The Investigation of the Organochlorine Pesticides Residues in Soil of Taiwan

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Introduction

Organochlorine Pesticides (OCPs) are hydrocarbon compounds containing multiple chlorine substitutions. They were introduced since 1940s and have been widely used in agriculture as pest control. There are four main types of OCPs: dichlorodiphenylethanes, chlorinated cyclodienes, chlorinated benzenes and chlorinated cyclohexanes. Nine of the 12 most hazardous persistent organic pollutants (POPs) targeted by the Stockholm Convention in 2001 are OCPs. Consequently, residual POPs might cause significant impacts on human health and the environment. The health risk of POPs has been widely debated globally in recent years and came to a consensus agreement of the Stockholm Convention on Persistent Organic Pollutants in 2001 that prohibit the production and use of these chemicals. Most of them have been banned or restricted in the industrialized world. However, some non-targeted OCPs such as Endosulfan, Lindane and DDT are still employed in developing countries for mosquito and malaria control. Organochlorine pesticides such as DDT, BHC, Lindane have been banned in Taiwan since 1977. In the same time, EPA Taiwan has been carrying out a systematic tracking on the residual concentration of organochlorine pesticides in environment with analytical tools such as GC/ECD for the past thirty years. Recently, we initiated the use of the isotope dilution method with HRGC/HRMS to analyze 26 organochlorines and their metabolites in environmental samples so as to determine the residual OCPs in a more accurate way. We have collected 100 soil samples from selected 16 counties of Taiwan. The average total concentration of 26 OCPs in soil samples is 4296 ng/kg d.w. and the concentrations ranged 164.8~39,183 ng/kg d.w.. The highest OCPs level found in the soil sample of Taiwan is still well below the official regulated risk threshold limit. The highest total concentration of samples 39,183 ng/kg is found in a site located at Taichung. The highest average total concentration is found in Taoyuan area. Those areas located in the east of Taiwan such as Taitung and Hualien exhibited lowest total average concentration. The ratio of DDT and its metabolites can be served as indicators for possible liable pollution sources as well as the degree of degradation. The ratio of Σ(DDD+DDE)/Σ(DDT+DDD+DDE) in the 95 out of 100 collected samples were found to be higher than 0.52 implicating that these DDT contamination in soil of Taiwan might be accumulated from the aged pollutants in the long past.

Material and methods

(1) Sample collection, extraction and clean-up

Samples were collected from 16 selected counties of Taiwan. 100 sampling sites were chosen based on the scale of agriculture in each county. Sampling time were scheduled from March to August during the busy agriculture season. The analyzed level of organochlorine in the soil samples can therefore reflect the use of pesticides in the land field. All samples were dried, ground and homogenized before being spiked with 13C-isotopes of the target compounds and extracted by Soxtherm with (1+1)Acetone/n-Hexane solvent mixture. Target compound standards and isotope labeled spiking solution were purchased from Chembridge Corporation. The extracts were concentrated to about 1 mL by turbo evaporation. Then we substitute the residual solvent with 1 mL hexane for subsequent pretreatment process. The extracts were cleaned up with Florisil SPE column. Gel permeation chromatography were used to remove the high molecular weight interference such as polymeric materials, humic acids, lipids and so on.

(2) HRGC/HRMS analysis

26 organochlorine pesticides were analyzed by isotope dilution in according to the official standard method NIEA

M905.00B of Taiwan EPA with high resolution mass spectrometer (HRMS) (AutoSpec Premier^{TM}) coupled with gas chromatograph equipped with cold injection system. Pesticides were chromatically separated with J&W (Agilent Technologies) DB-1701 column (30m×0.25mm×0.25μm).

Results and discussion

The concentrations of 26 organochlorine pesticides in soil samples ranged within 164.8~39,183 ng/kg d.w. The average concentration is 4296 ng/kg d.w.. All OCPs level found in the soil samples of Taiwan were well below the official risk threshold limit. The highest level were found in those sampling sites of Taoyuan and Taichung, of which the total average concentration fell between 10,000~15,000 ng/kg d.w.. The lower level range between 5,000~10,000 ng/kg d.w. were found in those sampling sites of New Taipei, Miaoli, Changhua, Yunlin and Chiayi. others The analyzed OCPs levels of other areas are under 5,000 ng/kg d.w. as shown in Tab.1. and Fig.1.

