Residue occurrence and potential risk assessment of HCHs and DDTs in campus surface soils: In case of Jilin University in Changchun, China

Jilong Lu, Wei Zhao, Qiaoqiao Wei, Yaru Hou, Junshi Si, Tong Li and Libin Zang*

College of GeoExploration Science and Technology, Jilin University, Changchun 130012, China

*Corresponding author. Tel: +86 13504453945 E-mail: zanglb13@jlu.edu.cn

Abstract. Hexachlorocyclohexane (HCH) and Dichlorodiphenyltrichloroethane (DDT) are typical Organochlorine pesticides (OCPs), which were widely used in pest control and insect infestation in China. This study aimed at researching the concentration, potential sources and potential risk of HCH and DDT in Jilin University in Changchun, China. A total of 45 surface soil samples were collected from five land-use types in Jilin University campuses, the contents of were determined by Gas Chromatography and Mass Spectrometry (GC-MS) with Soxhlet extraction pretreatment technology. The overall HCHs existed the pollution in some campuses, while the DDTs were relatively low without pollution. Results of composition analysis showed that HCHs in campus soils mainly came from the mixed use of technical HCHs and lindane, and DDTs were mainly from the input of historical dicofol products. The potential health risks of HCHs and DDTs to campus populations were very low, while the potential ecological risks of HCHs and DDTs individual isomers should be paid attentions to.

1. Introduction
Organochlorine pesticides (OCPs) represent an important group of persistent organic pollutants (POPs), its residues in soil are an ongoing concerned topic in the field of environment because of their nature characteristics of biological toxicity, persistence and long-distance migration. As the typical representative of OCPs, HCHs and DDTs have been identified as endocrine disruptors due to their characteristics of carcinogenic, teratogenic and mutagenic, and can be transmitted and enriched through the food chains. HCHs and DDTs can be found in a variety of environments such as water, air, river sediment, soil and even crops and food. While since their widely used for agriculture purpose, as well as the soil aggregation, atmospheric settlement and the high resistance to degradation in soil, the soil system may be the biggest reservoir and the second resource for HCHs and DDTs. There are many considerable reports about HCHs and DDTs residues in agriculture soil over these years, but few researches have been conducted to investigate the residues in urban campus soil.

In this paper, the residue levels, possible sources and their potential risks of HCHs and DDTs in campus soils of Jilin University with high population density were investigated. This study aimed at provide a reference for the campus construction and a guidance for soil environmental quality assessment and environmental pollution control in Changchun urban districts.
2. Methods and Materials

2.1. Study Area and Sampling

The study area was Jilin University seated in Changchun city which is located between N43°05’~45°15’; E124°18’~127°05’. Jilin University has six campuses with seven school yards as for its specific history development, including QWN (avant-garde southern campus), QWB (avangarde northern campus, NH(south lake campus), NL(nanling campus), CY(Chaoyang campus), XM(xinmin campus) and HP(peace campus). The campuses covered a total area of more than 6.6 million square meters, with the building area of more than 2.7 million square meters. The types of campus soil are mainly black soil and meadow black soil[15], but the soil structure of campus was complex and human disturbance was strong due to the non-agricultural construction and campus green space beautification or other factors.

Considering the different effects of human activities in different functional areas on HCHs and DDTs residues in soil, seven campuses of Jilin University were sampled in five functional zones, which were living, greening, teaching, sporting and experimental zone, respectively. This study collected 45 samples, which were representative and considered the uniformity of the functional area. Each composite sample was constituted by 4 sub-samples with approximate 500 grams of 0-20cm surface soil, unwanted materials were removed manually and collected soils were mixed thoroughly. The homogenized samples were collected in brown clean wide-mouth glass bottles which labeled indicated information, then transported ice preserved to the laboratory to store below 4℃until further extraction.

2.2. Sample Extraction and Clean-up

Extraction and clean-up of samples was carried out following the validated methods from the standard of Ministry of Environment protection of P.R.China(HJ613-2011 and HJ835-2017)[16,17].The extraction method was Soxhlet extraction.

2.3. Analysis determination and Quality Control

The determination of target compounds was carried out by using the Gas Chromatography and Mass Spectrometry (GC-MS)(PerkinElmer,ClarusSQ8),equipped with the HP-5 quartz capillary column (Agilent,USA,30m×0.32mm×0.25μm). Identification of the target compounds was based on the spectral retrieval and retention time with corresponding standards. The quantification of the analyses was performed by comparison to internal standard method comparing peak area in target compounds with the standards using six-level calibration curves (R2 value, 0.999).

