CHARACTERISTICS OF CONTAMINATION FOR DDT IN THE AIR AND SOIL IN REPUBLIC OF KOREA

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Introduction

Dichlorodiphenyltrichloroethane (DDT) is an insecticide and organochlorine pesticide that had been used extensively in the world for decades because of its low cost and excellent insecticidal effect since the 1940s. In the 1950s, various infectious diseases broke out in Republic of Korea (referred to as Korea) during the Korean War. US troops brought DDT and started to use it to eradicate lice. Since then, DDT had been used in large quantities as a pesticide in order to increase agricultural output. However, the excessive toxicity of DDT and the accumulation of high concentrations in living organisms had caused severe negative effects on human body and ecosystems. In 1969, the Korean government revised the "Pesticide Control Act" in order to prohibit the use of DDT by mandating users to receive 'permission for sale and the use of toxic pesticides'. Although almost 50 years have passed since the use and manufacture of DDT had been banned, not only the DDT used in other countries but also the DDT used in the past still affect our environment because of its long-term mobility and persistency.

DDTs is decomposed into isomers of DDDs, DDEs in accordance with the surrounding environment with the course of time and DDT pesticides are produced in the form of DDTs. Therefore, the ratio of DDTs, DDEs, and DDDs detected in the environment can determine the use of DDT insecticides and the change of DDT with environment and time.

This study was performed to understand the actual condition of contamination through o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT, p,p'-DDT concentration and changes in the ratio of isomers in the air and soil of Korea from 2008 to 2013.

Materials and methods

As a comprehensive monitoring survey on persistent organic pollutants (POPs) in Korea, data on samples taken from the air and soil were used in 2008 to 2013. Air samples were collected at 36 to 38 locations for three to four seasons each year. Samples were collected 24 hours per day and continuative 3 days with 750L/min flow by high volume air sampler (HV-1000F, SIBATA). Particles on glass fiber filter and gaseous phases in activated carbon felt (ACF) were extracted by soxhlet extraction with toluene for 24 hours and acetone for 4 hours, polyurethane form (PUF) were extracted by soxhlet extraction with dichloromethane for 24 hours. Soil samples were collected at 57 to 60 locations in the spring of each year. Each soil samples were collected at 5 points in total, 5cm diameter and 5 cm in depth, at one center point and four directions around within 5~10m in one place respectively, and they were mixed to collect more than 100g as dry weight. Soil was extracted by soxhlet extraction with toluene for 24 hours. Organochlorine pesticides (OCPs) were cleaned up by florisil cartridge (InertSep Fl 5g/20mL) after injecting the internal standard solution (Wellington Laboratories, ES-5465, Cambridge Isotope Laboratories, Inc., USA) into the extracts. The cartridge is activated with 10mL of n-hexane and then eluted with 100mL of n-hexane and 100mL of n-hexane solution containing dichloromethane (25% vol). After then, received elute was concentrated by vacuum rotary evaporator (Rotavapor R-215, BÜCHI Labortechnik AG, Switzerlnd) and inject the recovery standard

solution (2, 3′, 4′, 5-Tetrachlorobiphenyl) into the samples. The samples were concentrated by a nitrogen concentrator up to 10 μL and transferred to vial insert for analysis. All the air samples were analyzed using GC/HRMS from 2008 to 2013. Soil samples were analyzed using GC/LRMS from 2008 to 2012 and GC/HRMS in 2013.

Table 1. Analysis condition for organochlorine pesticides (2008-2012)

MS / GC	HRMS / Agilent 6890A GC	LRMS / Perkin Elmer Clarus500 GC
Sample type	Air	Soil
Column	HT-8 capillary column, 30m × 0.25㎜ID × 0.25㎛	Ultra-2 capillary column, 50m × 0.2㎜ID × 0.33㎛
Carrier Gas	Helium (99.9999%) 1.0mL/min	Helium (99.9999%) 1.0mL/min
Injector Temp.	260℃	250℃
Temp. program	120℃ for 1min, 10℃/min to 180℃ and hold for 2min, 4℃/min to 210℃ and hold for 1min 10℃/min to 300℃ and hold for 12min	100℃ for 0.3min, 10℃/min to 200℃ and hold for 3min, 2.5℃/min to 280℃ and hold for 1min 56℃/min to 300℃ and hold for 2min
Ion source Temp.	240℃	210℃
Detection	Selective ion monitoring	Selective ion monitoring

