

# ASSESSMENT AND ESTIMATION OF ORGANOCHLORINE PESTICIDES (OCPs) IN THE AMBIENT AIR, SOUTH KOREA

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## Introduction

Organochlorine pesticides (OCPs) had been widely used in the agriculture to increase the production during the last several decades. They were defined as Persistent Organic Pollutants (POPs) under the "Stockholm Convention on POPs". They possess the properties such as the bioaccumulation, toxicity, persistence, and long range transportation by wind or water stream. The production and use of toxic OCPs have been banned or restricted by the Agricultural Chemicals Control Act in Korea since 1970s.

However, because of their physicochemical properties, OCPs are ubiquitously distributed around the earth and present in air, water, soil and biota. Among the 12 POPs, in this research, we measured about 8 OCPs such as aldrin, dieldrin, endrin, chlordane, heptachlor, toxaphene, DDT, mirex from 2008 to 2009 under Korean POPs monitoring program. This program was started to determine the status in environmental media (ambient air, surface water, sediment, and soil) and to establish a new strategy on POPs (S. K. Shin, et al., 2011; J. S. Park, et al., 2011).

The objective of the work was to assess the concentration of POPs and its seasonal variation in the ambient air. Comparison of results with the other countries has also been carried out.

## Materials and methods

Air samples were collected from 37 sites across South Korea over 4 seasons in 2009. Sampling regions were classified as 11 industrial, 5 rural, 9 commercial areas, and 12 residential areas. Sites were selected to consider the several conditions such as a potential source, population, and affective possibility for human and ecosystem. Sampling was conducted for 24hr with high volume air sampler, which consisted of QFF (Quartz Fiber Filter), 2 PUFs (Poly Urethane Form) and ACF (Activated Carbon Filter) during 3 days on each season. Total volume of air sample was roughly 1,000 m<sup>3</sup> with flow rate of 700 L/min (S. K. Shin., et al. 2011; KMoE. 2010).

All sample filters (1 QFF, 2 PUFs, 1ACF of a sample) were extracted using 500 mL dichloromethane for 24hr, and then concentrated by a rotary evaporator and transferred with 10 mL hexane. Before the purification, each sample was spiked with a <sup>13</sup>C<sub>12</sub>-labeled recovery standard (ES-5349, CIL, USA). Purification was done by using Florisil SPE and activated carbon column. First, the selected fraction was loaded on SPE cartridge (InterSep FL, 5 g/20 mL, GL science) and eluted with 50 mL hexane (1st fraction) and 150 mL of 25% dichloromethane/hexane (2nd fraction). Then, the second fraction was concentrated to about 1 mL and loaded once again on SPE cartridge (Supel-clean Envi-carb, 3 mL tube, Supelco) and eluted with 10 mL hexane. Finally, the elute was combined with 1st fraction (50 mL hexane) and reduced to a final volume of 100 µL by blowing down under a gentle stream of nitrogen and spiked with <sup>13</sup>C<sub>12</sub>-labeled 4,4-diCB and 2,3,4,5-tetraCB (EC-5350, CIL., USA) as internal standards. Analysis of OCPs was done by using high resolution gas chromatography/high resolution mass spectrometry (HP 6890/Micromass Autospec Ultima) with Rtx-CL Pesticides 2 capillary column (30 m x 0.25 mm ID x 0.25 mm film thickness). The instrumental analysis was carried out in splitless mode with helium (99.9999%) as a carrier gas at an injector temperature of 280 °C. The source temperature was 280 °C in EI mode (35 eV). The MS was operated over 10,000 resolutions by using selected ion monitoring (SIM).

All analytical procedures were monitored using QA/QC guideline available in the Korean official method on POPs. Field, laboratory and glassware blank were extracted and analyzed in the same manner as a sample. The recoveries of <sup>13</sup>C<sub>12</sub>-labeled OCPs in all samples were ranged from 50 to 120%. Reported data (i.e., over the MDL) were corrected with field blank. Concentrations below MDLs were noted as "ND" (not detected) (G. Z. Jin, et al. 2013; J. S. Park, et al. 2011; S. K. Shin, et al. 2011; KMoE. 2010; NIER, 2007).

