Spatiotemporal variations of chlorinated paraffins in PM$_{2.5}$ from Chinese cities: Implication of the shifting and upgrading of its industries[☆]

Di Liu [a, 1], Qilu Li [b, a, 1], Zhineng Cheng [a], Kechang Li [a], Jun Li [a], Gan Zhang [a, *]

[a] State Key Laboratory of Organic Geochemistry and Guangdong Provincial Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] School of Environment, Henan Normal University, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Xinxiang, Henan 453007, China

ARTICLE INFO

ABSTRACT

To highlight the levels and distributions and to assess the risk of human exposure of chlorinated paraffins (CPs) in PM$_{2.5}$ in China, the concentrations and homologue patterns of short−chain chlorinated paraffins (SCCPs) and medium−chain chlorinated paraffins (MCCPs) in PM$_{2.5}$ from 10 cities in China were studied in 2013 and 2014. The mean concentrations of ΣSCCPs and ΣMCCPs were 19.9 ± 41.1 ng m^{-3} and 15.6 ± 18.6 ng m^{-3}, respectively. Unexpectedly, the highest pollution levels occurred in two central cities (Xinxiang and Taiyuan) rather than in well−known eastern megacities such as Beijing, Nanjing, Shanghai, and Guangzhou. By comparing with earlier research, it has indicated the trend of CPs industry shifting from large eastern cities to small and medium-sized cities in central China to some extent. In addition, the composition pattern of SCCPs demonstrated an obviously differences from previous studies, with C$_{11}$ and Cl$_7$ predominating and accounting for 45.1% and 24.9%, respectively. Meanwhile, the ratio of MCCPs/ SCCPs in most cities was less than 1.00 except for Guangzhou (1.92), Shanghai (1.29), and Taiyuan (1.11). Combined with the results of correlation analysis and principal component analysis, the observed pollution characteristics of CPs in PM$_{2.5}$ had similar sources, which were more influenced by the ratio of MCCPs/SCCPs than by organic carbon, elemental carbon, temperature, population, and gross domestic product. Overall, the composition of CPs reflected the characteristics of local industrial production and consumption, and also implied efforts of Chinese enterprises to reduce the content of short carbon groups of CPs production. The CPs mainly deposited in head airways during the process of entering the human respiratory system. However, at the present levels, there was no significant carcinogenic effect for human health.

1. Introduction

Atmospheric particulate pollution has recently become a global problem, particularly fine particles with a median aerodynamic diameter <2.5 μm (PM$_{2.5}$), which not only affect the transportation and diffusion of organic pollutants but also one of the main factors that threatening human health (Pöschl, 2005; Brauer et al., 2012). The result of a previous study indicated that non−occupational human exposure to fine particulate matter (PM$_{2.5}$) is an important pathway for the inhalation uptake of pollutants (Chaney et al., 2017). Furthermore, PM$_{2.5}$ has been classified as carcinogenic by the International Agency for Research on Cancer (Hsu et al., 2017) and has been recognized as the cause of increased mortality and morbidity rates even at very low levels (Li et al., 2013; Lanzinger et al., 2015; Feng et al., 2016). In China, PM$_{2.5}$ pollution is becoming increasingly serious with the rapid development of urbanization and industrialization (Liu et al., 2016b; Zhang et al., 2017b). The rate caused by PM$_{2.5}$ pollution in 2015 accounted for 1.75‰, or approximately 2.62 million people and 31.14% of all deaths in China (Xie et al., 2018). In the past decade, relatively high PM$_{2.5}$ concentrations that severely exceeding the national ambient

air quality standards of China (Grade II: 75 μg m^{-3}) have been observed in 165 Chinese cities (Zhang and Cao, 2015), and many organic contaminants with relatively high toxicity have been detected in PM$_{2.5}$ including polycyclic aromatic hydrocarbons (Martellini et al., 2012), polychlorinated biphenyls (Xu et al., 2005), organochlorinated pesticides (Wang et al., 2008), halogenated flame retardants and chlorinated paraffins (CPs) (Liu et al., 2016a). Chinese citizens have experienced the potential hazards of PM$_{2.5}$ far in excess of those of coarse particles, because they can be deposited much more deeply in the lungs (Ohura et al., 2005).

Chlorinated paraffins (CPs), a large class of structurally complex organic pollutants containing 30−70% chlorine can be classified into three groups according to their carbon chain length: short chain CPs (SCCPs, C$_{10}$−C$_{13}$), medium chain CPs (MCCPs, C$_{14}$−C$_{17}$), and long chain CPs (LCCP, C$_{18}$−C$_{30}$) (Fiedler, 2010; Chaemfa et al., 2014). In particular, SCCPs have been listed as a new persistent organic pollutants (POPs) since 2017 from the Stockholm Convention (UNEP, 2017). CPs have attracted an increasing attention in the past two decades, as they were considered to be persistent in the environment, bio−accumulative, and have high toxicity and long−range transport potential (Geng et al., 2015; Tomy et al., 1999; Wang et al., 2012) because of their physico-chemical properties, such as high values of octanol/water partition coefficients and vapor pressures (Glüge et al., 2013). A variety of industrial applications such as polyvinyl chloride production, metal−working fluids, and flame retardants in plastics are heavily reliant on the use of CPs (Chen et al., 2018). Because almost all CPs are artificial synthesized and there are no known natural sources of CPs (Fiedler, 2010), these industries are considered as the primary sources of CPs contamination in different environmental media including the atmosphere (Li et al., 2012; Diefenbacher et al., 2015), sediment (Pan et al., 2018), soil (Xu et al., 2016; Bogdal et al., 2017), bio (Du et al., 2018; Casà et al., 2019), and human body (Thomas et al., 2006; Qiao et al., 2018). But information on the levels and fate of CPs in atmospheric fine particles are still limited (van Mourik et al., 2015).

European and North American countries have gradually reduced their production and consumption due to the high toxicity of SCCPs as early as the beginning of the century (Marvin et al., 2003; Barber et al., 2005). And then, China became the major global producer and consumer of CPs, and its production has exhibited sustained growth, reaching 1,000 thousand tons in 2013 (Glüge et al., 2016). The high concentrations of CPs were observed in the city's environment in most provinces of China (Cao et al., 2019; Chen et al., 2018; Harada et al., 2011; Zhan et al., 2017), including air that is closely linked with human life. As early as 2008, the atmospheric concentration of SCCPs was substantially higher in China than in other Asian countries, and the SCCPs pollution in each country was mainly from national sources (Li et al., 2012). Li et al. have reported that the concentrations of SCCPs in PM$_{2.5}$ of Jinan ranged from 9.80 to 105 ng m^{-3} (Li et al., 2019). However, there are relatively few studies on monitoring data of CPs in PM$_{2.5}$ and its risk of human exposure in China. Thus, it is necessary to study the levels and distributions of CPs in PM$_{2.5}$ in representative Chinese cities.

PM$_{2.5}$ samples from 10 China cities were collected by high volume active samplers simultaneously from October 2013 to August 2014. This is the first study of chlorinated paraffin in PM$_{2.5}$ in urban atmosphere on a large scale of China. SCCPs and MCCPs in all samples were extracted by dichloromethane (DCM) and measured by high resolution gas chromatography electron capture negative ionization low resolution mass spectrometry (HRGC-ECNI-LRMS). The purposes of this study were to (1) report the concentration levels and homologue profiles of CPs in PM$_{2.5}$ in China; (2) explore the probable factors influenced on spatial and temporal distribution; (3) assess the health risk of human exposure to CPs in PM$_{2.5}$.

