

MONITORING OF HCHs(HEXACHLOROCYCLOHEXANE ISOMERS; α -, β -, γ -HCH) OF AMBIENT AIR, SOIL, FRESH WATER AND RIVER SEDIMENT IN KOREA

Ok Gon^{1,2}, Kim C-S¹, Jung B-G^{1,2}, Lee S-H^{1,2}, Hwang S-M^{1,2}, and Park N-J^{1,2}.

¹Graduate school of Earth Environmental Engineering and ²Dioxin Research Center,
Pukyong National University, 599-1 Daeyon 3 dong, Namgu, Busan, 608-737, Korea

Abstract

This study was carried out to confirm the concentration level of HCH in the Korean environment (water, sediment, soil, and atmosphere), and particularly, in this time, monitoring results of the atmosphere are presented for the first time in Korea. Samples were collected from ambient air, soil, water, and sediments at 29 sites. In the sampling, soil samples were collected under the following conditions: width (30 cm) x vertical (30 cm) x depth (5 cm), and sediment samples were collected using a grab sampler (25x40x30 cm). Water samples were collected using a 4L glass bottle. After collection, samples were stored in a refrigerator. Ambient air samples were collected using a High Volume Air sampler. Particularly, α -HCH was confirmed as the highest concentration among the three isomers from ambient air samples. The concentration of α -HCH in ambient air ranged from 0.68 to 19.49 $\mu\text{g}/\text{m}^3$, representing the highest concentration level in the Kimhae plain of the southern area.

Introduction

It is indicated that Hexachlorocyclohexane (HCH) is the most abundant organochlorine pesticide for distribution in Arctic water and air by results of transportation.¹

As worldwide use of HCH declines, however, the frequency of detection and the levels detected in the environment should continue to decrease. The concentration of HCH was confirmed as a low level in environment media such as air, water, soil, and sediment,² but it was widespread distribution.³

HCH compounds can be expressed that toxicity, persistency, bio-accumulation according to their relatively high stability and using for long time. Especially, these pesticides have been continued detection in air, soil, surface water, ground water, and drinking water because of long range transportation through environment media and atmospheric process.^{4,5,6,7}

UNEP were suggested to the persistence organic pollutants (POPs) unintentionally of three kinds from by-products such as dioxins and dioxin like compounds and pesticides of nine kinds. While recently, Mexico government was proposed to the UNEP that include in POPs to the HCH.⁵⁻⁶

It is summarized that Hexachlorocyclohexane (HCH) is a synthetic chemical consisting of eight isomers. Only four of these isomers— α -HCH, β -HCH, γ -HCH, and δ -HCH—are of commercial significance. γ -HCH, commonly referred to as lindane, is used as seed treatment for barley, corn, oats, rye, sorghum, and wheat. It is also used in very small quantities as a prescription medication for the treatment of scabies and head lice in humans.² Especially, insecticide γ -HCH (lindane) can be included > 99% γ -HCH, also Technical-grade HCH can be consisted of approximately 60–70% α -HCH, 5–12% β -HCH, 10–15% γ -HCH, 6–10% δ -HCH, and 3–4% ϵ -HCH.^{2,7}

This study was carried out to confirm the concentration level of HCH in the Korean environment (water, sediment, soil, and atmosphere), and particularly, in this time, monitoring results of the atmosphere are presented for the first time in Korea.

Materials and Methods

Sampling and preparation

Ambient air samples were collected using a High Volume Air sampler (HVAS; SHBATA, JAPAN). The sample holder was constructed following the procedure; GF (Glass Filter), PUF (Polyurethane Foam), ACF (Activated Carbon Filter), PUF, and did Surrogate (13 C Labeled POPs 12 kinds 10ng) spiking on above PUF part of the first stage PUF. The velocity of flow is 500 L/min, and sample collection was carried out for 24 hr.