The meteorological data such as temperature, velocity and direction of wind, were obtained from automatic measuring station and local weather station.

## Results and discussion

**Level of OCPs in ambient air:** Average concentrations of DDT and chlordanes were detected as  $6.264 \pm 4.567$ ,  $4.015 \pm 2.162$   $\text{pg}/\text{m}^3$  in ambient air, respectively. The mean concentration of dieldrin and heptachlors were detected as  $0.254 \pm 0.239$ ,  $0.752 \pm 0.539$   $\text{pg}/\text{m}^3$  respectively (KMoE, 2010). Other OCPs such as Aldrin, toxaphene, and mirex were not detected in air samples.

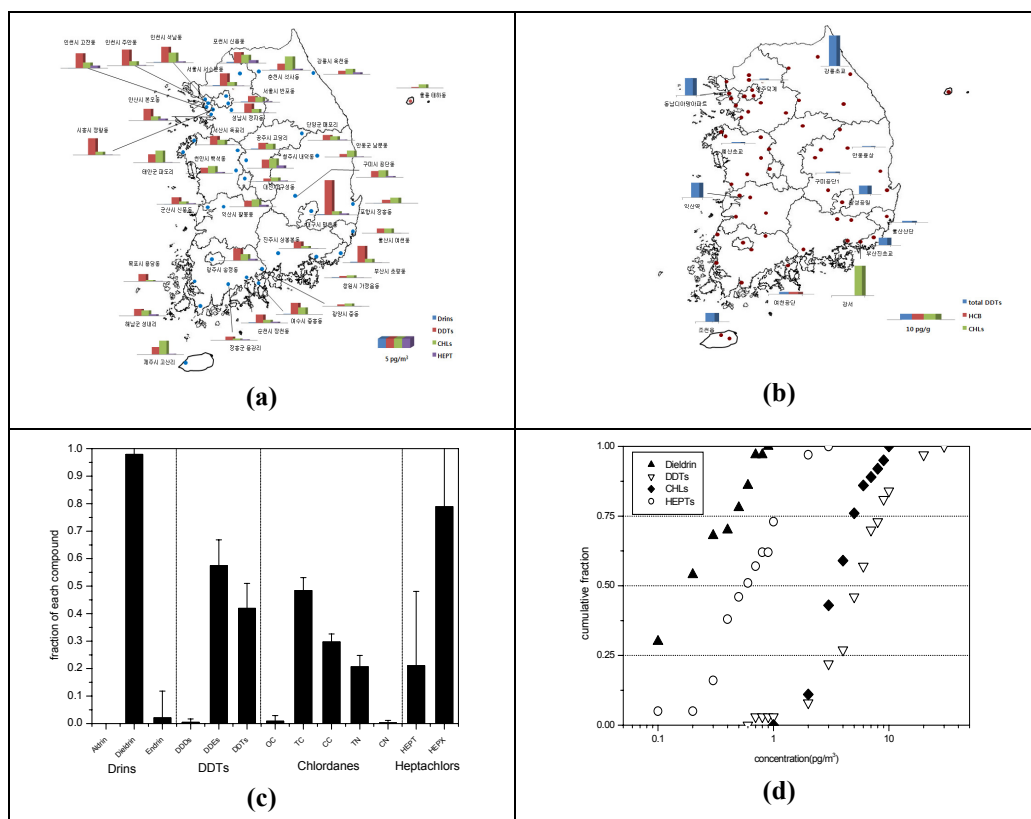


Fig 1. Spatial distribution (annual average) level of OCPs in Korea (a) air, (b) soil (c) Fraction of OCPs metabolites, (d) Cumulative fraction of OCPs concentration  
OC: Oxychlordane, HEPT: Heptachlor, HEPX: Heptachlor epoxide, TN: trans-nonachlor  
CN: cis-nonachlor, TC: trans-chlordane, CC: cis-chlordane

Figure 1 (c) indicated that among the drins, dieldrin fraction was high (98%). Dieldrin itself has been used as pesticides. However, endrin has got the tendency to be broken down as dieldrin because of the difference in the chemical properties. The total DDT was separated as DDD, DDE, and DDT.

