SEASONAL CHARACTERISTICS OF CONTAMINATION FOR ORGANOCHLORINE PESTICIDES IN AMBIENT AIR IN REPUBLIC OF KOREA

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Introduction

Organochlorine pesticides (OCPs) belong to persistent organic pollutants (POPs) and were used extensively in agriculture, forestry, and home pest control, until most were banned in the 1970s and 1980s. These pollutants target the central nervous system and many of them are suspected to cause cancer. Organochlorines pesticides such as dichloro diphenyl trichloroethane (DDT) and lindane tend to be very persistent, breaking down exceedingly slowly once released into the environment. This property made them attractive insecticides to be investigated, since often just single application would be effective for months. But this makes them dangerous for people and the environment because they can be incorporated into ecosystems and food chains where they can persist for years.

These persistent pollutants tend to be poorly soluble in water but highly soluble in fat; a combination of properties that causes them to be stored in the fatty tissues of animals, called bioaccumulation. As a result of bioaccumulation, the levels of OCPs in a person can be much higher than levels in the environment or in food.

To achieve effective management to OCPs, the monitoring plans over long term and national wide are necessary because these pollutants influence the humans getting exposure through inhalation.

This study was performed to evaluate the level and contamination characteristics of OCPs especially focused on DDT and Hexachlorocyclohexane (HCH) in national atmosphere where distinctive seasonal characteristics of these exist.

Materials and methods

As a comprehensive monitoring survey on POPs in Korea, 108 ambient air samples taken from 36 locations in four seasons were studied in 2013. Samples were collected 24 hours per day and continuative 3 days with 0.7 m3/min flow by high volume air sampler (HV-1000F, SIBATA). Particles on glass fiber filter and gaseous phases in activated carbon felt (ACF)/polyurethane form (PUF) were extracted by soxhlet extraction with toluene and acetone for 16 hours. The extracts were spiked with internal standard solution (Wellington Laboratories, Canada and ES-5465, Cambridge Isotope Laboratories, Inc., USA). The OCPs were eluted florisil cartridge (InertSep Fl 5g/20mL). There are two fractions in florisil column. The first fraction of florisil column was used 10mL hexane and discarded. After then, the second fraction with 100mL hexane solution containing dichloromethane (25% vol) was received. Received elute was concentrated by vacuum rotary evaporator (Rotavapor R-215, BÜCHI Labortechnik AG, Switzerland) and 2, 3′, 4′, 5-Tetrachlorobiphenyl was added to the sample as an internal standard. The samples were concentrated to 10 μL with flowing nitrogen, transferred to micro volume inserts, and sealed until analysis.

Table 1. Summary of HRMS analysis condition for organochlorines pesticides MS

GC	Agilent 7890A GC	Remarks
Column	DB-5 capillary column, 30m × 0.25㎜ ID × 0.2㎛	
Injection Volume	1μL	
Carrier Gas	Helium 1.0mL/min	
Auxiliary Temp.	300℃	
Injector Temp.	260℃	
Temp. program	100℃ for 1min, 20℃/min to 180℃, 2.5℃/min to 210℃ and hold for 1min 10℃/min to 330℃ and hold for 10min	
Ion source Temp.	260℃	
Detection	Selective ion monitoring	

The samples were analyzed using an Agilent 7890A gas chromatography and HRGC/HRMS Autospec Premier and a DB-5 capillary column (30 m × 0.25 mm × 0.2μm, Restek, USA). Helium was used as the carrier gas at a flow rate of 1 mL/min. Samples (1 μL) were injected by the auto sampler under a splitless mode at a temperature of 260°C. The oven temperature program was the following: 100°C for 1 min, 20°C/min to 180°C, 2.5°C/min to 210°C and 210°C for 1 min, 10°C/min for 330°C, and 300°C for 10 min. The ion source temperature of the mass spectrometer was 260°C. The compounds were quantified in the selected ion mode, and the calibration curve was quantified with the internal standard.

Results and discussion

The production and use of DDT is banned from 1973 in Republic of Korea, as 941tons of DDT was used during 1946 to 1973. The DDT metabolizes to DDE and DDD after releasing to the environment and concentration of DDT is expressed by sum of DDT and their metabolite DDE and DDD. This study also examined the o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT, p,p'-DDT and calculated sum of metabolite, ΣDDT.

Table 1 is annual mean concentration of organochlorines pesticides and Table 2 is seasonal concentrations. Only o,p'-DDD, o,p'-DDD, o,p'-DDE were detected in summer except during spring and winter. On the other hands, p,p'-DDE, o,p'-DDT, p,p'-DDT were detected with all samples in winter, spring and summer.

