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Trace Organic Contaminants in Sediments from Deep-sea Basin near Dokdo, Korea

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Abstract : Trace organic contaminants in deep-sea sediments near Dokdo were analyzed. Total PAHs concentration ranged 14.8-314 ng/g dry weight and high molecular weight PAHs were dominant. The highest PAHs concentration was detected at A19 which located at Ulleung Basin. Most of organochlorines were under detection limit. Among the detected organochlorines, DDT compounds were dominant and followed by HCHs and HCB. Butyltin compounds and most of organophosphorus pesticides were not detected. Vertical distribution of PAHs showed typical sub-surface maximum and decreasing trends depending on depth. The highest PAHs concentration reached 454 ng/g. Some organochlorines, DDT, HCH was detected and also showed decreasing trends. Other target organic pollutants were not detected in core sediments. Abnormally high level of PAHs concentration in A19 was discussed and the input sources were inferred to be the transport of sludge derived pollutant dumped at dumping site "Byung" by deep current.

Key words : Trace organic contaminants, Sediment, Core, Deep-sea, Deep current.

1. Introduction

The deep-sea and its ecosystems are considered to be one of the last regions on earth that are little, or not at all, influenced by human activity. But the deep-sea is not as pristine as it is supposed to be, it may even turn out to be the ultimate global sink for persistent organic pollutants in the marine environment, like the soil of the forests is in the terrestrial environment (Krämer *et al.* 1984; Froescheis *et al.* 2000). In an aqueous environment, the physico-chemical properties of persistent, hydrophobic, semivolatile contaminants require that they accumulate in biota or that they are adsorbed on particles (bio- and geo-accumulation). As a result, persistent organic pollutants will follow any movement of particles or organic matter in the oceanic system and therefore will be transported to the remote sites of the deep-sea as well.

Deep-sea basin near Dokdo in this study is Ulleung basin where water depth is more than 2,000 m deep. There are only limited human activity and very limited input of anthropogenic materials. Therefore deep-sea near Dokdo has been thought to be pristine area. In order to understand geographical and vertical distribution of trace organic contaminants in this area, deep-sea sediments were collected and analyzed under strict quality control.

Trace organic contaminants considered here include several categories (Table 1). Polycyclic aromatic hydrocarbons (PAHs) are known to be produced by incomplete combustion processes and are constituents of crude oil or refined products. PAHs originated at high temperatures (pyrogenic) are dominated by the parent species, while crude oils (petrogenic) contain a wide range of alkyl-derivatives. The low molecular weight PAHs have a significant acute toxicity, whereas some the high molecular weight PAHs show high carcinogenic potential (McElroy *et al.*, 1989; Stein *et al.*, 1990).

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Table 1. List of target compounds analyzed in this study.

Chlorinated Pesticides	Polycyclic Aromatic Hydrocarbons
Pentachlorobenzene	Naphthalene
Hexachlorobenzene	2,-Methylnaphthalene
	1-Methylnaphthalene
HCHs	Biphenyl
α -HCH, β -HCH, γ -HCH,	2,5-Dimethylnaphthalene
δ -HCH	Acenaphthylene
	Acenaphthene
Chrodane related compounds	2,3,5-Trimethylnaphthalene
α -Chlordane, γ -Chlordane,	Fluorene
cis-Nonachlor, trans-Nonachlor,	Phenanthrene
Oxychlordane,	Anthracene
Heptachlor, Heptachlor epoxide	1-Methylphenanthrene
	Fluoranthene
Aldrin, Dieldrin	Pyrene
Endrin	Benz[a]anthracene
Endosulfan	Chrysene
Mirex	Benzo[b+k]fluoranthene
	Benzo[e]pyrene
DDT compounds	Benzo[a]pyrene
<i>o,p'</i> -DDE, <i>p,p'</i> -DDE,	Perylene
<i>o,p'</i> -DDD, <i>p,p'</i> -DDD,	Indno(1,2,3-cd)pyrene
<i>o,p'</i> -DDT, <i>p,p'</i> -DDT	Dibenz[a,h]anthracene
	Benzo[ghi]perylene
Polychlorinated Biphenyl congeners	Butyltin Compounds
PCB8, PCB18, PCB28, PCB29,	Tributyltin, Dibutyltin,
PCB44, PCB52, PCB66, PCB87,	Monobutyltin
PCB101, PCB105, PCB110,	Organophosphorous Pesticides
PCB118, PCB128, PCB138,	Diazin, IBP, Dichlorvos,
PCB153, PCB170, PCB180,	Parathion, Methylparathion,
PCB187, PCB195, PCB200,	chlorpyrifos
PCB206, PCB209	

Polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides such as hexachlorobenzene (HCB), HCH isomers (HCHs), Chlordanes (CHLs), DDT, and its derivatives (DDTs) have been detected in sediments for over the last 30 years. Despite a 1970s ban on the use of PCBs and DDTs in many countries including Korea, these compounds are ubiquitous and persistent in various environmental media (Khim *et al.* 1999).

Organotin compounds are among the most widely used organometallic chemicals. Production of organotins has increased for various purposes since their first biocidal application in the early 1920s (Shim *et al.* 1999). Tributyltin (TBT) used as biocidal additive for antifouling paints has received much attention since its adverse effects on oyster farms near marina were revealed in the early 1980s (Alzieu, 1986). Many industrialized countries have regulated

the use of TBT in anti-fouling paints and also banned in Korea since 2000.

In many countries, restrictions have been imposed on the use of organochlorine pesticides. This has shifted the use patterns away from organochlorines toward organophosphorus and carbamate pesticides. Most organophosphorus and carbamate pesticides are regarded as being non-persistent, but residues of some organophosphorus pesticides are persisting for extended periods in organic soils and in surrounding drainage systems (Harris and Miles, 1975).

2. Materials and methods

Five surface sediment and one core samples were taken around Dokdo (Fig. 1). The sampling took place during May 2000 cruise of R/V Onuri. Sediment samples were taken using Box corer and sediment core was sampled at St. A19 using acryl liner. The samples were immediately frozen by dry ice and stored at the freezer before laboratory analysis. Packing and storage of the samples followed the normal NS&T protocol of US NOAA (Lauenstein and Cantillo, 1998).

The analytical procedures of PAHs and organochlorines in sediments followed the method of Sloan *et al.* (1993) after some modifications. Briefly, The dried sediment samples were spiked with 300 ng of deuterated surrogates for PAHs (naphthalene-*d*₈, acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂, and perylene-*d*₁₂) and 10 ng of surrogate for organochlorines (OCs) (DBOFB, PCB 103, PCB 169) and then extracted by Soxhlet for 6-8 hrs with 200 ml of methylene chloride. The sample extracts were extensively cleaned up by a Si/Al column chromatography and HPLC with size exclusion column (Krahn *et al.*, 1988). Terphenyl-*d*₁₄ (PAH) and tetrachloro-*m*-xylene (TCMX, OCs) was used as instrumental internal standard. Polycyclic aromatic hydrocarbons and organochlorines were identified and quantified using GC/MS, and GC/ECD, respectively.

The analytical procedure used on the sediment sample is a modification of the method suggested by Shim *et al.* (1999). Air-dried sediments were ground and weighed to about 5 g in 50 ml polypropylene centrifuge tubes. The samples were spiked with triphenyltin chloride and digested with 10 ml of 6 N HCl, then subsequently extracted with 20 ml methylene chloride with tropolone (0.1%) by shaking for 3 h. After 10 min centrifugation (4,000 rpm), 2 ml of organic extracts were transferred to 15 ml glass test tubes and concentrated to about 25 μ l under a gentle stream of nitrogen. Then the samples were resuspended in 2 ml *n*-hexane and derivatized with 250 μ l of 2 M propylmagnesium