According to the results of 2009 survey, DDE fraction was 58% of the total DDT, and DDT was 42% of the total DDT. As DDE was formed as a metabolite by the decomposition of DDT, if DDT is used at present, its concentration will be higher than the DDE. However, due to the decomposition of DDT used in the past, DDE is present in a higher than DDT. If the volatilization from soil which is a domestic source of DDTs, is predominant, its level in the air possess close relation with that of soil. Because DDTs have been used in agriculture and these have the property of semi volatility from soil.

Heptachlor epoxide, a degradation product of heptachlor, had been observed at higher concentration in atmosphere than heptachlor. This clearly indicates that it is greater resistant to biodegradation while being readily converted from heptachlor (J. S. Park, et al. 2011; H.G. Yeo, et al. 2011; KMoE 2009).

**Comparison of OCPs among other countries:** The levels of OCPs in the atmosphere of Korea were similar to that of other countries. The levels of spatial distributions of OCPs in an ambient air reveal that those were found to be the highest in coastal region (includes metropolitan city, coastal region, industrial area, etc.) of South Korea and consistent with previous studies such as impacts of anthropogenic and unknown emission sources (KMoE. 2009; KMoE. 2010).

**Seasonal variation of OCPs in air:** Seasonal variation of OCPs was observed as higher concentrations in summer and lower in winter period (Fig. 3a). It is likely to be associated with their temperature, which is a driven force, re-volatilization from historical source and recent application of some OCPs. Atmospheric distributions of POPs are significantly influenced by meteorological patterns. The Korean peninsula was affected by strong seasonal variation of meteorological conditions such as direction of wind, speed, temperature, humidity etc.

The highest concentration of DDTs was observed in summer followed by fall, spring, and winter. Also concentration of *p,p'*-DDE (main metabolite of DDTs) was predominant in summer. It found that OCPs level in air increased with increase of ambient temperature due to temperature dependent factor such as volatilization from soil and sediment. This result indicates that soil is a potential source of DDTs in Korea even though its level is low.

