



Occurrence and gas/particle partitioning of short- and medium-chain chlorinated paraffins in the atmosphere of Fildes Peninsula of Antarctica



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HIGHLIGHTS

- The concentration of CPs in Antarctic was much lower than that of low latitudes.
- Long-range atmospheric transport was a major input way of CPs to the Antarctic.
- CPs with shorter carbon chain and less chlorines was relatively easier to migrate.
- Absorption mechanism showed a relatively significant effect on partitioning of CPs.

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ABSTRACT

Chlorinated paraffins (CPs) were measured in air samples at a remote air monitoring site established in Georgia King Island, Fildes Peninsula of Antarctica (Great Wall Station, China) to study the long-range atmospheric transport of these anthropogenic pollutants to the Antarctic. Gas- and particle-phase CPs were collected using polyurethane foam plugs (PUF) and glass fiber filters (GFF) respectively during summertime of 2012. The total atmospheric levels of SCCPs and MCCPs ranged from 9.6 to 20.8 pg m^{-3} (average: 14.9 pg m^{-3}) and 3.7–5.2 pg m^{-3} (average: 4.5 pg m^{-3}), respectively. C_{10} and C_{11} carbon chain homologues with Cl_5 and Cl_6 chlorine atoms predominated in SCCP formula groups both in gas- and particle-phase. Significant linear correlation was found between gas/particle partition coefficients (K_p) and sub-cooled liquid vapor pressures (p_l°) ($R^2 = 0.437$, $p < 0.01$), as well as K_p and octanol–air partition coefficients (K_{OA}) ($R^2 = 0.442$, $p < 0.01$). Absolute slope values of two regression models (0.31 and 0.39) were less than 0.6 indicating that the way of absorption into organic matter of aerosol played a more important role on atmospheric partitioning and transferring of CPs in remote Antarctic area. Both the Junge–Pankow model and the K_{OA} -based model tended to underestimate the sorption of lower chlorinated CPs and overestimate the sorption of highly chlorinated CPs.

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1. Introduction

Chlorinated paraffins (CPs) are a group of chlorinated derivatives of *n*-alkanes and classified as short-chain chlorinated

paraffins (SCCPs, C_{10} – C_{13}), medium-chain chlorinated paraffins (MCCPs, C_{14} – C_{17}), and long-chain chlorinated paraffins (LCCPs, $\text{C}_{>17}$) according to their carbon chain length (Tomy et al., 1998). They have especially attracted extensive concern worldwide due to their environmental persistence (Barber et al., 2005; Iozza et al., 2008; Friden et al., 2011; Zhao et al., 2013), higher toxicity (Warnasuriya et al., 2010) and bioaccumulation potential (Houde et al., 2008; Zeng et al., 2011). SCCPs have been placed on toxic

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release inventory in the European Union, Japan and Canada, and classified as priority toxic substances in the United States (UNEP, 2009). Meanwhile, in 2007, SCCPs have been also reviewed as a new candidate of persistent organic pollutants (POPs) by the Stockholm Convention on POPs.

Previous studies have indicated that long-range atmospheric transport is a primary way of migration for semi-volatile organic compounds (SVOCs) (Wania et al., 1999; Wang et al., 2009; Na et al., 2011). Two mechanisms of absorption into the organic matter (OM) and adsorption onto the particulate surface (corresponding to two predicted models, i.e., J–P model based on adsorption (Pankow, 1994) and K_{OA} -model based absorption (Harner et al., 1998) are introduced to describe the gas/particle partitioning of SVOCs (Dachs and Eisenreich, 2000; Helm and Bidleman, 2005; Chen et al., 2006; Vardar et al., 2008; Gaga and Ari, 2011; Yang et al., 2013). SCCPs are a group of ubiquitous SVOCs with a wide range of logarithmic sub-cooled liquid vapor pressure ($\log p_L^*$) (from -2.29 for $C_{10}Cl_5$ to -6.58 for $C_{13}Cl_{10}$ at $25^\circ C$, Drouillard et al., 1998) and can exist in both gas- and particle-phase (Wang et al., 2012). Furthermore, the wide range of p_L^* can make a significant difference in partitioning coefficient (K_p) between gas- and particle-phases for various CP formula groups, and as a result their atmospheric transport potential could vary greatly. Therefore, the partitioning coefficient could be an essential aspect with regard to the atmospheric fate of CPs.

As a new type of global pollutants, information regarding the atmospheric level and distribution of SCCPs in remote North Polar regions provided an evidence for the long-range atmospheric transport of SCCPs. For example Borgen et al. (2000) reported that atmospheric levels of SCCPs in the Norwegian Svalbard and Bear Island ranged from 9 to 27 pg m^{-3} and 1.8 – 10.6 ng m^{-3} , respectively. The Antarctica region, especially the Georgia King Island of Fildes Peninsula, has become the research focus area for the SVOCs, e.g. PAHs, PCBs and PBDEs (Na et al., 2011; Li et al., 2012a,b). However, investigation about the long-range atmospheric transport and environmental behavior and fate of CPs in this area has been never reported. In this study, the remote air monitoring during summertime in Antarctic area was carried out to investigate the concentrations, distribution and gas-particle partitioning of CPs. Furthermore, the comparisons of CPs partitioning between the measured data and the predicted data from J–P model and K_{OA} -model were also carried out to explore the factors influencing the atmospheric behavior and fate of CPs.