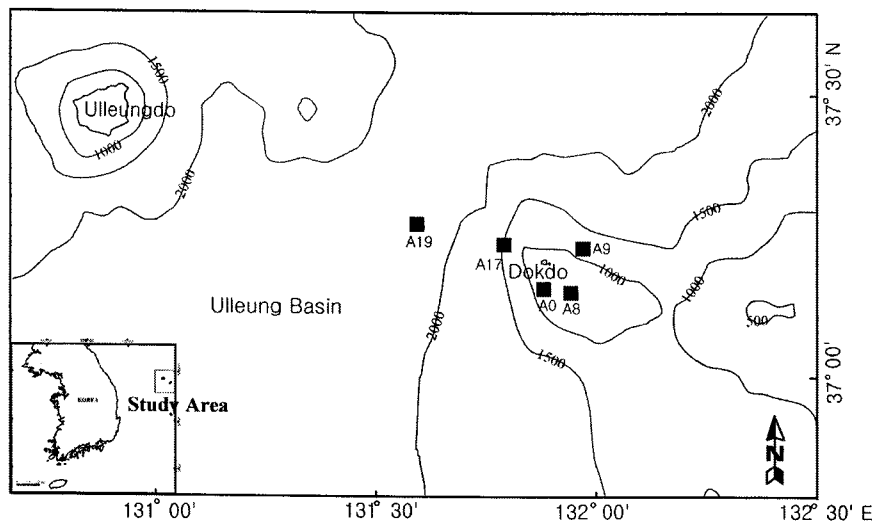


Fig. 1. Location map of surface sediment sampling sites near Dokdo. Core sediment samples were taken at A19.

chloride for 20 min. The remaining Grignard Reagent was neutralized with 4 ml of 0.4 N sulfuric acid. The organic phase was recovered by centrifugation and cleaned up on 2 g of activated florisil. The cleaned extracts were concentrated again and spiked with tetrabutyltin as an internal standard, and then analyzed by gas chromatograph (Hewlett Packard 5890 Series II) equipped with a capillary column (SPB-1, 30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness) and a flame photometric detector. The gas chromatograph operating condition was reported elsewhere (Shim *et al.*, 1999).

Determination of the organophosphorus pesticides in sediment samples was performed using of the method of Yu *et al.* (2001). About 5 g of freeze-dried sediment sample was taken into a pre-cleaned extraction thimble in Soxhlet apparatus and extracted using hexane : acetone mixture (50:50). The extract was rotary vacuum evaporated to 2 ml and further concentrated to 0.5 ml by gentle nitrogen stream. The concentrated extracts were cleaned up by Florisil column. The eluent was concentrated to 1 mL then subjected to GC/NPD analysis.

Detection limit for each compounds are 0.001-0.005 ng/g dw (OCPs), 0.001-0.003 ng/g dw (PCBs), 0.05-0.25 ng/g dw (PAHs), 1 ng Sn/g dw (BTs), and 1 ng/g dw (OPs). The acceptable range for surrogate recovery was 40-120%, and if any sample deviate this criterion, that was reanalyzed. Procedural blank was analyzed with same batch of real sample. The criteria for procedural blank were none of target compounds exceeds 3 times the method detection limit. Certified reference materials (CRM) were also analyzed for quality assurance and target compounds in CRM satisfied the certified values.

Table 2. Trace organic contaminants in surface sediments from deep-sea near Dokdo.

	A0	A8	A9	A17	A19
¹ TOC (%)	1.47	3.21	3.61	3.98	2.09
² PAHs	29.3	14.8	118	37.1	314
³ PCB	nd	nd	0.011	nd	nd
⁴ OCPs	1.89	0.165	2.97	2.70	3.04
⁵ OPs	nd	nd	nd	nd	nd
⁶ BTs	nd	nd	nd	nd	nd

¹Total organic carbon.

²Sum of 24 target PAHs.

³Sum of 22 isomers.

⁴Sum of DDTs, HCHs, HCBs, CHLs, and Dieldrins.

⁵Sum of six organophosphorous pesticides.

⁶Sum of mono, di, and tributyltin.

*Not detected.

3. Results and discussion

Surface sediments

Polycyclic aromatic hydrocarbons

Total PAH concentrations in surface sediments ranged 14.8-314 ng/g dry weight (Table 2). Relatively low concentrations (14.8-37.1 ng/g) were found near Dokdo, while the highest concentration was found away from Dokdo, that site is more than 2,000 m deep. Concentration of total PAHs at A19 is several magnitude or order higher than other sites.

