THE NATIONWIDE MONITORING OF PAHS AND OCPS IN SURFACE SEDIMENTS FROM THE FOUR MAJOR RIVER BASINS IN KOREA

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Abstract

We analyzed micropollutants contamination (13 organochlorine pesticides [OCPs] and 16 polycyclic hydrocarbons [PAHs]) in sediments from major 4 river basins in Korea and tried to investigate the source identification of these contaminants. The ΣPAHs concentration in river sediments ranged from ND to 1756 ng/g and the average values of Han river, Nakdong river, Yeongsan river and Geum river were 103.3±300.1, 66.6±167.2, 44.1±44.3 and 50.5±49 ng/g-dry, respectively. The highest ΣPAHs concentration was detected near the petro-chemical factories. Particularly, 3- and 4-ring PAHs (Phenanthrene, Fluoranthene, Pyrene, Benzo[b]fluoranthene, Chrysene, Benzo[a]anthracene, Anthracene and Benzo[k]fluoranthene) were most abundant. ΣPAHs concentration in sediments from the lake was higher than those from river. The average concentration of Σ PAHs in lake samples was 205.4 ng/g ranging from 4.0 to 2,987 ng/g-dry. The ΣDDTs concentration ranged from ND to 9.04 ng/g-dry with an average 1.03±0.69 ng/g-dry. *p,p'*- DDE was dominant compound and accounted for 61% of DDTs.

Introduction

These days, many synthetic organic compounds have been made and emitted into environment. Particularly, persistent organic pollutants (POPs) have been regarded as hazardous compounds in the past decades worldwide. Some organochlorine pesticides (OCPs) are regulated as POPs and 16 polycyclic aromatic hydrocarbons (PAHs) have been listed as priority control pollutants by the Environmental Protection Agency of the USA (U.S.EPA)[1]. They are of environmental issue due to their widespread distribution in the environment and potential toxicity to organisms. Although OCPs have been officially banned over 30 years ago in Korea, residues of OCPs still have been detected in food, soil, sediment and biota[2]. The organic compounds are emitted by mainly anthropogenic processes through various routes[1]. Lots of these emitted contaminants are accumulated in sediment through industrial wastewater discharge, atmospheric deposition of vehicle exhaust and industrial stack emission[3]. If the loading of these contaminants is large enough, these contaminats might disrupt the ecosystem directly and indirectly and moreover, the sediment can be resuspended in the disturbing condition and the contaminants would reenter the aquatic environment and circulate in ecosystem. In order to understand occurrence of these contaminants in river ecosystem, it is necessery to elucidate their distribution and sources in sediment. Therefore, in this study, we tried to identify the source of 13 OCPs and 16 PAHs in sediment samples from 4 major river basins in Korea through nationwide monitoring of these compounds.

Materials and Methods

Sampling. 195 individual samples were taken from the 4 major river basins (Han: 54, Nakdong: 60, Geum: 44, Youngsan: 37) in Korea. Surface sediment were taken with a grab sampler. Sediment samples were sieved with 63 µm sieve to remove coarse particles and homogenize samples.

Analytical procedures. Analysis of 13 OCPs (α-BHC, β-BHC, γ-BHC, δ-BHC, ε-BHC, α-Endosulfan, β-Endosulfan, *o,p'*-DDE, *p.p'*-DDE, *o,p'*-DDD, *p.p'*-DDD, *o,p'*-DDT and *p.p'*-DDT) and 16 priority PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[*a*]anthracene, Chrysene, Benzo[*b*]fluoranthene, Benzo[*k*]fluoranthene, Benzo[*a*]pyrene, Indeno[*1,2,3-cd*]pyrene, Benzo[*g,h,i*]perylene and Dibenzo[*a,h*]anthracene) was implemented. Extraction were performed using accelerated solvent extractor (ASE) with a mixture of acetone and hexane (1:1, v/v). Then, the extracts were preconcentrated to 2~3 mL with turbo vap. Before clean-up procedure, deuterated PAHs and OCPs were spiked into each sample as internal standard. All sediment extracts were passed through 6 g of activated silica gel packed in a glass column for cleanup and additional florisil cleanup was carried out before silica gel cleanup to remove residual oil. Eluents were concentrated under a gentle stream of purified nitrogen and adjusted to 0.5 mL with recovery standard. The amounts of PAHs and OCPs were determined by gas chromatography-electron impact mass spectrometry using Agilent 6890 GC equipped with a DB5-MS column (60m*0.32mm*0.25µm film thickness; J&W Scientific, USA). Recoveries of PAHs were 65.4±16.5% and those of OCPs were 60.2±9.1%. The detection limit of quantitations (LOQs) set on a signal-to-noise ratio of 10 were 0.5 ng/g-dry for PAHs and 0.1 ng/g-dry for OCPs, respectively.