2. Materials and methods

2.1. Sample collection

PM$_{2.5}$ samples were collected from 10 cities in China: Beijing (BJ), Chengdu (CD), Lanzhou (LZ), Wuhan (WH), Taiyuan (TY), Guiyang (GY), Xinxiang (XX), Guangzhou (GZ), Nanjing (NJ) and Shanghai (SH). These cities were classified into three categories by geographic location: Eastern (BJ, SH, NJ, and GZ), Central (TY, XX, and WH), and Western (LZ, CD, and GY). Four sampling periods were selected to represent the four seasons: autumn (October 22 to November 13, 2013), winter (December 30, 2013 to January 20, 2014), spring (March 30 to April 20, 2014), and summer (June 26 to August 24, 2014). Detailed sampling information is provided in Table S1. Four PM$_{2.5}$ samples were collected per season in each city and the total number of samples was 156. Among them, the samples collected in spring and summer in GY were lost in the mail.

The sampling sites were located on rooftops approximately 10−15 m above ground in densely inhabited districts of these cities, such as residences or schools. Each sample was collected for 24 h using high−volume sampler (Andersen Instruments, Inc., Smyrna, GA, USA; GMW Associates, San Carlos, CA, USA) operated at 300 L min^{-1}. Whatman® quartz microfiber filters (20.3 × 25.4 cm) were wrapped in clean aluminum foil and baked at 450 °C for 5 h before use, sealed in Teflon bags, and transported to the sampling sites. All of the samples were wrapped, sealed, and transported to the laboratory, and stored at −20 °C until further analysis. More detailed sampling information is available in the Supporting Information (SI).

2.2. Extraction and analysis

As a complex mixture, CPs challenge the analytical technique owing to thousands of isomers and unavailable commercial standards materials (Schinkel et al., 2018a; Schinkel et al., 2018b). The treatment procedures and instrumental analysis for CPs in the PM$_{2.5}$ samples can be found in the previous studies (Chaemfa et al., 2014; Li et al., 2012; Xu et al., 2016), which were based on the method described by Reth et al. (2005). Filters were Soxhlet extracted with 50 mL DCM for 24 h. Before extraction, 20 ng ^{13}C-trans-chlordane was spiked as recovery surrogate and 3 g activated copper sheet (1 × 1 cm) was added to remove sulfur element. Then the extract was solvent-exchanged to hexane by rotary evaporation (about 1 mL) and cleaned up by a multilayer silica-gel column. The column was comprising of 3 g 3% deactivated neutral alumina, 3 g 3% deactivated neutral silica gel, 2 g 50% (w/w) H$_2$SO$_4$ sulfuric acid − silica gel, and 1 g anhydrous Na$_2$SO$_4$ from bottom to top. The collected eluent was concentrated to approximately 25 μL under a gentle nitrogen stream. Prior to an instrumental analysis, 20 ng ^{13}C$_8$-mirex was added to the extracts as the internal standard.

Extracts containing SCCPs (C$_{10-13}$ with Cl$_{5-10}$) and MCCPs (C$_{14-17}$ with Cl$_{6-10}$) were analyzed by HRGC-ECNI-LRMS (Agilent 7890-5975C, Santa Clara, CA, USA). Capillary column was DB-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness) and carrier gas was Helium with a constant flow of 1.0 mL min^{-1}. The oven temperature program started at 120 °C for 1 min, and then raised with 15 °C min^{-1} to 290 °C and held for 15 min. Each 2 μL sample extract was injected in the splitless mode at 280 °C. Temperatures of mass selective detectors source and quadrupole were 200 and 150 °C, respectively. The highest and second abundant isotopes of the [M-Cl]$^{-}$ ions of SCCPs and MCCPs were recorded in the selected ion monitoring (SIM) mode (dwell time of 30 ms per ion).

2.3. Quality assurance/quality control

Solvent blanks and field blanks were used to assess possible contamination and instrument stability. The entire analytical process was strictly monitored to achieve high standards of quality control (QC) and quality assurance (QA). The method detection limit (MDL) was generally calculated as the mean blank values plus three times the standard deviation (SD) except when compounds were not found in the field blanks, it was calculated as three times the instrumental detection limit (IDL). In this study, the MDL values for SCCPs and MCCPs are 0.17 ng m^{-3} and 0.13 ng m^{-3}, respectively. The recoveries for ^{13}C$-$trans$-$chlordane ranged between 75.1% and 104.2% for all the samples, with an average of 83.9%. Solvent blank was not detected. Field blank levels were 1.18 $\pm$ 0.36 ng m^{-3} for SCCPs and 0.40 $\pm$ 0.15 ng m^{-3} for MCCPs. The Final results were corrected based on field blanks.

2.4. Respiratory deposition and health risks

Human exposure to pollutants mainly occurs through food intake, skin contact, dust ingestion, and inhalation. Particulate pollutants have the ability to get into respiratory system by breath exposure, an uncontrollable exposure route. PM$_{2.5}$ can even get into the lungs and alveoli with negative health impacts. CPs deposition fluxes of PM$_{2.5}$ in different human regions, including HA (head airways, including nose, mouth, pharynx, and larynx), TB (tracheobronchial region), and AR (alveolar region) were studied to assess the human exposure status based on ICRP model (Hinds, 1999). The equations of deposition flux (D) are as follows:

$$DF_{HA,i} = IF_i \times \left(\frac{1}{1 + \exp(6.84 + 1.183 lnD_{p,i})} + \frac{1}{1 + \exp(0.924 - 1.885 lnD_{p,i})} \right) \tag{1}$$

$$DF_{TB,i} = \frac{0.00352}{D_{p,i}} \times \left(\exp\left(-0.234 \left(lnD_{p,i} + 3.40 \right)^2 \right) + 63.9 \exp\left(-0.819 \left(lnD_{p,i} - 1.61 \right)^2 \right) \right) \tag{2}$$

$$DF_{AR,i} = \frac{0.0155}{D_{p,i}} \times \left(\exp\left(-0.416 \left(lnD_{p,i} + 2.84 \right)^2 \right) + 19.11 \exp\left(-0.482 \left(lnD_{p,i} - 1.362 \right)^2 \right) \right) \tag{3}$$

$$IF_i = 0.5 \times \left(1 + \exp\left(-0.06 \times D_{p,i} \right) \right) \tag{4}$$

$$D_j = \sum \left(DF_{j,i} \times C_i \right) \times V \tag{5}$$

where $DF_{j,i}$ is the deposition fraction, IF is the inhalable fraction, $D_{p,i}$ is the average particle size (2.5 μm), D_j is the deposition flux of different regions, and V (1.56 m^3 h^{-1}) is the average respiration rate at different activity levels (sitting, light exercise, and high exercise) (Hinds, 1999).

European Food Safety Authority used the margin of exposure (MOE) to assess the potential genotoxic and carcinogenic risk of chemicals as follows (Zhuo et al., 2019):

$$MOE = \frac{NOAEL}{EDI} \tag{6}$$

$$EDI = \frac{C \times IR \times T}{BW} \tag{7}$$

where NOAEL is the no-observed-adverse-effect-level, for SCCPs and MCCPs are 100 mg d^{-1} kg^{-1} and 23 mg d^{-1} kg^{-1}, respectively (Bureau, 2007a,b). EDI is Estimated daily intake, C is the concentrations of chemical, IR is the inhalation rate, T is the average time, BW is the body weight of person.

2.5. Data analysis

The data were mainly analyzed by two software programs, Statistica 10 (StatSoft, Tulsa, OK, USA) was used to run variance analysis and correlation analysis, and Origin 9.0 (Origin Lab., Northampton, MA, USA) for principal component analysis (PCA). Prior to PCA, the data matrix was standardized to eliminate the influence of different units and to give each determined variable an equal weighting.