Most of studies have focused on the contamination of PAHs in the nearshore industrialized or urbanized regions (Table 3). As much as 10,000 ppm of PAHs was found in the heavily contaminated harbor (Simpson *et al.*, 1996).

Table 3. Comparison of PAHs data in this study with other studies.

Location	Sample No.	Target Analytes	Range	Instrument	Reference
<i>Nearshore</i>					
Kyunggi Bay (Korea)	66	24	9.1 -1400	GC/MS	Kim <i>et al.</i> (1999)
Kitimat Harbor (Canada)	20	16	nd -10,000,000	GC/FID	Simpso <i>et al.</i> (1996)
Casco Bay, Maine (USA)	53	24	16 -20,798	GC/MS	Kennicutt <i>et al.</i> (1994)
Western Mediterranean (Europe)	23	26	1 -20,500	GC/MS	Baumar <i>et al.</i> (1998)
Fjords (Norway)	119	13	262 -784,296	GC/MS, FID	Naes & Oug (1998)
Sydney Harbor (Australia)	124	17	nd -380,000	GC/MD	McCread <i>et al.</i> (2000)
Nationwide (Korea)	92	24	1.19 -28,640	GC/MD	MOMAF (2001)
<i>Deep-sea</i>					
Dokdo	5	24	14.8 -314	GC/MD	This study
Abyssal plain (North Atlantic)	1	3	8	GC/MD	Laflamme & Hites (1978)
Navarin Basin (Alaska)	19	16	20 -40	GC/MS, FID	Venkatesan & Kaplan (1982)
Deep-sea floor (Central Pacific)	20	15	0.81 -60.6	GC/MS	Ohkouch <i>et al.</i> (1999)

However there exists only few studies concerning deep-sea sediments. Total PAHs in the deep-sea sediments from central Pacific ranged from 0.81 to 60.6 ng/g dry weight (Ohkouchi *et al.*, 1999). Other studies reported that total PAHs concentration in the abyssal plain (Laflamme and Hites, 1978) and outer continental shelf (Venkatesan and Kaplan, 1982) are far less than 100 ng/g dry weight. The highest concentration in A19 is comparable to those of moderately polluted regions Korean coastal area where total PAHs in surface sediments ranged from 1.19 ng/g (sand) to 28,640 ng/g with geometric mean of 290 ng/g dw (MOMAF,

2001).

Most of the target compounds were detected because large quantities of samples (15 g dry weight) were used for increasing detection limit. According to the composition of each site, two groups were defined. Group A comprises A0, A8 and group B stands for A9, A17 and A19. High molecular weight (molecular weight ≥ 202) PAHs were dominant, which account for 61% and 81% in group A and B, respectively. In group A, molecular weight (MW) 276 + 278 was predominant and followed by 252. While MW 252 was most dominant and followed by 128, 202+228 in group B (Fig. 2). These apparent compositional differences are mainly due to the input sources and will be discussed later.

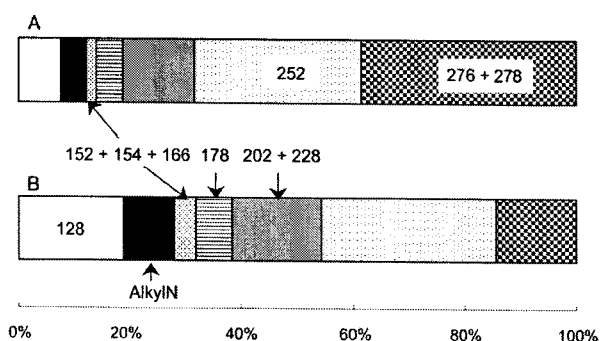


Fig. 2. Average composition profiles of PAHs in surface sediments near Dokdo. A. average of A19 and A9. B. Other sites. MW128: naphthalene; alkyl N: sum of C1 naphthalene, 2,6 dimethylnaphthalene, 1,3,5 trimethylnaphthalene; 152 + 154 + 166: sum of biphenyl, acenaphthene, fluorene; 178: sum of phenanthrene, anthracene; 202+228: sum of fluoanthene, pyrene, benzo[a]anthracene, chrysene, 252: sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo [e]pyrene, benzo[a]pyrene, perylene; 276 + 278: Indeno (1,2,3-cd)pyrene, dibenz[a,h]anthracene, benzo [ghi]perylene.

