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Sources and health risks of PM_{2.5}-bound polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in a North China rural area

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ABSTRACT

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are typical persistent organic pollutants (POPs), which have high toxicity, bioaccumulation and long-distance transfer capability. Daily variation, sources of PCBs and OCPs in PM_{2.5} are rarely explored in polluted rural area. Here, the sources and health risks of the PCBs and OCPs were evaluated for 48 PM_{2.5} samples collected in winter 2017 in Wangdu, a heavy polluted rural area in the North China Plain. The average diurnal and nocturnal concentrations of Σ_{18} PCBs and Σ_{15} OCPs were 1.74–24.37 and 1.77–100.49, 11.67–408.81 and 16.89–865.60 pg/m³, respectively. Hexa-CBs and penta-CBs accounted for higher proportions (29.0% and 33.6%) of clean and polluted samples, respectively. Hexachlorobenzene (HCB) was the dominant contributor to OCPs with an average concentration of 116.17 pg/m³. Hexachlorocyclohexane (Σ HCHs) and dichlorodiphenyltrichloroethane (Σ DDTs) were the other two main classes in OCPs with the average concentrations of 4.33 and 15.89 pg/m³, respectively. β -HCH and *p,p'*-DDE were the main degradation products of HCHs and DDTs, respectively. The principal component analysis and characteristic ratio method indicated both waste incineration and industrial activities were the main sources of PCBs, contributing 76.8% and 12.7%, respectively. The loadings of OCPs were attributed to their application characteristics and the characteristic ratio method reflected a current or past use of OCPs. Health risk assessment showed that the respiratory exposure quantity of doxin-like PCBs (DL-PCBs) and the lifetime cancer risk from airborne OCPs exposure was negligible, while the other exposure modes may pose a risk to human bodies.

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Introduction

PM_{2.5} is an important atmospheric pollutant and has significant impacts on air quality, visibility, human health and global climate (Gao et al., 2018; Huang et al., 2014). The components of PM_{2.5} mainly involve water soluble ions, organic compounds and metal elements (Tao et al., 2013; Yao et al., 2016). Organic aerosols account for a high proportion (30%–90%) in PM_{2.5} and consists of thousands of harmful constituents (Cao et al., 2018a; Tan et al., 2016). Among these constituents, organochlorines (OCs), including polychlorinated biphenyls (PCBs) and organochlorines (OCPs) have attracted many interests (Ding et al., 2015; Gong et al., 2018).

Polychlorinated biphenyls and organochlorine pesticides are substances of environmental persistence, bioaccumulation, long distance migration and high toxicity (Fu et al., 2018; Muller et al., 2017). They are typical persistent organic pollutants (POPs), which have the characteristics of high octanol-water partition, low water-solubility, high lipid solubility, which can cause bioaccumulative effect that magnifies step by step via food chain (Die et al., 2015; Zhu et al., 2017). Although PCBs has been banned in the 1970–1980s, PCBs keep emitting from the obsolescent industrial goods and incineration of Cl-containing materials (Han et al., 2010). Among 209 sorts of PCBs, 12 sorts of dioxin-like PCBs (DL-PCBs) have been demonstrated to have potential endocrine disruption, irritation and carcinogenicity (Pham et al., 2019). OCPs have been massively used in 1950s–1980s as the main pesticides for agricultural production and pest control, with the quantities of 4.9 million tons and 0.4 million tons for HCHs and DDTs, respectively. Since the restriction of OCPs in the 1970s, the degradation product such as *o,p'*-DDE, *o,p'*-DDD or γ -HCH also exist in the environment (Socorro et al., 2016; Xu et al., 2011). Wang et al. (2018) found the half-time values of HCHs and DDTs in atmosphere were more than 30 years, so the residuals of the POPs in environment could not be ignored over the recent several decades. Due to their detrimental properties of OCPs, PCBs, many researches have concerned in their detecting and analyzing, as well as their long-range atmospheric transport (Degrendele et al., 2016; Kuzu, 2016).

Atmospheric transport is a dominant way moving the organic compounds from the emission sources to the remote regions (Wu et al., 2017). Suspending PM_{2.5} can work efficiently as a carrier to transfer PCBs and OCPs in the environment. Ubiquitous suspending particles in the atmosphere are able to enter the humans via different ways (food, breath and skin) and are considered to result to great potential threat to humans (Gallistl et al., 2017; Rusin et al., 2019). The PCBs accumulated in humans mainly come from diet, while breathing exposure could not be ignored (Die et al., 2015).

PCBs and OCPs can enter into atmosphere via sources emissions, soil suspension and air-sea exchange (Kim Oanh et al., 2015; Rugner et al., 2019). Due to their special properties as POPs, the researches of PCBs and OCPs have been very prevalent and many studies have reported the concentrations of PCBs and OCPs worldwide (Dvorščak et al., 2015; Kuzu, 2016; Wang et al., 2018). However, the comprehensive assessment on PM_{2.5}-bound PCBs and OCPs in North China was very rare so far (Ding et al., 2015), so it was essential to study the concentrations, sources, and risk assessment of PCBs and OCPs in China.

