OCCURRENCE OF PERSISTENT ORGANIC POLLUTANTS IN SOUTH KOREA: SPATIAL DISTRIBUTION AND TEMPERAL TRENDS (2001~2008)

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Introduction

The Stockholm Convention was ratified by the Republic of Korea in January 2007 to protect human health and the environment from persistent organic pollutants (POPs) by reducing or eliminating releases to the environment. Public concern on POPs re-emerged in the 1990s due to studies describing endocrine disrupting effects of some POPs. Recently, we need to review of POPs information on POPs to evaluate the management status including inventories, sources, fate, and distribution in South Korea.

In the Republic of Korea, public concern over POPs was initiated by the dioxin release from waste incinerators in 1997, and the emission of PCDDs/DFs was included in regulations. Since 2001, comprehensive projects have been performed to establish the national emission inventory of some priority POPs (dioxins). The early regulation was focused on classical POPs. Most of the organochlorine pesticides (OCPs) were banned from use in South Korea, during the early stages of POPs control in the late 1960s, and in 1980, two pesticides (heptachlor and toxaphene) were also banned from use in South Korea. HCB and Mirex were neither imported nor produced in South Korea as pesticides. PCBs were imported from abroad and the use of electric heaters with PCB-containing dielectric fluids was legally regulated for the first time in 1979. Waste containing concentrations of PCBs greater than 2 ppm was classified as specific hazardous waste by the KMOE (Shin et al., 2006).

In this study, 13 compounds including the dirty dozen POPs (OCPs, PCDDs/DFs, and PCBs) and one new group of POPs (PFAs) in the South Korean environment were reviewed. The number and volume of the literature indicates that the Korean POP studies have focused on legacy POPs (i.e., dioxins, PCBs, and OCPs). The literature review on these compounds includes project reports either performed or funded by the KMOE or NIER except for the PFAs.

Materials and methods

Mass concentrations of POPs were determined by gas chromatography (GC) with electron capture detector (ECD) and confirmed by GC with mass spectrometry (GC/MS) in the National Institute of Environmental Research (NIER), Republic of Korea. This laboratory amended the Korean official method for POPs and has successfully participated in international proficiency tests in 2007~2009. The quality control procedures followed the POPs official analytical method prepared by the KMOE. The following relevant criteria were performed for each batch, amongst others: Reagent blanks were analyzed by the performance of a complete analysis using the solvents and reagents only, in the absence of any sample. Different quality control samples of certified reference material were analyzed. The recovery rates of the internal standards in the samples as well as those of the analytes in the QC/QA samples were in the range of 40~120% which met the requirements of the official method. Calibration was based on a multilevel (5 levels) calibration curve including a bracketing calibration to control the drift of the relative response.

Results and discussion:

Dioxin-like compounds (PCDDs/DFs, co-PCBs): Beginning in 1999, the investigations of dioxin-like compounds such as PCDDs/DFs and co-PCBs were performed by NIER on a nationwide scale. Long-drawn-out monitoring for the environmental matrix includes ambient air, soil, and sediment. The levels indicate that the concentrations of dioxin-like compounds decrease gradationally by year. The concentration range of PCDD/DFs was from ND to 0.617 and the average was 0.028 pg TEQ/m^3 in 2008. The urban province of Gyeonggi tends to show relatively high concentration compared with other investigated areas in Korea. The concentration of dioxin-like compounds in sediment and soil in Korea were similar to annual levels except for the concentration measured in 2005. The level range of PCDD/DFs was from 0 to 0.648 pg TEQ/L and the average was 0.072 pg

TEQ/L in 2008. The investigations of PCDD/DFs were performed by NIER extensively in the soil around incinerators from 2004 to 2007. The results suggest that the levels tend to decrease with increasing distance from the incinerators. The highest value was 153.229 pg TEQ/g in 2006.

