

SPATIAL DISTRIBUTIONS OF HEXACHLOROCYCLOHEXANES, PENTACHLOROBENZENE AND ENDOSULFANS IN SOILS ACROSS SOUTH KOREA

Kim EJ¹, Park Y-M², Park J-E², Kim J-G^{1*}

¹ Department of Environmental Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju, Jeollabukdo 561-675, Republic of Korea;

² National Institute of Environmental Research, Environmental research Complex, Kyungseo-Dong, Seo-Gu, Incheon 404-708, Republic of Korea

Introduction

Organochlorine pesticide (OCP) contamination in the environment has given serious cause of concern due to their toxicity, persistence in the environment, bioaccumulation, and potential for long-range environmental transport¹. Heavily used OCPs in the past are dispersed throughout the global environment due to their environmental and biological persistence, and the residues continue to influence on the environment and ecosystems¹. Accordingly, six OCPs such as hexachlorocyclohexanes (lindane (γ -HCH), α -, β -HCHs), chlordecone, pentachlorobenzene (PeCBz) and endosulfans were added to the Stockholm Convention's annexes in 2009 and 2011². Therefore, in order to implement the Stockholm Convention, systematic assessments of the newly added chemicals in the environment are required.

In South Korea, HCHs had been widely used between 1950s and 1970s and its production and use were banned in 1969 and 1979 for lindane and technical HCH, respectively, but HCHs have been detected in various environmental media³⁻⁵. PeCBz was used as an intermediate in manufacture of pentachloronitrobenzene (quintozene) and as a mixture with PCBs in electrical equipment. The use of quintozene was banned in 1989, but PeCBz could continue to be released from various sources as a byproduct such as metal production and combustion of solid waste, coal, and biomass⁶. Endosulfan has been widely used until recent times and the use was banned in 2010. Chlordecone has never been produced or used in Korea.

Soil acts as an important sink for OCPs in the environment. Thus, the release of OCPs from the contaminated soils is a potential source of pollution to the atmospheric environment. In this study we monitored HCHs, PeCBz, endosulfans and chlordecone in soils from 33 sites across South Korea in order to evaluate the spatial distributions and potential sources of these OCPs in Korean soils. Moreover, we estimated the air-soil exchange by monitoring atmospheric levels of OCPs at the four selected sites. This is the first nationwide monitoring of these OCPs in South Korea. Therefore, these data can provide important information for government's implementation of the Stockholm Convention.

Materials and methods

Soil samples were collected at 33 sites consisting of 8 industrial, 13 urban, 11 agricultural and 1 control sites across South Korea (Fig. 1). Sampling was conducted between April 2010 and May 2012. At each site, five soil subsamples were taken from 0-5 cm below the surface, bulked into one sample and homogenized to obtain a composite soil sample. Air samples were collected from 4 sites consisting of 2 industrial, 1 urban and 1 agricultural sites when soil sampling was conducted. Air sampling was composed of 24 hour sampling using high volume air sampler on three consecutive days. OCPs were extracted from samples using a Soxhlet extraction for 24 hours with toluene/acetone (8:2, v/v) for soil and DCM for air samples. The extracted were subsequently cleaned and fractionated with a Florisil solid phase extraction (SPE) cartridge and activated carbon cartridge. OCPs were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry with a DB-5MS capillary column (60 m, 0.25 mm ID, 0.32 μ m film thickness).

