# Enrichment of persistent anthropogenic pollutants in the ocean dumping zone of Korea

Sang Hee Hong*, Won Joon Shim, Un Hyuk Yim, Narayanan Kannan, Jin Youngnu, Jong Ho Won, Gi Myung Han

Oil & POPs Research Group, Korea Ocean Research & Development Institute, 391 Jangmok-ri, Jangmok-myon, Geoje-shi 656-834, Korea

## Introduction

The Yellow Sea is a semi-enclosed body of water bounded by the Chinese mainland to the west, the Korean Peninsula to the east, and a line running from the north bank of the mouth of the Yangtze River (Chang Jiang) to the south side of Cheju Island. This international water body, one of the 50 large LMEs (large marine ecosystems) in the world, supports substantial populations of fish, invertebrates, marine mammals, and sea birds which in turn support partially 600 million people living on its basin. The Yellow Sea is presently threatened by both land- and sea-based sources of pollution resulting from extensive economic development in the coastal zone. The major industrial and agricultural wastes to this LME come from the three littoral countries that share this water, namely, Democratic People's Republic of Korea, the People's Republic of China and the Republic of Korea. Offshore waste dumping may add up this burden, for example, Korea has an offshore dumping site called 'Byung' in the middle of Yellow Sea. Ocean dumping is the dumping or placing of materials into designated place in the ocean, often on the continental self. Ocean dumping has been conducted since 1988 in Korea. Dumping activity is legally permitted at three regions within Korean waters, among which one is located in the western side of Korea and two is in the eastern side. Disposal of such waste at sea introduces anthropogenic contaminants to the pristine marine environment directly and expose the marine organisms to acute or chronic toxic effects. Contaminated seafood will ultimately affect human health. In the present study, we collected surface sediments and benthic organisms from the Yellow Sea including dumping site in order to assess the contamination of PBDEs in the Yellow Sea and the consequences of dumping activity to YSLME.

## Materials and Methods

### *Sampling*

Surface sediment and benthic organisms were collected during cruises in R/V Eardo in September 2004 and August 2007, respectively. Surface sediments samples were collected from 38 stations including 19 stations inside the dumping site (DS) "Byung". Sampling sectors are named A-line, B-line, and DS-line according to the sampling locations (Figure 1). Surface sediment samples were collected using Smith-McIntyre grab sampler. To understand the bioconcentration of POPs, several benthic species such as clam, polychaeta, and shrimp was collected at the middle of the Yellow Sea and at dumping site. The collected samples were immediately frozen and transferred to the laboratory for analysis.

### *Chemical analysis*

*PBDE analysis*

The sediment samples were prepared for PBDE analysis in accordance with previously reported

method (Hong et al., 2005; Hong et al., 2007) that includes silica gel and alumina column chromatography, size-exclusion high pressure liquid chromatography (HPLC), and multilayer silica gel column chromatography for clean-up and chemical separation. Determination of PBDE congeners were according to Zhu and Hites (2003) using an Agilent 6890 series gas chromatograph coupled to an Agilent 5975 mass spectrometer with helium as the carrier gas. The mass spectrometer was operated in electron capture negative ionization mode (ECNI) using methane as the reagent gas. Selected ion monitoring of the two bromide ions at m/z 79 and 81 was used to detect the PBDEs. The internal standard PCB198 was used as a retention time reference, and BDE-139 was used as the internal standard to quantitate all the PBDE congeners. PCB-189 was used as a recovery standard which eluted in the middle of the retention range of all the congeners; thus, it provides satisfactory response factors for all congeners investigated. Total PBDE indicates the sum of BDEs 17, 28, 47, 99, 100, 118, 115, 153, 154, and 183. WMF-01 from Wellington laboratories was used as a reference material which contains certified reference values for BDE congeners 28, 47, 99, 100, 153 and 154.