3. Results and discussion

3.1. Spatiotemporal distribution of concentrations

The mean concentrations of ΣSCCP and ΣMCCP in PM$_{2.5}$ samples in 10 cities were 19.9 $\pm$ 41.1 ng m^{-3} (1.98$-$274 ng m^{-3}) and 15.6 $\pm$ 18.6 ng m^{-3} (1.27$-$312 ng m^{-3}), respectively (Table 1). The total highest annual average concentration was detected at XX with 68.7 ng m^{-3} (42.8 and 25.9 ng m^{-3} of SCCPs and MCCPs, respectively) and followed by TY (63.6 ng m^{-3}, with 28.8 ng m^{-3} and 34.8 ng m^{-3}), whereas the lowest concentrations (14.2 ng m^{-3}, with 8.23 ng m^{-3} and 6.02 ng m^{-3}) were observed in NJ (Fig. 1A and B). In addition, we found that MCCPs exhibited relatively weaker variation among the 10 cities than SCCPs (Fig. S1), likely because MCCPs could easily adsorbed to fine particulates with higher molecular weight and lower vapor pressure (Zhou et al., 2018). Most previous studies measured SCCPs in the atmosphere but fewer investigated SCCPs and MCCPs in PM$_{2.5}$. Only Huang et al. reported SCCPs and MCCPs concentrations in PM$_{2.5}$ from Beijing (Huang et al., 2017) and Li et al. reported SCCPs concentrations in PM$_{2.5}$ from Jinan (Li et al., 2019). From Table 1, it could be observed that the mean concentration of SCCPs (14.9 ng m^{-3}) in the previous report was relative lower than this study and the mean concentration of MCCPs (1.9 ng m^{-3}) was just about one-tenth of the present result in Beijing. While the concentration of SCCPs in Jinan (38.7 ng m^{-3}) was two times higher than the average concentrations in 10 cities of this study. On global scale, our results were generally higher than those in Japan (SCCPs: 0.28$-$14.2 ng m^{-3}),

Table 1
The SCCPs and MCCPs concentration in PM$_{2.5}$ in this study and in previous study (ng m^{-3}).

| Region	City	SCCPs					MCCPs					SCCP and MCCP				Total	ref
		Autumn	Winter	Spring	Summer	ΣSCCPs	Autumn	Winter	Spring	Summer	ΣMCCPs	Autumn	Winter	Spring	Summer		
Eastern	BJ	34.0 (15.2)	48.1 (18.1)	6.17 (2.84)	8.70 (0.40)	24.2 (210)	15.7 (12.9)	39.7 (18.7)	1.98 (0.92)	3.89 (0.87)	15.3 (18.6)	49.7 (27.9)	87.8 (36.7)	8.15 (3.74)	12.6 (1.19)	39.6 (39.2)	this study
	NJ	5.03 (4.04)	5.99 (2.72)	2.36 (0.43)	19.0 (29.9)	8.23 (15.6)	3.50 (2.85)	3.48 (2.06)	1.37 (0.07)	15.1 (25.3)	6.02 (13.2)	8.49 (6.89)	9.47 (4.80)	3.73 (0.49)	34.1 (55.3)	14.2 (28.7)	
	SH	5.25 (3.52)	20.1 (24.2)	3.46 (2.08)	2.86 (0.48)	8.00 (13.6)	8.56 (7.30)	30.9 (40.0)	3.89 (3.18)	3.76 (1.27)	12.0 (22.3)	13.8 (10.8)	51.0 (64.1)	7.35 (5.22)	6.62 (1.70)	20.0 (36.0)	
	GZ	11.5 (15.3)	12.6 (19.2)	23.3 (39.9)	3.47 (1.65)	12.7 (22.2)	20.3 (28.7)	15.3 (25.1)	35.4 (53.8)	6.73 (3.40)	19.4 (31.4)	31.8 (44.0)	27.9 (44.3)	58.7 (93.7)	10.2 (5.02)	32.1 (53.5)	
Central	TY	78.2 (131)	13.4 (5.18)	13.1 (16.3)	10.5 (3.48)	28.8 (65.9)	85.5 (151)	18.2 (9.53)	23.8 (39.6)	11.8 (4.57)	34.8 (76.5)	164 (282)	31.5 (14.3)	36.8 (55.9)	22.4 (7.89)	63.6 (142)	
	XX	85.2 (99.9)	73.5 (95.1)	14.7 (6.03)	8.41 (1.08)	42.8 (67.7)	50.6 (71.4)	51.3 (64.8)	5.47 (3.23)	2.49 (0.70)	25.9 (47.2)	136 (171)	125 (160)	20.2 (9.18)	10.9 (1.65)	68.7 (115)	
	WH	5.70 (1.93)	89.4 (124)	5.16 (2.24)	2.98 (0.46)	25.8 (67.0)	2.42 (0.83)	23.7 (32.0)	2.01 (0.90)	1.55 (0.26)	7.43 (17.3)	8.13 (2.70)	113 (134)	7.17 (3.03)	4.53 (0.68)	33.2 (76.6)	
Western	LZ	17.7 (7.16)	27.5 (17.2)	4.36 (0.92)	9.29 (2.01)	14.7 (12.4)	3.94 (1.57)	18.2 (15.3)	1.71 (0.64)	2.18 (0.42)	6.51 (9.84)	21.7 (8.71)	45.7 (32.3)	6.07 (1.54)	11.5 (2.42)	21.2 (21.7)	
	CD	12.5 (5.44)	25.8 (37.2)	3.82 (1.10)	8.50 (2.82)	11.8 (16.4)	15.6 (7.77)	26.4 (39.7)	2.92 (1.44)	2.60 (1.01)	10.9 (18.3)	28.1 (12.6)	52.2 (76.9)	6.75 (2.53)	11.1 (3.80)	22.7 (34.5)	
	GY	11.4 (10.7)	39.9 (50.1)	–	–	23.6 (33.6)	4.74 (6.20)	37.3 (47.6)	–	–	18.7 (32.8)	16.1 (16.9)	77.2 (97.8)	–	–	42.3 (66.3)	
10 cities		45.5 (104)	64.7 (81.6)	17.2 (18.6)	13.8 (18.6)	19.9 (41.1)	20.3 (53.2)	27.3 (32.9)	8.72 (22.8)	5.57 (8.90)	15.6 (18.6)	45.5 (104)	64.7 (81.6)	17.2 (36.8)	13.8 (18.6)	35.5 (72.5)	
	Beijing	–	–	–	–	14.9 (9.2–19.6)	–	–	–	–	1.7 (0.6–2.7)	–	–	–	–	–	Huang et al. (2017)
	Ji'nan	–	–	–	–	38.7 (9.80–105)	–	–	–	–	–	–	–	–	–	–	Li et al. (2019)
	Japan	–	–	–	–	2.26 (0.12–14.2)	–	–	–	–	–	–	–	–	–	–	Li et al. (2012)
	South Korea	–	–	–	–	2.06 (0.60–8.96)	–	–	–	–	–	–	–	–	–	–	Li et al. (2012)
	India	–	–	–	–	8.11 (nd-47.4)	–	–	–	–	4.83 (nd-38.2)	–	–	–	–	–	Chaemfa et al. (2014)
	UK	–	–	–	–	185–3430	–	–	–	–	811–14500	–	–	–	–	–	Barber et al. (2005)
	Norway	–	–	–	–	1.8–10.6	–	–	–	–	–	–	–	–	–	–	Borgen et al. (2002)