Quality control included sample blank to check for the cross-contamination during the experiment, random duplicate samples(sd<35%). The recoveries of surrogate spiked in matrix were in the range of 58%–97%. The average of duplicate analysis was used in calculations. Method detection limit was 0.04mg·kg⁻¹, and result of blank sample is lower than this value.

3. Results and discussion

3.1. The concentration of HCHs and DDTs in campus soil

Concentrations of total and individual HCH and DDT isomers in campus soil of Jilin University were presented in Table 1. The highest concentration of HCHs were detected in experimental zone of CY campus and greening zone of XM campus, which was 2.496mg·kg⁻¹ and 1.548mg·kg⁻¹ respectively. The average concentration of ΣHCHs in campus soil of Jilin University was higher than the primary environment background value(0.01mg·kg⁻¹)while below the second screening value(1.0m·kg⁻¹), basis on the Chinese Environmental Quality Standard (GB15618-2008)[18], among which 43 samples were between the primary and second background value. The concentration of total HCHs and its isomers of different functional areas was compared and the result showed that experimental zone>greening zone>sporting zone>living zone >teaching zone.
Table 1 Statistical parameters of HCH and DDT concentrations in campus samples of Jilin University (0-20cm; N=45)(mg·kg⁻¹ dry weight).

| Compounds | Minimum | Maximum | Mean | Geometric | Standard | LODs | DF(%) |
|-----------|---------|---------|------|-----------|----------|------|-------|
| α-HCH     | 0.004   | 0.788   | 0.121| 0.090     | 0.124    | 0.07 | 100   |
| β-HCH     | 0.009   | 0.760   | 0.124| 0.073     | 0.165    | 0.06 | 100   |
| γ-HCH     | 0.001   | 0.851   | 0.075| 0.032     | 0.143    | 0.06 | 100   |
| δ-HCH     | 0.003   | 0.132   | 0.023| 0.016     | 0.026    | 0.1  | 83    |
| ΣHCHs     | 0.018   | 2.496   | 0.343| 0.226     | 0.434    |      |       |
| p,p'-DDE  | 0.001   | 0.063   | 0.007| 0.004     | 0.011    | 0.04 | 100   |
| p,p'-DDD  | 0.000   | 0.092   | 0.004| 0.002     | 0.014    | 0.08 | 100   |
| o,p'-DDT  | 0.001   | 0.026   | 0.007| 0.005     | 0.006    | 0.08 | 82    |
| p,p'-DDT  | 0.000   | 0.081   | 0.005| -         | 0.013    | 0.09 | 62    |
| ΣDDTs     | 0.003   | 0.239   | 0.023| 0.013     | 0.037    |      |       |

(SD: Standard Deviation; LODs: limits of detection; DF: Detection frequencies)

Concentration of ΣDDTs (p,p'-DDE, p,p'-DDD, p,p'-DDT and o,p'-DDT) ranged from 0.003mg·kg⁻¹ to 0.239mg·kg⁻¹, with 0.023mg·kg⁻¹ as average(Table 1). The average of ΣDDTs was lower than 0.05mg·kg⁻¹ which the primary environment background value(GB15618-2008), but one sample of experiment area in QWB campus was higher than the screening value. The comparison of DDTs and its isomers among different functional area was similar with HCHs.

3.2. Possible Sources of HCHs and DDTs in campus soil

HCH is available as technical HCH or lindane agriculture formulations in soil, generally. Technical HCH is composed of α-HCH(60%~70%), β-HCH(5%~12%), γ-HCH(10%~15%), δ-HCH(6%~10%) and some other HCH isomers(3%~4%)[19,20]. The average concentration of HCH isomers compounds decreased in the order of β-HCH>α-HCH>γ-HCH>δ-HCH. The estimated ratio of α-HCH/γ-HCH in this study ranged from 0.9-3, with a total mean of 1.6, which reflected a mixed source of both HCH forms in campus soil and without the fresh input of technical HCH.

