

Short- and Medium-Chain Chlorinated Paraffins in Air and Soil of Subtropical Terrestrial Environment in the Pearl River Delta, South China: Distribution, Composition, Atmospheric Deposition Fluxes, and Environmental Fate

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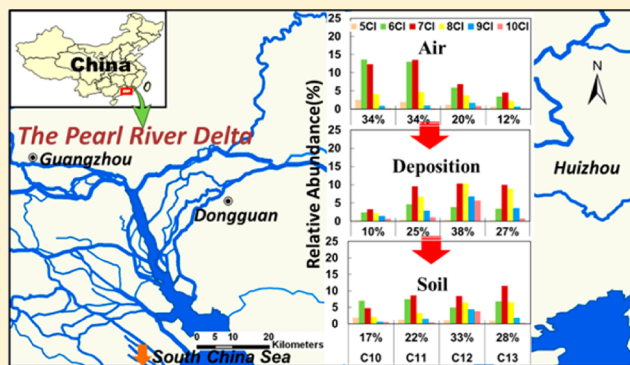
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Supporting Information

ABSTRACT: Research on the environmental fate of short- and medium-chain chlorinated paraffins (SCCPs and MCCPs) in highly industrialized subtropical areas is still scarce. Air, soil, and atmospheric deposition process in the Pearl River Delta of South China were investigated, and the average SCCP and MCCP concentrations were 5.2 $\mu\text{g}/\text{sampler}$ (17.69 ng/m^3) and 4.1 $\mu\text{g}/\text{sampler}$ for passive air samples, 18.3 and 59.3 ng/g for soil samples, and 5.0 and 5.3 $\mu\text{g}/(\text{m}^2\text{d})$ for deposition samples, respectively. Influenced by primary sources and the properties of chlorinated paraffins (CPs), a gradient trend of concentrations and a fractionation of composition from more to less industrialized areas were discovered. Intense seasonal variations with high levels in summer air and winter deposition samples indicated that the air and deposition CP levels were controlled mainly by the vapor and particle phase, respectively. Complex environmental processes like volatilization and fractionation resulted in different CP profiles in different environment matrixes and sampling locations, with $\text{C}_{10-11} \text{Cl}_{6-7}$ and $\text{C}_{14} \text{Cl}_{6-7}$, $\text{C}_{10-12} \text{Cl}_{6-7}$ and $\text{C}_{14} \text{Cl}_{6-8}$, and $\text{C}_{11-12} \text{Cl}_{6-8}$ and $\text{C}_{14} \text{Cl}_{7-8}$ dominating in air, soil, and atmospheric deposition, respectively. Shorter-chain and less chlorinated congeners were enriched in air in the less industrialized areas, while longer-chain and higher chlorinated congeners were concentrated in soil in the more industrialized areas. This is suggesting that the gaseous transport of CPs is the dominant mechanism responsible for the higher concentrations of lighter and likely more mobile CPs in the rural areas.



INTRODUCTION

Chlorinated paraffins (or polychlorinated n-alkanes, PCAs), including short-chain chlorinated paraffins ($\text{C}_{10}\text{--}\text{C}_{13}$, SCCPs), medium-chain chlorinated paraffins ($\text{C}_{14}\text{--}\text{C}_{17}$, MCCPs), and long-chain chlorinated paraffins ($\text{C}_{18}\text{--}\text{C}_{30}$, LCCPs), are highly complex technical mixtures theoretically containing more than 10 000 structural isomers,¹ which have been industrially produced as additives in lubricants and metal-working fluids, as flame retardants in plastics and sealants, and as plasticizers in polyvinyl chloride (PVC) for more than 70 years.^{2,3} They have similar properties (e.g., persistent, hydrophobic, and semi-volatile) compared to some persistent organic pollutants (POPs) like PCBs, toxaphene, and DDT.^{1,4} Meanwhile, SCCPs are under review by the Stockholm Convention as a potential “new” category of POP due to their persistence,

bioaccumulation, long-range transport potential, and toxic character.^{5,6} As reported, SCCPs show chronic toxicity in aquatic organisms and are carcinogenic in rats and mice.⁷ The toxicity of MCCPs is lower compared to SCCPs, but they are widely used and show higher concentration levels than SCCPs.^{2,8} As a consequence of their widespread and unrestricted use,⁹ persistence, and tendency to bioaccumulate,^{10,11} CPs have become ubiquitous in the environment and are routinely detected in most natural environmental compartments,^{3,12–15} as well as the human living environment.^{16–18}

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Once released, semivolatile organic chemicals (SOCs), like CPs, are cycling between the atmosphere and terrestrial environment over long periods of time as they move toward equilibrium between environmental compartments,^{19,20} because they are persistent and can undergo long-range atmospheric transport (LRAT). Emissions through gaseous diffusion are considered to be the most important pathway for the transfer of SOCs from soil to atmosphere,²¹ while atmospheric deposition is an important input for delivering both gaseous and particle bound SOCs to terrestrial ecosystems.²² Meanwhile, atmospheric transport is said to be the major pathway for SOCs transport to rural areas.²³

Despite increasing attention over CPs over the past decade, there is still lack of insight on the environmental partition and fate of CPs in different matrixes, especially in the developing countries like China,^{13,15,23,24} where the largest production and export of CPs in the world takes place without restriction.²⁵ Consequently, the extensive production (600 000 tons in 2007) and usage of CPs suggest that the potential for contamination and impact to humans and the environment is very high, rendering the need for such studies in China imperative.