Higher detection ratio are found than most previous reports. Up to 81% Organochlorine pesticides are detected in all samples possibly due to that HRGC/HRMS has lower detection limit compared with traditional GC/ECD and GC/MS. Pentachlorobenzene, Hexachlorobenzene, BHC, Chlordane, DDT and their metabolites are found in most samples of this study as shown in Fig.2. As we compare the analyzed data between OCPs and their metabolites, the detection ratio of OCPs metabolites are very close to the ratio of their OCPs originates. The only exception is Oxychlordane of which its detection ratio is 18% that is much lower as compared with the number of 90% for both Chlordane and Nonachlor. Residual Chlordane and Nonachlor in soil metabolized to Oxychlordane generally took a long time, but the half-life of Oxychlordane is much shorter than those of Chlordane and Nonachlor. Oxychlordane in soil tends to metabolize into other compounds in a short time. We observed that the average level of chlordane in soil (144 ng/kg d.w.) was higher than that of nonachlor(75 ng/kg d.w.). One possible explanation can be attributed to the slower rate of metabolism of chlordane in soil.

As regard to the acute toxicity, carcinogenic and residual level of OCPs are shown in Fig.3. It is obvious that DDTs and their metabolites have biggest triangle area, therefore their residual level in soil should be of more concern in Taiwan. The second OCPs group that are worthwhile to be noticed include Aldrin and Endosulfans. Although the residual level (182 ng/kg d.w.) of Aldrin is relatively lower than other OCPs and its detection ratio is only 67%, it is advised to keep alert due to its potential high toxicity and carcinogenic. Endosulfans has the second highest residual level (364 ng/kg d.w.) and also has high toxicity. Though Endosulfans have been banned by the Stockholm Convention since 2011, there is still possibility to observe occasional discharge of this chemical to the environment and impacts on bio system and human health need to be continuously monitored.

Some of previous research works revealed that the half-lives of DDTs in soil are about two years or longer. It is reported in some previous research papers that DDTs will last longer than eight years in tissue before being metabolized to DDDs and DDEs. In this study we found that p,p'-DDE and p,p'-DDD were detected in all samples (100 %) while p,p'-DDT was found in only less than 30% of collected soil samples. Similar phenomenon are observed in the case of o,p′-DDE, o,p′-DDD and o,p′-DDT family group. Residual data of these congeners reflects the widely usage of DDTs in the past. Nevertheless, the average concentrations of DDTs (3,047 ng/kg d.w.) found in all soil samples of this investigation are far below the regulated level for soil (3 mg/kg d.w.).

F_{DDTs} is a frequently used indicator for the degree of DDT degradation as show below:

$$\mathbf{F_{DDTs} = \Sigma (DDD+DDE) / \Sigma (DDT+DDD+DDE)}$$

For the fresh DDT, the F_{DDTs} will generally fall within the lower range of 0.52. On the other hand, aged DDT contaminations usually exhibit higher values. As illustrated in Fig.4, F_{DDTs} of all 95 samples are higher than 0.52. It implied that little fresh DDT has been found in these samples as shown in Fig.3. The only two site that have lower F_{DDTs} than 0.52 are both found in samples collected from sites in Kaohsiung. Further investigation is needed to confirm whether it is due to illegal use of the banned pesticides or it is coming from other sources into this area via some transmission path.

The concentration distribution of the 26 targeted OCPs in Tainan, Yunlin and Chiayi counties are very similar possibly due to that the topographic features and their agriculture activitiese are quite similar in these three areas. However, the average total concentration of Tainan (1,035 ng/kg d.w.) is five times lower than the other two areas (6,539 and 6,333 ng/kg d.w.). One possible explanation is that due to Tainan is located in more south part of Taiwan. Average temperature in the year is higher and has generally more sunny days. It is possible that more and faster OCPs in soil will be metabolized. The average total concentration of Tainan is therefore lower and close to Kaohsiung (1,611 ng/kg d.w.) that are both located in the south ends of Taiwan. The concentration distribution of the 26 OCPs in those samples collected from sites of Changhua, Miaoli and Nantou varied from each other significantly. We attribute these differences to the complex agricultural product and pesticides applcation patterns in the past years.

Acknowledgments

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Table 1 Summary of Total OCPs concentration in soil of Taiwan

Area	Sampling sites	Concentration range (ng /kg d.w.)	Average (ng /kg d.w.)	Area	Sampling sites	Concentration range (ng /kg w.w.)	Average (ng /kg d.w.)
Taipei	1	4148~4148	4148	Changhua	8	1152~20932	6299
New Taipei	3	2312~10045	5396	Yunlin	10	601~26133	6539
Yilan	3	2848~7873	4683	Chiayi	9	705~15302	6333
Taoyuan	5	2431~27197	11544	Tainan	12	183~5443	1036
Hsinchu	4	525~3336	2122	Kaohsiung	6	443~4709	1611
Miaoli	4	2308~9693	5958	Pingtung	9	1060~3405	1973
Taichung	6	3226~39183	10129	Taitung	6	174~2178	867
Nantou	8	225~4221	2906	Hualien	6	165~946	556

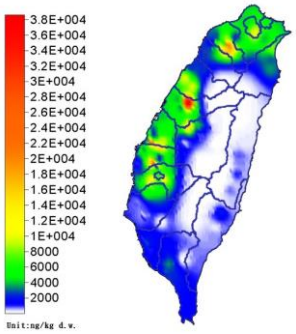

Figure 1 concentration distribution of 16 Areas.