Figure 1 shows the levels of dioxins in the soil and sediment by year. These ranges of concentration included the levels of the nationwide investigation in 2008. The concentrations of dioxins in the sediment samples did not largely change from 1999 to 2008.

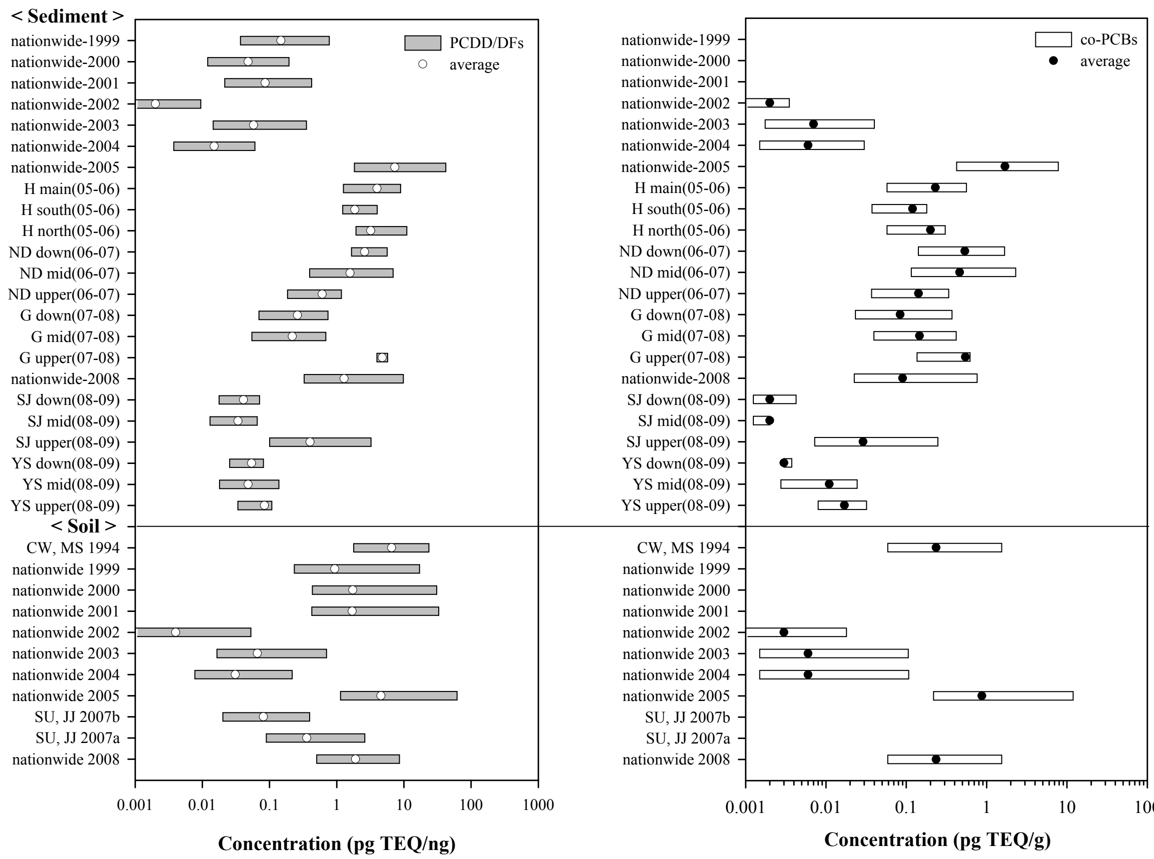

Figure 1. Concentration range and mean values of dioxin-like compounds in sediment and soil in Korea. Nationwide 1999~2006 (NIER, 2006a), nationwide 2008 (NIER, 2009a), H main, south, north (Han river main stream, south stream, north stream, NIER, 2006c), ND down, mid, upper (Nakdong river downstream, midstream, upper stream, NIER, 2007c), G down, mid, upper (Geum river downstream, midstream, upper stream, NIER, 2008), SJ down, mid, upper (Seomjin river downstream, midstream, upper stream, NIER, 2009b), YS down, mid, upper (Youngsan river downstream, midstream, upper stream, NIER, 2009b) , CW, MS (Changwon, Masan city, Lee et al., 2009), SU, JJ (Seoul, Jeonju city, Im et al., 2002).