Generally, the technical grade DDTs are composed of 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE, <0.5% p,p'-DDD, and some other unidentified compounds[21]. In this study, p,p'-DDE and o,p'-DDT were the main forms of DDTs in campus soil. The value of o,p'-DDT/p,p'-DDT was far greater than 0.3 which suggested that the DDT contaminants in campus were mainly from the input of historical dicofol products. The ratio of p,p'-DDE/p,p'-DDT and (DDD+DDE)/DDT were higher than the critical value, which indicated that DDTs in campus soil had undergone a long time degradation and there were no introduction of new sources. The value of DDD/DDE indicated that the DDTs contaminant in campus was mainly degraded under the aerobic conditions.

3.3. Ecological Risk of HCH and DDT in campus soil

Ecological risk assessment refers to the effective prediction of the possible ecological effects caused by toxic pollutants in the soil and the method of assessing the probability of risk occurrence [22]. In this study, the currently food chain model was used to evaluate the ecological risk of OCPs owning to the obvious amplification effect of OCPs (such as DDTs) in the food chains. Some researchers took soil invertebrates as the research objects, and calculated the concentrations of α-HCH, β-HCH, γ-HCH that can cause 50% of species occurrence ecological risk in soil were 0.1mg·kg⁻¹, 0.04mg·kg⁻¹ and 10mg·kg⁻¹, respectively[23]. Some other researchers calculated the critical levels of DDTs to soil organisms, birds and mammals by simple food chain model based on the principle of food chain enrichment, which were 0.01mg·kg⁻¹, 0.011mg·kg⁻¹ and 0.19mg·kg⁻¹ respectively [24]. According to the above recommended guideline level, the ecological risk assessment of HCHs and DDTs in campus soil was carried out.
3.4. Human Health Risk of HCHs and DDTs in campus soil

Health risk assessment refers to the process of probability assessment on the impact of toxic chemicals on human health. The specific steps include pollutant hazard identification, determination of human exposure pathway, calculation of exposure does and the exposure risk assessment[25]. In this study, the USEPA health risk assessment model was used to assess the health risk of HCH and DDT in campus soil of Jilin University.

The carcinogenic risk and non-carcinogenic risk of HCHs and DDTs in campus soil under three exposure routes were all in the order of ingestion>dermal contact>inhalation. The carcinogenic risk of HCHs was higher than that of DDTs, but both they were less than $10^{-6}$ (the acceptable risk level). The carcinogenic risk of HCHs and DDTs to adult was all higher than that to children. The carcinogenic and non-carcinogenic risks of HCHs and DDTs in campus soil of Jilin University were lower than the acceptable risk level, indicating that the human health risk of HCHs and DDTs in campus soil was very low, even can be ignored.

4. Conclusion

On basis of GB15618-2008, the HCHs level in campus soils could be classified as little pollution while two samples in CY campus experimental zone and XM campus greening zone may exist serious pollution, DDTs level might be categorized as no pollution.

The residual HCHs in the campus soil of Jilin University were mainly α-HCH and β-HCH and they mainly came from the used of industrial HCH in the history with a long residual time and the components had been transformed. The main residual forms of DDTs were p,p'-DDE and o,p'-DDT and they mainly came from the pollution of dicofol in the history, and had been degraded for a long time in the soil.

Some ecological risks of HCHs existed in campus soil of Jilin University. The exposure health risks of HCHs and DDTs in campus soil of Jilin University were very low without harm to the campus population.

Acknowledgements

The authors are grateful to the supports from the Agricultural Geology Projects of China Geological Survey (No.12120105111208) and the State Key Research and Development Program (No.2016YFC060606)

