Levels, Potential Sources and Risk Assessment of Organochlorine Pesticides in Atmospheric Particulate Matter at Regional Background Site

Juan Liu^{1,2}, Hui-Yu Wang^{1,2}, Shan-Jun Song³, Hui-Chun Ma⁴, Wen-Tao Sun¹, Lei Wang^{4**}, Yan Wang⁵, Xian-Liang Yi⁶, Li-Qiong Guo⁷, Peng-Hui Li^{1,2,8*}

¹ School of Environmental Science and Safety Engineering, Tianjin University of Technology, Tianjin 300384, China

² Tianjin Key Laboratory of Hazardous Waste Safety Disposal and Recycling Technology, Tianjin 300384, China

³ National Institute of Metrology, Beijing 100029, China

⁴ Hebei research center for Geoanalysis, Hebei 071000, China

⁵ School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

⁶ School of Food and Environment, Dalian University of Technology, Panjin 124221, China

⁷ Department of Occupational and Environmental Health, School of Public Health, Tianjin Medical University, Tianjin 300070, China

⁸ Tianjin SF-Bio Industrial Bio-Tec Co., Ltd, Tianjin 300462, China

ABSTRACT

Forty-eight PM_{2.5} samples were collected from June to August 2015 at the summit of Mount Tai. The samples were analyzed to determine the concentrations, potential sources and health risk of organochlorine pesticides (OCPs). Total OCPs concentration in PM_{2.5} ranged from 20.5 to 331 pg m⁻³. Hexachlorocyclohexane (HCHs) were the most abundant compounds. The sources of OCPs used potential source contribution function (PSCF), back trajectory analysis and principal component analysis suggested that the southwest agricultural areas and southeast regions of Mount Tai were the significant contributions regions of OCPs. Both old residual and new input were considered to the contribution of OCPs contamination. Human health risk assessment was carried out by non-carcinogenic health hazard quotient (HQ). The HQ values through inhalation and dermal contact ranged from 9.28×10^{-12} to 6.56×10^{-3} , indicating a negligible risk of the study area.

Keywords: PM_{2.5}; Organochlorine pesticides (OCPs); Concentration; Long-range transport; Health risk.

INTRODUCTION

Organochlorine pesticides (OCPs), a group of persistent organic pollutants (POPs), were extensively used in agriculture from the 1950s to 1970s all over the world due to their low cost and the effective performance in controlling insects (Jin *et al.*, 2013). However, due to their high toxicity, carcinogenic property and resistance to degradation, OCPs are of special concern in previous studies (Bräuner *et al.*, 2011; Jiao *et al.*, 2018). The application of OCPs have been restricted in most of the developed and developing countries since 1980s. However, they were still widely detected in different regions because of the previous residues

(Bozlaker *et al.*, 2009; Zhou *et al.*, 2019). In atmosphere, OCPs mainly came from agricultural soil suspension and synthesis of chlorinated product (Chakraborty *et al.*, 2013), and can be transported over long distances from their sources and had been found in remote locations where they have never been used or produced (Kirchner *et al.*, 2016).

China was a major producer and consumer of OCPs in the world. Before they were prohibited in 1983, the total production of hexachlorocyclohexane (HCHs) and dichlorodiphenyltrichloroethane (DDT) in China was about 4.9 and 0.4 million tons, accounting for 33% and 20% of the total world production, respectively (Xu *et al.*, 2011). Studies concerning OCPs compounds in atmospheric environment have been performed in different regions of China (Han *et al.*, 2016; Wang *et al.*, 2008). In Beijing, the levels were found to be 212 pg m⁻³ for HCHs and 522 pg m⁻³ for DDTs in 2005, and their concentrations were decreased to 101 pg m⁻³ and 146 pg m⁻³, respectively in 2009 (Zhang *et al.*, 2011). However, through the global distillation and grasshopper effect, OCPs were detected in many background sites such as Antarctica (Dickhut *et al.*, 2005), and the

* Corresponding author.

Tel.: 86 22 60214203

E-mail address: lipenghui406@163.com

** Corresponding author.

E-mail address: wanglei8812@126.com

Arctic (Becker *et al.*, 2012) where had never used OCPs. Understand the long-range transport of OCPs in atmosphere can give important information for the global-scale existence and fates of these pollutants. In the present study, fine particle (PM_{2.5}) samples were collected at the summit of Mount Tai, which serves as a regionally background site and a unique environment to investigate the long-range transport of pollutants in troposphere (Liu *et al.*, 2017). OCP compounds were analyzed in collected PM_{2.5} samples, and the objectives of the present study were to (1) survey the regional pollution levels of OCPs in PM_{2.5}, (2) identify possible sources and long-range transport of OCPs from contaminated regions, and (3) provide comprehensive fundamental data for risk assessment of OCPs in atmospheric environment.