Note:
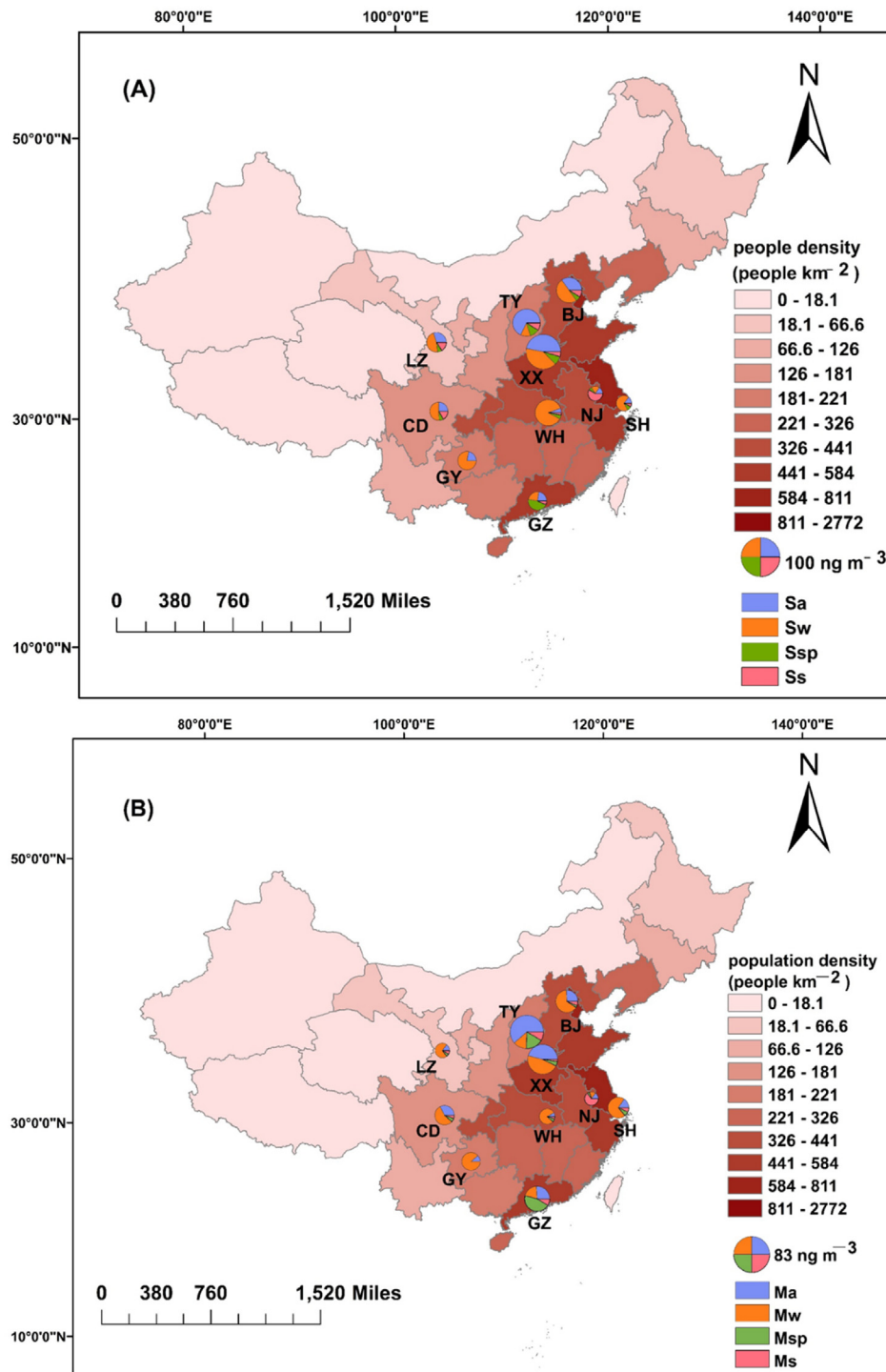
Fig. 1. The concentrations of SCCPs (A) and MCCPs (B) in 10 cities of China for 4 seasons. (autumn (a), winter(w), spring (sp), and summer (s)).

South Korea (SCCPs: 0.60–8.96 ng m^{-3}), India (SCCPs: 8.11 ng m^{-3}; MCCPs: 4.83 ng m^{-3}), UK (SCCPs: < 185–3430 pg m^{-3}; MCCPs: < 811–14500 pg m^{-3}), Norway/Bear Island (SCCPs: 1.8–10.6 ng m^{-3}) (Borgen et al., 2002; Barber et al., 2005; Li et al., 2012; Chaemfa et al., 2014).

For regional, central cities have the highest concentrations of CPs in PM$_{2.5}$ (54.9 ± 113 ng m^{-3}) with 32.2 and 22.6 ng m^{-3} of SCCP and MCCP, respectively. While the concentrations of CPs in eastern cities (26.8 ± 36.7 ng m^{-3}, with 13.5 and 13.3 ng m^{-3}) were the

same as that in western cities (25.7 ± 37.7 ng m^{-3}, with 15.2 and 10.5 ng m^{-3}) (Table 1). China's major production and consumer areas are located in Shandong, Jiangsu and Guangdong provinces on the eastern coast, and Henan province in the central region. Jiang et al. employed a gridded emissions inventory to estimate the atmospheric emissions of SCCP from 2008 to 2012 in China (Jiang et al., 2017), which indicated that Shandong, Jiangsu, Zhejiang, Henan, and Guangdong province were the primary emission producers. Similarly, in another study, the emission in Jiangsu province

(562.6 tons) was far greater than in other provinces in 2010−2014, followed by Zhejiang, Shandong, and Guangdong province, and Henan province came in ninth (Zhang et al., 2017a). However, the monitored concentrations in this study did not correspond to the previous research. The level of CPs in central cities (XX in Henan province and TY in Shanxi province) were extremely high, while the lowest value occurred in eastern cities (NJ in Jiangsu province). This contrast may need to consider the following reason. First, the disparate emissions rates from different applications of CPs in commercial production alone create variation in pollution measurements. The results from Jiang et al. indicated that CPs production accounted for 40.4% of the total emissions, which was the second highest contributor (Glüge et al., 2016). Meanwhile, the three major industries that consume CPs (metal cutting fluids, plasticizers, and flame retardants) were accounted for 47.4%, 9.1%, and 1.9%, respectively. Zhang et al. also considered metal working fluids as the largest producer of total atmospheric SCCPs emission in China (Zhang et al., 2017a). Moreover, the present results may reflect that CP−related factories are not allowed in great eastern metropolises but are unrestricted in medium and small cities or suburbs of central China to some extent under current Chinese environmental protection policies. Therefore, more attention should be given to toxic pollutant exposures in central cities with large population in the future.

3.2. Spatiotemporal variation of compositions

The percent relative abundances of SCCPs and MCCPs homologues of individual carbon chain groups and chlorine number groups were displayed in Fig. 2. The C_{11} and C_{14} homologues were the predominant carbon chain group in all of the sites, accounting for 45.1% and 57.5% of total SCCPs and MCCPs, respectively (Table S4). Based on the number of chlorine atoms, the SCCPs with

Cl_7 and Cl_8 groups were the most abundant congener groups, accounting for 24.9% and 20.3%, respectively (Table S5). While the MCCPs profiles were dominated by Cl_7 and Cl_6 groups, accounting for 41.3% and 33.4% of the total composition, respectively (Table S5). The variation of average fraction of SCCPs and MCCPs composition profiles between 10 cities are not obviously. D-value between the maximum and minimum were not exceeded 10%. Taken C_{14} for example, GZ with the highest mean value was 63.9% while LZ with the lowest value of 54.5%. As shown in Figs. S2 and S3, the seasonal variation of SCCPs and MCCPs homologue profiles in most cities were in the agreement condition.