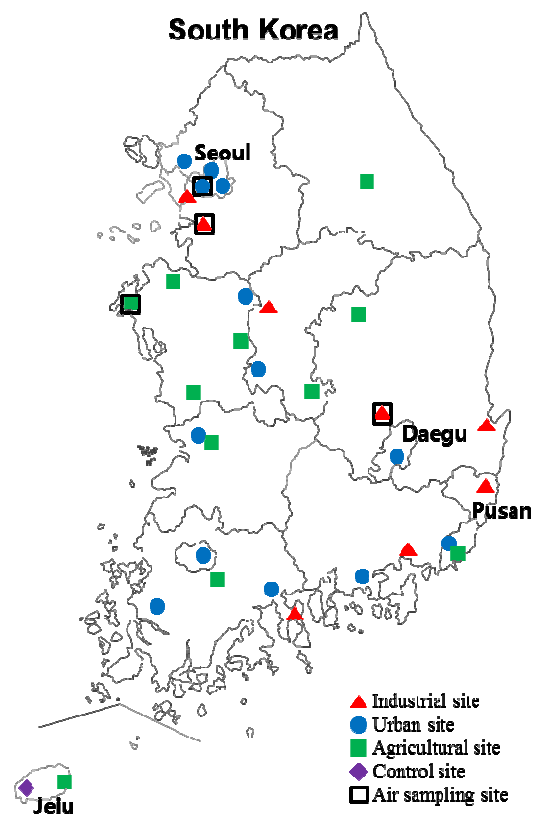


Figure 1. Locations of sampling sites in South Korea

Results and discussion

Levels and spatial distributions of OCPs in soils.

The concentrations of Σ HCH (α -, β -, γ -HCH), PeCBz and Σ endosulfans (α -, β -endosulfan, endosulfan sulfate) in soil samples are summarized in Figure 1. Chlordecone was not detected in any samples in this study, which reflected no history of its application in Korea. The average concentrations of Σ HCHs in soil samples were 0.073 ng/g with range of ND and 0.449 ng/g, which is lower than those in natural (0.65 ng/g) or agricultural (4 ng/g) soils in South China⁷ and comparable to those in urban and industrial impacted area (0.5 ng/g) of Estonia⁸. No significant difference was observed among industrial, urban, and agricultural soils ($p > 0.05$), which indicates that HCHs were evenly distributed in soils all over the country. PeCBz was detected in all soil samples except control site. The PeCBz concentrations in soil samples were ranged from 0.003 to 0.531 ng/g with an average of 0.086 ng/g, which is similar to the levels measured from Shanxi Province in China (0.144 ng/g)⁹ and those from Estonia (0.1 ng/g)⁸. The industrial soils (0.135 ng/g) showed the highest levels of PeCBz followed by the agricultural soils (0.086 ng/g) and the urban soils (0.05 ng/g). This indicates that PeCBz in soils were influenced by industrial activities as well as agricultural applications in the past. The concentrations of endosulfans in soil samples were ranged from 0.058 to 8.42 ng/g with an average of 2.19 ng/g. Endosulfan is the most recently used pesticide investigated in this study. Thus, it is quite natural that endosulfan showed higher concentrations than HCBs or PeCBz in soils. The agricultural soils showed obviously higher level of endosulfans (4.10 ng/g) than those of industrial (1.27 ng/g) or urban (1.51 ng/g) soils, which reflected its recent uses at the agricultural sites.

