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Residual characteristics of HCHs and DDTs in soil and dust of some parks in Ulaanbaatar, Mongolia

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Abstract: The residual characteristics of HCHs and DDTs in park soils and dusts in Ulaanbaatar, Mongolia were determined by GC-ECD to evaluate their potential pollution risk. The residual concentrations of total HCHs and DDTs in the park soil samples were ranged in 11.36-53.14 $ng \cdot g^{-1}$ and 11.96-24.70 $ng \cdot g^{-1}$ while it was ranged in 32.28-92.68 $ng \cdot g^{-1}$ and 13.45-24.41 $ng \cdot g^{-1}$ in the park dust samples, respectively. We have studied the ratio of α-HCH/γ-HCH in order to determine pollution sources which may come from either technical HCHs or lindane. The study revealed that concentration of DDTs in soil has direct correlation on usage rate of the dicofol and technical DDT in the sampling area. The soil pollution assessments based on the single pollution index of HCHs and DDTs indicated that Ulaanbaatar city's park soil and dust were not polluted with these compounds.The single pollution index of HCHs reached to 1.85 in A park dust samples，indicating the park dust environment was potentially polluted.

Keywords: Ulaanbaatar, Organochlorine pesticide, pollution assessment

INTRODUCTION

Organochlorine pesticides (OCPs) are environment typical Persistent Organic Pollutants (POPs) [1-5]. Although they has been observed to persist in the plants, animals, water, soil, sediment and other organisms due to refractory to highly chemical stability [3], biodegradation and long-term residual resistance to bioaccumulation along the food chain [5-12]. The soil is the material basis of human survival, agricultural ecosystem carrier material and energy exchange [13]. Therefore, the OCPs residue analysis in soil and dust contributed to reveal the deeper dynamics and pesticide contamination in the soil. So the environment risk assessments of OCPs in soil are great practical significance to the ecological environment. With the rapid industrialization, urbanization and population growth of Ulaanbaatar, more and more pollutants emit into the environment. The content of OCPs in the city parks soil was analyzed as a research object.

This paper presents the current status of OCPs residual concentrations in soil and dust samples obtained from Botanical garden, Central Tower Public Park, Memorial status garden, Khar khorin children's garden and National Amusement Park in Ulaanbaatar city (Fig.1).

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MATERIALS AND METHODS

Reagents and Standards: Acetonitrile, acetone, n-hexane, methylene chloride, calcium chloride, pure anhydrous sodium sulfate, sulfuric acid, activated carbon, silica gel.

Standard samples: HCHs, DDTs mixed standard sample (including: α-HCH, β-HCH, γ-HCH, δ-HCH; p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-DDD), purity 93%-99%.

Sample collection: Surface soil sampling (soil and dust) for analysis was conducted at four different spots from 0-30 cm depth in the circular area with a diameter of 50m in Ulaanbaatar city within the period of September to October in 2013. The soil samples were well mixed and the weight of each sample was 300 to 500g. The samples were packed in polyethylene bags. They were freeze-dried and stored at -20°C until the extraction.

Sample extraction and pre-treatment: Samples were extracted using accelerated solvent extractor (ASE-350) with n-hexane and acetone. A 5 g (dried through a 60 mesh sieve) soil and dust samples mixed with anhydrous Na_2SO_4 were extracted in a 34 ml stainless steel vessel with n-hexane:acetone (1:1) at 120°C and 10.3 MPa for 5 min heat-up followed by 10 min static extraction [14].