Average concentration levels of DDT were 7.060pg/Sm3 in urban area, 3.406 pg/Sm3 in suburban area, 3.442 pg/Sm3 in industrial area and 3.505 pg/Sm3 in background area.

Table 2. Summary of annual mean concentration (pg/Sm3) of organochlorines pesticides

Compounds	Mean	STDEV	Max	Min	Median	N > LOD
o,p'-DDD	0.119	0.096	0.631	<LOD[a]	0.454	7
p,p'-DDD	0.114	0.119	0.800	<LOD[a]	0.495	6
o,p'-DDE	0.170	0.096	0.678	<LOD[a]	0.406	11
p,p'-DDE	3.042	1.615	7.926	<LOD[a]	2.531	34
o,p'-DDT	1.037	0.548	3.988	<LOD[a]	1.045	31
p,p'-DDT	1.117	0.865	5.884	<LOD[a]	1.073	28
∑DDTs	5.599	3.210	19.831	<LOD[a]	4.318	34
α-HCH	23.240	11.532	64.918	<LOD[a]	19.778	34
β-HCH	1.918	0.785	5.332	<LOD[a]	1.784	34
γ-HCH	9.175	3.733	25.491	<LOD[a]	8.044	34

[a]<LOD : less than limit of detection

Table 3. Summary of seasonal mean concentration (pg/Sm^3) of organochlorines pesticides

Compounds	winter	spring	summer
o,p'-DDD	<LOD[a]	<LOD[a]	0.334
p,p'-DDD	<LOD[a]	<LOD[a]	0.342
o,p'-DDE	<LOD[a]	<LOD[a]	0.509
p,p'-DDE	1.510	2.006	5.609
o,p'-DDT	0.061	0.488	2.563
p.p'-DDT	0.302	0.677	2.372
ΣDDTs	1.873	3.172	11.751
α-HCH	11.275	18.921	39.523
β-HCH	1.102	1.200	3.453
γ-HCH	7.127	6.032	14.367
Temp.	-0.7	14.1	26.8

[a]<LOD : less than limit of detection

Hexachlorocyclohexane (HCH) is a manufactured chemical that exists in eight chemical forms called isomers. One of these forms, γ-HCH (commonly called lindane) is produced and used as an insecticide on fruit, vegetables. Technical-grade HCH is used as an insecticide and typically contained 10-15% γ-HCH as well as the alpha (α), beta (β), delta (δ), and epsilon (ε) forms of HCH. Virtually all the insecticidal properties resided in γ-HCH. The technical-grade HCH has not been produced or used in Republic of Korea since 1979. But HCH is possible to transport from one phase to another, so it would be vaporized or rescattered from soil to ambient when the temperature is raised; and it is adsorbed again from ambient to soil when temperature is dropped again. Fig 1 shows seasonal characteristics of isomers of DDT and HCH; and it can also figure out that most of isomers increase as temperature increase.

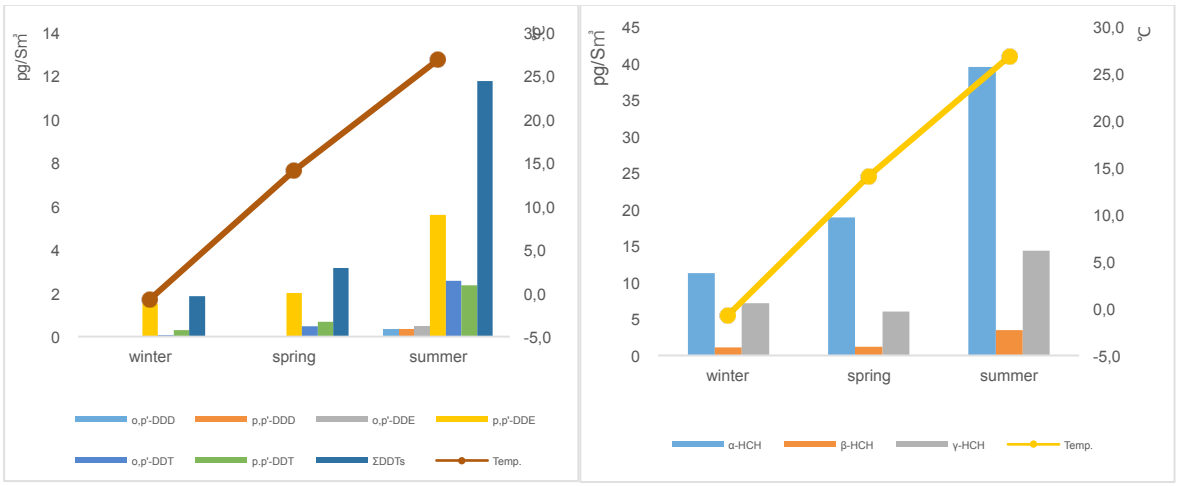

Fig 1. Seasonal and temperature dependence characteristics of isomers of DDT and HCH