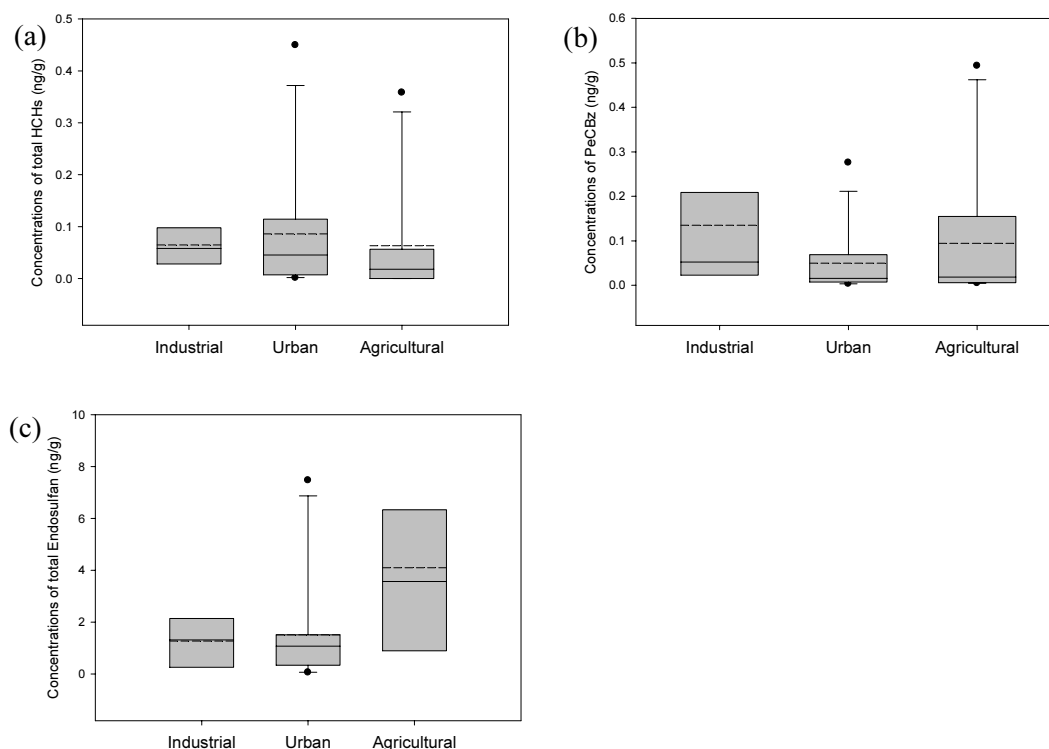


Figure 2. Levels of organochlorine pesticides in industrial, urban, and agricultural soils in South Korea. (a) total hexachlorocyclohexanes (α -, β -, γ -HCHs), (b) pentachlorobenzene, and (c) total endosulfans (α -, β -endosulfan, and endosulfan sulfate). A solid line within the box indicates the median value and a dashed line indicates the mean value.

Soil-air exchange: proportions of HCH and endosulfan isomers in soil and air.

In order to study the influence of soil-air exchange, OCPs in ambient air samples were further studied with soil samples at the four selected sites. The average concentrations of OCPs in the selected soil samples were 0.064, 0.079, 1.53 ng/g for Σ HCH, PeCBz and Σ endosulfans, respectively. The levels of OCPs in air samples were 27.9, 74.7, and 162 $\mu\text{g}/\text{m}^3$ for Σ HCH, PeCBz and Σ endosulfans, respectively. The β -isomer represented 69-100% of total HCHs in the soil samples, while α and γ -isomers represented 70-95% of total HCHs in air samples (Fig 3). Since the β -HCH isomer is the most persistent and the least volatile, high levels of β -HCH isomer in soils indicate the use of local technical HCH in the past¹⁰. On the other hand, high α - and γ -HCHs in atmospheric samples indicates higher volatility of these compounds as compared to β -HCH. The α - to γ -HCH isomer ratio could provide useful clue about the source of HCH: higher ratio (4-7) indicates the technical HCH source, while lower ratio (<1) indicates the lindane source¹⁰. In this study, α - to γ -HCH isomer ratio was 2.67 and 1.65 for soil and air, respectively, which was lower than the ratio of technical HCH. The lower ratio indicates the historical use of technical HCHs few decades ago and also possible input of long range transported lindane used in other areas⁵. Endosulfan sulfate was the dominant isomer in soil samples accounting for 72-92% of total endosulfans (Fig 3). Endosulfan sulfate is a major degradation product of α - and β -endosulfan. Therefore, major degradation of endosulfans to endosulfan sulfate seemed to occur in soil after applied in soils. On the other hand, α -endosulfan was the dominant isomer in the air representing 80% of total endosulfans, which is consistent with the results of previous study¹¹. The α - to β -endosulfan ratio of the commercially used endosulfan was about 2, but the averaged ratio observed in this study was 0.8 for soil and 5.0 for air samples. The low α - to β -isomer ratio of soil might be caused by faster degradation¹² and higher volatilization¹¹ of α -isomer in soil than β -isomer endosulfan.