In the previous studies, C_{10} was the dominant profiles with 55.47% relative mass fraction of SCCPs and MCCPs in Beijing (Huang et al., 2017) and Jinan (34% ± 8%) (Table S4) (Li et al., 2019). It is well known that C_{10} group was the previously predominant proportion in atmospheric CPs and mainly three commercial products of China (Table S4). These compositional variations could be due to the differences in sampling sites and sampling periods between these studies. Apart from this, the chlor−alkali industry in China has also been committed to decreasing the production and the use of short carbon group CPs, it may be a contributing factor. Other factors, such as metalogical parameters (i.e., temperature), may also influence the pattern, which will be discussed in section 3.3. The ratio of MCCPs/SCCPs, which act as an indicator for contamination degree and direct local source emission or long-range transport of CPs in the regional environment (Pan et al., 2018; Qiao et al., 2017), can also support this viewpoint. In this study, the mean ratio of MCCPs/SCCPs in all cities was 0.79. It also presented obvious spatial differences, in most cities was less than 1.00 except for GZ (1.92), SH (1.29), and TY (1.11). Additionally, although this ratio in BJ (0.492) did not exceed 1.00, it made rings round the previous study (0.114) (Huang et al., 2017). For regional scale, the ratio in eastern cities (1.02) was almost two times than that in central cities (0.66) and
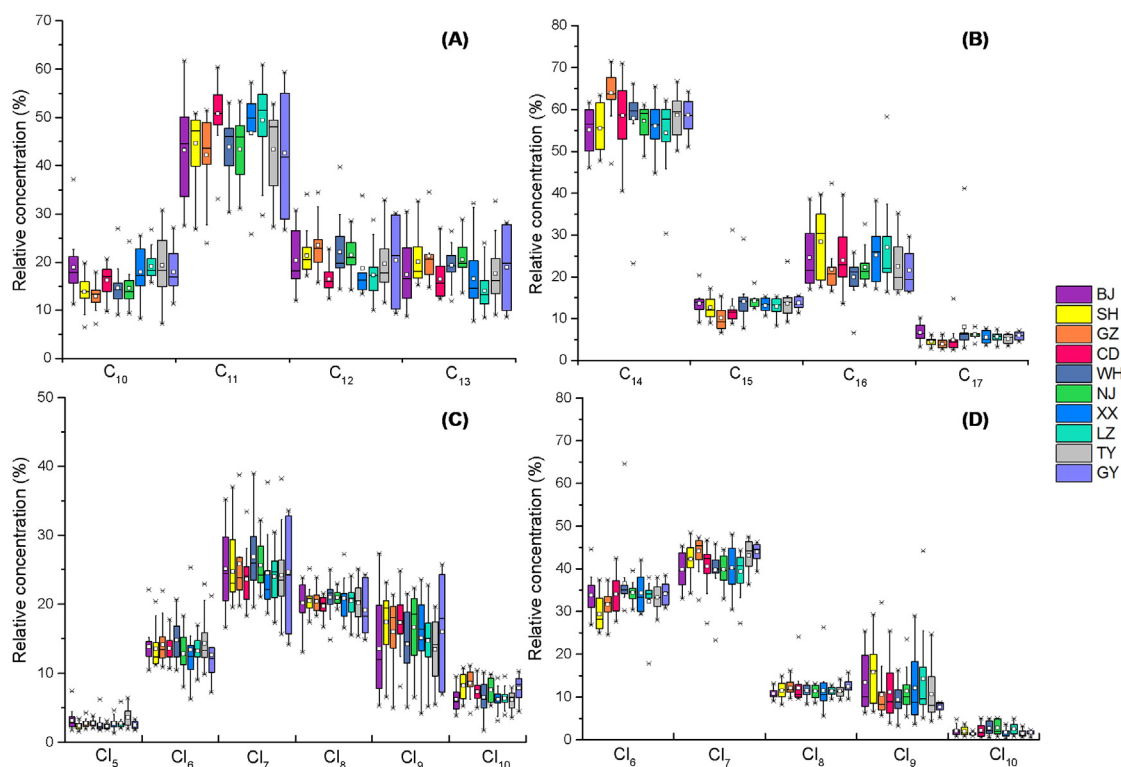

Fig. 2. The relative mass compositions of SCCPs and MCCPs at different carbon ((A) and (B)) and chlorine degrees ((C) and (D)) (The asterisk represents extreme value, the small square means average value, the line means medium value, the lower and upper ends of the box are the 25th and 75th percentiles of the data).

western cities (0.56) (Table S6).

Since SCCPs are listed as POPs, China has recently been trying to reduce the content of short−chain components in industrial products. It was supported by the significant increase in the ratio of MCCPs/SCCPs in sediment, such as from Pearl River Estuary (Chen et al., 2011) and Laizhou Bay (Pan et al., 2018). Furthermore, the present results of the atmospheric $PM_{2.5}$ also indicated that the production and the utilization of SCCPs were probably replaced by MCCPs in considerable part of eastern cities. In contrast, the central and western cities were still mainly producing and using of SCCPs.

3.3. Impact factors and sources analysis

CPs have been proven to have no natural sources (Zhang et al., 2017a) and are mostly produced locally (Li et al., 2012). Some previous studies have pointed out that the pollution characteristics of CPs are mainly influenced by CP products, application, meteorological parameters, and so on (Wei et al., 2016). So, what were the main factors and potential sources contributing to the distribution detail above?

3.3.1. Meteorological parameters and $PM_{2.5}$ properties

Table S7 has shown the correlation between the concentrations of CPs components and $PM_{2.5}$ concentrations, organic carbon (OC), elemental carbon (EC), temperature (°C), relative humidity (%RH), and atmospheric pressure (P) for all 10 cities. CPs homologues were significantly correlated with OC, EC ($p < 0.01$) and with $PM_{2.5}$ concentrations ($p < 0.05$) but a negative correlation existed between CP groups and °C and %RH. This was partly because $PM_{2.5}$ contains organic matter (Ye et al., 2017), especially the higher molecular weight homologues with larger octanol−air partition (K_{OA}) (Wang et al., 2012). The present SCCPs and MCCPs concentrations of most cities in winter were significantly higher than those in other seasons had reflected that high temperature did not cause an increase in the concentration of CPs in fine particles (Fig. 1). The similar phenomenon was observed in Beijing (Huang et al., 2017) and Jinan (Li et al., 2019).

3.3.2. Industry production and application

Table S7 also shown the correlation between the concentrations of CPs components with population (PP) and gross domestic product (GDP). It could be clearly seen that the significant positive correlation ($p < 0.01$) between SCCPs and MCCPs groups. This was in line with the fact that CPs industrial production in China did not strictly distinguish between different carbon lengths (Li et al., 2018). And yet it was worth to note that the relationships between SCCPs, MCCPs, PP, and GDP were negative. This contradicted the results of previous researches (Li et al., 2012; Zeng et al., 2017) suggested that the population and GDP of city may not the main controlling factor of CPs pollution. Apart from the central cities, there were apparently positive relationships ($p < 0.01$) between the SCCPs concentrations and each carbon chain groups concentrations in the eastern and western cities (Tables S8−10). To sum up, the pollution characteristic of CPs in $PM_{2.5}$ may be more susceptible to the production and utilization as pointed out in the previous studies (Li et al., 2012).

3.3.3. PCA: production and utilization

As shown in Fig. 3, the first and second principle components accounted for 87.4% and 8.54% of the variation, respectively. The red points represent CPs congeners, and the blue line represents the city pattern. In general, most CPs congeners gathered in the area with low PC1 and PC2 scores in $PM_{2.5}$, indicating they may affect by fine particles. In the space of PC1, several compounds had positive PC1 values, and SCCPs and MCCPs were separate from each other
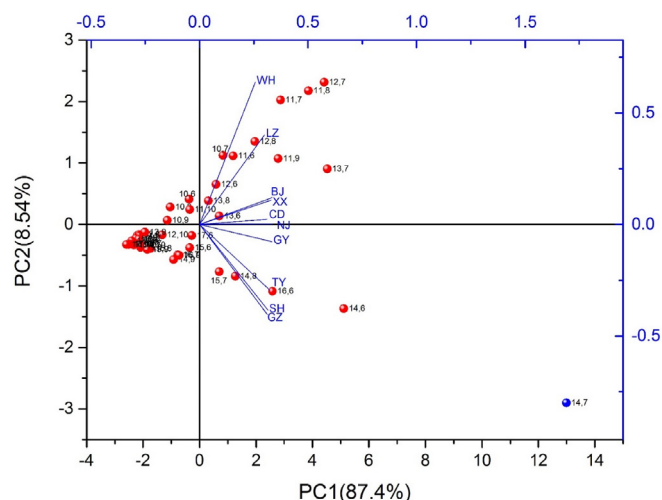