EXPERIMENT AND METHOD

Sampling

The sampling was carried out in the meteorological monitoring station on Mount Tai (117°06'E, 36°16'N, 1532.7 m A.S.L), located in free troposphere, is one of the highest peaks in northern China. A total of 48 PM_{2.5} samples were collected from June 15 to August 11, 2015, using a high-volume air sampler (HI-Q 7386, Inc. San Diego, manufactured by Environmental Products Company, CA, USA) at a flow rate of 1000 L min⁻¹ with 24-h sampling intervals. Before sampling, the quartz fiber filter (QFF; 203 × 254 mm, Munktell, Sweden) was heated at 600°C for 2 h to eliminate organic substances, and equilibrated at controlled environment condition (relative humidity of 35% ± 1% and temperature of 22 ± 2°C) for 48 h (U.S. EPA, 2001). Then they were weighed using a microbalance (balance sensitivity ± 0.001 mg, Mettler Toledo XP6). After sampling, the quartz filters were wrapped by aluminum foil, packaged in polyethylene bags, transported to laboratory as soon as possible. After weighed in controlled conditions described above, samples were stored at -20°C until analysis.

Sample Analysis

Filters were extracted by accelerated solvent extraction (ASE 300, Dionex, Sunnyvale, US). The extraction procedures were repeated twice, which was operated with

a mixture solvent of n-hexane/acetone (1:1, v/v) at 100°C and 1500 psi. The extract was concentrated by a rotary evaporator and then reduced to 1 mL under a gentle stream of nitrogen, transferred into a glass vial for analysis.

The OCPs were analyzed using a gas chromatography-mass spectrometer (GC-MS) (7890B-5977A, Agilent Technologies, USA) equipped with a fused silica capillary DB-5MS column (30 m × 0.25 mm × 0.25 μm) using selective ion monitoring mode. The inlet, transfer line, and ion source temperature were 250°C, 260°C, and 230°C, respectively. 2 μL of each sample was injected in the splitless mode.

Quality Assurance and Quality Control (QA/QC)

Strict QA/QC procedures were performed during analysis processes. Laboratory and field blanks were prepared and analyzed in the same manner as samples, and OCPs were not detected in these blanks. The method detection limit (MDL) were as follows: 1 pg m⁻³ for Hexachlorobenzene (HCB) and α-HCH; 1.5 pg m⁻³ for β-HCH, γ-HCH and δ-HCH; 2.0 pg m⁻³ for heptachlor, heptachlor epoxide and aldrin; 25 pg m⁻³ for p,p'-DDT and mirex. Concentrations below the method detection limit were regarded as the lowest values. Samples were analyzed in triplicate with relative standard deviations (RSDs) less than 13%. The recoveries were 61% ± 23% in the PM_{2.5} samples.

RESULTS AND DISCUSSION

OCPs Concentration

Ten OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, p,p'-DDT, HCB, heptachlor, heptachlor epoxide, mirex and aldrin) were detected in this present study (Table 1). The concentration of ΣOCPs in PM_{2.5} ranged from 20.5 to 331 pg m⁻³, with an average of 60.3 ± 53.3 pg m⁻³.

HCHs used to be a dominant commercial insecticide. In this study, HCHs (ΣHCH, sum of α-HCH, β-HCH, γ-HCH, and δ-HCH) exhibited the highest concentration, with an average of 29.0 ± 28.1 pg m⁻³. The concentrations were comparable to those observed in air samples from background sites such as the Atlantic Ocean (3 pg m⁻³ for α-HCH and 22 pg m⁻³ for γ-HCH) (Jaward *et al.*, 2004) and Singapore (1.38 ± 0.86 pg m⁻³ for α-HCH, and 1.36 ± 1.84 pg m⁻³ for

Table 1. OCPs concentrations (pg m⁻³) in atmospheric particles of Mount Tai from June 2015 to August 2015.

Compounds	Mean (pg m ⁻³)	Range (pg m ⁻³)	FD%
α-HCH	1.46 ± 3.15	ND-22.0	27
β-HCH	10.3 ± 14.7	ND-85.3	43
γ-HCH	5.91 ± 5.41	ND-26.4	75
δ-HCH	11.3 ± 8.34	ND-37.2	46
p,p'-DDT	5.80 ± 12.1	ND-61.3	40
HCB	3.65 ± 3.49	ND-14.8	78
Heptachlor	3.72 ± 4.90	ND-30.3	65
Heptachlor epoxide	3.50 ± 2.88	ND-14.6	41
Mirex	10.1 ± 10.9	ND-49.3	84
Aldrin	4.48 ± 5.46	ND-34.4	75
ΣHCH	29.0 ± 28.1	8.79-108	
ΣOCP	60.3 ± 53.3	20.5-331	

γ -HCH) (He *et al.*, 2009) (Table 2). They were lower than some regions, such as the South China Sea ($67 \pm 33 \text{ pg m}^{-3}$ for α -HCH, and $771 \pm 310 \text{ pg m}^{-3}$ for γ -HCH) (Lin *et al.*, 2012; Zhang *et al.*, 2007), Taihu Lake ($74 \pm 45 \text{ pg m}^{-3}$ for α -HCH, and $46 \pm 24 \text{ pg m}^{-3}$ for γ -HCH) (Qiu *et al.*, 2004), and Korea background sites (71.3 pg m^{-3} for HCHs) (Jin *et al.*, 2013).