2. Materials and methods

2.1. Air sampling

Air sampling was conducted from January 16th to February 8th, 2013, using a high-volume air sampler (HiVol, Type 2031, Qingdao, China) on a mountain (40 m above ground level) in Georgia King Island, Fildes Peninsula of Antarctica (Great Wall Station, China; latitude: $62^\circ 12'59'' S$; longitude: $58^\circ 57' 52'' W$). Twenty four air samples were collected on 48 h intervals by HiVol equipped with a glass fiber filter (GFF) to capture particles and a PUF plug for the gas-phase CPs (as listed in Table 1). After sampling, PUF and GFF were wrapped in aluminum foil and stored in freezers at $-20^\circ C$. The HiVol operated at an average flow rate of $1.0 \text{ m}^3 \text{ min}^{-1}$ and the total sampled air volume averaged about 2880 m^3 . In addition, six cleaned QFFs and PUFs processed as field blanks were exposed to the atmosphere for 10 min, then wrapped in aluminum foil and stored in freezers at $-20^\circ C$. The total suspended particulate (TSP) in air was determined by weighing the mass difference of GFF before and after sampling.

Table 1

Sampling parameters and statistical results of CPs (pg m^{-3}) in atmosphere of Georgia King Island, Antarctica.

Sampling volume	Mean = $3450 \text{ (m}^3)$									
	Ambient temperature Mean = $15.6 \text{ } \mu\text{g m}^{-3}$									
Ambient temperature	Mean = $-5^\circ C$, mean = $0^\circ C$									
	TSP concentration									
Gas-phases (PUF)				Particle-phases (GFF)				Total		
Min	Max	Arithmetic mean	SD	Min	Max	Arithmetic mean	SD	Arithmetic mean	SD	
Σ SCCPs	7.8	18.8	13.5	4.0	1.9	2.6	1.7	0.2	14.9	4.1
Σ MCCPs	3.0	4.5	3.8	0.6	0.5	0.9	0.7	0.1	4.5	0.60
Σ CPs	10.9	23.3	17.3	4.3	1.8	2.8	2.5	0.4	19.4	4.5

2.2. Sample pretreatment

Both PUF and GFF were extracted and analyzed separately to obtain information on the respective gas- and particle-phases. Before extraction, a surrogate standard of $10 \text{ } \mu\text{L } ^{13}\text{C}_6\text{-}\alpha\text{-HCH}$, (100 ng mL^{-1}) was added into the sample. PUF and GFF were soaked for 12 h with 400 mL and 100 mL hexane/dichloromethane (DCM) (1:1, v:v) respectively, and then extracted in an ultrasonic bath for 30 min. The raw extracts were evaporated to about 5 mL with a rotary evaporator, and the concentrates were subsequently transferred to a multilayer column for further clean-up. Detailed information on the chemicals and materials, and further clean-up procedure were provided in the Supplementary Information (SI).

2.3. Instrument analysis and quantification

The instrument analysis was performed on a 5973i triple quadrupole mass spectrometer coupled with a 6890A GC at ECNI mode (Agilent, U.S.A). An aliquot of $1 \text{ } \mu\text{L}$ of the final extract was injected into a DB – 5 ms ($15 \text{ m} \times 0.25 \text{ mm i.d.} \times 0.25 \text{ } \mu\text{m}$ film thickness, J&W Scientific, U.S) capillary column at pulse splitless mode. The injector temperature was $275^\circ C$. Helium was used as carrier gas at a constant flow of 1.0 mL min^{-1} and methane (99.995% purity) as reagent gas at a flow rate of 2 mL min^{-1} . The oven temperature program was as follows: 1 min isothermal at $100^\circ C$, increased to 160 at $30^\circ C \text{ min}^{-1}$, held for 5 min, then ramped to 310 at $30^\circ C \text{ min}^{-1}$, and held for 13 min. The two most abundant isotopes of the $[\text{M}-\text{Cl}]^-$ ion were selected for the quantitative and qualitative ions. In order to minimize the interference in SCCP quantification from MCCP congener groups, with which five carbon atoms more and two chlorine atoms less (e.g. $C_{10}Cl_6$ and $C_{15}Cl_4$, $C_{10}Cl_7$ and $C_{15}Cl_5$, $C_{11}Cl_6$ and $C_{16}Cl_4$, and $C_{11}Cl_7$ and $C_{16}Cl_5$), three-time injections were one by one conducted to monitor three homologues groups containing the similar quantitative ions, i.e., C_{10} -CPs and C_{15} -CPs group, C_{11} -CPs and C_{16} -CPs group, and C_{12} -CPs and C_{17} -CPs group. In addition, another injection was conducted to monitor both C_{13} -CPs and C_{14} -CPs. The chromatographic peak areas of SCCP congeners were first corrected by removing the interference from MCCP congeners according to the method described by Zeng et al. (2011), and then the quantifications of SCCPs and MCCPs were conducted using the procedure described by (Reth et al., 2005), respectively.

2.4. Quality control

Strict quality controls were implemented to ensure the accuracy and reliability of the data. All equipment was thoroughly rinsed with dichloromethane before experiment, and the sample preparations were conducted in a super clean lab to avoid background contamination. PUF and GFF were pre-cleaned three times with dichloromethane (300 mL each time) before taking to Antarctic.

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