Fig. 3. The principle component analysis (PCA) of CPs congeners (red points) and 10 cities (blue lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(SCCPs: $C_{13}Cl_7$, $C_{12}Cl_7$, $C_{11}Cl_8$, $C_{11}Cl_7$, $C_{10}Cl_7$, $C_{11}Cl_6$, and so forth; MCCPs: $C_{14}Cl_7$, $C_{14}Cl_6$, $C_{16}Cl_6$, $C_{14}Cl_8$, and $C_{15}Cl_7$). These CPs congeners had some consistency with the dominant congeners, particularly $C_{14}Cl_7$ was an obvious outlier with an extremely large PC1 and negative PC2 values. In the space of PC2, all of the points were divided into two groups, SCCPs and MCCPs. Most SCCPs congeners presented positive scores, and all MCCPs congeners were located in the area with negative PC2 values, similar to a previous study (Chaemfa et al., 2014). Li et al. found the composition of CP-42 in different provinces was relatively consistent, with $C_{13~15}$ as the main components. While the composition of CP-52 and CP-70 implied significant difference, but most of them are mainly short ($C_{12~13}$) and medium chain groups (C_{14} and $C_{16~17}$) (Li et al., 2018). These also support the results of this study to some extent.

All of the city areas had positive PC1 scores (Fig. 3), which exhibited slight variation. In the space of PC2, three groups can be seen in 10 cities. WH and LZ were in group 1 with positive PC2 values. Group 2 combines BJ, XX, CD, NJ, and GY, which presented low PC2 scores. For Group 3, TY, SH, and GZ exhibited negative values. The aggregation of cities was mainly controlled by the MCCPs/SCCPs ration in each city (Table S2). For example, the three cities of Group 3 have a ratio greater than 1.0 (1.11, 1.31, and 1.66, respectively). Besides, the relative mass fraction or the concentration of SCCPs and MCCPs congeners also affected the grouping. As shown in Fig. 2A, C_{11} congeners accounted for a large proportion of SCCPs. Meanwhile, C_{14} congeners had an extremely high relative concentration, and Cl_7 congeners also had the highest relative concentrations in this study (Fig. 2D). This led to the grouping of WH and LZ, although WH has a higher ratio of MCCPs/SCCPs. On the basis of the above results, we deduced that the composition of CPs production and varied consumption style were the possible impact factors for the variation observed among the different groups.

3.4. Human deposition

CPs have been detected in different media and pose a potential ecological threat to the environment (Gao et al., 2018). As mentioned above, CPs are easier associated with fine particulate contamination and then the inhalation exposure risk should be concerned when serious $PM_{2.5}$ pollutions are frequently found in Chinese cities (Pui et al., 2014). On the basis of the mentioned above

calculations, the total deposition of PM$_{2.5}$ was dominated by deposition in the *HA*, indicating that this was the main deposition region followed by *AR*, which also had high deposition levels. The CPs deposition fluxes of PM$_{2.5}$ samples in *HA*, *TB*, and *AR* were 23.1, 2.18, and 3.87 ng h^{-1}, respectively. Due to the lack of CPs migration coefficient (air to skin), and the skin exposure was much lower than inhalation exposure (Gao et al., 2018; Luo, 2015), the CPs skin exposure was not studied.

The CPs inhalation exposure via PM$_{2.5}$ were also estimated. Table S11 presented the calculated MOE of all ages, the values range of SCCPs and MCCPs were 2.22×10^4–6.74×10^4 and 2.45×10^4–9.70×10^4 and 5.45×10^3–1.65×10^4 and 6.01×10^3–2.38×10^4 for male and female, respectively. EPA considered MOE value less than 1000 to indicate a "high risk finding." Hence, it implied the present calculated exposure of SCCPs and MCCPs in 10 cities of China may not have significant carcinogenic effect for human health considering concentration from gas phase that did not analyzed in this study.

4. Conclusion

The mean concentrations of ΣSCCPs and ΣMCCPs in PM$_{2.5}$ in China cities during 2013–2014 were 19.9 ± 41.1 ng m^{-3} and 15.6 ± 18.6 ng m^{-3}, respectively. This were significantly higher than those in the atmospheric of some different geographical region, such as Europe, North America and south Asia countries. The highest CPs concentrations had observed in central China (Small and medium-sized cities) but not in eastern China (well-known megacities). The C$_{11}$ homologues were predominant carbon formula groups in SCCPs with average proportion of 45.1% instead of C$_{10}$ congeners in the previous studies and the ratio of MCCPs/SCCPs in some eastern cities was higher than 1.00. By correlation analysis and principal component analysis, the pollution characteristics of CPs in PM$_{2.5}$ had mainly influenced by locally industrial production and consumption than by OC, EC, temperature, PP, and GDP. Additionally, the total deposition of PM$_{2.5}$ was dominated by deposition in the HA and there was no significant carcinogenic effect for human health in cities of China. Due to there is still existed serious PM$_{2.5}$ pollution in North China which is a densely populated area, further researches on CPs pollution characteristics, source analysis and human health risks of PM$_{2.5}$ should be carried out under the background of industrial transfer and upgrading.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work.

CRediT authorship contribution statement

Di Liu: Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Investigation, Writing - review & editing. **Qilu Li:** Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Investigation, Writing - review & editing. **Zhineng Cheng:** Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Investigation, Writing - review & editing. **Kechang Li:** Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Investigation, Writing - review & editing. **Jun Li:** Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Investigation, Writing - review & editing, Project administration, Resources. **Gan Zhang:** Conceptualization, Methodology, Data curation, Formal analysis, Writing - original draft, Investigation, Writing - review & editing, Funding acquisition, Supervision.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113853.

References

Barber, J.L., Sweetman, A.J., Thomas, G.O., Braekevelt, E., Stern, G.A., Jones, K.C., 2005. Spatial and temporal variability in air concentrations of short-chain (C10−C13) and medium-chain (C14−C17) chlorinated n-alkanes measured in the U.K. Atmosphere. Environ. Sci. Technol. 39, 4407−4415.

Bogdal, C., Niggeler, N., Glüge, J., Diefenbacher, P.S., Wächter, D., Hungerbühler, K., 2017. Temporal trends of chlorinated paraffins and polychlorinated biphenyls in Swiss soils. Environ. Pollut. 220, 891−899.

Borgen, A.R., et al., 2002. Polychlorinated alkanes in ambient air from Bear Island. Organohalogen Compd. 59, 303−306.

Brauer, M., Amann, M., Burnett, R.T., Cohen, A., Dentener, F., Ez-zati, M., Henderson, S.B., Krzyzanowski, M., Martin, R.V., VanDingenen, R., Van Donkelaar, A., 2012. Exposure assessment for estimation of the global burden of disease attributable to outdoor air pollution. Environ. Sci. Technol. 46, 652−660.

Cao, D.D., Gao, W., Wu, J., Lv, K., Xin, S.Z., Wang, Y.W., Jiang, G.B., 2019. Occurrence and human exposure assessment of short- and medium-chain chlorinated paraffins in dusts from plastic sports courts and synthetic turf in beijing, China. Environ. Sci. Technol. 53, 443−451.

Casà, M.V., van Mourik, L.M., Weijs, L., Mueller, J., Nash, S.B., 2019. First detection of short-chain chlorinated paraffins (SCCPs) in humpback whales (Megaptera novaeangliae) foraging in Antarctic waters. Environ. Pollut. 250, 953−959.