Results and Discussion:

PAHs and OCPs contents in surface sediment samples

Total concentration of 16 PAHs in surface sediments from the Korean major river basins varied from ND to 1,756 ng/g-dry. The averages of 16 PAHs in sediment from 4 rivers were 103.3±300.1, 66.6±167.2, 44.1±44.3 and 50.5±49 ng/g-dry, respectively (Table 1). The highest ΣPAHs concentration was detected at the sampling point near the petro-chemical factories. The other highly contaminated samples were taken at the points located near industrial complex. 3- and 4-ring PAHs (Phenanthrene, Fluoranthene, Pyrene, Benzo[*b+k*]fluoranthene, Chrysene, Benzo[*a*]anthracene and Anthracene) were most abundant (72%), which is consistent with previous studies[1]. Pyrene was the most predominant component in this study and sum of Pyrene, Fluoranthene, Benzo[*b*]fluoranthene, and Phenanthrene explained for 60% of total concentration. These predominant compounds were detected at all the river basins with similar distribution pattern (Figure 1). Phenanthrene was detected at most of samples with 97% of detection frequency. PAHs in sediment samples from the lake were higher than those from river. Average of 16 PAH concentration in lake samples was 205.4 ng/g-dry ranging from 4.0 to 2,987 ng/g-dry. The distribution patterns of PAHs in lake samples were similar with those in river samples. These concentration levels of PAHs in river and lake were similar with or a little bit lower than those of previous reports in European countries and United State[1]. Also, the PAHs levels in all sediment samples in this study were satisfied with ERL (Effect range low) in SQG (Sediment quality guideline) of NOAA (National oceanic and atmospheric administration) [4].

Only DDTs among target OCPs were detected in this study and their levels were lower than PAHs. However, in other study, it was reported that DDTs accounted for 77% of the total organochlorine pesticide concentrations in sediment[5]. The concentration of DDTs ranged from ND to 9.041 ng/g-dry with an average 1.03±0.69 ng/g-dry. These levels were remarkably low compared with major ten DDTs consumer countries such as India, China, America and Egypt (ND - 1,700 ng/g-dry)[7-11]. Comparing with SQG (NOAA), 20% of whole samples in this study exceeded ERL (Effect range low,1.58 ng/g-dry) of ΣDDTs but pretty below than ERM (Effect range median, 46.1 ng/g-dry)[4].

The source identification of PAHs and OCPs

It is known that there are two types of potential anthropogenic sources of PAHs: petrogenic and pyrogenic sources. These sources were originated from crude and refined petroleum (i.e., petrogenic source) and combustion of fossil fuel such as coal and petroleum and biomass such as grass and wood etc (i.e., pyrogenic source). Some molecular ratios of specific hydrocarbons have been developed to distinguish PAHs sources generated from different sources. Phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), Indeno[*1,2,3-cd*]pyrene (IP) and benzo[*g,h,i*]perylene (BP) were normally used to obtain these ratios. An/(An+Ph) ratio < 0.1 is usually taken as an indication of petroleum, while the ratio over 0.1 indicates dominance of combustion. Fl/(Fl+Py) ratio < 0.4 is attributed to petrogenic source, ratio > 0.5 is suggested wood and coal combustion, while between 0.4 and 0.5 is regarded as petroleum combustion. IP/(IP+BP) ratio less than 0.2 is corresponded to petroleum pollution, higher than 0.5 for grass, wood or coal combustion, and between 0.2 and 0.5 for petroleum combustion[1]. The results of these ratios in this study were shown in Figure 3. An/(An+Ph) ratio for most of samples ranged from 0.02 to 0.35, which may suggest that the majority of PAHs in Korean river basin was derived from pyrogenic source. This kind of source is confirmed by two other ratios, Fl/(Fl+Py) and IP/(IP+BP) were ranged from 0.23 to 0.71 and 0.20 to 0.50, respectively. Some of sampling sites were related with petrogenic source and located in the close proximity of petroleum area in graph. This result indicates the presence of additional petrogenic source except pyrogenic source in Korean river basin.