The Pearl River Delta (PRD), encompassing southern Guangdong Province, Hong Kong, and Macao, is located in the south coast of China and is strongly influenced by the Asian monsoon system. It has been considered one of the most rapidly developing regions in China over the last three decades, with an area of 42 794 km² and a population of 41 million. Moreover, Dongjiang River, one of the tributaries of the Pearl River, supplies fresh water for many cities including Guangzhou, Dongguan, Shenzhen, and Hong Kong. Highly developed industries located at the adjacent area of the watershed, resulting in the escape of various chemicals, may pose a potential pollution to the river and the surrounding ecosystem. Previous studies suggested that the fate of SOCs can be influenced by the Asian monsoon,²⁶ and model analysis also indicated that the outflow of polycyclic aromatic hydrocarbons from the PRD can be transported to northern mainland China, the South China Sea, or even to the Pacific Ocean and beyond under particular weather conditions.²⁷ Therefore, analysis of CP concentrations in air, soil, and deposition in the PRD is not only necessary for the environmental quality of the region but also essential for the understanding of the fate and potential impact of CPs in the nearby and faraway regions as well.

So far, no study has focused on the fate of CPs in air, soil, or the process that govern the interactions between those two compartments. In this direction, the study was designed to study the occurrence of CPs in air and soil and to assess the distribution, composition, and environmental processes that govern the fate of SCCPs and MCCPs in the highly developed PRD region of South China, which can be considered as characteristic of subtropical environments.

MATERIALS AND METHODS

Detailed descriptions of the materials and methods are presented in Supporting Information.

Sampling. Totally, 40 passive air samples (PUFs) at 20 sites,²⁸ 60 top soils (0–5 cm) at 60 sites,²⁹ and 44 bulk atmospheric depositions (wet and dry) at 11 sites,³⁰ along Dongjiang River within the eastern PRD, were collected during December 2009 to September 2010 (Figure 1). Each deposition sampler was installed together with a passive air sampler, while additional passive air samplers were spread along this river. Field blanks were carried out simultaneously with

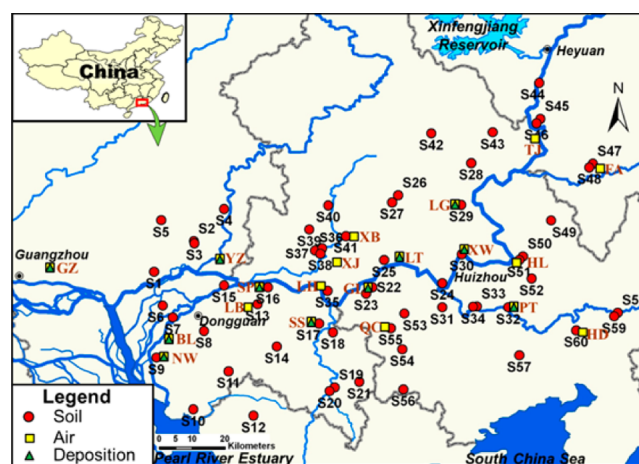


Figure 1. Map of sampling locations.

samples to assess the possible contaminations. For the details, please check Supporting Information 1 and published papers.^{28–30}

Sample Preparation and Analysis. *Extraction.* PUF disk and soil samples were spiked with ¹³C₁₀-trans-chlordane (¹³C-TC) as surrogate standard and were Soxhlet extracted with DCM for 48 h. Atmospheric deposition samples were passed through glass-fiber filter (GF/F). Glass fiber filters were Soxhlet extracted with DCM for 48 h. Water samples were extracted by XAD resins and eluted with methanol and DCM. The methanol was separated from the DCM by liquid–liquid extraction. The DCM portions were combined and dehydrated.

Clean-up. The extracts were initially cleaned up through a column containing sulfuric acid–silica gel and then purified with a multilayer column filled with anhydrous Na₂SO₄, florisil (2% deactivated), neutral silica gel (3% deactivated), and neutral alumina (3% deactivated) from top to bottom.