Chaemfa, C., Xu, Y., Li, J., Chakraborty, P., Hussain Syed, J., Naseem Malik, R., Wang, Y., Tian, C.G., Zhang, G., Jones, K.C., 2014. Screening of atmospheric short- and medium-chain chlorinated paraffins in India and Pakistan using poly-urethane foam based passive air sampler. Environ. Sci. Technol. 48, 4799−4808.

Chaney, R.A., Sloan, C.D., Cooper, V.C., Robinson, D.R., Hendrickson, N.R., McCord, T.A., Johnston, J.D., 2017. Personal exposure to fine particulate air pollution while commuting: an examination of six transport modes on an urban arterial roadway. PLoS One 12.

Chen, M.Y., Luo, X.J., Zhang, X.L., He, M.J., Chen, S.J., Mai, B.X., 2011. Chlorinated paraffins in sediments from the Pearl River delta, south China: spatial and temporal distributions and implication for processes. Environ. Sci. Technol. 45, 9936−9943.

Chen, H., Lam, J.C.W., Zhu, M.S., Wang, F., Zhou, W., Du, B.B., Zeng, L.X., Zeng, E.Y., 2018. Combined effects of dust and dietary exposure of occupational workers and local residents to short- and medium-chain chlorinated paraffins in a mega E-waste recycling industrial park in south China. Environ. Sci. Technol. 52, 11510−11519.

Diefenbacher, P.S., Bogdal, C., Gerecke, A.C., Glüge, J., Schmid, P., Scheringer, M., Hungerbühler, K., 2015. Short-chain chlorinated paraffins in zurich, Switzerland−Atmospheric concentrations and emissions. Environ. Sci. Technol. 49 (16), 9778−9786.

Du, X.Y., Yuan, B., Zhou, Y.H., Benskin, J.P., Qiu, Y.L., Yin, G., Zhao, J.F., 2018. Short-, medium-, and long-chain chlorinated paraffins in wildlife from paddy fields in the Yangtze river delta. Environ. Sci. Technol. 52, 1072−1080.

ECB, 2007a. European Union Risk Assessment Report. Alkanes, C10-13, Chloro. European Chemicals Bureau, European Commission.

ECB, 2007b. European Union Risk Assessment Report. Alkanes, C14-17, Chloro. European Chemicals Bureau, European Commission.

Feng, S.L., Gao, D., Liao, F., Zhou, F.R., Wang, X.M., 2016. The health effects of ambient PM$_{2.5}$ and potential mechanisms. Ecotoxicol. Environ. Saf. 128, 67−74.

Fiedler, H., 2010. Short-Chain Chlorinated Paraffins: Production, Use and International Regulations, edˇeds. Springer, Berlin Heidelberg.

Gao, W., Cao, D.D., Wang, Y.J., Wu, J., Wang, Y., Wang, Y.W., Jiang, G.B., 2018. External exposure to short- and medium-chain chlorinated paraffins for the general population in beijing, China. Environ. Sci. Technol. 52, 32−39.

Geng, N.B., Zhang, H.J., Zhang, B.Q., Wu, P., Wang, F.D., Yu, Z.K., Chen, J.P., 2015. Effects of short-chain chlorinated paraffins exposure on the viability and metabolism of human hepatoma HepG2 cells. Environ. Sci. Technol. 49, 3076−3083.

Glüge, J., Bogdal, C., Scheringer, M., Buser, A.M., Hungerbühler, K., 2013. Calculation of physicochemical properties for short- and medium-chain chlorinated

paraffins. J. Phys. Chem. Ref. Data 42 (2), 2–12.

Glüge, J., Wang, Z.Y., Bogdal, C., Scheringer, M., Hungerbühler, K., 2016. Global production, use, and emission volumes of short-chain chlorinated paraffins – a minimum scenario. Sci. Total Environ. 573, 1132–1146.

Harada, K.H., Takasuga, T., Hitomi, T., Wang, P., Matsukami, H., Koizumi, A., 2011. Dietary exposure to short-chain chlorinated paraffins has increased in beijing, China. Environ. Sci. Technol. 45, 7019–7027.

Hinds, W.C., 1999. Aerosol Technology: Properties, Behavior and Measurement of Airborine Particles. Wiley Interscience, New York.

Hsu, C.Y., Chiang, H.C., Chen, M.J., Chuang, C.Y., Tsen, C.M., Fang, G.C., Tsai, Y.I., Chen, N.T., Lin, T.Y., Lin, S.L., Chen, Y.C., 2017. Ambient PM2.5 in the residential area near industrial complexes: Spatiotemporal variation, source apportionment, and health impact. Sci. Total Environ. 590–591, 204–214.

Huang, H.T., Gao, L.R., Xia, D., Qiao, L., Wang, R.H., Su, G.J., Liu, W.B., Liu, G.R., Zheng, M.H., 2017. Characterization of short- and medium-chain chlorinated paraffins in outdoor/indoor PM10/PM2.5/PM1.0 in Beijing, China. Environ. Pollut. 225, 674–680.

Jiang, W.Y.H., Huang, T., Mao, X.X., Wang, L., Zhao, Y., Jia, C.H., Wang, Y., Gao, H., Ma, J.M., 2017. Gridded emission inventory of short-chain chlorinated paraffins and its validation in China. Environ. Pollut. 220, 132–141.

Lanzinger, S., Schneider, A., Breitner, S., Stafoggia, M., Peters, A., 2015. Associations between ultrafine and fine particles and mortality in five central European cities - results from the UFIREG study. Environ. Int. 88, 44–52.

Li, Q.L., Li, J., Wang, Y., Xu, Y., Pan, X.H., Zhang, G., Luo, C.L., Kobara, Y., Nam, J.J., Jones, K.C., 2012. Atmospheric short-chain chlorinated paraffins in China, Japan, and South Korea. Environ. Sci. Technol. 46, 11948–11954.

Li, P., Xin, J., Wang, Y., Wang, S., Li, G., Pan, X., Liu, Z., Wang, L., 2013. The acute effects of fine particles on respiratory mortality and morbidity in Beijing, 2004-2009. Environ. Sci. Pollut. Res. 20, 6433–6444.

Li, T., Gao, S.X., Ben, Y.J., Zhang, H., Kang, Q.Y., Wan, Y., 2018. Screening of chlorinated paraffins and unsaturated analogues in commercial mixtures: confirmation of their occurrences in the atmosphere. Environ. Sci. Technol. 52, 1862–1870.

Li, H.J., Li, J.K., Yu, H.Z, Li, H., Yang, L.X., Chen, X.F., Cai, Z.W., 2019. Seasonal variations and inhalation risk assessment of short-chain chlorinated paraffins in PM2.5 of Jinan, China. Environ. Pollut. 245, 325–330.

Liu, D., Lin, T., Shen, K.J., Li, J., Yu, Z.Q., Zhang, G., 2016a. Occurrence and concentrations of halogenated flame retardants in the atmospheric fine particles in Chinese cities. Environ. Sci. Technol. 50, 9846–9854.

Liu, J.K., Zhu, L.J., Wang, H.H., Yang, Y.L., Liu, J.T., Qiu, D.D., Ma, W., Zhang, Z.M., Liu, J.L., 2016b. Dry deposition of particulate matter at an urban forest, wetland and lake surface in Beijing. Atmos. Environ. 125, 178–187.

Luo, P., 2015. Size-Dependent Distribution and Inhalation Exposure of Particle–Bound Semivolatile Organic Contaminants. University of Chinese Academy of Sciences, Guangzhou.

Martellini, T., Giannoni, M., Lepri, L., Katsoyiannis, A., Cincinelli, A., 2012. One year intensive PM2.5 bound polycyclic aromatic hydrocarbons monitoring in the area of Tuscany, Italy. Concentrations, source understanding and implications. Environ. Pollut. 164, 252–258.