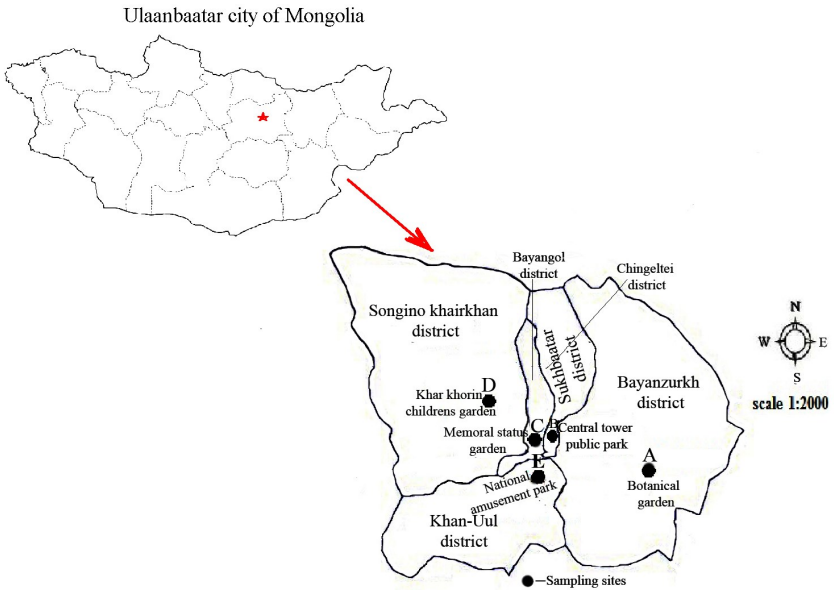

Fig. 1. Locations of soil sampling sites from Ulaanbaatar city

The extracts were concentrated to 2-3 mL using rotary evaporator (35°C-40°C), transfer to Florisil column for further purification. The extract is purified in a Florisil small column which have the layers of activated carbon with 1 cm deep and anhydrous Na_2SO_4 with 1cm deep. The column was eluted with 15 ml n-hexane and dichloromethane (1:1). The elution was done with 20 ml 1:1 n-hexane and dichloromethane. The extract was evaporated by nitrogen to 1-2 mL before gas chromatographic (GC-ECD) analysis and quantification.

Sample Analysis: Samples were measured by an Agilent-7890A gas chromatograph using a ^{63}Ni electron capture detector and DB-5 fused silica capillary column (30m×0.25mm×0.25µm). The carrier gas was high purity nitrogen (0.6 ml/min). The injector and detector temperatures were 250°C and 280°C, respectively. The oven temperature was initially set at 100°C and programmed to 160°C (10°C/min) to hold time of 2 min, and again ramped to 260°C at 4°C/min and held for 10 min.

RESULTS AND DISCUSSIONS

Parks soil and dust residual HCHs and DDTs

HCHs: The concentrations of ∑HCHs (α-HCH, β-HCH, γ-HCH and δ-HCH) in the surface soil and dust samples from five parks in Ulaanbaatar city were 11.36-53.14 $ng \cdot g^{-1}$ and 32.28-92.68 $ng \cdot g^{-1}$ dry weight, respectively (Table 1). Compared with data acquired by studies conducted in the present study area from Ulaanbaatar, it was lower than those of soil samples (HCHs: 0.02-0.81$ng \cdot g^{-1}$ and DDTs: 0.06-4.28$ng \cdot g^{-1}$) [15]. Both HCHs had high detectable ratios, β-HCH residues were detected in soil samples of studied parks The concentrations of HCH isomers in soil and dust samples arranged in the following order: β-HCH> α-HCH> δ-HCH> γ-HCH and β-HCH> γ-HCH> α-HCH> δ-HCH (Fig 2-3.).

The highest content of β-HCH in soil samples mainly caused by the β-HCH which arranged special

Table1. Residue concentrations of HCHs in parks soil and dust from Ulaanbaatar city ($ng \cdot g^{-1}$)

	Soil samples*					Dust samples*				
	A	B	C	D	E	A1	B1	C1	D1	E1
α-HCH	2.52	0.48	2.95	2.24	2.94	5.89	2.67	3.64	2.4	4.13
β-HCH	35.9	8.35	28.44	26.51	45.02	71.46	21.87	19.65	83.47	26.9
γ-HCH	0.7	2.03	1.42	1.56	1.46	11.92	3.98	5.02	3.47	4.96
δ-HCH	6.34	0.51	1.91	1.47	3.72	3.4	3.76	3.69	2.21	1.37
∑HCH	45.46	11.36	34.72	31.78	53.14	92.68	32.28	31.99	91.56	37.35
α/γ-HCH	3.6	0.2	2.1	1.4	2.0	0.5	0.7	0.7	0.7	0.8