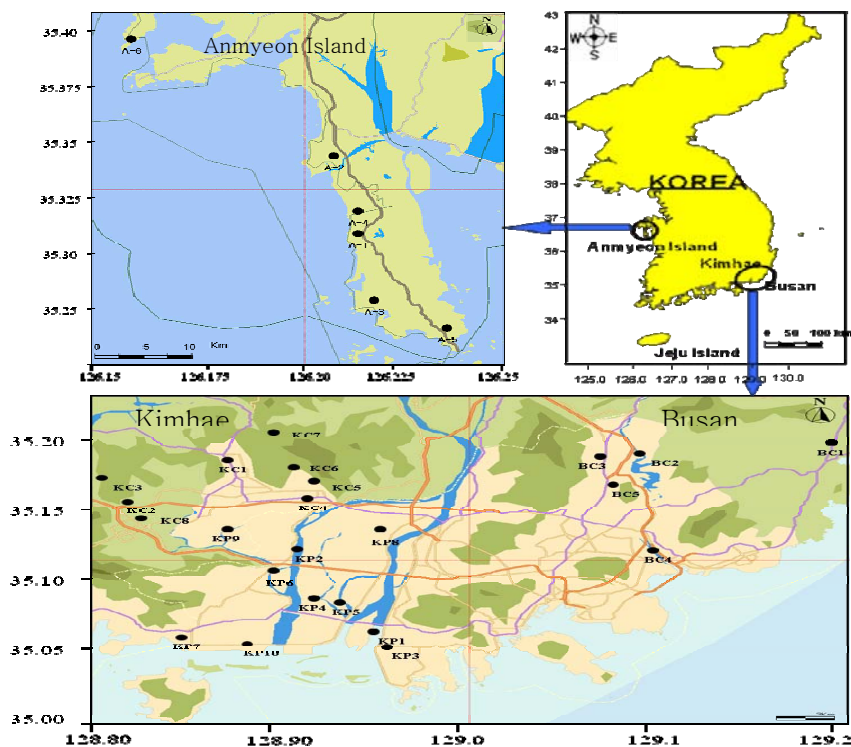


Fig.1. Map of sampling area of 29 sites for ambient air, soil, water and sediment.

Fig.1 shows sampling area of 29 sites. Samples were collected to the ambient air, soil, water and sediments in 29 sites. In the sampling, soil samples were collected in following condition; to width (30 cm) x vertical (30 cm) x depth(5 cm) and sediment samples were collected using a grab sampler(25x40x30cm). Water samples were collected using glass bottle of 4L capacity. After collection, samples were stored in refrigerator.

-Extraction-

Glass Filter, PUF and Activated Carbon Filter of Ambient air samples were Soxhlet extracted for 24hr using acetone and toluene solvent and concentrated using a rotary evaporator and finally changeover by n-hexane.

Water samples were added of 30g sodium chloride and surrogate STD (13 C-POPs, 1ug/mL) 10 uL. Extraction was carried out two times using n-Hexane 50 mL and for remove to water used anhydrous sodium sulfate and finally concentrated to 10ml using a rotary evaporator.

Sediment samples were freezing dried, and soil samples were treated to remove of moisture by anhydrous sodium sulfate 10g against soil sample 10g. After that, surrogate STD (13 C-POPs, 1ug/mL) 10 uL were spiked and extracted using Acetone 25 mL and extracted 3 times for 30 minutes by ultrasonic. After that, 5% sodium chloride of 250ml was added with extraction solution and liquid-liquid extracted using n-hexane 50ml, that it was carry out 2 times and for remove to water added anhydrous sodium sulfate and finally concentrated to 5ml using a rotary evaporator and N₂ gas.

-Clean up-

Extracts solution were treated for clean up as following on condition; in the Florisil Column(15mm (φ) x 300mm (L) : Filling up by Quartz wool and charges by 2g anhydrous sodium sulfate (Anhyd.Na₂O₄), 10g activated Florisil (18 hours in 200°C vitality), 2g anhydrous sodium sulfate.

In the first (To begin with), Pre-clean up of Florisil column was carried out by 5% diethylether with n-hexane (5:95) 100ml. After that, extract solutions with care poured for column and which was eluted as following; Flow out 20% diethylether with n-hexane (5:95) 100ml solvent and after flow out using solvent by 5% diethylether with n-hexane (5:95) 100ml. After concentrated to 10ml used rotary

evaporator and finally concentrated to 0.1ml using N₂ gas to the instrumental analysis by HRGC/HRMS. The samples were analyzed by HRGC/HRMS(6890 GC coupled to a JEOL JMS-700D HRMS), and quantification were carried out according to 13C labeled surrogate with internal standard and syringe spiking standard of five mixing compounds of 13C-PCBs by RRF Method.