Table 2. Analysis condition for organochlorine pesticides (2013)

MS / GC	HRMS / Agilent 7890A GC
Sample type	Air, Soil
Column	CLPesticides2 capillary column, 30m × 0.25㎜ID × 0.2㎛
Carrier Gas	Helium (99.9999%) 1.0mL/min
Injector Temp.	260℃
Temp. program	30℃ for 1min, 20℃/min to 180℃, 0.5℃/min to 186.5℃, 10℃/min to 250℃, 40℃/min to 300℃ and hold for 4.4min
Ion source Temp.	260℃
Detection	Selective ion monitoring

Results and discussion

From the results of DDT analysis in Korean air and soil from 2008 to 2013, the concentration of DDT tended to decrease with time. Also, most of the DDTs exist as p, p'-DDE in which DDTs were decomposed, and the order of isomers is DDEs> DDTs> DDDs. Looking at the correlation between isomers, p,p'-DDT and p,p'-DDE are inversely correlated.

Table 3 and Table 4 show the concentration of DDT detected from 2008 to 2013, in order to identify the contamination characteristics of DDT still being detected, even 50 years have passed since the ban on the use of

DDT in Korea. Table 3 is summary of annual mean concentration of DDT in the air from 2008 to 2013. It was the highest at 6.913 pg/Sm^3 in 2010 and gradually decreased year by year, reaching 4.235 pg/Sm^3 in 2013. Table 4 is summary of annual mean concentration of DDT in soil from 2008 to 2013. It was 4.576 ng/g in 2008 and 0.869 ng/g in 2013.

Table 3. Summary of annual mean concentration (pg/Sm^3) of DDT in the air

Compound	o,p'-DDD	p,p'-DDD	o,p'-DDE	p,p'-DDE	o,p'-DDT	p,p'-DDT	∑DDT
2008	0.014	0.021	0.127	2.882	1.038	1.155	5.237
2009	0.033	0.024	0.227	3.328	1.253	1.399	6.264
2010	0.063	0.075	0.272	3.894	1.188	1.421	6.913
2011	0.017	0.018	0.080	2.680	0.608	0.774	4.177
2012	0.008	0.058	0.035	2.138	0.585	0.661	3.485
2013	0.119	0.523	0.203	2.101	0.650	0.639	4.235

Table 4. Summary of annual mean concentration (ng/g) of DDT in soil

Compound	o,p'-DDD	p,p'-DDD	o,p'-DDE	p,p'-DDE	o,p'-DDT	p,p'-DDT	∑DDT
2008	0.093	0.462	0.023	2.689	0.124	1.184	4.576
2009	0.070	0.478	0.012	2.207	0.083	0.875	3.725
2010	<LOD	<LOD	<LOD	0.461	0.012	0.299	0.771
2011	<LOD	<LOD	<LOD	0.209	<LOD	0.258	0.467
2012	<LOD	<LOD	<LOD	0.331	<LOD	0.137	0.468
2013	0.024	0.113	0.005	0.484	0.035	0.209	0.869

<LOD : less than limit of detection

Fig 1 shows the ratio of DDT isomers in the air and soil to determine whether DDT was recently used. Most isomers were present in the p,p'- isomer form, among them, the ratio of p, p'-DDE, in which DDTs were decomposed over time, was the highest in both air and soil. Isomers of DDT are p,p'-DDE>p,p'-DDT>o,p'-DDT in the air, and p,p'-DDE>p,p'-DDT>p,p'-DDD in soil, and these three substances accounted for more than 90% of the total.