The concentrations of p,p'-DDT (average: $5.80 \pm 12.1 \text{ pg m}^{-3}$) in this study were comparable to those in the China marginal seas ($5.1 \pm 5.1 \text{ pg m}^{-3}$ for p,p'-DDT) (Lin *et al.*, 2012), Korea background sites (3.5 pg m^{-3} for DDTs) (Jin *et al.*, 2013) and the Indian Ocean (5.9 pg m^{-3} for p,p'-DDT) (Wurl *et al.*, 2006). But they were significantly lower than results analyzed in particle samples in Beijing, China ($273 \pm 695 \text{ pg m}^{-3}$) (Wang *et al.*, 2008), remote area of Turkey ($74 \pm 163 \text{ pg m}^{-3}$) (Ozcan and Aydin, 2010), Durban, South Africa ($15.0 \pm 11.7 \text{ pg m}^{-3}$) (Batterman *et al.*, 2008), and gas samples in Tai Lake ($124 \pm 91 \text{ pg m}^{-3}$ for p,p'-DDT) (Qiu *et al.*, 2004) and the South China Sea ($58 \pm 65 \text{ pg m}^{-3}$ for p,p'-DDT) (Zhang *et al.*, 2007).

HCB was mainly used for producing pentachlorophenol sodium, wood preservation and pesticide for schistosoma (Wang *et al.*, 2008). In this study, the average concentration of HCBs ($3.65 \pm 3.49 \text{ pg m}^{-3}$) were comparable to those measured at the points in Durban, South Africa ($4.7 \pm 2.7 \text{ pg m}^{-3}$) (Batterman *et al.*, 2008), but much lower than those observed over Korea background sites ($15\text{--}256 \text{ pg m}^{-3}$) (Jin *et al.*, 2013) and Beijing ($53.7 \pm 28.1 \text{ pg m}^{-3}$) (Wang *et al.*, 2008).

Heptachlor is an organochlorine cyclodiene insecticide isolated from technical chlordane in 1946. It was used primarily in termite, ant and soil insect control in seed grains and on crops, as well as in the home (Wang *et al.*, 2008). It was banned in Japan since 1970s, and had not been registered for use in Mongolia, Russia and China (excluding Taiwan, which banned in 1989) (UNEP, 2003). In this study, the concentration of heptachlor ranged from ND to 30.3 pg m^{-3} (average $3.72 \pm 4.90 \text{ pg m}^{-3}$) were comparable to the results detected in remote area, Turkey ($3 \pm 9 \text{ pg m}^{-3}$) (Ozcan and Aydin, 2010); higher than Korea background sites (0.41 pg m^{-3}) (Jin *et al.*, 2013); but significantly lower than those regions, such as Beijing ($99.9 \pm 190 \text{ pg m}^{-3}$) (Wang *et al.*, 2008).

Heptachlor epoxide was found in 41% samples in this study, ranged from ND– 14.6 pg m^{-3} and averaged $3.50 \pm 2.88 \text{ pg m}^{-3}$. This non-systemic stomach and contact insecticide was used primarily against soil insects and termites, as well as cotton insects, grasshoppers, some crop pests and mosquitoes (Batterman *et al.*, 2008). Karlsson *et al.* (2000) reported heptachlor epoxide levels of $0.82 \pm 1.9 \text{ pg m}^{-3}$ at Lake Malawi, and Batterman *et al.* (2008) reported the average concentration lower than the detection limit in Durban, South Africa, which were slightly lower than our measurements.

It was worth noticing that aldrin had never been used in large amounts in China, but it was detected in most of samples on Mount Tai (range: ND– 34.4 pg m^{-3} , average $4.48 \pm 5.46 \text{ pg m}^{-3}$). This concentration was higher than that in Korea background sites (ND– 0.65 pg m^{-3} , 0.08 pg m^{-3})

(Jin *et al.*, 2013), but significantly lower than those in Beijing ($376 \pm 542 \text{ pg m}^{-3}$) (Wang *et al.*, 2008). Aldrin was also detected in sediments and surface water from Guanting Reservoir and in most samples of water from Qiantang River (Zhou *et al.*, 2006). Due to its persistence and semi-volatility, aldrin can enter atmosphere by volatilization from sediments and surface water, resulting in a large-scale pollution through “the Grasshopper Effect” or long-range transport (Wang *et al.*, 2008; Wania *et al.*, 2010).

Mirex is a stomach insecticide that has been used to control fire ants in the southeastern US, leaf cutters in South America, harvester termites in South Africa, western harvester ants in the US and mealybugs in Hawaii. It also has been used as a fire retardant in plastics, rubber, paint, paper and electrical products (Batterman *et al.*, 2008). It has not been produced or used in Korea, Mongolia, Russia and Japan, but it was detected in some of these areas such as the study on Korea background sites (Jin *et al.*, 2013). In China, it was used as termiticide in some regions (UNEP, 2003). The levels of mirex in this study ranged from ND to 49.3 pg m^{-3} , with an average of $10.1 \pm 10.9 \text{ pg m}^{-3}$. The concentration was higher than that in Korea background sites (range: ND– 0.78 pg m^{-3} , average: 0.04 pg m^{-3}) (Jin *et al.*, 2013).