*A: Botanical garden, B: Central tower public park, C: Memoral status garden, D: Kharkhorin children's garden, E: National amusement park

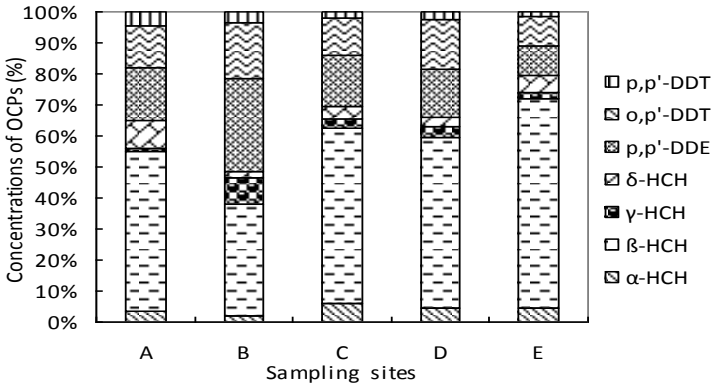

Fig. 2. The composition profiles of OCPs in park soil from Ulaanbaatar city

characteristic compared to the other isomers of Cl atom in space [16] where the molecular structure of all Cl atoms and carbon frames can be strongly existed on the same plane of symmetry [17]. Technical HCHs includes 60-70% α-HCH, 10-12% γ-HCH, 5-12% β-HCH and 6-10% δ-HCH [5, 18].

The ratio of *α*-HCH/*γ*-HCH has been used to identify whether the pollution source comes from technical HCH or lindane. The ratio of α-HCH/γ-HCH ranged in 3-7 is a source indicator for technical production and technical HCH [18, 19], while it is close to 0 for Lindane [20, 21].

In this study α-HCH/γ-HCH ratio were ranged from 0.2 to 3.6. The ratios were above 3 in most of park soils showing the sources can be a mixture of lindane and technical HCH. In the case of soil for park A, the ratio was the highest (3.6) indicating the HCHs can solely come from technical HCH. Main polluted components of HCHs were β-HCH and γ-HCH in dust samples and α-HCH/γ-HCH ratio ranges from 0.5 to 0.8 which indicating that the lindane is main contributor to pollution source.

DDTs: The concentrations of ∑DDTs (p,ṕ'–DDE, o,p'-DDT and p,p'- DDT) were ranged from 11.96 to 24.70 $ng \cdot g^{-1}$ and from 13.45 to 24.41 $ng \cdot g^{-1}$ in the surface soils and dust samples in parks of Ulaanbaatar city. Distribution of DDTs isomers were p,p'-DDE> o,p'-DDT> p,p'-DDT with concentrations of 6.12-11.92 $ng \cdot g^{-1}$, 4.25-9.71 $ng \cdot g^{-1}$ and 0.82-3.07 $ng \cdot g^{-1}$, respectively. (Table 2.). The concentration of p,p'-DDE and o,p'-DDT isomers were higher than other isomers in the total DDTs. The concentration of p,p'-DDT was lower than that of other isomers in the park soils. The p,p'-DDE is a DDTs metabolic degradation products, DDT aerobic degradation to DDE and p,p'-DDT could be biodegraded to p,p'-DDE aerobic conditions [21]. The DDT/DDE ratio was reported <0.8 in technical DDT [18]. The ratio of o,p'-DDT/p,p'-DDT has been used to identify whether the soil pollution source of the technical DDT. The ratio of o,p'-DDT/ p,p'-DDT ranged from 0.2-0.3 for technical DDTs [5, 18] and 1.3-9.3/or higher for technical mixture in dicofol, o,p'-DDT easier degradation to p,p'-DDT in soil [19]. In this study, the ratio of DDT/DDE in soil samples was ranged from 0.7 to 1.2 while the o,p'-DDT/ p,p'-DDT ratio was varied from 3 to 6 which suggesting that pollution source comes from technical DDT and dicofol.