Marvin, C.H., Painter, S., Tomy, G.T., Stern, G.A., Braekevelt, E., Muir, D.C.G., 2003. Spatial and temporal trends in short-chain chlorinated paraffins in lake ontario sediments. Environ. Sci. Technol. 37, 4561–4568.

Ohura, T., Noda, T., Amagai, T., Fusaya, M., 2005. Prediction of personal exposure to PM2.5 and carcinogenic polycyclic aromatic hydrocarbons by their concentrations in residential microenvironments. Environ. Sci. Technol. 39, 5592–5599.

Pan, X.H., Tang, J.H., Tian, C.G., Li, J., Zhang, G., 2018. Short- and medium-chain chlorinated paraffins in sediments from the Laizhou Bay area, North China: implications for transportation from rivers to marine environment. Environ. Pollut. 243, 1460–1468.

Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angew. Chem. Int. Ed. 44, 7520–7540.

Pui, D.Y.H., Chen, S.C., Zuo, Z.L., 2014. PM2.5 in China: measurements, sources, visibility and health effects, and mitigation. Particuology 13, 1–26.

Qiao, L., Gao, L.R., Xia, D., Huang, H.T., Zheng, M.H., 2017. Short- and medium-chain chlorinated paraffins in sediments from the middle reaches of the Yangtze River: spatial distributions, source apportionment and risk assessment. Sci. Total Environ. 575, 1177–1182.

Qiao, L., Gao, L.R., Zheng, M.H., Xia, D., Li, J.G., Zhang, L., Wu, Y.N., Wang, R.H., Cui, L.L., Xu, C., 2018. Mass fractions, congener group patterns, and placental transfer of short- and medium-chain chlorinated paraffins in paired maternal and cord serum. Environ. Sci. Technol. 52, 10097–10103.

Reth, M., Zencak, Z., Oehme, M., 2005. New quantification procedure for the analysis

of chlorinated paraffins using electron capture negative ionization mass spectrometry. J. Chromatogr. A 1081 (2), 225–231.

Schinkel, L., Bogdal, C., Canonica, E., Cariou, R., Bleiner, D., McNeill, K., Heeb, N.V., 2018a. Analysis of medium-chain and long-chain chlorinated paraffins: the urgent need for more specific analytical standards. Environ. Sci. Technol. Lett. 5, 708–717.

Schinkel, L., Lehner, S., Heeb, N.V., Marchand, P., Cariou, R., McNeill, K., Bogdal, C., 2018b. Dealing with strong mass interferences of chlorinated paraffins and their transformation products: an analytical guide. Trends Anal. Chem. 106, 116–124.

Thomas, G.O., Farrar, D., Braekevelt, E., Stern, G., Kalantzi, O.I., Martin, F.L., Jones, K.C., 2006. Short and medium chain length chlorinated paraffins in UK human milk fat. Environ. Int. 32 (1), 34–40.

Tomy, G.T., Stern, G.A., Lockhart, W.L., Muir, D.C.G., 1999. Occurrence of C10–C13 polychlorinated n-alkanes in Canadian midlatitude and arctic lake sediments. Environ. Sci. Technol. 33, 2858–2863.

UNEP, 2017. POPS/COP.8/SC/8-11. Listing of Short-Chain Chlorinated Paraffins.

van Mourik, L.M., Leonards, P.E.G., Gaus, C., de Boer, J., 2015. Recent developments in capabilities for analysing chlorinated paraffins in environmental matrices: a review. Chemosphere 136, 259–272.

Wang, X.F., Li, X.H., Cheng, H.X., Xu, X.B., Zhuang, G.M., Zhao, C.D., 2008. Organochlorine pesticides in particulate matter of Beijing, China. J. Hazard. Mater. 155, 350–357.

Wang, T., Han, S.L., Yuan, B., Zeng, L.X., Li, Y.M., Wang, Y.W., Jiang, G.B., 2012. Summer–winter concentrations and gas-particle partitioning of short chain chlorinated paraffins in the atmosphere of an urban setting. Environ. Pollut. 171, 38–45.

Wei, G.L., Liang, X.L., Li, D.Q., Zhuo, M.N., Zhang, S.Y., Huang, Q.X., Liao, Y.S., Xie, Z.Y., Guo, T.L., Yuan, Z.J., 2016. Occurrence, fate and ecological risk of chlorinated paraffins in Asia: a review. Environ. Int. 92–93, 373–387.

Xie, Z., Qin, Y., Zhang, L., Zhang, R., 2018. Death effects assessment of PM2.5 pollution in China. Pol. J. Environ. Stud. 27, 1813–1821.

Xu, D.D., Dan, M., Song, Y., Chai, Z.F., Zhuang, G.S., 2005. Concentration characteristics of extractable organohalogens in PM2.5 and PM10 in Beijing, China. Atmos. Environ. 39, 4119–4128.

Xu, J., Gao, Y., Zhang, H., Zhan, F., Chen, J., 2016. Dispersion of short- and medium-chain chlorinated paraffins (CPs) from a CP production plant to the surrounding surface soils and coniferous leaves. Environ. Sci. Technol. acs.est.6b03595.

Xu, J.Z., Gao, Y., Zhang, H.J., Zhan, F.Q., Chen, J.P., 2016. Dispersion of short- and medium-chain chlorinated paraffins (CPs) from a CP production plant to the surrounding surface soils and coniferous leaves. Environ. Sci. Technol. 50, 12759–12766.

Ye, Z., Liu, J., Gu, A., Feng, F., Liu, Y., Bi, C., Xu, J., Li, L., Chen, H., Chen, Y., Dai, L., Zhou, Q., Ge, X., 2017. Chemical characterization of fine particulate matter in Changzhou, China, and source apportionment with offline aerosol mass spectrometry. Atmos. Chem. Phys. 17, 2573–2592.

Zeng, L.X., Lam, J.C.W., Horii, Y., Li, X.L., Chen, W.F., Qiu, J.W., Leung, K.M.Y., Yamazaki, E., Yamashita, N., Lam, P.K.S., 2017. Spatial and temporal trends of short- and medium-chain chlorinated paraffins in sediments off the urbanized coastal zones in China and Japan: a comparison study. Environ. Pollut. 224, 357–367.

Zhan, F.Q., Zhang, H.J., Wang, J., Xu, J.Z., Yuan, H.P., Gao, Y., Su, F., Chen, J.P., 2017. Release and gas-particle partitioning behaviors of short-chain chlorinated paraffins (SCCPs) during the thermal treatment of polyvinyl chloride flooring. Environ. Sci. Technol. 51, 9005–9012.

Zhang, Y.L., Cao, F., 2015. Fine particulate matter (PM2.5) in China at a city level. Sci. Rep. 5, 14884.

Zhang, B.Y., Zhao, B., Xu, C., Zhang, J.B., 2017a. Emission inventory and provincial distribution of short-chain chlorinated paraffins in China. Sci. Total Environ. 581–582, 582–588.

Zhang, X.D., Du, J., Huang, T., Zhang, L.M., Gao, H., Zhao, Y., Ma, J.M., 2017b. Atmospheric removal of PM2.5 by man-made Three Northern Regions Shelter Forest in Northern China estimated using satellite retrieved PM2.5 concentration. Sci. Total Environ. 593–594, 713–721.

Zhou, W., Shen, M.J., Lam, C.W.J., Zhu, M.S., Liu, L.Y., Chen, Hui, Du, B.B., Zeng, L.X., Zeng, E.Y., 2018. Size-dependent distribution and inhalation exposure characteristics of particle-bound chlorinated paraffins in indoor air in Guangzhou, China. Environ. Pollut. 121, 675–682.

Zhuo, M.H., Ma, S.T., Li, G.Y., Yu, Y.X., An, T.C., 2019. Chlorinated paraffins in the indoor and outdoor atmospheric particles from the Pearl River Delta: characteristics, sources, and human exposure risks. Sci. Total Environ. 650, 1041–1049.