In this work, we collected 48 PM_{2.5} samples during the Campaign of Oxidation Potential research for air pollution in winter (COPPER) in a North China rural area and measured the concentrations of PCBs and OCPs in the samples. The respective concentrations of PCBs and OCPs during diurnal time and nocturnal time are presented in comparison with the values from the earlier publications. The principal component analysis and characteristic ratio method are deployed to identify their sources. The environmental risks of PM_{2.5}-bound PCBs and OCPs are assessed based on their concentrations. This study can provide a fundamental data support for the local pollution control.

1. Experiments and methods

1.1. Sample collection

The Campaign of Oxidation Potential research for air pollution in winter (COPPER) was conducted at the Wangdu site (38.67°N, 115.25°E) in Baoding city, Hebei province, which locates at a rural area surrounded by wide farms and scattering villages. The PM_{2.5} samples were collected with a high volume air sampler (HIVOL-CVALD, Thermo Fisher Scientific, USA) at a flow rate of 1.13 m³/min, which was placed 3 m above the ground. The PM_{2.5} samples were collected on quartz fiber filters (20 cm × 25 cm, Whatman, UK), which had been pre-baked at 650°C for 4 hr to remove any absorbed organic and inorganic materials. The collection time for every sample lasts 11 hr, i.e., 8:00–19:00 and 20:00–7:00. Twenty-four diurnal and 24 nocturnal samples were collected from 4th to 27th November, 2017. The filters were wrapped in aluminum foil after sampling and stored at -20°C before analysis. The filters were weighed under 25°C and 40% relative humidity (RH).

1.2. Chemicals and reagents

¹³C-labeled stock solutions of PCBs were obtained from Wellington Laboratories, Inc. (Ontario, Canada) and ¹³C-labeled stock solutions of OCPs were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Hexane (Honeywell, New Jersey, USA) and dichloromethane (Honeywell, New Jersey, USA) were pesticide analysis grade and used for sample pretreatment. Silica gel packing (DaMao, Tianjin, China) was baked in a muffle furnace at 650°C for 8 hr. Acidified silica gel (44%, W/W) was prepared by mixing 100 g of activated silica gel with 43 mL of 98 vol.% H₂SO₄. Analytical grade anhydrous sodium sulfate (DaMao, Tianjin, China) was ultrasonically cleaned in hexane solution.

1.3. Sample pretreatment and instrumental analysis

The samples were extracted with accelerated solvent extraction (ASE350 Dionex, Thermo Fisher Scientific, USA) with the dichloromethane (DCM)/*n*-hexane (1:1, V/V) as the extraction solvent. Spiked with ¹³C labeled internal standard, 1/8 of filter samples were cut into pieces and placed in an ASE cell (22 mL). Extractions were performed by four cycles at 100°C and 2 MPa, 5 min of heating, an 8 min static extraction, a flush volume of 70% and a N₂ purge time of 60 sec. The extracts were concentrated to 2–3 mL and cleaned on a multilayer-silica column consisting of 2 g copper powder, 2 g anhydrous Na₂SO₄, 2 g activated silica gel and 6 g acidified silica gel (44%, W/W) from top to bottom. The extracts were eluted with 100 mL hexane/DCM (1:1, V/V), and the extracts were concentrated to near dryness and added with ¹³C labeled injection internal standard (Cao et al., 2018b; Fu et al., 2018).

OCPs and PCBs were analyzed using a gas chromatograph (Tarce 1310, Thermo Fisher Scientific, USA) coupled to a high-resolution mass spectrometer (DFS, Thermo Fisher Scientific, USA). The oven temperature program was as follows: 80°C for 1 min, increased at 30°C/min to 190°C, followed by 2.5°C/min to 230°C, then increased at 20°C/min to 260°C and hold for 12 min, finally followed by 20°C/min to 320°C and hold for 23 min. Helium was used as the carrier gas, and 1 μ L of extracts were injected using an auto sampler in splitless mode. Eighteen sorts of PCB congeners and fifteen sorts of OCPs of the filter samples were quantified (Fu et al., 2018).

1.4. Quality assurance

The recoveries of the ¹³C labeled internal standards were 40%–110% for PCBs and OCPs. The method limits of quantitation (MLOQs) for PCBs and OCPs were 0.00097–0.084 and 0.00080–0.097 pg/m³, respectively. The procedural blanks samples were

also performed using the same pretreatment and instrumental methods to check the blank interference for every 8 samples. All the concentration of the analyzed pollutants in procedural blanks were below 10% of that in the filter samples.

1.5. Health risk assessment and statistical analysis

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin, whose toxic equivalent factor (TEF) defined as 1, was used for assessing the TEF of 12 dioxin-like PCBs. The TEF of 12 dioxin-like PCBs were shown in Appendix A Table S5 and the toxic equivalent quantity (TEQ) of the PCBs were calculated by the concentration and TEF following Eq. (1) (Cao et al., 2018b; Zhu et al., 2017). As for HCHs and DDTs, the risk were evaluated via lifetime average daily dose (LADD) and incremental lifetime cancer risk (ILCR) following Eqs. (3) and (4), while slope factor (SF) defined as carcinogenic slope coefficient via inhalation exposure.