Dicofol is potential substance and original drug

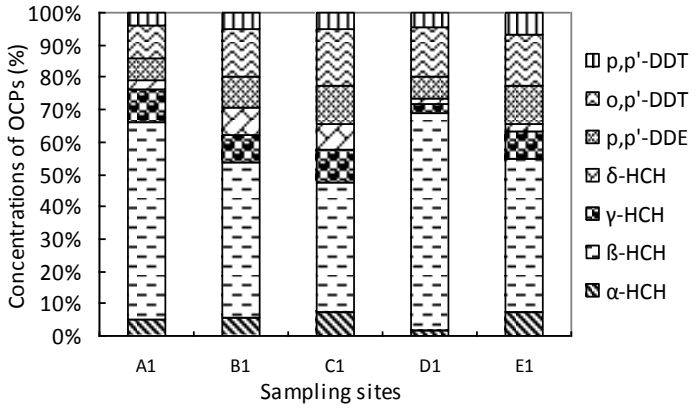

Fig. 3. The composition profiles of OCPs in park dust samples from Ulaanbaatar city

Table 2. Residue concentrations of DDTs in parks soil and dust from Ulaanbaatar city (ng·g^{-1})

	Soil samples					Dust samples				
	A	B	C	D	E	A1	B1	C1	D1	E1
p,p'-DDE	11.92	6.89	8.39	7.61	6.12	7.76	4.52	5.83	7.96	6.74
o,p'-DDT	9.71	4.25	5.88	7.6	6.41	12.08	6.7	8.48	19.32	8.88
p,p'-DDT	3.07	0.82	1.12	1.23	1	4.57	2.23	2.59	5.52	3.81
∑DDTs	24.7	11.96	15.39	16.44	13.54	24.41	13.45	16.9	32.8	19.43
DDT/DDE	1.1	0.7	0.8	1.2	1.2	2.1	2.0	1.9	3.1	1.9
(o,p' / p,p')-DDT	3.2	5.2	5.3	6.2	6.4	2.6	3.0	3.3	3.5	2.3

*Note：DDT=o,p'-DDT+p,p'-DDT, DDE=p,p'-DDE

production for DDTs, high levels of DDTs in degradation products exist. The park soils were polluted by basic source of technical DDTs and dicofol. Additionally, concentrations of DDTs were low in the studied samples. Thus, DDTs source was atmospheric deposition in three-park soil. The result shows that Ulaanbaatar's park soils are belonging to non-point pollution source.

The ∑HCHs residual concentration was higher/more than ∑DDTs in parks and dust samples. A major isomers of DDTs residues in park dust samples were p,p'-DDE and o,p'-DDT. The DDT/DDE ratio was ranged from 1.9 to 3.0 when the o,p'-DDT/p,p'-DDT ratio was from 2.3 to 3.0 in different park dust samples. The main pollution sources of DDTs were dicofol used in all dust samples. In addition, the climatic condition (dry and cold) in the study area can be basically influenced to microbial activity which became very low and inhibit chemical behavior. Therefore, microbial degradation and chemical transformation of DDTs are very slow with low efficiency in the studied soil.

Assessment of HCHs and DDTs for soil pollution: The soil environmental quality was evaluated using with single pollution index and soil quality (soil pollutants elements and substance) standards of Mongolia. Single pollution index method developed by Swedish scholar Hakanson [22] was employed to assessment the potential risk of OCPs pollution. It represents based on quantitative analysis method to evaluate soil pollution. The single factor pollution index calculation formula as follows:

$$Pi = \frac{Ci}{Si}$$

Among them,

P_i: Single pollution index of soil;

C_i: Determination of soil pollution concentrations;

S_i: Pollutants quality standards

Single pollution index and soil contamination exceeding data of HCHs and DDTs are presented in Figure 4. The single pollution index of HCHs and DDTs were less than 1, and exceeded the standard in A and B samples, which suggests the park soil environment was not polluted. However, single pollution index of HCHs was reached to 1.06 for park E soil sample showing a potential pollution.