Organochlorine pesticides (OCPs): The concentrations of DDTs, chlordanes, heptachlors, drins in ambient air of the various locations are listed in Table 2. The levels of DDTs in Korea were from sub 0.1 to 47.6 pg/m^3 and the average was 5.24 pg/m^3. These ranges were lower than those of other countries, especially Mexico shows the highest values, 2360 pg/m^3 in the rural area. The levels of chlordanes were in the relatively low range and the ranges of heptachlor and drins in Korea were similar to those of Japan. Table 2 shows the range values of OCPs in sediment samples of various locations in Asia. The levels of DDTs varied from 0.53 to 73.73ng/g in Korea and the average was 10.68ng/g. These values of DDTs were higher than those of other Asian nations and the levels of drins were similar to those of other countries. A comprehensive comparison of OCP levels in recently collected soil from various locations in Korea and in the world is presented in the following table. It can be recognized that among the reported locations in the world, the levels of OCPs in Korea in soil samples are similar to other countries levels.

Table 2. Concentration range values of OCPs in ambient air of various locations in Korea.

Matrix	∑DDTs	∑CHLs	∑HEPT	Aldrin	Dieldrin	Endrin	Reference
Air (pg/m^3)	<0.1~47.6 (5.24)	<0.1~39.0 (5.76)	<0.1~9.20 (1.28)	<0.1~3.57 (0.10)	<0.1~4.32 (0.53)	<0.1~1.41 (0.03)	Korea 2008
Sediment (ng/g)	0.53~73.73 (10.68)	0.55~10.73 (4.84)	0.53~1.31 (1.02)	<0.5~0.66	<0.5~1.01	<0.5	NIER 2009
Soil (ng/g)	0.53~73.73 (10.68)	0.55~10.73 (4.84)	0.53~1.31 (1.02)	<0.5~0.66	<0.5~1.01	-	NIER 2009
Soil (ng/g)	ND~149 (4.76)	ND~3.19 (0.095)	ND~0.87 (0.025)	-	-	-	NIER 2009
Soil (ng/g)	ND~59.34 (2.5)	ND~0.11 (0.003)	0~0.59 (0.016)	-	-	-	NIER 2009

∑DDTs : sum of *p,p*'-DDT, *p,p*'-DDE, *p,p*'-DDD, *o,p*'-DDT, *o,p*'-DDE, *o,p*'-DDD
∑CHLs : sum of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, oxychlordane
∑HEPT : sum of heptachlor, heptachlor epoxide

Occurrence of Perfluoroalkylated compounds (PFAs) : Perfluoroalkyl acids (PFAs) including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have emerged as one group of contaminants of most concern in recent years due to their endocrine disrupting effect and carcinogenic toxicity (Beach et al., 2006; Harada and Koizumi, 2009). However, few data are available on the environmental levels of these chemicals in Korea. These polar compounds are difficult to remove during water-treatment processes because they are readily soluble in water. Therefore, there has been increasing concern about the level in water. Several studies have reported the concentrations of PFOS and PFOA in surface water and sea water in Korea. In the KMOE report, Gamak Bay was a remote area and the others were industrial areas. The concentration of PFOS was relatively greater in the water flowing into the Shihwa Lake and Gwangyang bay. PFOA was detected with the highest concentration influent water of the Shihwa Lake as shown in Figure 2. The levels of PFOS and PFOA in sediment in Korea were similar to the values among all sampling sites, excluding the stream sediment of the Shihwa Lake.