Results and Discussion

Table-1. Concentration level(pg/m³ and ng/g dry wt)of HCH in Ambient air, Soil, Watr and Sediment from Rural and Urban in Korea

	Compounds	Urban, Kimhae- South Area (n=8)	Urban, Busan- South Area (n=5)	Rural, Anmendo -East Area (n=6)	Rural, Kimhae- South Area (n=10)
Ambient Air	α -HCH	0.68-13.10	0.77-6.81	6.92-16.24	1.65-19.49
	β -HCH	n.d-0.41	n.d	n.d	n.d-0.72
	γ -HCH	n.d-3.75	0.16-1.22	2.08-3.96	0.45-3.91
Soil	α -HCH	n.d-0.02	n.d-0.05	n.d	n.d-0.06
	β -HCH	n.d-0.09	n.d-0.17	n.d-0.13	n.d-0.14
	γ -HCH	n.d-0.06	n.d-0.05	n.d	n.d-0.06
Water	α -HCH	n.d	n.d	n.d	n.d-0.21
	β -HCH	n.d-0.81	n.d	n.d	n.d-2.58
	γ -HCH	n.d-7.26	0.18-11.04	n.d-0.38	0.24-20.15
Sediment	α -HCH	n.d	n.d	n.d	n.d
	β -HCH	n.d-0.11	n.d-0.11	n.d-0.06	n.d-0.21
	γ -HCH	n.d	n.d	n.d	n.d

-Ambient Air-

In the mainly, α -HCH and γ -HCH were detected in ambient air samples among to the three isomers. Particularly, α -HCH was confirmed most highest concentration within of three isomers from ambient air samples. Concentration of α -HCH in ambient air ranged from 0.68 to 19.49pg/m³, presented highest concentration level in Kimhae plain of southern area.

This concentration levels was evaluated by similar to compare with ambient air from Kattegat channel of Sweden and in Alabama of American.⁸ However, these concentration levels confirmed low 1/10 more than average concentration of 168pg/m³ in China Qingdao,⁹ as well as low than concentration of Nittaga, Maki, Ysubame, Jouzo and Yaihko in Japan.¹⁰

Also, concentration of γ -HCH was presented 0 - 3.96pg/m³ in ambient air, and these concentration levels were lower than 6 ~ 18pg/m³ of Alabama, and it was appeared by level of 1/3 compare to Alabama. These results were very lower level by comparing with 3.5~110pg/m³ of Sweden Kattegat channel and 86pg/m³ average concentration of Qingdao in China.^{9,11}

Result of this study, Concentration trend of HCH from ambient air were showed that plain area and urban of plain area surrounding city was higher levels rather than urban of downtown area. Also, Concentration level of isomers showed a sequence to pattern such as α -HCH > γ -HCH > β -HCH in ambient air, and Rural site(Anmen-do) of East area can be take effecting of transportation from China because of this site has nonexistence source as background area.

-Soil-

In the case of soil, 4 site among Urban 13 site were detected, and 10 site detected among Rural 16 site. β -HCH isomer was highest concentration level among HCH isomers by 0.17ng/g. However, this result was lower concentration level than Crop Pearl River delta, Paddy and Natural soil of China.¹²

-Water-

In the case of water, concentration of γ -HCH was showed higher compare with α -HCH and β , and the concentration of γ -HCH, a range is n.d - 20.15ng/L in Kimhae plain area. Concentration of γ -HCH is lower level compare to China Chentang river's 0.89 - 77.56ng/L in water sample.¹³

-Sediment-

In the case of sediment, only detected β -HCH, and level of concentration was presented n.d - 0.21ng/g and the concentration is low level compare to Minjang river.¹⁴

References

1. Macdonald *et al.* Canadian Arctic Contaminants Assessment Report 2000.
2. ATSDR, A Toxicological Profile for Hexachlorocyclohexane. 2005.
3. Tanabe S. et al., J Oceanogr Soc Jpn. 1982; 38:137-148.
4. Bidleman T.et al. , Environ. Sci. Technol. 2007; 41, 2688-2695
5. UNEP. Stockholm Convention on Persistent Organic Pollutants(POPs). 2001.
6. UNEP. New chemicals for control under POPs Convention. 2005.
7. Kutz et al. Rev Environ Contam Toxicol. 1991; 120:1-82.
8. Bidleman T. and A.D Leone., Environmental Pollution, 2004; 128; 49-57.
9. Lammel G. et al., Atmospheric Environment, 2007; 41, 452-464.
10. Murayama H.et al . Chemosphere, 2003;52, 683-694.
11. Sundqvist K.et al., Environmental Pollution. 2004 ; 128, 73-83.
12. Li J. et al., Science of the Total Environmental, 2006 ; 372, 215-224.
13. Zhou R. et al., Journal of Hazardous Materials, 2006 ; A 137, 68-75.
14. Zhang Z.L. et al., Chemosphere, 2003; 52, 1423-1430.