Table 3. The value of single pollution index and pollution degree [22]

Pollution degree	Non-pollution	Potential pollution	Slight pollution	Heavy pollution
P_i	$P_i \leq 1$	$1 < P_i \leq 2$	$2 < P_i \leq 3$	$P_i > 3$

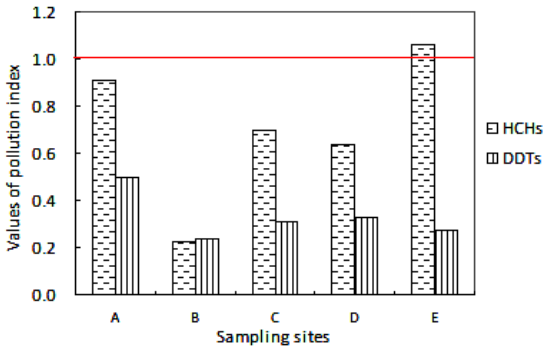

Fig. 4. Comparison of soil pollution index values of HCHs and DDTs in park soil from Ulaanbaatar

Assessment HCHs and DDTs for dust pollution: The results of HCHs and DDTs pollution assessment for dust samples are presented in Fig 5. The single pollution index of HCHs reached to 1.85 in park A

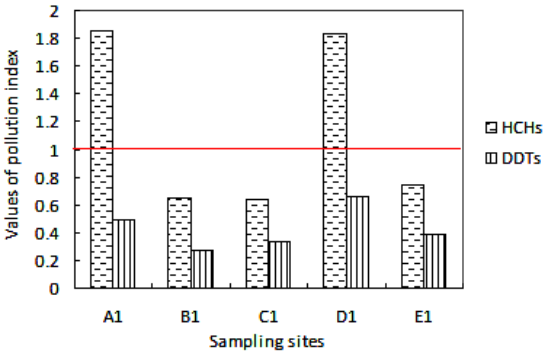

Fig. 5. Comparison of soil pollution index values of HCHs and DDTs in park dust from Ulaanbaatar

dust samples，indicating the park dust environment was potentially polluted. However, individual pollution index for other park dust samples were less than 1. This is highly suggested that park dust environment was not polluted. The single pollution index of DDTs were 0.27-0.66, which presenting non-polluting of DDTs in each park dust samples.

CONCLUSIONS

This study was investigated the distribution and concentrations of HCHs and DDTs in soil and dust from some parks in Ulaanbaatar city. Conclusions are as follows:

1. The total HCH conentrations were ranged from 11.36 to 53.14 ng·g^{-1} while the total DDT levels were varying from 11.96 to 24.7 ng·g^{-1} in these soil samples. A concentration of the HCHs and DDTs depends on human activity such as a usage of technical products or lindane and dicofol in the studied park soil samples. Soil environment was not contaminated by HCHs and DDTs.
2. The total concentrations of HCH and DDT were ranged from 32.28 to 92.68 ng·g-^{1} and from 13.45 to 24.41 ng·g^{-1} in the dust samples, respectively. The β-HCH and o,p'-DDT were dominant components. The HCHs and DDTs residues in the dust samples originated mainly from the use of lindane and dicofol.