Source Identification of OCPs

The concentrations and ratios of some marker OCP compounds can give the indication of the impact from different emission sources. For example, technical HCH and lindane was considered to be the major contribution of HCHs in environment. Technical HCH consisted of α -HCH (55%–80%), β -HCH (5%–14%), γ -HCH (8%–15%) and δ -HCH (2%–16%), while lindane was made up of more than 95% γ -HCH (Rodríguez-Garrido *et al.*, 2010). The sources of HCHs can be estimated by the ratio of α -HCH/ γ -HCH. If this ratio is lower than 3, HCHs was from the recent use of lindane. If the ratio is between 3 and 7, the source of HCH comes from fresh input of technical HCH. The ratio higher than 7 represents history use of technical HCH (Ozcan and Aydin, 2010). In the present study, the ratio of α -HCH/ γ -HCH is between 0.03 and 1.62, indicating HCHs was from recent use of lindane after technical HCH was banned (Huang *et al.*, 2014; Ji *et al.*, 2015).

To further explore the potential sources of OCPs components, principal component analysis (PCA) was applied by using SPSS version 21. The principle of PCA was to describe the covariance relationship of several variances based on some common components, which was expected to explain most of the variance in analysis results. (Cheng *et al.*, 2017). During the analysis, several factors can be subsequently divided by a certain factor interrelation, and the higher loading in factor represented more contribution to specific variation in data. In this present study, factor loadings higher than 0.6 was supposed to they can be suitable to identify source categories, and the score plot of eigenvalues >1 were considered to be able to explain the variance in output data (Ji *et al.*, 2015; Widiana *et al.*, 2017). Finally, the emission source represented by a component

Table 2. A comparison of OCP concentrations with literature values (pg m^{-3}).

Site	α -HCH	β -HCH	γ -HCH	δ -HCH	p,p'-DDT	HCB	heptachlor	heptachlor epoxide	mirex	aldrin	Reference
Mount Tai, China (particle phase)	1.46 ± 3.15	10.3 ± 14.7	5.91 ± 5.41	11.3 ± 8.34	5.80 ± 12.1	3.65 ± 3.49	3.72 ± 4.90	3.50 ± 2.88	10.1 ± 10.9	4.4 ± 5.46	This work
Singapore (particle phase)	1.38 ± 0.86	0.35 ± 0.54	1.36 ± 1.84	1.62 ± 0.62	0.16 ± 0.14	-	-	-	-	-	He et al. (2009)
Durban, South Africa (particle phase)	0.09 ± 0.15	-	-	-	15.0 ± 11.7	0.10 ± 0.12	-	0.05 ± 0.09	-	0.00 ± 0.01	Batterman et al. (2008)
Beijing, China (particle phase)	69.9 ± 88.8	39.7 ± 48.9	54.2 ± 31.5	54.2 ± 31.5	273 ± 695	53.7 ± 28.1	99.9 ± 190	300 ± 436	-	376 ± 542	Wang et al. (2008)
remote area, Turkey (particle phase)	< dl	2 ± 7	6 ± 14	9 ± 29	74 ± 163	-	3 ± 9	< dl	-	< dl	Ozcan and Aydin (2010)
Korea background sites (gas + particle phase)	71.3^a	-	-	-	3.50	80	0.41	-	0.04	0.08	Jin et al. (2013)
Atlantic Ocean (gas + particle phase)	3	-	22	-	-	-	-	-	-	-	Jaward et al. (2004)
Taihu Lake, China (gas phase)	74 ± 45	-	46 ± 24	-	124 ± 91	-	-	-	-	-	Qiu et al. (2004)
Indian Ocean (gas phase)	3.2	-	13.8	-	5.9	-	-	-	-	-	Wurl et al. (2006)
China marginal sea (gas phase)	13 ± 8.1	-	110 ± 76	-	5.1 ± 5.1	-	-	-	-	-	Lin et al. (2012)
South China Sea (gas phase)	67 ± 33	-	771 ± 310	-	58 ± 65	-	-	-	-	-	Zhang et al. (2007)
Durban, South Africa (gas phase)	1.5 ± 1.0	-	-	-	27.0 ± 18.0	4.50 ± 2.40	-	0.58 ± 0.75	-	10.1 ± 14.2	Batterman et al. (2008)
remote area, Turkey (gas phase)	209 ± 267	77 ± 147	71 ± 169	64 ± 94	42 ± 104	-	15 ± 38	< dl	-	1 ± 3	Ozcan and Aydin (2010)
Lake Malawi, Southern Africa (gas phase)	9.4 ± 9.0	5.3 ± 8.6	25 ± 42	-	12 ± 27	11 ± 7.5	44 ± 66	0.82 ± 1.9	0.51 ± 0.44	257 ± 338	Karlsson et al. (2000)

-; not analyzed;

dl: detection limit;

a: HCH data were reported as sum of α -HCH, β -HCH, γ -HCH, δ -HCH.

could be determined by the source profiles of pollutants contained in this component (Papaoikonomou *et al.*, 2018). As is shown in Fig. 1, two factors accounted for 69.7% of the total data factors. The first principal component (PC1) explained 39.0% of total variance, showing high loading for p,p'-DDT, α -HCH, β -HCH, mirex and heptachlor. p,p'-DDT was banned as a pesticide in China in 1983. α -HCH and β -HCH were the main components of technical HCHs, which was identified as the residues of old use (α -HCH/ γ -HCH ratio lower than 3). Heptachlor was the matrix of heptachlor epoxide, can be identified as previous usage before heptachlor. Thus, PC1 is assumed to be relatively old use of pesticides. The second principal component (PC2) with 30.7% of the variability occurred the high loading on γ -HCH, δ -HCH, HCB and heptachlor epoxide. The presence of γ -HCH could point to the contribution of lindane of recently use. HCB was widely used fungicides in China and emitted as byproduct from chlorinated industry, such as polyvinyl chloride plastics, synthetic rubber, metal production, dye and various combustion processes (Huang *et al.*, 2014). Heptachlor epoxide was derived by heptachlor in environment. Thus, PC2 could reflect the presence of OCPs from recently use.