The investigations of PFOS in domestic or overseas ambient air have been reported a few data. The levels of PFOS and PFOA in ambient air (particles and gas phase) have been measured in Cheonju (n=9) in Korea. The concentration ranges of PFOS and PFOA were ND~8.02 pg/m^3, 1.68~6.94 pg/m^3, respectively (Kim et al., 2009). These levels were similar to the values of Morioka and Iwate in Japan, Albany in USA and Germany. The concentration mean values of PFOS were 0.7, 1.2, 2.34, 1.1 pg/m^3, respectively (Harada et al. (2005), Kim and Kannan (2007), Dreyer and Ebinghaus (2009)).

Conclusion

Due to their persistent, bioaccumulative, and toxic properties, POPs are worldwide categorized as priority pollutant group to be prohibited in their use and distribution, or removed from the environment. Long-range transportation of POPs has resulted in relevant international efforts such as the Stockholm Convention. The present study exhibits the analysis results collected from national reports of KMOE and NIER published since 2000. Emission, contamination and exposure levels in environments for both classical and emerging POPs were reviewed within governmental management plans. Most studies focused on the 12 POPs such as organochlorinated pollutants and little on emerging POPs such as PFAs.

The concentrations of many classical POPs were less than the environmental quality criteria suggested by government agencies, except for a few 'hot spots'. Due to a lack of sufficient information, additional information from monitoring studies is needed for certain sites. Therefore, the Ministry of Environment in Korea has started the nationwide monitoring surveys (for classical and emerging POPs) of 167 sites (2009~2011).

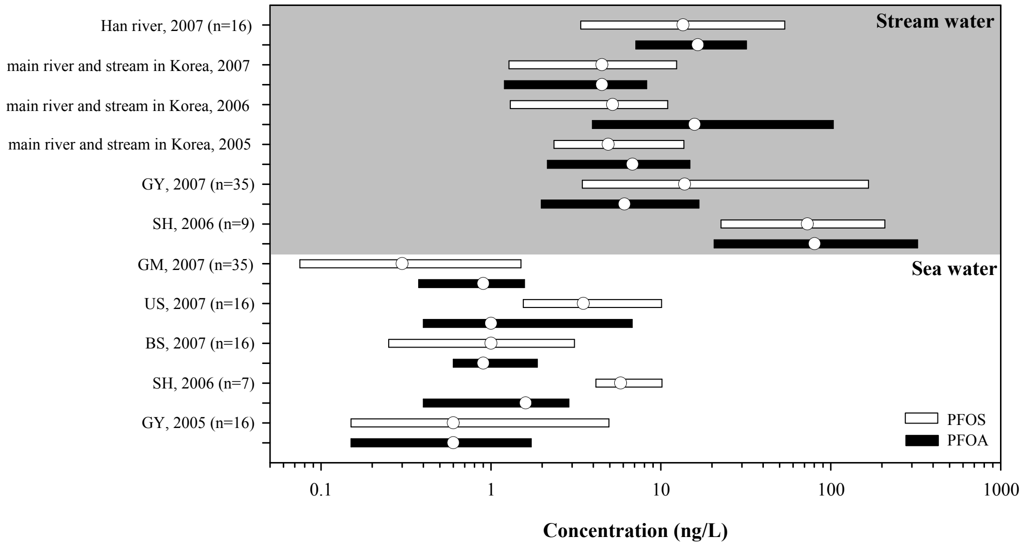

Figure 2. Concentration range and mean values of PFOS and PFOA in water in Korea. Main river and stream, 2005 : Han river, Nakdong river, Geum river, Sapkyo stream, Youngsan river, 2006 : Han river, Nakdong river, Geum river, Sapkyo stream, 2007 : Han river, Nakdong river, Geum river, Youngsan river, Seomjin river, Sapkyo stream, GY : Gwangyang bay, SH : Shihwa Lake, GM : Gamak bay, US : Ulsan bay, BS : Busan bay (KMOE report, 2009), Han river, 2007 (Shin et al., 2009).

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