The principal component analysis (PCA) was performed using SPSS 17.0. No rotation technique was applied to PCA.

$$\Sigma\text{TEQ} = \Sigma C_i \times \text{TEF}_i \quad (1)$$

$$\text{ADD} = \frac{\Sigma\text{TEQ} \times \text{InhR} \times \text{ED}}{\text{BW}_{\text{adult}}} \quad (2)$$

$$\text{LADD} = \frac{C \times \text{EF}}{\text{AT}} \times \left(\frac{\text{InhR}_{\text{child}} \times \text{ED}_{\text{child}}}{\text{BW}_{\text{child}}} + \frac{\text{InhR}_{\text{adult}} \times \text{ED}_{\text{adult}}}{\text{BW}_{\text{adult}}} \right) \quad (3)$$

$$\text{ILCR} = \text{LADD} \times \text{SF} \quad (4)$$

where ΣTEQ , C_i , TEF_i , ADD, LADD, and C are total toxic equivalent quantities, concentration of individual PCB, toxic equivalent factor of individual PCB, average daily dose, lifetime average daily dose and average concentration of individual OCP, respectively; InhR and BW represents the inhalation rate and average body weight, respectively; EF, ED and AT represents the exposure frequency, exposure duration and average time, respectively. The values of the specific parameters were shown in Appendix A Table S2. When ILCR was lower than 10^{-6} , the substance was considered to have no cancer risk. When ILCR value was in the range of 10^{-6} – 10^{-4} , it was considered to have potential cancer risk. When ILCR was higher than 10^{-6} , it was considered to have certain cancer risk.

1.6. Water soluble ions and organic carbon (OC)/elemental carbon (EC) analysis

A punched-out section (47 mm diameter) of filters was submerged in a small beaker with 10 mL ultrapure water, sealed and sonicated for 15 min. The extract was filtered with a 0.45 μm Teflon filter to remove any insoluble species. The extracts were analyzed via an ion chromatograph (940 Professional IC, Metrohm, Switzerland) equipped with a Metrosep A supp16-250 separation column and a Metrosep C6 analytical column for water soluble inorganic ions (Li^+ , Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+ , Cl^- , K^+ , SO_4^{2-} , NO_3^- , PO_4^{3-}).

OC and EC fractions of the filters were analyzed by a thermal/optical carbon analyzer (DRI Model 2015, Atmoslytic Inc., Canada) according to the IMPROVE protocol. Four OC fractions (OC1, OC2, OC3, and OC4 acquired at 140, 280, 480, and 580°C in helium (He) atmosphere) and three EC fractions (EC1, EC2, and EC3 evolved at 580, 740, and 840°C in 98 vol.% He/2 vol.% O_2 atmosphere) were produced. The 635 nm wavelength was for pyrolysis adjustment.

2. Results and discussion

2.1. Concentrations of PCBs and OCPs

2.1.1. PCBs

Five classes of PCB congeners were investigated in our studies, they are tri-CBs (PCB28), tetra-CBs (PCB52, 77 and 81), penta-CBs

(PCB101, 105, 114, 118, 123 and 126), hexa-CBs (PCB-138, 153, 156, 157, 167 and 169), hepta-CBs (PCB-180 and 189), respectively. The seven standard individual congeners (PCB 28, 52, 101, 138, 153 and 180) selected by EPA to represent a wide range of chlorination were also included. Concentrations of $\Sigma_{18}\text{PCBs}$ in $\text{PM}_{2.5}$ were in the range of 1.74–24.37 pg/m^3 with an average of 6.46 pg/m^3 for diurnal time and from 1.77–100.49 pg/m^3 with a mean value of 24.34 pg/m^3 for nocturnal time. The highest concentration of $\Sigma_{18}\text{PCBs}$ appeared in nocturnal time on 16th November. The differences between diurnal time and nocturnal may be attributed to their different boundary layer height and emission source. The boundary layer height decreased and the pollutant concentration increased (Cao et al., 2018b). Meanwhile, there existed the phenomenon of incineration waste furtively at night in the local area. Moreover, according to the China Statistic Yearbook (2018), the citizens in Hebei province produced 7.0 million tons of household waste in 2017, more than one third of which were disposed via incineration. As shown in Fig. 1a, the concentrations of ΣPCBs at nocturnal time were 3–4 folds higher than that at diurnal time, it is mainly because the waste incineration was performed furtively by the local residents at night and released hazardous substances, such as PCDDs or PCBs. The ratio of pollutant concentration and EC (elemental carbon) concentration may indicate the primary source of pollutants (Gao et al., 2012). If the values had statistically significant differences for diurnal time and nocturnal time, the primary source may be the dominant reason causing the concentration discrepancy. Otherwise, the boundary layer height may be the main reason. The values were 1.02×10^{-6} and 2.64×10^{-6} for diurnal time and nocturnal time (significant difference, $p < 0.01$), respectively, further demonstrating that the concentration increase of ΣPCBs was attributed to the primary emission. It is known that waste incineration is the main source of chloride (Zacco et al., 2014), while there is a positive correlation between chloride and ΣPCBs ($r = 0.6$) in these samples. As shown in Fig. 1a, the ΣPCBs were much higher at night from 11th to 16th November and the maximum is up to 100.49 pg/m^3 , which exceeded more than 10 times of the average. Moreover, the chloride concentrations of these nights were equally in a high level (maximum is 12.20 $\mu\text{g}/\text{m}^3$), which indicated that the behavior of waste incineration occurred nearby during this period and released amounts of PCBs and other chlorides. The concentrations of ΣPCBs in other days were in a moderate level and may mainly come from industrial activities.