REFERENCES

1. Nan Shu-qing, *et al.* (2009) Residues of HCHs, DDTs and Theirs Structures in Soils of Different Typical Agro-Yielding Areas. *J. Environmental Monitoring in China*, **25**(6), 81-84.
2. Mishra M., Kumar B., Singh S.K., *et al.* (2011) Hexachlorohexana (HCH) and Dichlorodimethyl-trichloroethane (DDT) in soils from Northern Uttar Pradesh, India. *J. European Journal of Experimental Biology,* **1**(3), 162-168.
3. Lu Hong-xuan., Liu Wei-guo. (2013) Determination of residues of twenty kinds of Organochlorine pesticides in soil with ASE technology and GC coupled with electron capture detector. *J. Applied Chemical Industry,* **42**(3), 546 -548.
4. Liu Xiu-fen., Lao Wen-jian., Bi Xin-hui., *et al*. (2002) Determination of Organochlorine pesticides in ABALONE samples from Antarctic. *J. Chinese Journal of Analytical Chemistry,* **9**, 1035-1037.
5. Annette S.M., Qi Sh.H., Wang Y.H., *et al*. (2009) Distribution and Sources of Organochlorine pesticides (OCPs) in Karst Cave, Guilin, China. *J. Academia Arena,* **1**(1), 47-56.
6. Yuan Xu-yin., Wang Yu., Chen Jun. *et al*. (2003) Organochlorine residues of sediments in Taihu Lake and Its Risk evaluation. *J. Environmental Science,* **24**(1), 121-125.
7. Ritter L., Solomon K.R., Forget J, *et al*. (2007) Persistent Organic Pollutants. United Nations Environmental Programme.
8. Wang Xiang-qin., Qi Shi-hua., Li Jie., *et al*. (2008) Organochlorine pesticides in sediments from Honghu Lake, China. *J. Journal of Environmental Science and Engineering,* **2**(1), 22-30.
9. Barriada-Pereira M., Gonz´alez-Castro M.J., Muniategui-Lorenzo S, *et al*. (2005) Organo-chlorine pesticides accumulation and degradation products in vegetation samples of a contaminated area in Galicia (NW Spain). *J. Chemosphere,* **58**, 1571–1578.
10. Shi Shuang-xin., Zhou Li., Shao Ding-ding., *et al*. (2007) Studies residues of Organochlorine pesticides POPs in the soils in Beijing Area. *J. Research of Environmental Science,* **20**(1), 24-29.
11. Jabir H.S., Riffat N.M. (2011) Occurrence and source identification of organochlorine pesticides in the surrounding surface soils of the Ittehad Chemical Industries Kalashah Kaku, Pakistan. *J. Environmental Earth Sciences,* **62**, 1311-1321.
12. Wei He., Ning Qin., Qi-Shuang He, *et al*. (2012) Characterization, ecological and health risks of DDTs and HCHs in water from a large shallow Chinese lake. *J. Ecological Informatics*, **12**, 77-84.
13. Zhao Qi-guo. (2008) Improving knowledge of soil, innovating modern pedology. *J. Acta Pedological Sinica,* **45**(5), 771-777.
14. You J., Weston D.P., Lydyl M.J. (2004) A Sonication Extraction Method for the Analysis of Pyrethroid, Organophosphate, and Organochlorine pesticides from sediment by Gas Chromatography with an electron-Capture Detection. *J. Environmental Contamination and Toxicology*, **47**, 141-147.
15. Mamontova E.A., Tarasova E.N., Ganchimeg D., *et al.* **(**2011) Persistent organic pollutants (PCBs and OCP) in air and soil from Ulaanbaatar and the Lake Hovsgol region, Mongolia. *J. Mongolian Journal of Chemistry,* **12**(38), 69-77.
16. Kalbitz K., Popp P., Geyer W., *et al.* (1997) β-HCH mobilization in polluted wetland soils as influenced by dissolved organic matter. *J. Science of Total Environment,* **204**, 37-48.
17. Mackay D., Shium W.Y., Ma K.C. (1997) Illustrated Handbook of Physical–chemical properties of Environmental Fate of Organic Chemicals [B]. Lewis Publishers, Boca Raton, FL.
18. Mukherjee D.P., Kumar B., Kumar S., *et al.* (2011) Occurrence and distribution of pesticide residues in selected seasonal vegetables from West Bengal. *J. Archives of Applied Science Research*, **3** (5), 85-93.
19. Zhang Z.L., Huang J., Yu G., *et al*. (2004) Occurrence of PAHs, PCBs and organochlorine pesticides in Tonghui River of Beijing, China. *J. Environmental Pollution,* **130**, 249-261.
20. Wu Zhi-sheng., Xie Guan-gyan., Yan Guo-yi., *et al*. (2009) Residual characteristics of HCHs and DDTs

in agricultural soils from Guangzhou. *J. Ecology and Environmental Sciences,* **18**(4), 1256-1260.

21. Zhang Hong-yan., Gao Ru-tai., Jiang Shu-ren., *et al.* (2006) Spatial variability of Organochlorine pesticides (DDTs and HCHs) in surface soils of Farmland in Beijing, China. *J. Scientia Agricultural Sinica,* **39**(7), 1403-1410.
22. Hakanson L. (1980) Ecological risk index for aquatic pollution control. *J. A sedimentological approach. Water Research,* **14**, 975–1001.