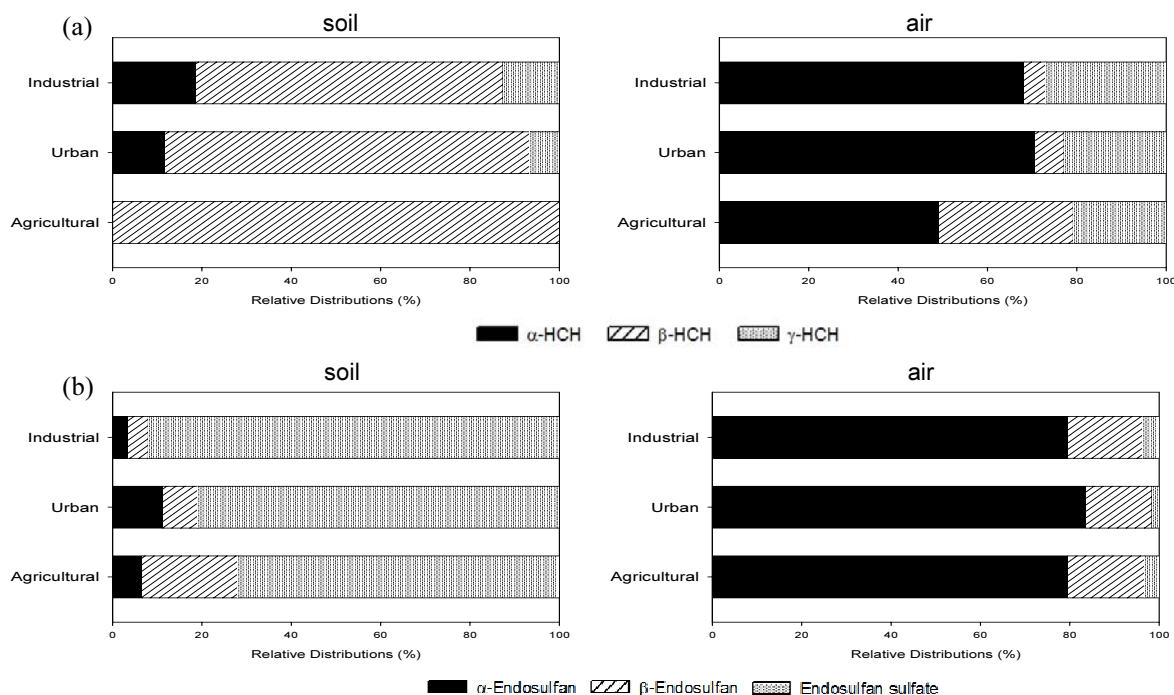


Figure 3. Relative distributions of (a) HCH and (b) Endosulfan isomers in industrial, urban, and agricultural soils and air of South Korea

Acknowledgements

This work was supported by research funds of Korean National Institute of Environmental Research.

References

1. Jones KC, de Voogt P. (1999); *Environ Pollut.* 100(1–3), 209-21
2. UNEP. <http://www.pops.int>.
3. Kim S-K, Oh JR, Shim WJ, Lee DH, Yim UH, Hong SH, Shin YB, Lee DS. (2002); *Marine Pollut Bull.* 45, 268-79
4. Hong SH, Yim UH, Shim WJ, Li DH, Oh JR. (2006); *Chemosphere.* 64(9), 1479-88
5. Jin G-Z, Kim S-M, Lee S-Y, Park J-S, Kim D-H, Lee M-J, Sim K-T, Kang H-G, Kim I-G, Shin S-K, Seok K-S, Hwang S-R. (2013); *Atmos Environ.* 68(0), 333-42
6. Bailey RE, Wijk Dv, Thomas PC. (2009); *Chemosphere.* 75, 555-64
7. Li J, Zhang G, Qi S, Li X, Peng X. (2006); *Sci Tot Environ.* 372, 215-24
8. Roots O, Roose A, Kull A, Holoubek I, Cupr P, Klanova J. (2010); *Environ Sci Pollut Res.* 17, 740-9
9. Liu GR, Cai MW, Zheng MH, Nie ZQ, Liu WB, Lv P, Su GJ, Gao LR, Xiao K. (2011); *Bull Environ Contam Toxicol.* 86, 535–8
10. Willett KL, Ulrich EM, Hites RA. (1998); *Environ Sci Tech.* 32, 2197-207
11. Hapeman CJ, McConnell LL, Potter TL, Harman-Fetcho J, Schmidt WF, Rice CP, Schaffer BA, Curry R. (2013); *Atmos Environ.* 66, 131-40
12. Zhao C, Xie H, Zhang J, Xu J, Liang S. (2013); *Chemosphere.* 90(9), 2381-7