Reference

[1] Ali U, Syed JH, Malik RN, et al. 2014. Organochlorine pesticides (OCPs) in South Asian region: A review. Sci Total Environ 476-477: 705-717.
[2] Zhang JJ, Wang Y, Hua DL. 2017. Occurrence, distribution and possible sources of organochlorine pesticides in peri-urban vegetable soils of Changchun, Northeast China. Hum Ecol Risk Assess. 23(8): 2033 - 2045
[3] Zhi H, Zhao Z and Zhang L 2015. The fate of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water from Poyang Lake, the largest freshwater lake in China. Chemosphere.119: 1134-1140.
[4] Yuan L, Qi S, Wu X, et al. 2013. Spatial and temporal variations of organochlorine pesticides (OCPs) in water and sediments from Honghu Lake, China. J Geochem Explo. 132:181-187.
[5] Pan G, Hu MY, Guan CC, et al. 2019. Surveillance results of HCHs and DDTs residues of five marine products from Taizhou shallows. Preventive Medicine. 31:622-624.
[6] Peng SY, Peng PA, Kong DM, et al. 2019. Distribution characteristics and Ecological Risk Assessment of Organochlorine Pesticides in Sediments of Zhanjiang Bay. Environ Sci. 40:1734-1741.
[7] Sun YX, Hao Q, Xu XR, et al. 2014. Persistent organic pollutants in marine fish from Yongxing Island, South China Sea: levels, composition profiles and human dietary exposure assessment. Chemosphere. 98: 84-90.
[8] Taghizadeh SF, Badibostan H, Hayes AW, et al. 2019. Residues levels of pesticides in walnuts of Iran and associated health risks. Hum Ecol Risk Assess.1-14.

[9] Yu HY, Li FB, Yu WM, et al. 2013. Assessment of organochlorine pesticide contamination in relation to soil properties in the Pearl River Delta, China. Sci Total Environ.447:160-168.

[10] Guo Y, Yu HY and Zeng EY 2009. Occurrence, source diagnosis, and biological effect assessment of DDT and its metabolites in various environmental compartments of the Pearl River Delta, South China: a review. Environ Pollut.157:1753-1763.

[11] Kafaei R, Arfaeinia H, Savari A, et al. 2020. Organochlorine pesticides contamination in agricultural soils of southern Iran. Chemosphere.240:124983.

[12] Zhou Q, Wang J, Meng B, et al. 2013. Distribution and sources of organochlorine pesticides in agricultural soils from central China. Ecotox Environ Safe.93:163-170.

[13] Wang XN, Wu CY, Sun YN, et al. 2011. Urban Soil Character in Changchun City (in Chinese). Inner Mongolia Agri Sci tech.2011(3):35-37.

[14] Environmental Protection Administration of China. 2017. Soil and Sediment-Determination of organochlorine pesticides Gas chromatography/Mass spectrometry (HJ835-2017).

[15] Environmental Protection Administration of China. 2011. Soil-Determination of dry matter and water content-Gravimetric method (HJ613-2011).

[16] Environmental Protection Administration of China. 2008. Environmental quality standard for soils (GB 15618-2008).

[17] Kumar B, Verma VK, Mishra M, et al. 2014. DDT and HCH (Organochlorine Pesticides) in Residential Soils and Health Assessment for Human Populations in Korba, India. Hum Ecol Risk Assess.20:1538-1549.

[18] Vijgen J, de Borst B, Weber R, et al. 2019. HCH and lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue. Environ Pollut.248:696-705.

[19] Gao J, Zhou H, Pan G, et al. 2013. Factors influencing the persistence of organochlorine pesticides in surface soil from the region around the Hongze Lake, China. Science Total Environ.443:7-13.

[20] Tang JF, Feng J, Li G, et al. 2018. Occurrence and possible sources of organochlorine pesticides in soils of Ningbo, East China. Earth Env Sci T R So.109:495-500.

[21] Lu JL, Wang XH, Hao LB, et al. 2008. Residues Characteristics of DichloroDiphenyltrichloroethylene in Agricultural Soil in the Middle Jilin Province (in Chinese). Journal of Jilin University (Earth Science Edition).38(5):859-863.

[22] Urzelai A, Vega M and Angulo E 2000. Deriving ecological risk-based soil quality values in the Basque Country. Sci Total Environ.247(2-3):279-284.

[23] Jongbloed RH, Traas TP and Luttik R 1996. A Probabilistic Model for Deriving Soil Quality Criteria Based on Secondary Poisoning of Top Predators II. Calculations for Dichloro-diphenyltrichloroethene (DDT) and Cadmium. Ecoto Environ Safe.34(3):279-306.

[24] Liu MX, Yang YY, Yun XY, et al. 2016. Occurrence, sources, and cancer risk of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in agricultural soils from the Three Gorges Dam region, China. J Soil Water Conserv.71:327-334.

[25] Siriwong W, Thirakhupt K, Siticharoenchai D, et al. 2009. Risk Assessment for Dermal Exposure of Organochlorine Pesticides for Local Fishermen in the Rangsit Agricultural Area, Central Thailand. Hum Ecol Risk Assess.15:636-646.