The chlorine number distribution of PCBs in different pollution levels was shown in Fig. 2. The concentrations of $\Sigma_{18}\text{PCBs}$ were 8.45, 9.98 and 23.03 pg/m^3 for clean days ($\text{PM}_{2.5} < 75 \mu\text{g}/\text{m}^3$), light-polluted days ($75 \mu\text{g}/\text{m}^3 < \text{PM}_{2.5} < 150 \mu\text{g}/\text{m}^3$) and heavy-polluted days ($\text{PM}_{2.5} > 150 \mu\text{g}/\text{m}^3$), respectively. The incremental concentrations of PCBs accompanied with $\text{PM}_{2.5}$ concentration indicated that the PCBs may be affected by the local emission source. As shown in Fig. 2, for the light polluted days and heavy polluted days, penta-CBs accounted for a higher proportion, followed by tri-CB, tetra-CB and hexa-CB, and hepta-CB. While for the clean days, hexa-CBs took for a higher proportion, followed by tri-CB, penta-CB, tetra-CB and hepta-CB.

The detection ratios of all the congeners were more than 90% in $\text{PM}_{2.5}$ in both diurnal time and nocturnal time. Individual congeners PCB 28, 77, 101, 118 were the main congeners among the PCBs with the concentration of 0.96, 0.61, 0.69, and 0.40 pg/m^3 for diurnal time and 5.80, 1.97, 1.52 and 1.62 pg/m^3 for nocturnal time, respectively. The higher concentration may be due to their persistence in the environment, which was consistent with other studies (Chavhan et al., 2012).

2.1.2. OCPs

OCPs in the atmosphere usually came from the usage of pesticides in agriculture and soil-air or water-air exchange from farmland soil or industrial wastewater. HCHs (α -HCH, β -HCH and γ -HCH), DDTs (o,p' -DDE, o,p' -DDD, o,p' -DDT, p,p' -DDE, p,p' -DDD and p,p' -DDT) and HCB are the three dominant groups of OCPs in $\text{PM}_{2.5}$. Moreover, the three OCPs have been detected in sorts of environmental medium (soil, water and sediment).

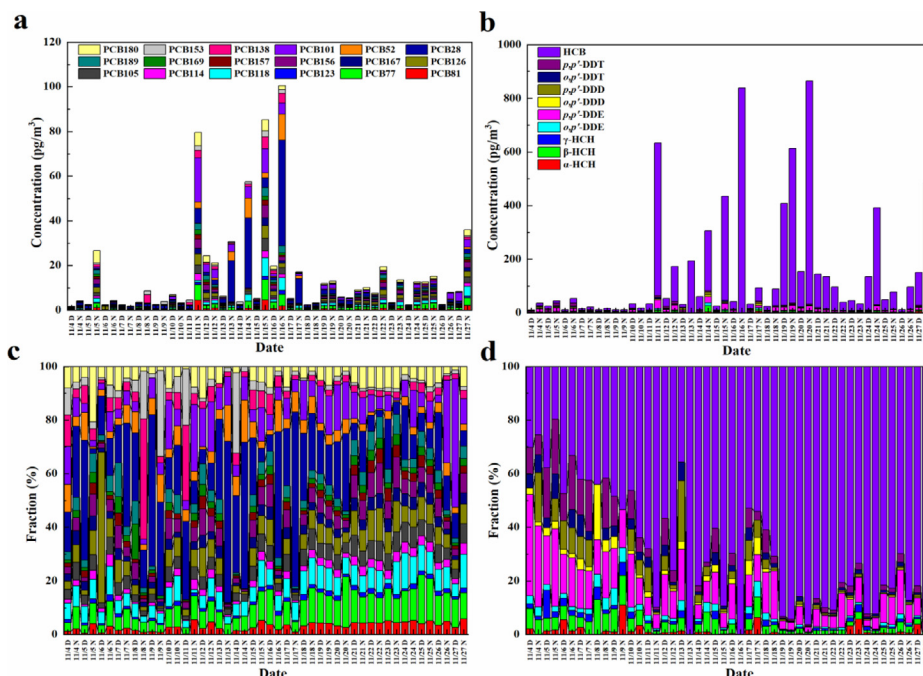


Fig. 1 – Concentrations of (a) polychlorinated biphenyls (PCBs) and (b) organochlorine pesticides (OCPs) in PM_{2.5} and congener profiles of (c) PCBs and (d) OCPs. DDT: dichlorodiphenyltrichloroethane; DDE: dichlorodiphenyldichloroethene; DDD: dichlorodiphenyldichloroethane; HCH: hexachlorobenzene; D: day; N: night.

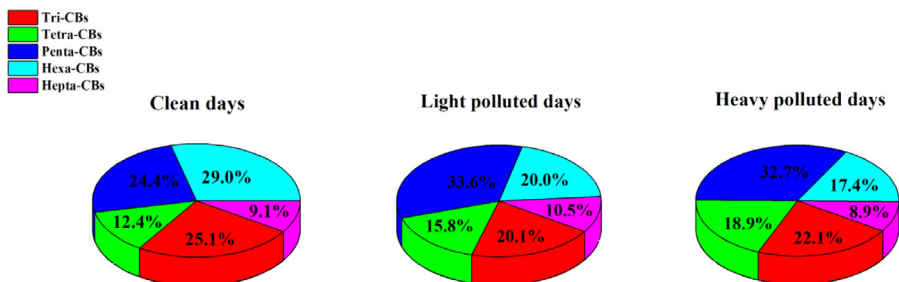


Fig. 2 – Mass fractions of different chlorine number of PCBs in different pollution levels.