Long-range Atmospheric Transport

To identify the transport patterns of OCPs and the influence of air mass transport on individual component, 24-hour air parcel back trajectories and potential source contribution function (PSCF) analysis were conducted by

the Hybrid-Single Particle Integrated Trajectories (HYSPLIT 4.8) and TrajStat, respectively. The back trajectories were clustered by cluster algorithm using HYSPLIT service (Yeh *et al.*, 2017). The PSCF analysis, combined with back trajectory results, was employed to identify the regional sources of organochlorine components. The study area was divided into some grid cells with equal size ($i \times j$), and the PSCF value in cell (i, j) was calculated by m_{ij}/n_{ij} multiple W_{ij} . Where m_{ij} and n_{ij} represented the number of concentration points loading in cell (i, j) and exceeding the threshold value in this cell, respectively. W_{ij} was an empirical weight function to reduce the uncertainty of results. In the present study, the grid cells with high values exceeding 0.9 were selected as potential regional sources (Li *et al.*, 2018; Tong *et al.*, 2018).

As shown in Figs. 2 and 3, all the air mass back trajectories classified into four types by source direction, namely, SE-air masses, SW-air masses, NW-air masses and NE-air masses, respectively (represented the air from southeast, southwest, northwest and northeast of Mount Tai). The SE-air masses represented travelled across Jiangsu and the Yellow Sea. The SW-air masses mainly from Henan and the western of Shandong province. The NW-air masses that most originated from continental areas in northern China crossed Inner Mongolia, Shanxi and Hebei province and reached the station. The NE-air masses were from Bohai strait and northeast of Shandong.

The largest proportion belonged to SE-air masses (31.3%), with the highest OCPs concentration (average 95.3 pg m^{-3}),

Fig. 1. Principal component analysis for OCPs.

Fig. 2. 24-h back trajectories of air masses during sampling period. **Fig. 3.** Regional sources analysis of (a) α -HCH, (b) p,p'-DDT, (c) HCB and (d) Aldrin using PSCF.

indicating that air masses from eastern coastal area was an important potential source region of OCPs on Mount Tai, which was coincident with the previous researches (Niu *et al.*, 2014; Ji *et al.*, 2015). OCPs applied as pesticides still have an impact on environment, and high concentrations for DDTs, HCHs, heptachlor had been reported in this region (Zhou *et al.*, 2013; Wang *et al.*, 2016; Sun *et al.*, 2017).

NW-air masses and NE-air masses accounted for 18.8% and 20.3% of air masses, and average OCPs concentrations were 54.1 pg m^{-3} and 36.2 pg m^{-3} , respectively. Some important OCP compounds had been influenced by NW-air masses and NE-air masses. α -HCH, p,p'-DDT, HCB and aldrin were associated with the air from the northwest of Mount Tai, which was consistent with the results from previous studies (Lammel *et al.*, 2007; Liu, 2014). Agricultural activities in these regions can still consume a lot of pesticides in past decades, and make contribution of OCPs in the environment (Niu *et al.*, 2014).

Toxicity Assessment

For atmospheric particles, exposure through inhalation and dermal contact could lead to adverse health effects. Health risk assessments for both inhalational and dermal exposures of OCPs were calculated in this study. The model was based on the Risk Assessment Guidance for Superfund, Vol. I: Human Health Evaluation Manual (U.S. EPA, 1989). Following two equations were used average daily dose (ADD) ($\text{mg kg}^{-1} \text{ day}^{-1}$) to estimate human health risks associated with inhalation (ADD_{inh}) and dermal contact (ADD_{derm}) (Wang *et al.*, 2018).

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (1)$$

$$ADD_{derm} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \quad (2)$$

where C is the concentration of OCPs (mg kg^{-1}). InhR is the inhalation rate ($\text{m}^3 \text{ day}^{-1}$). PEF is representative of the particle emission factor ($\text{m}^3 \text{ kg}^{-1}$). EF is the exposure frequency (days year⁻¹). ED represents the exposure duration (years). BW is the body weight (kg). AT is the averaging time (days). SA is the dermal exposure area (cm^2). AF is the dermal adherence factor ($\text{mg cm}^{-2} \text{ day}^{-1}$). ABS is the dermal adsorption fraction. These values of parameters

were referenced from the literature, showing in Table 3.