Organochlorine compounds

Among the detected organochlorine compounds, DDT compounds were the dominant organochlorines with the mean concentrations of 0.6 ± 0.89 ng/g and followed by HCHs (0.25 ± 0.41 ng/g) and HCB (0.05 ± 0.06 ng/g). While, the concentrations of PCB, aldrin, endosulfan II, mirex, and chlordane compounds were below the detection limit values. This contamination levels were apparently lower than those previously reported from the coastal zone of Korea with concentration range of 0.01-135 ng/g for Σ DDT, nd-4.38 ng/g for Σ HCH, nd-81 ng/g for HCB, and 0.09-199 ng/g for Σ PCB (MOMAF, 2001).

The concentration level of Σ DDT in surface sediments from the nearby Dokdo was comparable with that of Gulf of Alaska (0.17 ng/g), Bering Sea (0.006 ng/g), and Chukchi Sea (0.009 ng/g) (Iwata *et al.*, 1994), but lower than those of the Baltic Sea (1.9-6.9 ng/g; Strandberg *et al.*, 1998). Four sites (A0, A8, A9, and A19) out of five

sites showed relatively high DDT composition compared to total DDTs (0.6-0.8). The dominance of DDT might indicate recent input of DDT.

Among the four HCH compounds (α -, β -, γ -, δ - isomer), α -HCH was mostly abundant in surface sediments determined, and followed by β -HCH. Gamma- and δ - isomer were not detected at all sites. Hexachlorocyclohexane compounds are volatile organochlorines and hence are globally transported through the atmosphere. Numerous studies measured these compounds in various environmental matrix from open ocean, pristine Arctic and Antarctic where no local source exist (Iwata *et al.*, 1993; Muir *et al.*, 1995; Allen-Gill *et al.*, 1997; Hargrave *et al.*, 2000; Montone *et al.*, 2001). Among the HCH isomers, it is known that α -HCH has a strong tendency for global transportation. Therefore, α -HCH in sediment samples could be expected to be originated from the atmospheric deposition.

Other trace organic contaminants

Organotin compounds, especially butyltins, are used as biocide in antifouling paints to prevent ship hulls from fouling. Three target butyltin compounds (mono-, di- and tributyltin) were below detection limits for seawater (< 0.1-0.3 ng Sn/L) and sediments (< 1-3 ng Sn/g dry weight). In previous study, tributyltin (TBT) compound was detected in mussel sample (48 ng/g) from Dokdo (Shim, 2000). This is the quite low level of TBT in comparison with the mean TBT concentration (566 ng/g) in bivalves from the coastal environment of Korea (Shim, 2000), which indicates that there are boating activities, even limited, around the Island. When the rapid degradation of TBT in water column is taken into account (Seligman *et al.*, 1988), water depth of about 2000 m at the stations could be too deep to accumulate TBT in sediment up to above the detection limit.

In this study, six kinds of organophosphorus pesticides were used as target compounds (Table 1). Among them, chlorpyrifos was only detected in sediment samples with low level and low frequency, its concentration ranged from detection limit to 0.05 ng/g dry weight. It has been well known that organophosphorus pesticides are rapidly decomposed in environment and their half life range from several days to about twenty days in water system (Medina *et al.* 1999). Although large quantities were widely used in agricultural areas and high levels of concentration were determined in the Korea (Yu *et al.* 2001) and Japan (Tsuda *et al.* 1996), their low concentration in this studied area suggest that most of them are mixed and decomposed during the transportation.

