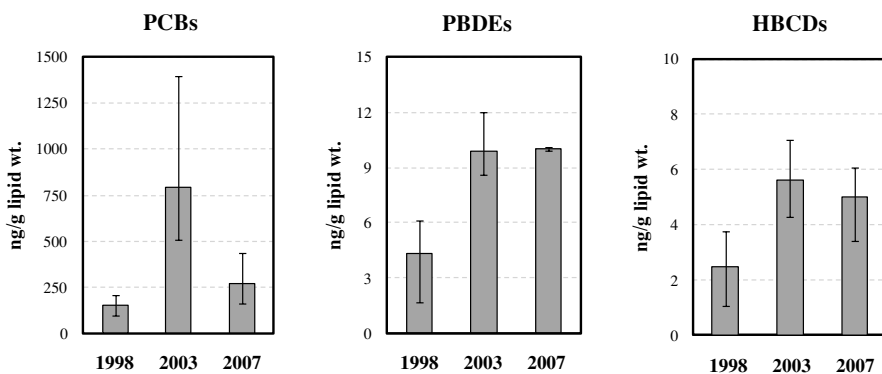


Fig. 5. Temporal variations of BFRs and PCBs in mussels from Jakarta Bay during 1998–2007 (PCBs = sum of 62 PCB congeners; PBDEs = sum of mono- to hepta-BDE; HBCDs = sum of 3 HBCD isomers; 1998: $n = 3$; 2003: $n = 3$; 2007: $n = 3$).

particulate matters. The prevalence of lower BDE-congeners in biota and gas-phase air (Fig. 4, cluster B) indicate selective bioaccumulation and preferable volatilization of these congeners.

Temporal variation

By utilizing mussel samples from Jakarta Bay during 1998–2007 (Sudaryanto *et al.*, 2007b; Ramu *et al.*, 2007; Fig. 5), PBDEs and HBCDs shows an increasing trend during that period (in contrast to PCBs in recent years), and thus environmental pollution by these compounds may be of great concern in the future.

SUMMARY

This paper provide information on the usefulness of *es*-BANK of Ehome University for understanding the occurrence, fate and behavior, human exposure and temporal trends of BFRs in Indonesia. From above results, it can be suggested that:

- BFRs are widely found in the environment and general population of Indonesia.
- Dietary (fish) and non-dietary sources (dust) are important pathways for BFRs intake by Indonesians.
- Deca-BDE commercial mixtures could be a major source of BFRs in Indonesia.
- Specific PBDE congeners have binding preference to particular environmental matrices or biota.
- BFRs in mussels from Jakarta Bay increased during the period 1998 to 2007.

Acknowledgments—This study was partly supported by grants from Global COE Program from the Japanese Ministry of Education, Culture, Sports, Science and Technology, and Japan Society for the Promotion of Science (JSPS); Grants-in-Aid for Scientific Research (S) (No. 20221003), (B) (No. 19780239) and (B) (No. 18310046) from JSPS; and the Global Environment Research Fund (RF-064), the Waste Management Research Grants (K1821 and K1836) from the Ministry of the Environment, Japan. The award of postdoctoral fellowship at Senior Research Fellow Center, Ehime University to A. Sudaryanto is acknowledged.