This study shows that major isomers of DDT is 61% of p,p'-DDE, 19% of p,p'-DDT, 13% of o,p'-DDT and the other isomers are below 1%. It means that p,p'-DDT was used long time ago when it has high ratio of p,p'-DDE and p,p'-DDT as p,p'-DDE is metabolite of p,p'-DDT. This result shows that ratio of p,p'-DDE and p,p'-DDT is 2.727±0.673 pg/Sm3.

The α-HCH seems to be existed high ratio in the atmosphere than the other isomers because it has high volatility. The ratio of α-HCH and γ-HCH can be used as a parameter which is recently being used either for technical-grade HCH or Lindane.

In this study, main isomer is α-HCH and average ratio of HCH isomers are 66% of α-HCH, 5% of β-HCH, 28% of γ-HCH. The ratio of α-HCH and γ-HCH is from 1.582 to 3.137 (average 2.49), and it is similar with mid-Atlantic atmosphere from 1.3±1 to 2.7±1.8 as shown in Fig 2.

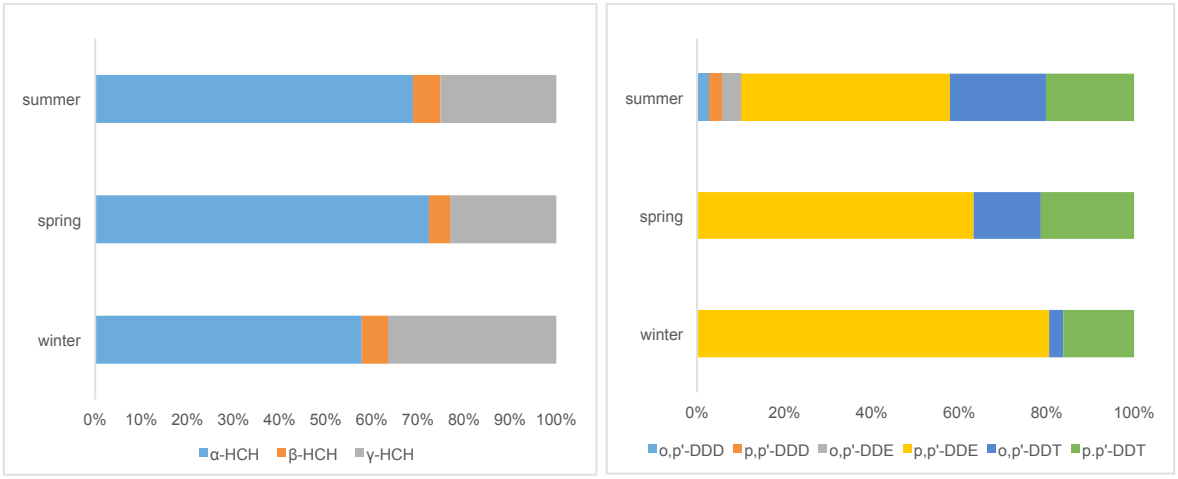

Fig 2. Seasonal profile pattern of isomers of DDT and HCH

The DDT and HCH have been designated as residual pesticide since 1970's in Republic of Korea as these were detected in the atmosphere and it was found that α-HCH exists at higher concentration than γ-HCH.

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References

1. A. Li, S. Tanabe, G. Jiang J.Giesy, P. Lam, Persistent organic pollutants in Asia: sources, distributions, transport and fate, Elsevier (2011) 31-157.
2. Q Li, X. Wang, R. Wang, H. Sui, W. Li, L. Lu, Seasonal trends and potential sources of ambient air OCPs in urban and suburban areas in Dalian, China, J. Environ. Monit. 13 (2011) 1816-1822.
3. G.G. Pandit, S.K. Sahu, Gas exchange of OCPs across the air-water interface at the creek adjoining Mumbai harbour, India, J. Environ. Monit. 3 (2001) 635-8.
4. F. Wania, D. Mackay, Tracking the distribution of persistent organic pollutants. Environ. Sci. Technol. 30 (1996) 390-396.
5. K. S. B. Miglioranza, M. Gonzalez, P. Ondarza, V. Shimabukuro, F. Isla, G. Fillmann, Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Rio Negro basin, Sci. Total Environ. 452-453 (2013) 275-285.