The concentrations of ΣOCPs ranged from 11.67 to 865.60 pg/m³ with an average of 137.37 pg/m³. Hexachlorobenzene (HCB) was the dominant contributor to OCPs with an average concentration of 116.17 pg/m³. Hexachlorocyclohexane (ΣHCHs) and dichlorodiphenyltrichloroethane (ΣDDTs) were the other two main classes in OCPs with the average concentrations of 4.33 and 15.89 pg/m³, respectively. As shown in Fig. 1d, the HCB accounted for an extremely higher proportion (84%). It is known that HCB had complex sources and it is mainly released via being used as the intermediates of pentachlorophenol and sodium pentachlorophenol or incineration of the chlorinated waste (Dong et al., 2019). The higher proportion may be attributed to the waste incineration in the area. Among the other OCPs, the HCHs and DDTs occupied relatively higher proportion (3.2% and 11.6%) compared with that of Mirex, Σchlordan and Σnonachlor (lower than 0.5%). Appendix A Fig. S1 showed the relative concentrations of the HCHs and DDTs congeners in different pollution levels, while β-HCH and p,p'-DDE presented extremely higher concentrations than other congeners, indicating that these two congeners were main degradation products of HCHs and DDTs, respectively.

With regards to OCPs, the 2 sorts of OCPs (HCHs, DDTs) did not present obvious diurnal-nocturnal and daily variation characteristics. As shown in Fig. 1b, the concentrations of ΣHCHs and

ΣDDTs were in a moderate level and did not change significantly during sampling period (4.33 ± 4.30 pg/m³ for HCHs and 15.88 ± 12.47 pg/m³ for DDTs, respectively). Moreover, the concentrations of DDTs and HCHs at nocturnal time were higher than that at diurnal time, it could be caused by the decreasing of chlorinated organic compounds during the decreasing of boundary layer height (Cao et al., 2018b). While in the Fig. 1b, the concentration of HCB at the beginning of the sampling was in a relatively low level and had a significant ascending after 11th November (maximum is up to 865.20 pg/m³) and it was mainly because the waste incineration occurred, for the concentration of Σ₁₈PCBs during that period also increased and had a similar rising trend as HCB. Furthermore, the higher concentration of HCB after 19th November may be related to other local primary emissions, such as coal combustion and some industrial activities. Meanwhile, the concentration of HCB at nocturnal time was much higher than that at diurnal time, indicating that waste incineration may play a crucial role of forming chlorinated organic compounds.

2.2. Comparative analysis with other areas

The concentrations of PCBs and OCPs in Wangdu are listed with previous studies for comparison in Table 1. Compared with other areas in China, ΣPCBs concentrations in Wangdu were higher than that in Shanghai (Die et al., 2015), Beijing (Zhu et al., 2017)

Table 1 – Comparison of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) concentrations in atmospheric particles from areas worldwide.

Sampling sites	Sampling time	Particle size	Σ PCBs (pg/m ³)	Σ OCPs (pg/m ³)	References
Lijiang, China	June 2009 to July 2013	PM _{2.5}	Σ_6 M-PCBs: 0.3-10.9	Σ_6 DDT: 0.3-128.4, Σ_3 HCH: 0.1-50, HCB: ND-94.0	Gong et al., 2018
Shanghai, China	May 2013 and October 2013	PM _{2.5}	Σ_{12} DL-PCBs: 0.37-7.61	NA	Die et al., 2015
Beijing, China	October 2013 to June 2014	PM _{2.5}	Σ_{19} PCBs: 2.0-36.3	NA	Zhu et al., 2017
Taiyuan, China	January 2006	PM _{2.5}	NA	Σ_4 DDT: 6.5-1500, Σ_4 HCH: 5.2-870, HCB:2.4-210	Fu et al., 2009
Jinan, China	July 2009 to June 2010	PM _{2.5}	NA	Σ_3 DDT: 5.3±2.43, Σ_4 HCH: 14.7±8.2	Xu et al., 2011
East China Sea, China	March 2015 to May 2015	PM _{2.5}	Σ_{24} PCBs: 17.0-43.0	NA	Wu et al., 2017
East China Sea, China	October 2011 to August 2012	PM _{2.5}	NA	Σ_4 DDT: 5.71 ± 3.91, Σ_2 HCH: ND-22.56	Ji et al., 2015
Kanpur, India	April 2013 to May 2013	PM _{2.5}	Σ_{18} PCBs: 254-432	NA	Goel et al., 2016
Gwangju, South Korea	October 2016 to April 2017	PM _{2.5}	Σ_6 M-PCBs: 1.40-8.20	Σ_3 DDT: ND-59.58, Σ_9 OCPs: 363.56-1172.22	Kim et al., 2019
Hochiminh, Vietnam	July 2016 to February 2017	PM _{2.5}	Σ_{12} DL-PCBs: 0.35-1.66	NA	Trinh et al., 2018
Yokohama, Japan	March 2002-February 2003	PM _{2.5}	Σ_{12} DL-PCBs: 0.42-2.2	NA	Kim et al., 2005
King George Island, West Antarctica	2011-2014	PM _{2.5}	NA	Σ_6 DDTs: 0.012-8.13, Σ_4 HCH: ND-9.26, HCB: 3.33-21.2	Wang et al., 2018
Istanbul, Turkey	February 2015	PM _{2.5}	Σ_{84} PCBs: 8.39-49.34	Σ_3 DDT: 2.54-35.62, Σ_4 HCH: 0.55-30.64	Kuzu, 2016
Brno, Czech Republic	October 2009 to October 2010	0.49-3.0 μ m	Σ_{12} DL-PCBs: ND-1.85	NA	Degrendele et al., 2014
Bizerte, Tunisia	March 2015 to January 2016	PM _{2.5}	Σ_{20} PCBs: 0.35-10.97	Σ_6 DDT: 0.07-2.88, Σ_4 HCH: ND-0.75, HCB: 0.01-2.27	Barhoumi et al., 2018
Zagreb, Croatia	2000-2003	PM _{2.5}	Σ_6 PCBs: 0.87-70.6	Σ_3 DDT: 4.35-78.10, Σ_4 HCH: 6.86-60.6, HCB: 0.96-22.8	Dvorščak et al., 2015
Baoding, China	4 November 2017 to 27 November 2017	PM _{2.5}	Σ_{18} PCBs: 1.74-100.49	Σ_6 DDT: 2.81-53.42, Σ_3 HCH: 0.66-25.51, Σ HCB:3.32-832.36	This study