REFERENCES

- La Guardia, M. J., R. C. Hale and E. Harvey (2006): Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.*, **40**, 6247–6254.
- Monirith, I., D. Ueno, S. Takahashi, H. Nakata, A. Sudaryanto, A. Subramanian, S. Karuppiyah, A. Ismail, M. Muchtar, J. Zheng, B. J. Richardson, M. Prudente, N. D. Hue, T. S. Tana, A. V. Tkalin and S. Tanabe (2003): Asia-Pacific Mussel Watch: Monitoring Contamination of persistent organochlorine compounds in coastal waters of Asian countries. *Mar. Pollut. Bull.*, **46**, 281–300.
- Ramu, K., N. Kajiwara, A. Sudaryanto, T. Isobe, S. Takahashi, A. Subramanian, D. Ueno, G. J. Zheng, P. K. S. Lam, H. Takada, M. P. Zakaria, P. H. Viet, M. Prudente, T. S. Tana and S. Tanabe (2007): Asian mussel watch program: Contamination status of polybrominated diphenyl ethers and organochlorines in coastal waters of Asian countries. *Environ. Sci. Technol.*, **41**, 4580–4586.
- Sudaryanto, A., N. Kajiwara, H. Iwata, A. D. Santoso, P. Hartono, Muawanah, R. Hayami, K. Omori and S. Tanabe (2005): Geographical distribution of polybrominated diphenyl ethers and organochlorine compounds in fish from Indonesia. *Organohalogen Comp.*, **67**, 598–601.
- Sudaryanto, A., I. Monirith, N. Kajiwara, P. Hartono, Muawanah, K. Omori, H. Takeoka and S. Tanabe (2007a): Levels and distribution of organochlorines in fish from Indonesia. *Environ. Int.*, **33**, 750–758.
- Sudaryanto, A., K. Ramu, T. Isobe, N. Kajiwara, S. Takahashi, I. E. Setiawan and S. Tanabe (2007b): Levels, distribution and temporal variation of brominated flame retardants in the environment of Indonesia. p. 27–30. In *Chemical Pollution and Environmental Changes*, ed. by S. Tanabe, H. Takeoka, T. Isobe and Y. Nishibe, *Proceedings of the 4th International Symposium on Pioneering Studies of Young Scientists on Chemical Pollutions and Environmental Changes, Matsuyama, Japan, November 17–19 2006*, Universal Academy Press, Inc.
- Sudaryanto, A., A. Eguchi, T. Isobe, I. E. Setiawan, A. S. Riyadi, M. Ilyas, I. Wahyono, S. Takahashi and S. Tanabe (2008): Brominated flame retardants and persistent organic pollutants in Indonesia: assessment of human exposure. *Organohalogen Comp.*, **70**, 2236–2239.
- Tanabe, S. (2006): Environmental Specimen Bank in Ehime University (*es-BANK*), Japan for global monitoring. *J. Environ. Monit.*, **8**, 782–790.
- Ueno, D., S. Takahashi, H. Tanaka, A. N. Subramanian, G. Fillmann, H. Nakata, P. K. S. Lam, J. Zheng, M. Muchtar, M. Prudente, K. H. Chung and S. Tanabe (2003): Global pollution monitoring of PCBs and organochlorine pesticides using skipjack tuna as a bioindicator. *Arch. Environ. Contam. Toxicol.*, **45**, 378–389.
- Ueno, D., N. Kajiwara, H. Tanaka, A. Subramanian, G. Fillmann, P. K. S. Lam, G. J. Zheng, M. Muchtar, H. Razak, M. Prudente, K. H. Chung and S. Tanabe (2004): Global pollution monitoring of polybrominated diphenyl ethers using skipjack tuna as bioindicator. *Environ. Sci. Technol.*, **38**, 2312–2316.
- Ueno, D., M. Alaei, C. Marvin, D. C. G. Muir, G. Macinnis, E. Reiner, P. Crozier, V. I. Furdui, A. Subramanian, G. Fillmann, P. K. S. Lam, G. J. Zheng, M. Muchtar, H. Razak, M. Prudente, K.-H. Chung and S. Tanabe (2006): Distribution and transportability of hexabromocyclododecane (HBCD) in the Asia-Pacific region using skipjack tuna as a bioindicator. *Environ. Pollut.*, **144**, 238–247.

- Watanabe, I. and S.-I. Sakai (2003): Environmental release and behavior of brominated flame retardants. *Environ. Int.*, **29**, 665–682.
- Wurl, O., J. R. Potter, C. Durville and J. P. Obbard (2006): Polybrominated diphenyl ethers (PBDEs) over the open Indian Ocean. *Atmos. Environ.*, **40**, 5558–5565.

A. Sudaryanto (e-mail: aguss@agr.ehime-u.ac.jp)