After the ADD was calculated, health hazard quotient (HQ) based on non-cancer toxic risk on humans can then be estimated by dividing the average daily dose to a specific reference dose (RfD).

$$HQ = \frac{ADD}{RfD} \quad (3)$$

The reference dose (RfD) ($\text{mg kg}^{-1} \text{ day}^{-1}$) values of α -HCH, β -HCH, γ -HCH, p,p'-DDT, heptachlor, aldrin and heptachlor epoxide is 0.8, 0.8, 0.3, 0.5, 0.5, 0.03 and 1.3×10^{-2} , respectively (Witczak and Abdelgawad, 2014). RfD is an estimation of maximum permissible risk on human populations through daily exposure. The threshold of RfD value can be used to indicate whether there is adverse health effect during a lifetime. $HQ > 1$ indicated likely adverse health effects, whereas $HQ \leq 1$ indicated unlikely adverse health effects (Witczak and Abdelgawad, 2014). The estimated HQ values of OCPs detected at Mount Tai were much lower than the acceptable level ($HQ \leq 1$) (Table 4), indicating exposure to PM_{2.5}-bound OCPs lead to an acceptable health effects in this region. However, the health effect of PM-bound OCPs had been highlighted in some regions in Northern China (Ding *et al.*, 2015), much research work should be conducted in the future.

CONCLUSIONS

Despite most OCPs have been restricted in China, many OCP compounds are still detected in PM_{2.5} at Mount Tai, a regional background site in Northern China owing to their persistence and transport in the environment. The concentration of total OCPs on Mount Tai ranged from 20.5 pg m^{-3} to 331 pg m^{-3} . HCHs were the most abundant OCP compounds, with an average concentration of 29.0 pg m^{-3} . The results of PCA, back trajectory and PSCF analysis signaled the dominant source of OCPs were from the southwest agricultural areas and southeast regions of Mount Tai. The HQ values of non-cancer toxic risk on humans were estimated to be in the range of 9.28×10^{-12} to 6.56×10^{-3} . All of values were far less than 1, suggesting that exposure to PM_{2.5}-bound OCPs would not lead to significant adverse health effects for general population.

Table 3. Introduction of each parameter.

Logogram	Parameters	Unit	Moderate dose
EF	Exposure frequency	days year ⁻¹	365
ED	Exposure duration	years	70
AT	Average time	days	70 × 365
InhR	Inhalation rate	$\text{m}^3 \text{ day}^{-1}$	20
SA	Dermal exposure area	cm^2	3300
AF	Dermal adherence factor	$\text{mg cm}^{-2} \text{ day}^{-1}$	0.2
ABS	Dermal adsorption fraction	-	0.1
PEF	Particle emission factor	$\text{m}^3 \text{ kg}^{-1}$	1.36×10^9
BW	Standard body weights	kg	61.5

Table 4. Health hazard quotient (HQ) of OCPs compounds through inhale and dermal, respectively.

Compounds	HQ (inhale)	HQ (dermal)
α -HCH	9.28×10^{-12}	4.17×10^{-5}
β -HCH	7.45×10^{-11}	3.34×10^{-4}
γ -HCH	1.11×10^{-10}	4.97×10^{-4}
p,p'-DDT	6.12×10^{-11}	2.75×10^{-4}
Heptachlor	4.21×10^{-11}	1.89×10^{-4}
Heptachlor epoxide	1.46×10^{-9}	6.56×10^{-3}
Aldrin	9.05×10^{-10}	4.06×10^{-3}

ACKNOWLEDGMENTS

Financial supports were provided by National Natural Science Foundation of China (41601548, 81602827, 21806158), Tianjin Municipal Education Commission Research Project (2017KJ244), Fundamental Research Funds of National Institute of Metrology China (AKY1720), Tianjin 131 innovative talent training project, Natural Science Foundation of Chongqing (cstc2018jcyjAX0776), Research Start-up Funding Project of Chongqing Technology and Business University (1756003) and Tianjin Special Commissioner Project (17JCTPJC53100).