Among target OCPs, p.p'-DDT was detected in only one sample and *p,p'*-DDE was dominant compound and accounted near 61% of total DDTs in this study (Figure 2). The result of this study shows that DDTs deposited in Korea river basin are more likely to be “weathered” residues derived from aged soil rather than from “fresh”

DDTs input because of DDTs banning by Korean government 30 years ago. DDT is generally degraded to metabolite at specific conditions and it is known that that DDT is biodegraded to DDE under aerobic conditions or to DDD under anaerobic conditions in the environment[13]. This result also suggests aerobic biodegradation of DDT in Korean main river basin.

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Table 1. PAHs concentration level of sediment from Korea river basin

Sampling site		River basins (unit : pg/g-dry)							
		HR	HL	NR	NL	YSR	YSL	GR	GL
∑16 PAHs	min	ND[a]	6.972	ND	5.757	2.520	4.041	1.544	10.60
	max	1756	458.2	969.3	2987	211.1	175.5	152.0	143.7
	mean	103.3	152.8	66.61	210.6	44.08	66.24	50.49	83.94
	S.D.	300.1	118.1	167.2	624.4	44.28	53.03	49.06	41.41
	DF[b]	33/34	20/20	36/38	22/22	26/26	11/11	29/29	15/15

Table 2. OCPs concentration level of sediment from Korea river basin

Sampling site		River basins (unit : pg/g-dry)			
		HL	NL	YSL	GL
∑13 OCPs	min	ND	ND	ND	ND
	max	9.041	1.509	1.000	6.496
	mean	2.155	0.561	0.352	1.075
	S.D.	2.550	0.474	0.375	1.547
	DF	29/34	19/22	9/11	14/15

* [a]ND, Not detected; [b]DF, Detection frequency of PAHs and OCPs at each river and lake sample group
* HR/L, Han river/lake; NR/L, Nakdong river/lake, GR/L, Geum river/lake; YSR/L, Yeongsan river/lake