NA: not available; ND: not detected; Σ_{12} DL-PCBs: Σ_{12} doxin-like polychlorinated biphenyls; Σ_6 M-PCBs: Σ_6 indicator polychlorinated biphenyls.

and East China sea (Wu et al., 2017) and even higher than that in southwest of China (Gong et al., 2018) and some high altitude regions (Zhang et al., 2018). When compared with other countries in Asia, the Σ PCBs concentrations were higher than that in South Korea (Kim et al., 2019), Japan (Kim and Masunaga, 2005) and Vietnam (Trinh et al., 2018), but were extremely lower than that in India (Goel et al., 2016). In comparison with other countries in the world, the concentrations were much higher than that in Tunisia (Barhoumi et al., 2018) and Czech Republic (Degrendele et al., 2014), while were comparable with that in Turkey (Kuzu, 2016) and Croatia (Dvorščak et al., 2015).

With regards to OCPs, compared with other areas in China, the concentrations were similar with the levels in Jinan (Xu et al., 2011), Lijiang (southwest city) (Gong et al., 2018) and East China sea (Ji et al., 2015), while were higher than that in some high altitude regions (Zhang et al., 2018). Some agricultural cities had higher concentrations compared with Baoding, such as Taiyuan (Fu et al., 2009). In comparison with other countries, the Σ OCPs concentrations were lower than that in South Korea (Kim et al., 2019) and higher than that in Tunisia (Barhoumi et al., 2018). Moreover, the concentrations were comparable with that in Turkey (Kuzu, 2016) and Croatia (Dvorščak et al., 2015).

In summary, the comparison demonstrated that OCPs and PCBs pollution levels in atmospheric particle were in a medium level.

2.3. Sources identification of PCBs and OCPs

In this work, we first use characteristic ratios method to estimate the sources, then use principal component analysis (PCA), a statistical model for multivariate data, to explore possible sources of the PCBs and OCPs. Eighteen sorts PCB congeners and fifteen sorts of OCPs were analyzed in software SPSS 17.0 and factor loadings were higher than 0.5, indicating they can match the possible source categories. The higher loading indicated the specific variable contributed more to the factor and expressed the degree of correlation with the principal component.

The results of characteristic ratios method of PCBs were shown in Fig. 3a, the ratio of (PCB126 + PCB169) / (PCB126 + PCB169 + PCB77) can be used to estimate the PCBs sources roughly. When the ratio was approximately 50%, the source can be defined as solid waste incineration, while the ratio approached 1%, the use of commercial product may be the primary source (Kishida et al., 2010). Moreover, some reports

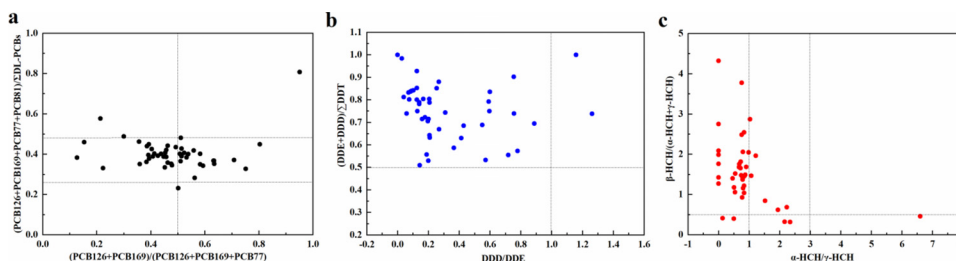


Fig. 3 – Scatter plots of (a) PCBs, (b) DDTs, and (c) HCHs in $PM_{2.5}$ samples in characteristic ratio method.