Core sediment

Polycyclic aromatic hydrocarbons

Core sediment samples were taken at A19 (Fig. 1), where trace organic contaminants and trace metal concentrations happened to be the highest (MOMAF, 2000). Total PAHs concentrations ranged 38.4-454 ng/g dry weight and showed decreasing trends depending on the depth. Subsurface (2-4 cm) showed the highest concentration and mid depth (16-19 cm) the lowest (Fig. 3). Core sediment can be divided into three groups according to principal component analysis (Fig. 4A). Group 1 comprises surface and sub-surface (0-7 cm), group 2 mid-depth (10-22 cm) and group 3 lowest depth (22-33 cm), respectively. High molecular weight PAHs account for most of variations of the total PAHs ($r^2 = 0.98$, $p < 0.01$) (Fig. 3, Fig. 4B).

Input source changes which could be inferred from PAHs composition, were distinct depending on each group. Molecular weight 276 + 278, i.e., indeno(1,2,3-cd), dibenzo[a,h]anthracene, benzo[ghi]perylene were dominant in group 1 and followed by 252 and 202 + 228. These high molecular weight PAHs which are primarily produced by incomplete combustion of carbonaceous materials, have high $\log K_{ow}$ values (6.04-6.86) and hence have high affinity to adsorb to particulate matter. However, the

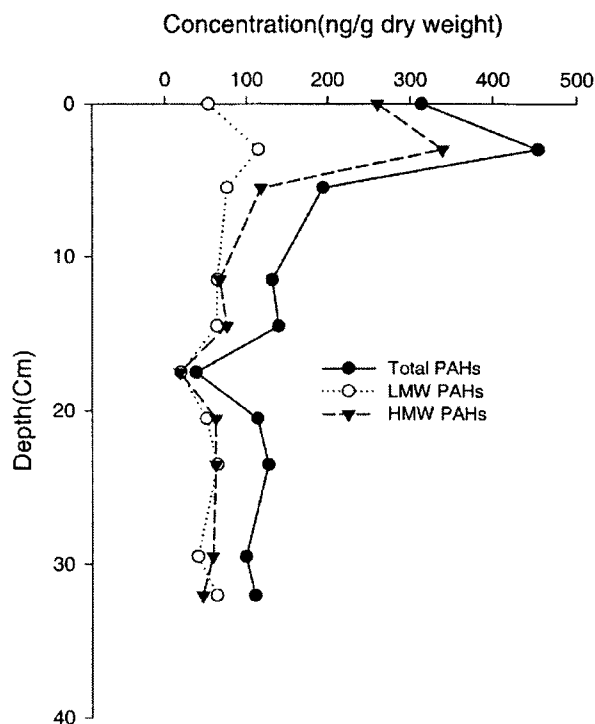


Fig. 3. Vertical distribution of total PAHs, low molecular weight and high molecular weight PAHs in core sediments from A19.

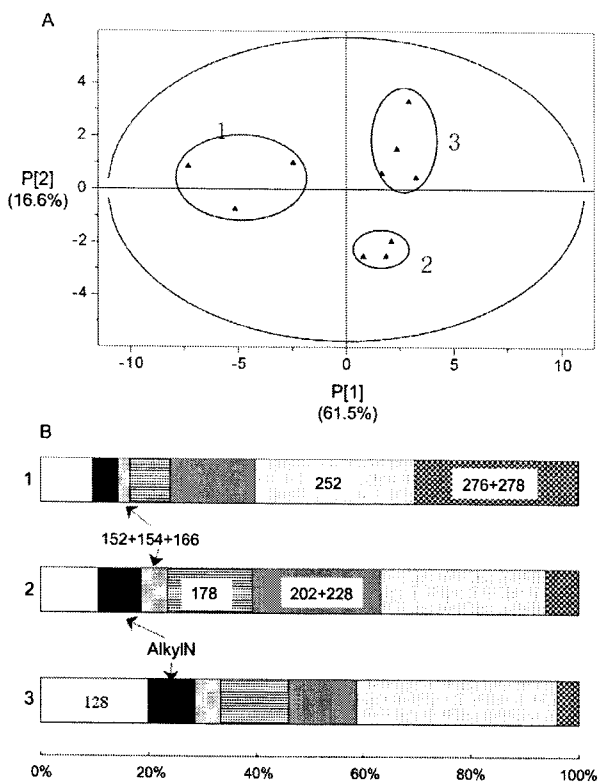


Fig. 4. Principal component analysis (A) and average composition profiles of sediment cores sampled at A19. 1. 0-7 cm, 2. 10-22 cm, 3. 22-33 cm. Refer to caption of Fig. 2 for acronyms.