REFERENCES

- Batterman, S.A., Chernyak, S.M., Gounden, Y., Matooane, M. and Naidoo, R.N. (2008). Organochlorine pesticides in ambient air in Durban, South Africa. *Sci. Total Environ.* 397: 119–130.
- Becker, S., Halsall, C.J., Tych, W., Kallenborn, R., Schlabach, M. and Man, S. (2012). Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere. *Atmos. Chem. Phys.* 12: 515–540.
- Bozlaker, A., Muezzinoglu, A. and Odabasi, M. (2009). Processes affecting the movement of organochlorine pesticides (OCPs) between soil and air in an industrial site in Turkey. *Chemosphere* 77: 1168–1176.
- Bräuner, E.V., Mayer, P., Gunnarsen, L., Vorkamp, K. and Raaschou-Nielsen, O. (2011). Occurrence of organochlorine pesticides in indoor dust. *J. Environ. Monitor.* 13: 522–526.
- Chakraborty, P., Zhang, G., Eckhardt, S., Li, J., Breivik, K., Lam, P.K., Tanabe, S. and Jones, K.C. (2013). Atmospheric polychlorinated biphenyls in Indian cities: Levels, emission sources and toxicity equivalents. *Environ. Pollut.* 182: 283–290.
- Cheng, J.H., Hsieh, M.J. and Chen, K.S. (2016). Characteristics and source apportionment of ambient volatile organic compounds in a science park in central Taiwan. *Aerosol Air Qual. Res.* 16: 221–229.
- Dickhut, R.M., Cincinelli, A., Cochran, M., and Ducklow, H.W. (2005). Atmospheric concentrations and air-water flux of organochlorine pesticides along the western Antarctic Peninsula. *Environ. Sci. Technol.* 39: 465–470.
- Han, Y., Li, X., Zhu, T., Lv, D., Chen, Y., Hou, L.a., Zhang, Y. and Ren, M. (2016). Characteristics and relationships between indoor and outdoor PM_{2.5} in Beijing: A residential apartment case study. *Aerosol Air Qual. Res.* 16: 2386–2395.
- He, J., Balasubramanian, R., Karthikeyan, S. and Joshi, U.M. (2009). Determination of semi-volatile organochlorine compounds in the atmosphere of Singapore using accelerated solvent extraction. *Chemosphere* 75: 640–648.
- Huang, T., Guo, Q., Tian, H., Mao, X., Ding, Z., Zhang, G., Li, J., Ma, J. and Gao, H. (2014). Assessing spatial distribution, sources, and human health risk of organochlorine pesticide residues in the soils of arid and semiarid areas of northwest China. *Environ. Sci. Pollut. Res.* 21: 6124–6135.
- Jaward, F.M., Barber, J.L., Booij, K., Dachs, J., Lohmann, R. and Jones, K.C. (2004). Evidence for dynamic air-water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environ. Sci. Technol.* 38: 2617–2625.
- Ji, T., Lin, T., Wang, F., Li, Y. and Guo, Z. (2015). Seasonal variation of organochlorine pesticides in the gaseous phase and aerosols over the East China Sea. *Atmos. Environ.* 109: 31–41.
- Jiao, L., Lao, Q., Chen, L., Chen, F., Sun, X. and Zhao, M. (2018). Concentration and influence factors of organochlorine pesticides in atmospheric particles in a coastal island in Fujian, Southeast China. *Aerosol Air Qual. Res.* 18: 2982–2996.
- Jin, G.Z., Kim, S.M., Lee, S.Y., Park, J.S., Kim, D.H., Lee, M.J., Sim, K.T., Kang, H.G., Kim, I.G. and Shin, S.K. (2013). Levels and potential sources of atmospheric organochlorine pesticides at Korea background sites. *Atmos. Environ.* 68: 333–342.
- Karlsson, H., Muir, D.C.G., Teixiera, C.F., Burniston, D.A., Strachan, W.M.J., Hecky, R.E., Mwita, J., Bootsma, H.A., Grift, N.P., Kidd, K.A. and Rosenberg, B. (2000). "Persistent chlorinated pesticides in air, water, and precipitation from the Lake Malawi area, Southern Africa. *Environ. Sci. Technol.* 34: 4490–4495.
- Kirchner, M., Jakobi, G., Körner, W., Levy, W., Moche, W., Niedermoser, B., Schaub, M., Ries, L., Weiss, P., Anritter, F., Fischer, N., Bernhard Henkelmann, B.H. and Schramm, K.W. (2016). Ambient air levels of organochlorine pesticides at three high alpine monitoring stations: Trends and dependencies on geographical origin. *Aerosol Air Qual. Res.* 16: 738–751.
- Lammel, G., Ghim, Y., Grados, A., Gao, H., Huhnerfuss, H. and Lohmann, R. (2007). Levels of persistent organic pollutants in air in China and over the Yellow Sea. *Atmos. Environ.* 41: 452–464.