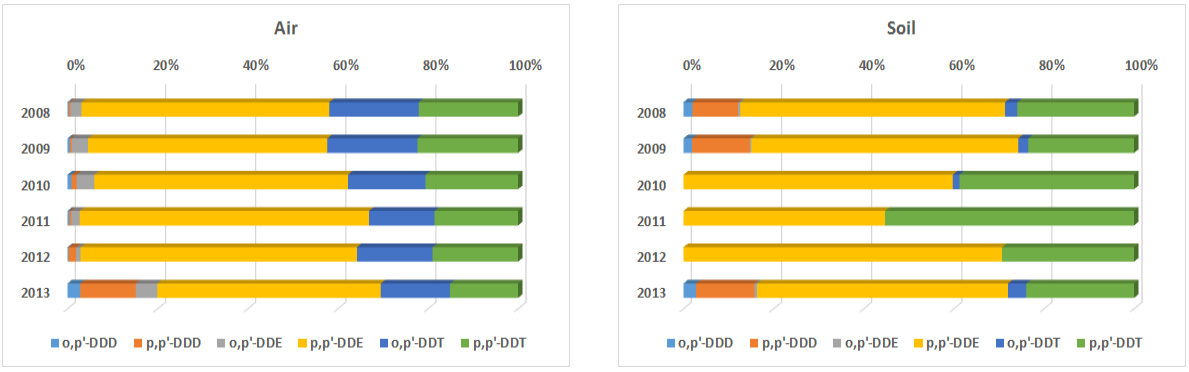

Fig 1. Annual profile pattern of isomers of DDT

p, p'-DDT were decomposed into p, p'-DDE in the aerobic state and p, p'-DDD in the anaerobic state depending on the surrounding condition. To understand the decomposition characteristics of p, p'-DDT, the correlation of p,p'-DDE/p,p'-DDT and p,p'-DDD/p,p'-DDT ratios is shown in Fig 2. p,p'-DDT and p,p'-DDE were inversely correlated with R^2=0.6333 in the air and R^2=0.8840 in soil, p, p'-DDD and p, p'-DDT were not correlated with R^2=0.0165 in the air and R^2=0.2876 in soil. That is, p,p'-DDT decomposed mostly into p, p'-DDE form over time, and the air and surface soil samples were aerobic condition.

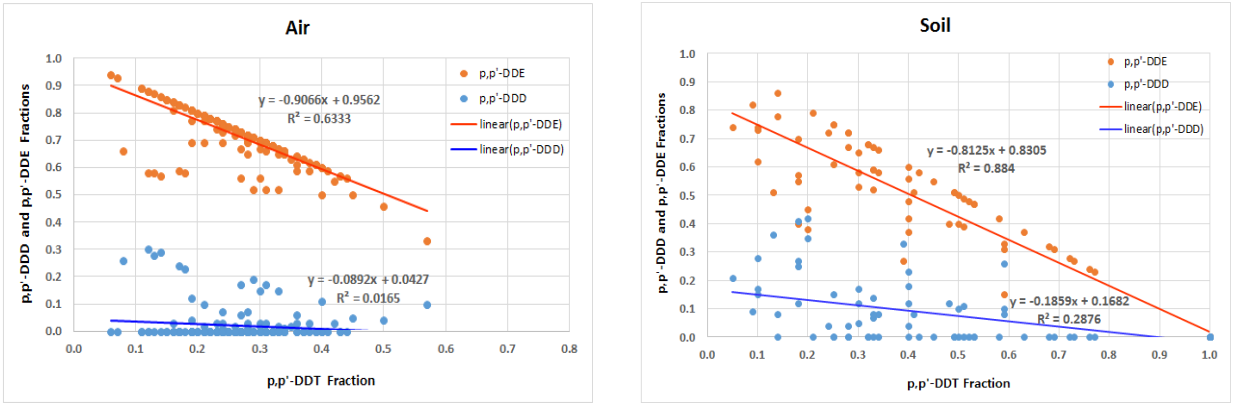

Fig 2. Relationships between the fractional values of p,p'-DDT and p,p'-DDD; p,p'-DDT and p,p'-DDE measured at air and soil

Even after a long period of time since the use of DDT, the detection of DDT seems to be due to the long-distance mobility and persistence of DDT used in the past. The concentration of DDT tended to decrease over time, and most of the remaining DDT is present as p,p'-DDE, which has been degraded over a long period of time, so it is considered that there is no additional use after banning DDT in Korea. Although DDT concentration is decreasing with time, it is still being detected and it is a harmful substance to human and environment, so continuous monitoring is needed.

Acknowledgements

This study was carried out part of Persistent Organic Pollutants Monitoring program under the budget of the Ministry of Environment, Republic of Korea.

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