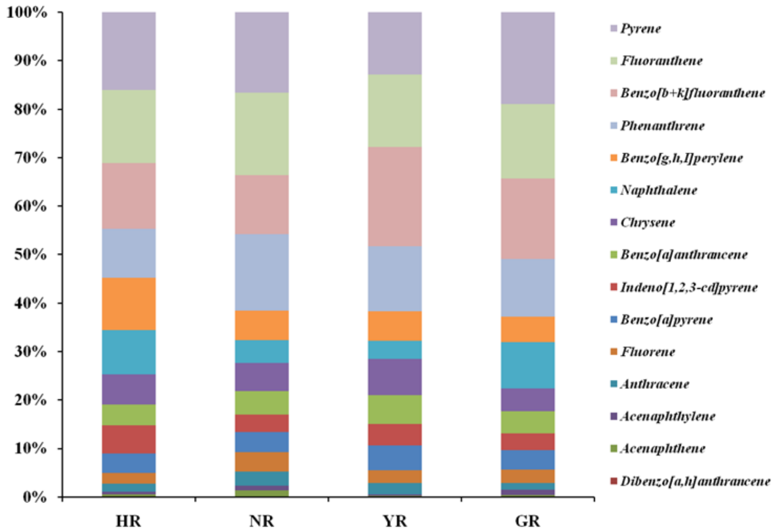

Figure 1: The distribution patterns of PAHs in each river basin

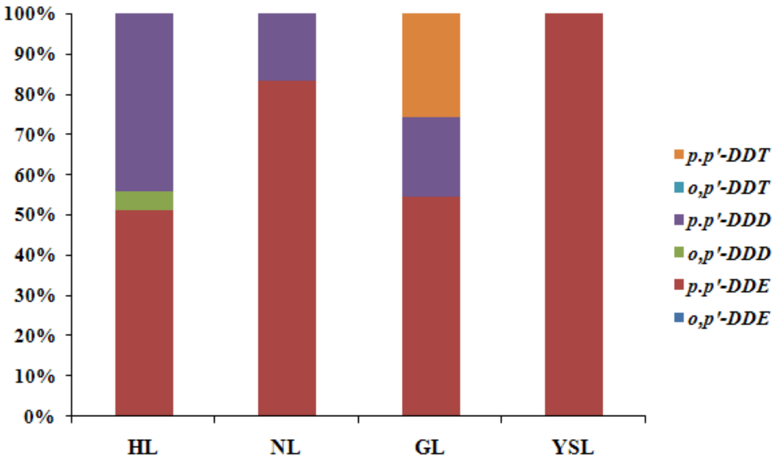

Figure 2: The distribution patterns of OCPs in each lake

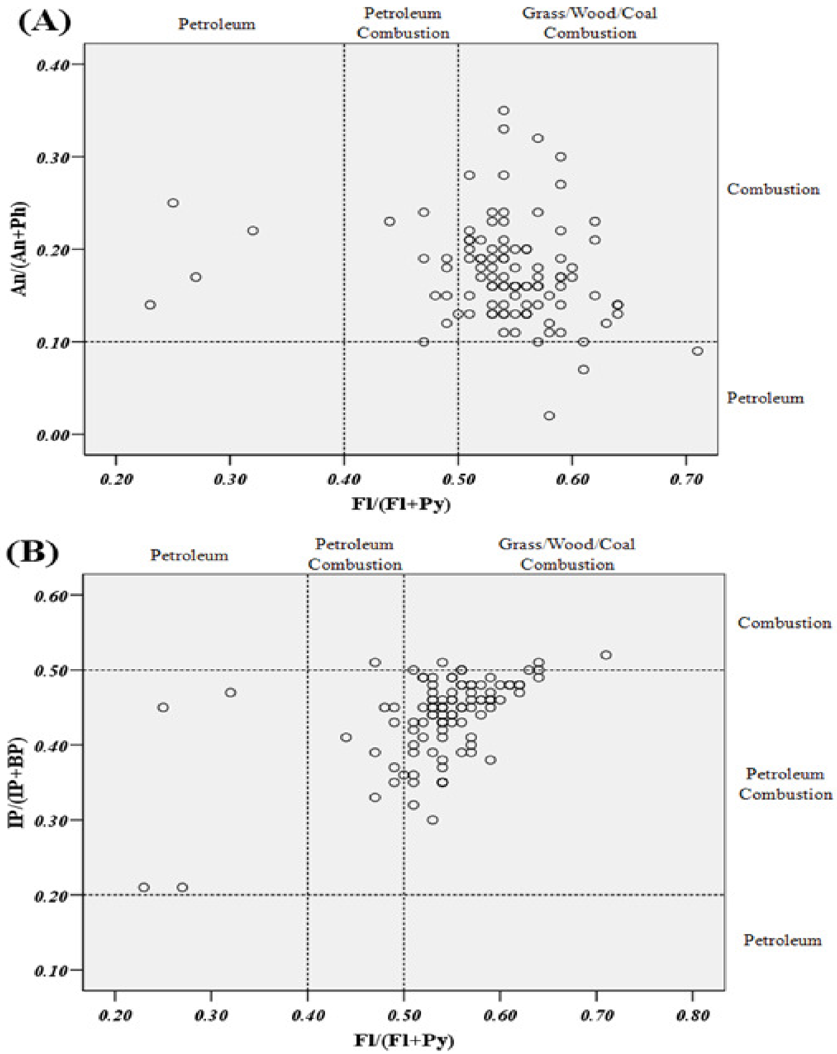

Figure 3. PAH cross plots for the ratios of (A) An/(An+Ph) vs Fl/(Fl+Py), (B) IP/(IP+BP) vs Fl/(Fl+Py)