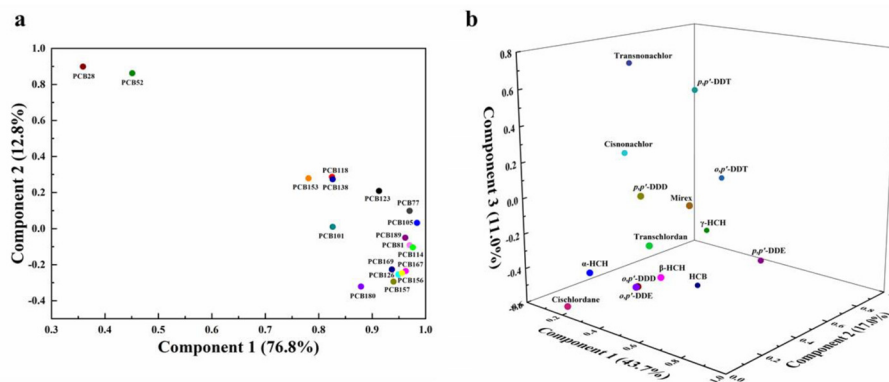


Fig. 4 – Principal components analysis (PCA) loading plots of (a) PCBs and (b) OCPs.

(Sakai et al., 1996; Takasuga, 1994) found that non-ortho DL-PCB (PCB77, PCB81, PCB126 and PCB169) accounted for 26%–48% of total DL-PCB in the smoke particle from solid waste combustion. As shown in the Fig. 3a, 80% of the samples were in the range of 40%–60% (X -axis) and in the range of 26%–48% (Y -axis), indicating that wasting incineration was the predominant factor.

Loading plots of all congeners in PCA were shown in Fig. 4a, the first principal component (PC1) accounted for 76.8% of the variability, while the second principal component (PC2) took for 12.7%. PC1 was highly loaded by PCB81 (0.970), PCB77 (0.970), PCB123 (0.913), PCB118 (0.926), PCB114 (0.976), PCB105 (0.984), PCB126 (0.949), PCB167 (0.963), PCB156 (0.956), PCB157 (0.940), PCB169 (0.937), PCB189 (0.962), while be moderately contributed by PCB118 (0.825), PCB101 (0.826), PCB138 (0.826), PCB153 (0.781), PCB180 (0.879). The characteristic product of incineration (PCB81, PCB77, PCB126, PCB169) (Sakai et al., 1996) showed high loading, so PC1 can be defined as waste incineration combining the results of characteristic ratios method. Moreover, PC2 showed higher loading for the congeners of PCB28 (0.899), PCB52 (0.862) and moderate loading for PCB138 (0.273), PCB153 (0.273). Appendix A Table S3 showed the mass fraction of the congeners in the commercial products Kane chlor (KC) and Aroclor series products, which closely matched the chlorinated PCB congeners (a mixture of Aroclor 1232, 1248 or KC 400) (Kim et al., 2004). Considering the industry distribution around the sampling site, it was inferred that the PC2 may be contributed by some industrial activities such as power plant or factories producing chlorinated materials or intermediates.

For the OCPs in the samples, characteristic ratios method was firstly used to evaluate the sources of HCHs and DDTs. It is known that HCHs exist in two forms, one is industrial HCHs consisting of α -HCH (6%–70%), β -HCH (5%–12%), γ -HCH (10%–12%), the other is Lindane consisting of 99% γ -HCH (Dvoršćak et al., 2015), the ratio of α -HCH/ γ -HCH can speculate the sources of HCHs as shown in Appendix A Table S4. Besides, the ratio of DDD/DDE indicates whether the DDTs degraded in an aerobic

or anaerobic environment shown in Appendix A Table S4. Moreover, the ratio of β -HCH/(α -HCH + γ -HCH) and (DDE+DDD)/ Σ DDT can speculate whether the HCHs or DDTs were degraded or input recently (Fu et al., 2018; Qadeer et al., 2019). When the value was more than 0.5, it suggested the HCHs came from historical degradation, but less than 0.5 implied that the region had new pollution input. As shown in Fig. 3c, the samples were in the range of (α -HCH/ γ -HCH) less than “1” and “ β -HCH/ α -HCH+ γ -HCH” more than “0.5”, the source of HCHs can be inferred as Lindane input and HCHs came from historical degradation. Moreover, as shown in Fig. 3b, the samples were in the area of “(DDD/DDE) less than “1” and “(DDE+DDD)/ Σ DDT” more than “0.5”, indicating that the DDTs degraded in an aerobic environment and also rooted in historical pollution.

Three factors accounted for 71.8% of the total in the PCA analysis. As shown in Fig. 4b, the first factor accounted for 43.7% of the total with the high loading on α -HCH (0.613), β -HCH (0.882), o,p' -DDE (0.898), p,p' -DDE (0.794), o,p' -DDD (0.892), p,p' -DDD (0.751). It was identified as the usage of industrial HCHs and DDTs. The second principal component (PC2) accounted for 17.1% of the variability, while the third principal component (PC3) took for 11.0%, which are inferred as the usage of Lindane or HCB and chlordane or nonachlor, respectively. The results implied that the compounds show some similar physicochemical properties, such as volatility, low vapor pressure, and persistence in environment (Dong et al., 2019). Their far-ranging usage for the control of pests in various crops has been identified as a new source of OCPs pollution in China.