*NP analysis*

Nonylphenol analysis followed the procedure of Li *et al*. (2003). Briefly, sediment samples were treated with 0.1 M HCl, digested for 10 min, and then extracted three times with dichloromethane. Ten nanograms of internal standard (IS) (hepthylphenol) were added to the samples before extraction. The extract was concentrated and solvent-exchanged to acetone for silyl derivatization. After derivatization, the sample was eluted with hexane using 1 g of Florisil. The elute was analyzed by Gas Chromatography (Shimadzu GC-17A)–Mass Spectrometry (Shimadzu MS QP-5000) with selected ion monitoring mode as described in Li *et al*. (2001). Macerated organisms were Soxhlet-extracted with dichloromethane for 16 h. The extract was concentrated, solvent-exchanged to hexane, and cleaned on Florisil column for lipid removal. 18 ml fraction of hexane was discarded and 6 ml dichloromethane fraction was subsequently collected for NP analysis. The dichloromethane fraction was solvent-exchanged to acetone. Stages such as silyl derivatization, cleanup and instrumental analysis that followed were similar to sediment sample analysis.

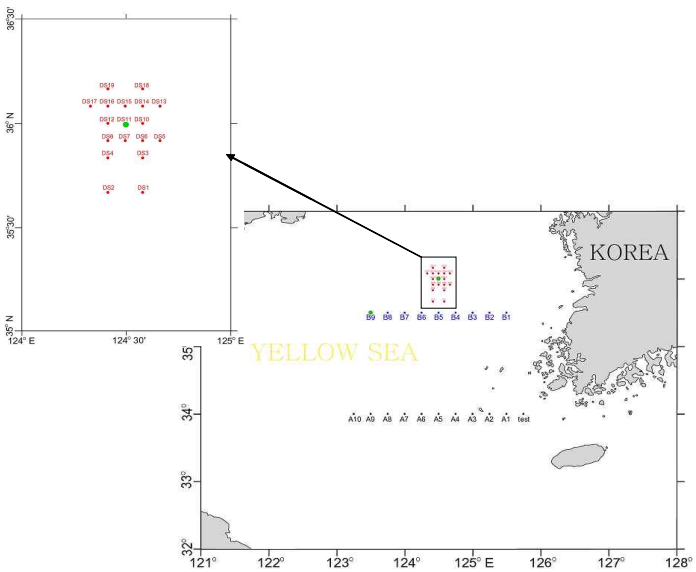


Figure 1. Sampling locations o surface sediments in the Yellow Sea DS indicates Korean ocean dumpin zone “Byung”.

**Results and Discussion**

A wide range of PBDE concentrations were recorded in sediment samples. 0.06-3.94 ng $g^{-1}$. Dumping sites accumulated higher levels of PBDE in comparison to the rest (A-line and B-line stations) (Figure 2). The concentrations of PBDEs in sediments of lines A- and B were relatively lower than those determined in overall Korean coastal sediments, while dumping site showed comparable levels to Korean coasts (Moon *et al*., 2007). The other persistent organic pollutant including dioxins, PCBs, and DDTs were also enriched in the dumping area (the data is not presented here). The elevated level of POPs in dumping site indicates that dumped wastes are accumulated in sediments within the site, and dumping activity could be a pollution source of anthropogenic chemicals in this offshore region.