- Li, P., Sato, K., Hasegawa, H., Huo, M.Q., Minoura, H., Inomata, Y., Take, N., Yuba, A., Futami, M., Takahashi, T. and Kotake, Y. (2018). Chemical characteristics and source apportionment of PM_{2.5} and long-range transport from northeast Asia continent to Niigata in Eastern Japan. *Aerosol Air Qual. Res.* 18: 938–956.
- Lin, T., Li, J., Xu, Y., Liu, X., Luo, C., Cheng, H., Chen, Y. and Zhang, G. (2012). Organochlorine pesticides in seawater and the surrounding atmosphere of the marginal seas of China: Spatial distribution, sources and air-water exchange. *Sci. Total Environ.* 435–436: 244–252.
- Liu, D. (2014). Organochlorinated compounds in the air at NAO, an eastern background site in China: Long-Range atmospheric transport versus local sources. *Aerosol Air Qual. Res.* 14: 1258–1268.
- Liu, J., Wang, Y., Li, P.H., Shou, Y.P., Li, T., Yang, M.M., Wang, L., Yue, J.J., Yi, X.L. and Guo, L.Q. (2017). Polycyclic aromatic hydrocarbons (PAHs) at high mountain site in North China: Concentration, source and health risk assessment. *Aerosol Air Qual. Res.* 17: 2867–2877.
- Niu, L., Xu, C., Xu, Y., Zhang, C. and Liu, W. (2014). Hexachlorocyclohexanes in tree bark across Chinese agricultural regions: Spatial distribution and enantiomeric signatures. *Environ. Sci. Technol.* 48: 12031–12038.
- Ozcan, S. and Aydin, M.E. (2010). Organochlorine pesticides in urban air: concentrations, sources, seasonal trends and correlation with meteorological parameters. *Clean-Soil, Air, Water* 37: 343–348.
- Papaoikonomou, K., Emmanouil, C., Vasilato, V., Diapoulis, E., Grigoratos, T., Zafirakou, A. and Kungolos, A. (2018). PM₁₀ and elemental concentrations in a dismantling plant for waste of electrical and electronic equipment in Greece. *Aerosol Air Qual. Res.* 18: 1457–1469.
- Qiu, X., Zhu, T., Li, J., Pan, H., Li, Q., Miao, G. and Gong, J. (2004). Organochlorine pesticides in the air around the Taihu Lake, China. *Environ. Sci. Technol.* 38: 1368–1374.
- Rodríguez-Garrido, B., Lú-Chau, T.A., Feijoo, G., Macías, F. and Monterroso, M.C. (2010). Reductive dechlorination of α -, β -, γ -, and δ -hexachlorocyclohexane isomers with hydroxocobalamin, in soil slurry systems. *Environ. Sci. Technol.* 44: 7063–7069.
- Sun, J., Pan, L., Tsang, D., Zhan, Y., Zhu, L. and Li, X. (2017). Organic contamination and remediation in the agricultural soils of China: A critical review. *Sci. Total Environ.* 615: 724–740.
- Tong, L., Zhang, J., Xu, H., Xiao, H., He, M. and Zhang, H. (2018). Contribution of regional transport to surface ozone at an island site of Eastern China. *Aerosol Air Qual. Res.* 18: 3009–3024.
- UNEP (2003). Regionally based assessment of persistent toxic substances: Global report. United Nations.
- Wang, B., Wu, C., Liu, W., Teng, Y., Luo, Y., Christie, P. and Guo, D. (2016). Levels and patterns of organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in Henan province, China. *Environ. Sci. Pollut. Res.* 23: 6680–6689.
- Wang, X., Li, X., Cheng, H., Xu, X., Zhuang, G. and Zhao, C. (2008). Organochlorine pesticides in particulate matter of Beijing, China. *J. Hazard. Mater.* 155: 350–357.
- Wang, Y., Fu, Y., Wang, C. and Wen, N. (2018). Dissimilar emission characteristics between bioaerosol and suspended particles from gaseous biofilters and bioaerosol health risk evaluation. *Aerosol Air Qual. Res.* 18: 1874–1885.
- Wania, F., Mackay, D., Li, Y.F., Bidleman, T.F. and Strand, A. (2010). Global chemical fate of α -hexachlorocyclohexane. 1. Evaluation of a global distribution model. *Environ. Toxicol. Chem.* 18: 1390–1399.
- Widiana, D.R., Tsai, J.H., Wang, Y.F., You, S.J. and Yang, H.H. (2017). Source apportionment of air pollution and characteristics of volatile organic compounds in a municipal wastewater treatment plant, North Taiwan. *Aerosol Air Qual. Res.* 17: 2878–2890.
- Witczak, A. and Abdelgawad, H. (2014). Assessment of health risk from organochlorine pesticides residues in high-fat spreadable foods produced in Poland. *J. Environ. Sci. Health., Part B* 49: 917–928.
- Wurl, O., Potter, J.R., Obbard, J.P. and Durville, C. (2006). Persistent organic pollutants in the equatorial atmosphere over the open Indian Ocean. *Environ. Sci. Technol.* 40: 1454–1461.
- Xu, H., Du, S., Cui, Z., Zhang, H., Fan, G. and Yin, Y. (2011). Size distribution and seasonal variations of particle-associated organochlorine pesticides in Jinan, China. *J. Environ. Monit.* 13: 2605–2611.
- Yeh, C.F., Lee, C.L. and Brimblecombe, P. (2017). Effects of seasonality and transport route on chemical characteristics of PM_{2.5} and PM_{2.5-10} in the East Asian Pacific Rim Region. *Aerosol Air Qual. Res.* 17: 2988–3005.
- Zhang, G., Li, J., Cheng, H., Li, X., Xu, W. and Jones, K.C. (2007). Distribution of organochlorine pesticides in the northern South China Sea: Implications for land outflow and air-sea exchange. *Environ. Sci. Technol.* 41: 3884–3890.
- Zhang, L., Huang, Y., Dong, L., Shi, S., Zhou, L., Zhang, T., Mi, F., Zeng, L. and Shao, D. (2011). Levels, Seasonal Patterns, and Potential Sources of Organochlorine Pesticides in the Urban Atmosphere of Beijing, China. *Arch. Environ. Contam. Toxicol.* 61: 159–165.
- Zhou, J., Liu, L., Xu, X., Yu, Y., Li, Y., Zhang, H. and Xu, Y. (2019). Atmospheric transport and bulk deposition of organochlorine compounds at leigongshan nature reserve in Southwestern China. *Aerosol Air Qual. Res.* 19: 1483–1492.
- Zhou, Q., Wang, J., Meng, B., Cheng, J., Lin, G., Chen, J., Zheng, D. and Yu, Y. (2013). Distribution and sources of organochlorine pesticides in agricultural soils from central China. *Ecotoxicol. Environ. Saf.* 93: 163–170.
- Zhou, R., Zhu, L., Yang, K. and Chen, Y. (2006). Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. *J. Hazard. Mater.* 137: 68–75.

Received for review, June 25, 2019

Revised, August 9, 2019

Accepted, August 10, 2019