2.4. Risk assessment of PCBs and OCPs

Considering the toxicity of PCBs and OCPs, it is important to evaluate the potential health risk on humans (Fu et al., 2018). PCBs can be absorbed easily in the stomach, lung or skin and accumulated in bodies (Qadeer et al., 2019). The PCBs accumulated in humans mainly come from diet, but breathing exposure

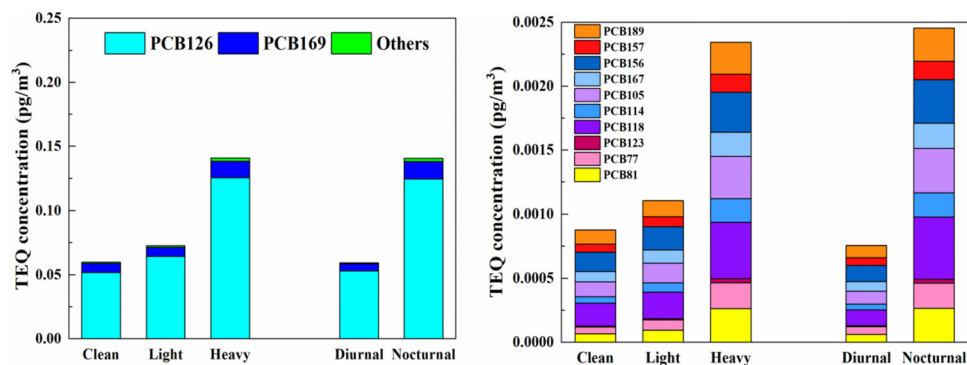


Fig. 5 – Toxic equivalent quantities (TEQs) of different pollution levels and time.

Table 2 – Average concentrations, lifetime average daily dose (LADD), slope factor (SF) and incremental lifetime cancer risk (ILCR) of the seven OCPs.

	Concentration (pg/m ³)	LADD (mg/(kg·day))	SF ((kg·day)/mg)	ILCR
α-HCH	0.90	2.70×10^{-12}	1.8	4.86×10^{-12}
β-HCH	2.65	7.97×10^{-12}	0.53	4.22×10^{-12}
γ-HCH	0.85	2.56×10^{-12}	0.53	1.36×10^{-12}
<i>o,p'</i> -DDT	1.26	3.80×10^{-12}	0.097	3.69×10^{-12}
<i>p,p'</i> -DDT	2.44	7.35×10^{-12}	0.097	7.13×10^{-12}
HCB	116.17	3.50×10^{-12}	0.46	1.61×10^{-12}
Chlordanes	0.64	1.94×10^{-12}	0.1	1.94×10^{-12}

HCB: hexachlorobenzene

could not be ignored (Die et al., 2015). The concentrations of ΣDL-PCBs ranged from 0.53 to 54.94 pg/m³. The toxic equivalent factors (TEFs) for PCBs normalized to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin activity are listed in Appendix A Table S5 and corresponding exposure quantity based on the concentrations and TEFs of DL-PCBs was calculated as Eq. (1) assuming the extreme condition (11 hr outdoors) and shown in Appendix A Fig. S2. As shown in Fig. 5, the TEQ concentrations of heavy polluted days are 2.4- and 1.9-fold higher than that of light polluted days and clean days, respectively. Compared with the other regions, the TEQ concentration in Wangdu (4–644 fg TEQ/m³) was 1–2 orders of magnitude higher than that in Taiwan (2–5 fg TEQ/m³) (Chi et al., 2008), Japan (2–15 fg TEQ/m³) (Kim and Masunaga, 2005) and South Korea (8–15 fg TEQ/m³) (Kim et al., 2011). Moreover, the nocturnal TEQ concentrations are 2.4-fold higher than the diurnal TEQ concentrations. When exposed in different pathways, the same individual may increase its health risk (Gallistl et al., 2017; Omar et al., 2019).

The lifetime average daily dose (LADD) and incremental lifetime cancer risk (ILCR) are used to evaluate the potential health risk of OCPs on humans. As shown in Table 2, LADD is in a relatively lower level and corresponding ILCR showed that it is unlikely to have any detrimental health effects. LADD and ILCR of *p,p'*-DDT, *o,p'*-DDT, α-HCH, β-HCH, γ-HCH, HCB and chlordanes indicated that their health risk can be ignorable. However, it still had some detrimental effects to humans via other exposure pathways, such as ingestion and dermal contact, which increased the risk levels of HCHs and DDTs. The cancer risk of OCPs in particles of Northern China was in a moderate level compared with that in Jinan (Xu et al., 2011) and Tunisia (Barhoumi et al., 2018). Although the health risk of PCBs and OCPs in atmospheric particle were not severe, the organochlorine compounds may enter other environmental mediums via air-soil or air-water exchange, which could be accumulated in the plant or seafood and create health risk to human bodies simultaneously.

3. Conclusions

The PM_{2.5}-bound PCBs and OCPs in the rural area of North China were analyzed to explore their concentration characteristics, sources, and health risk. The concentration of the chlorinated compounds in Wangdu was comparable with other areas. Among the eighteen PCBs, tri-PCBs and penta-PCBs are the primary congeners of PCBs, while the HCB was the dominant pesticide of the fifteen OCPs. The PCA analysis indicated that the sources of PCBs were due to waste incineration and industrial activities. The OCPs such as DDTs, HCHs and chlordanes were mainly from the use of pesticides. The exposure quantity of PCBs was in a medium level and may have a potential risk to humans. Moreover, the ILCR values of *p,p'*-DDT, *o,p'*-DDT, α-HCH, β-HCH, γ-HCH, chlordanes and HCB indicated that the potential effect of the seven OCPs could be ignorable but other exposure pathways should be noticed. This work provides basic data for pollution control and risk assessment of PCBs and OCPs in the atmosphere in Northern China.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.03.051.

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