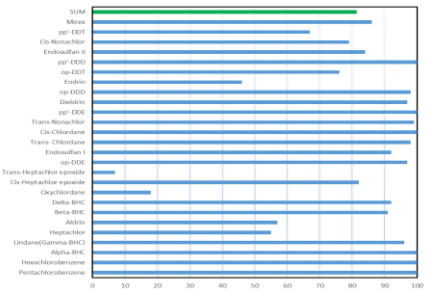

Figure 2 Detected percentage of 26 OCPs.

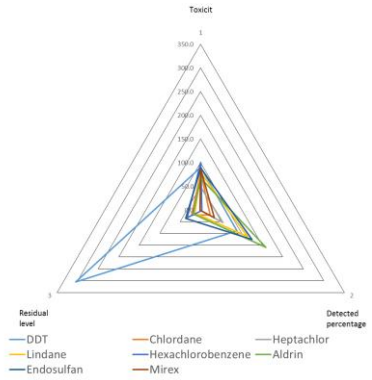

Figure 3 Impact estimate of 26 OCPs in soil.

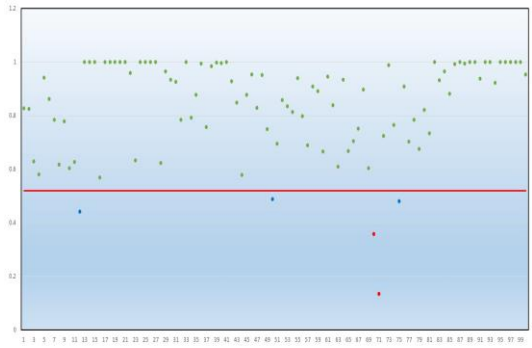

Figure 4 Index for evaluating the degradation of DDT in soil.

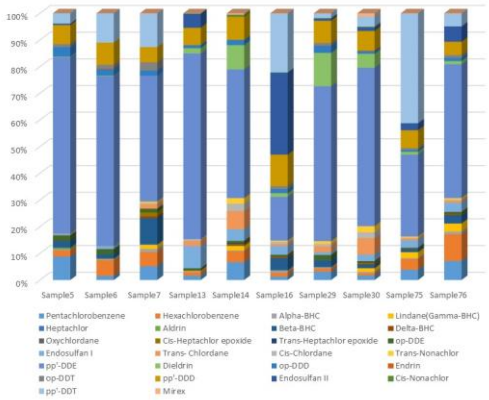

Figure 5 concentration distribution of 26 OCPs in Yunlin

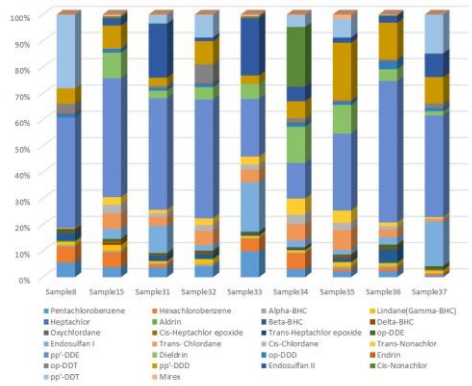

Figure 6 concentration distribution of 26 OCPs in Chiayi

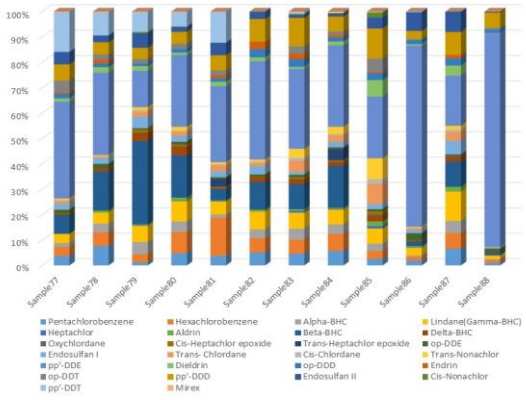

Figure 6 concentration distribution of 26 OCPs in Tainan

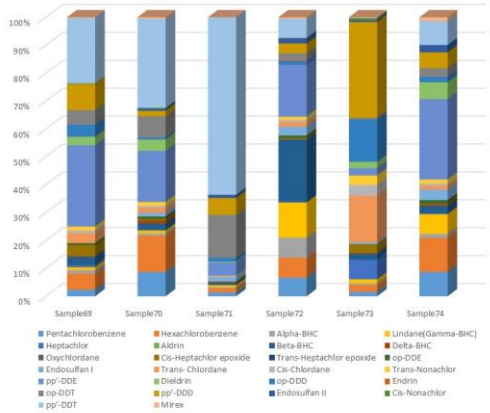

Figure 7 concentration distribution of 26 OCPs in Kaohsiung