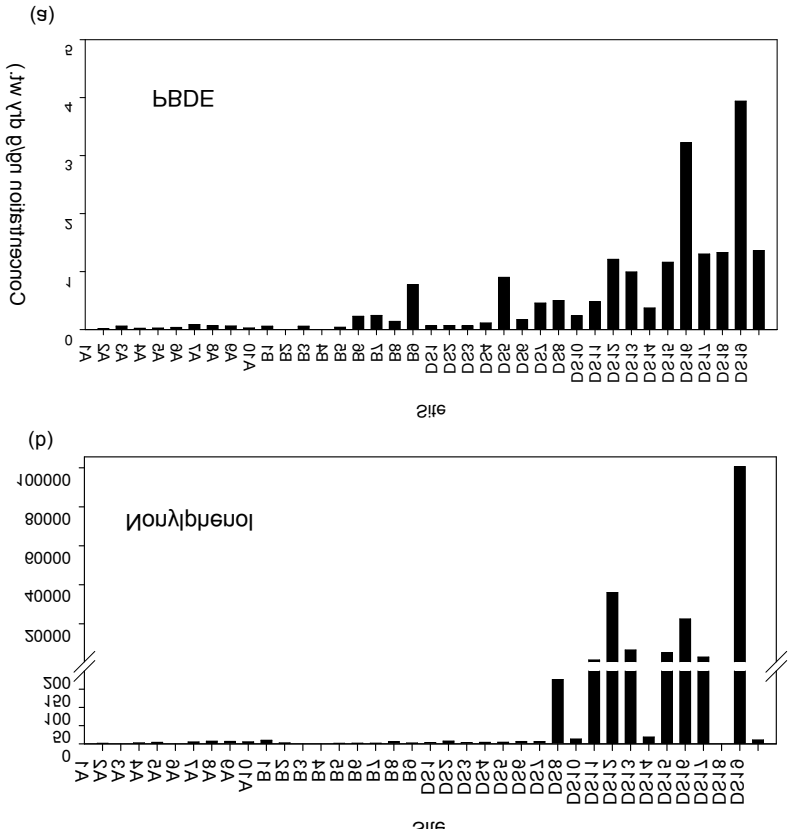


Figure 2. Levels of PBDEs and nonylphenols in surface sediment from the Yellow Sea

In addition to PBDE, nonylphenol (NP) was also determined in the samples. Nonylphenol is a very potent endocrine, disrupting chemical and degradation product of non-ionic surfactant, alkylphenol polyethoxylates entering aquatic environments via industrial and municipal wastewater discharges due to their widespread usage in cleaning products and industrial processes (Giger et al., 1984; Rice et al., 2003; Cheng et al., 2006). As a waste and sewage tracer, nonlyphenol has been applied. The extraordinary concentration of nonylphenol in dumping sites was observed. The extraordinary concentration of nonylphenol in dumping sites is the evidence of direct dumping of

waste and sewage sludge (Figure 2). Interestingly, the spatial distribution pattern of NP is well matched with that of PBDE.

PBDEs were also detectable in benthic species of Yellow Sea. Like sediment, the benthic organisms in the dumping site showed higher levels of PBDEs than other parts, which implies that contaminated sewage increases the tissue residue level in that area and possibly implying biomagnification in the food chain. The levels of PBDEs in polychaeta from the dumping were higher than those observed in Masan Bay (5-25 ng/g dry wt), one of the industrialized bays of Korea. Regular monitoring of POPs and other hazardous toxic chemicals in sediments and biota around dumping site should be conducted, and integrated environmental risk assessment is required.

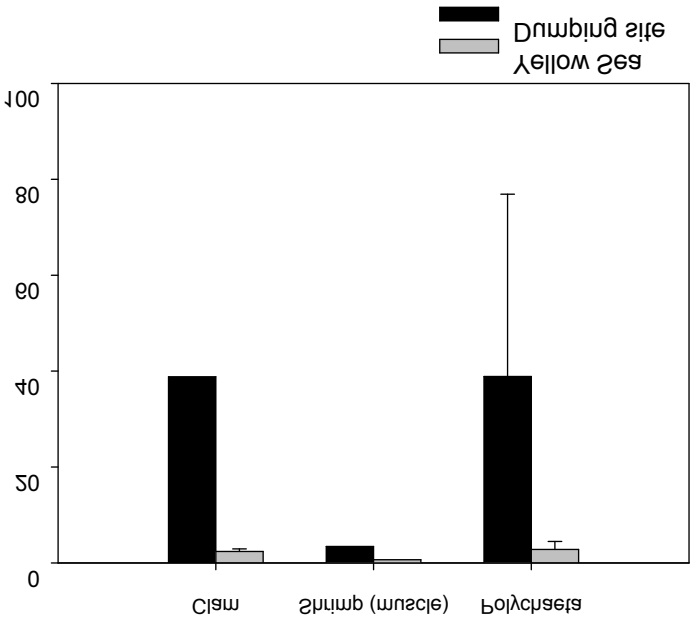


Figure 3. PBDEs in benthic organisms of Yellow Sea.

**Acknowledgement**

This work was supported by grants-in-aid from the Ministry of 389 Environment as a part of Eco-Technopia-21 Program (Grant No. 390 20010032).

**References**

Hong SH, Yim UH, Shim WJ, Oh JR. 2005. Environ Sci Technol 39(19):7380
Hong SH, Kannan N, Jin YN, Shim, WJ. 2007. Organohalogen Comp 69:2690
Li D, Park J, Oh JR. 2001. Analytical Chemistry 73:3089
Li D, Park J, Oh JR. 2003. Journal of Chromatography A 1012: 207
Moon H-B, Kannan K, Lee S-J, Choi M. 2007. Chemosphere 66:243
Zhu LY., Hites RA. 2003. Anal. Chem. 75:6696