portion of MW 252 increases depending on depth and reached 34% in group 3. Naturally occurring PAHs, perylene which is known to be made by diagenesis in the presence of precursor compounds, account for these phenomena. The portion of perylene increased from 2.9% in surface sediments to 32.6% in deep sediment. According to Wakeham *et al.* (1980), perylene account for 70-90% of total PAHs in more than 1 m depth. In this study apparent increase of perylene less than 30 cm depth support the mechanism of perylene formation.

Organochlorine compounds

Similar with surface sediments, PCB compounds were not detected at all depth of core sediments. The highest concentrations of Σ DDT and Σ HCH were found at surface zone (0-2 cm) of core sediments. At the depth of 0-2 cm of core sediment, DDT composition (53%) was relatively higher than those of its metabolites, DDD and DDE, similar to surface sediment (60%), while DDE only determined at the lower depth. At surface layer, high proportion of DDT compound indicate the recent input of DDT compound.

While DDTs were only found within the depth of 0-7 cm, HCHs were detected at all layers of sediment core. The concentrations of HCH compounds ranged from 0.06 to 0.48 ng/g. At all depth, α -HCH was the major isomer and followed by β -isomer, while γ and δ -isomer was not determined. In surface layer, the ratio of α - to β -isomer was 6.0, which corresponds to that of original HCH mixture (α : β -isomer = 55-80%, 5-14%) (Walker *et al.*, 1999). However, the ratio decreased according to the depth and this decreasing trend of α -/ β -HCH would be due to high persistency of β -HCH among HCH compounds (Willet *et al.*, 1998). Other target contaminants were not detected and this might due to their lack of input sources and rapid degradation.

Input sources

Limited input sources lead study area relatively free of organic pollutants. However elevated concentrations of PAHs (314 ppb in A19) in deep-sea basin away from Dokdo brought about the question related to its sources. This abnormally elevated concentration is not confined to PAHs compounds. Some trace metals like manganese, mercury, and arsenic concentration also showed factors or order of magnitude higher than other sites (MOMAF, 2000). Atmospherically transported elements like lead didn't showed such elevation. Likewise, PAHs in remote areas are usually explained by atmospherically transported and deposited (Hites and Laflamme, 1980). But their geographical distribution should be uniform or at least have compositional consistency. As previously mentioned, geographical distribution and composition didn't support that they have been originated similar sources. Especially in core sediments there were distinct differences according to depth and these might be due to the source changes in the past.

Deep current which flows counterclockwise around the study area was simulated by Chang *et al.* (2000). This current pass through the dumping site "Byung". Into this dumping site, wastes disposal was initiated from 1988. Recently (1995-2000), 13.3 million tons of sludges from industrial wastewater have been dumped into this area (MOST, 2001). Takada *et al.* (1994) reported transport of organic pollutants derived from dumped sludge through the water column and accumulation on the deep-sea floor. They also observed resuspended surface sediments, which have high concentration of organic pollutant can be further dispersed by deep water transport processes. Speed of deep current in Ulleung basin reaches 5 cm/s and this could be influential vector of organic pollutants derived from dumped sludge or resuspended sediments in dumping site.

There is only limited data related on status and geochemical

processes of trace organic contaminants in the deep-sea. Considering that the deep-sea basin plays important role for final reservoir of these contaminants, further studies should be done. Deep-sea basin near Dokdo in this study happened to be possessing elevated levels of trace organic contaminants, especially PAHs. Relationship between input sources like dumping activity and large-scale oceanographic processes such as deep current, air-sea interaction should be further backed up by sediment trap, water-borne contaminants, expansion of study area and atmospheric deposition.

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