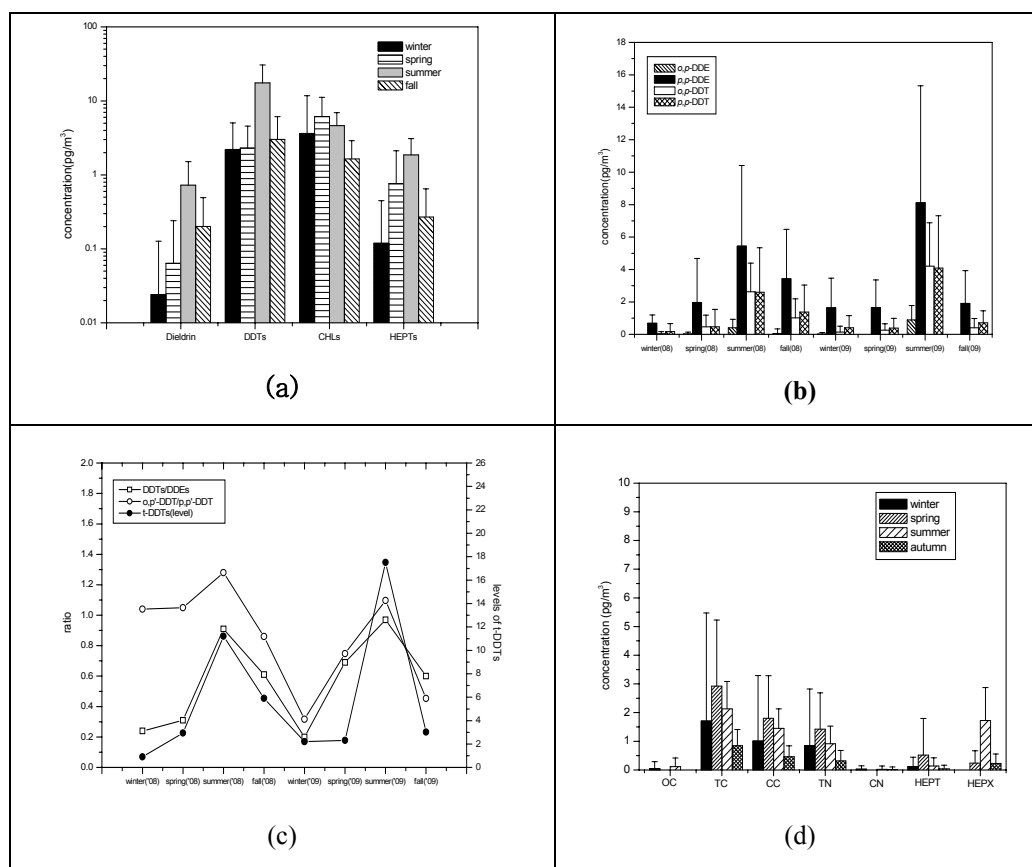


Fig 2. Seasonal variations of (a) OCPs in air (2009), (b) DDTs' metabolites (2008-2009) (c) Ratio of DDT and its metabolites for 4 seasons, (d) Level of metabolite for chlordane and heptachlor

A small value of *p,p'*-DDT/ *p,p'*-DDE ratio is indicative of aged DDTs and a value much greater than 1 indicates a fresh application due to degradation of DDTs to DDEs in environment. The ratio of *o,p'*-DDT/*p,p'*-DDT is also indicative of the contamination source type. The concentration ratio of *o,p'*-DDT/*p,p'*-DDT in formulated dicofol samples ranged from 1.3 to 9.3 with a mean of 7.0. Due to difference in physicochemical property of DDT

congeners, the fractionation of DDT isomers during soil-air exchange would lead to the changes in the ratios of *o,p'*-DDT/*p,p'*-DDT. This resulted in a calculated ratio of 0.74-0.96 for technical DDT and 28 for dicofol type DDT in the air (Ding et al., 2009; Liu et al., 2009). This ratio in dicofol was much higher than that in technical DDTs. And in the environment, *o,p'*-DDT metabolizes more easily than *p,p'*-DDT. This result indicates that DDTs contamination source in the air is potentially not dicofol type application but technical type. The concentration of chlordanes in air, seasonally increased in summer parallel to the increase of temperature and decreased in winter.

The metabolites such as oxychlordane and heptachlor epoxide showed the same temporal pattern such as lower levels in winter and higher levels in summer due to photo degradation from chlordanes and heptachlor. Chlordane degrades into oxychlordane and heptachlor epoxide in environmental media and *trans*-chlordane is easier to degrade than *cis*-chlordane. Therefore *trans/cis*-chlordane ratio is used to distinguish between aged and fresh chlordanes. The ratio of *trans/cis*-chlordane in technical mixtures was reported as about 1.17.

1. The concentration of DDTs and chlordanes were detected as  $6.264 \pm 4.567$ ,  $4.015 \pm 2.162$  pg/m<sup>3</sup> in ambient air, respectively. And the concentration of dieldrin and heptachlors were detected as  $0.254 \pm 0.239$ ,  $0.752 \pm 0.539$  pg/m<sup>3</sup> respectively. Other OCPs such as aldrin, toxaphene, and mirex in air were not detected.
2. Heptachlor epoxide, a degradation product of heptachlor, was observed in a much higher concentration than heptachlor in the atmosphere. This indicates that it is greater resistant to biodegradation while being readily converted from heptachlor.
3. The levels of OCPs in Korean air were similar to that of other countries..
4. This ratio in dicofol was much higher than that of technical DDTs. And in the environment, *o,p'*-DDT metabolizes more easily than *p,p'*-DDT. This result indicates that DDTs contamination source in the air is potentially not dicofol type application but technical type.
5. The concentration of chlordanes in air seasonally increased in summer parallel to the increase of temperature and decrease in winter.

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