Instrumental Analysis. SCCPs (C_{10–13} with Cl_{5–10}) and MCCPs (C_{14–17} with Cl_{6–10}) were simultaneously analyzed by gas chromatography electron capture negative-ion low resolution mass spectrometry. Three SCCPs (51.5%, 55.5%, and 63%Cl), three MCCPs references (42%, 52%, and 57% Cl) from Dr. Ehrenstorfer co., and their mixtures (Table S2, Supporting Information) were used to establish a linear correlation between chlorine content and total response factor (see Figure S1, Supporting Information). The analytical method was based on previous studies^{31,32} with slight modifications to improve the identification of possible interferences caused by the CP congeners themselves (Table S1, Supporting Information). The identification of CP congener groups was performed by comparison of retention time, signal shape, and correct isotope ratio according to Reth and Oehme³² and the quantification method followed the work of Reth et al.³¹ and Iozza et al.³³

QA/QC. Procedural and field blank levels were 22.6 ± 4.5 ng for SCCPs and 19.9 ± 4.2 ng for MCCPs. The method detection limits (MDLs) were defined as the average of all blanks analyzed plus 3 times the standard deviation. The MDLs of SCCPs and MCCPs were estimated at 1.2 and 1.1 ng/g for soils, 122 and 110 pg/m³ for PUF, and 11.8 and 10.9 ng/(m² d) for deposition. The recoveries of 7 spiked samples (SCCPs 5 μg; MCCPs 5 μg; ¹³C-TC 10 ng) were in the range of 82–96%, 74–80%, and 81–90%, respectively. The recoveries of ¹³C-TC from all environmental samples were 75–109%. The

quantitative results in this study were all corrected for the blanks but not for surrogate recoveries.

RESULTS AND DISCUSSION

Concentrations of CPs in Air. As presented in Figure 2a, the air concentrations of SCCPs and MCCPs for the whole sampling period (approximately 70 days) were in the range of 0.28–7.79 $\mu\text{g}/\text{sampler}$ and 0.03–6.76 $\mu\text{g}/\text{sampler}$ in winter and 0.59–31.2 $\mu\text{g}/\text{sampler}$ and 0.23–67.9 $\mu\text{g}/\text{sampler}$ in summer, respectively. On the basis of published sampling

rates for SCCPs from PUFs (4.2 m^3/d),⁶ the SCCP air levels ranged between 0.95 to 26.5 ng/m^3 in winter and 2.01 to 106 ng/m^3 in summer. Ever since 2007, SCCPs have been under review by the Stockholm Convention as candidate POPs, the research of CPs has become an emerging scientific issue. However, still only little attention has been paid to the fate of CPs in the environment. CP levels in the atmosphere have been reported but mostly using active air samplers.^{34–38} Using passive air samplers to assess air concentration of CPs was first presented by Barber et al.³ in Lancaster in 2003 with SCCPs and MCCPs in the range of 0.22–9.1 and 0.56–29 $\mu\text{g}/\text{sampler}$ in a 12 week sampling period, which were comparable with those in the present study. Besides, our results were comparable to the air concentrations of SCCPs all over China but higher than those in Japan and South Korea in 2008.⁶

The air concentrations of CPs varied widely with the sampling sites (Figure 2a). Spatial distribution showed that a gradient of CP concentrations from more to less industrialized areas was discovered, mainly impacted by the proximity to primary point sources. Most of the high CP concentrations (e.g., site NW and SS) were located in the Dongguan City, a highly industrialized city with dense metal processing workshops or PVC manufactories, while the lower levels were found in the developing Huizhou City (including part of Heyuan City).

The CP concentrations in air proved to be strongly seasonal, with summer concentrations being much higher in all sites. The study area is located in South China and is characterized by the subtropical monsoon climate with high temperatures in summer (average: 23.6 °C) and particularly cool temperatures in winter (average: 14.8 °C). High temperatures enhance the evaporation potential of CPs to the atmosphere leading to increases in air concentrations, thus in the passive air samples collected during the warm period. The ratios of MCCPs/SCCPs (M/S) in air also showed a seasonal variation with 0.7 ± 0.8 in winter and 0.5 ± 0.4 in summer.

The relative abundance of different CP homologue groups based on carbon atoms and chlorine atoms for air samples was presented in Figures 3, S2, and S3, Supporting Information, respectively. For SCCPs, the compositions in air samples changed obviously in different sampling sites with $\text{C}_{10-11}\text{Cl}_{6-7}$ being the dominant groups (Figures 3a and S2a, Supporting Information). Congeners with high number of carbon and/or chlorine atoms ($\text{C}_{12-13}\text{Cl}_{8-10}$) were enriched close to Dongguan City (e.g., site SS) compared to those in the rural areas of Huizhou City (e.g., site PT and HD). Higher chlorinated congeners with longer carbon chain have relatively lower volatility³⁹ and thus have lower transport potential than less chlorinated and shorter-chain congeners. The air SCCP homologue patterns in the present study were quite constant, characterized by C_{10} -CPs accounting for about 40% of the total SCCPs different from those of various commercial CP mixtures from Germany and England⁴⁰ and North America and UK,³⁵ as well as China.²³ A significant trend of decreasing vapor pressures with increased carbon-chain length and degree of chlorination has been observed for SCCPs.³⁹ Thus, besides the variation of homologue patterns due to the differences in the market formulations, the fractionation during the environmental processes may also change the CP patterns. Short-chain SCCPs are more easily emitted and transported than long-chain SCCPs and MCCPs; therefore, the likely elevated proportion of C_{10} -SCCP in the Chinese commercial CP mixtures and air samples may pose high environmental risk to remote areas in

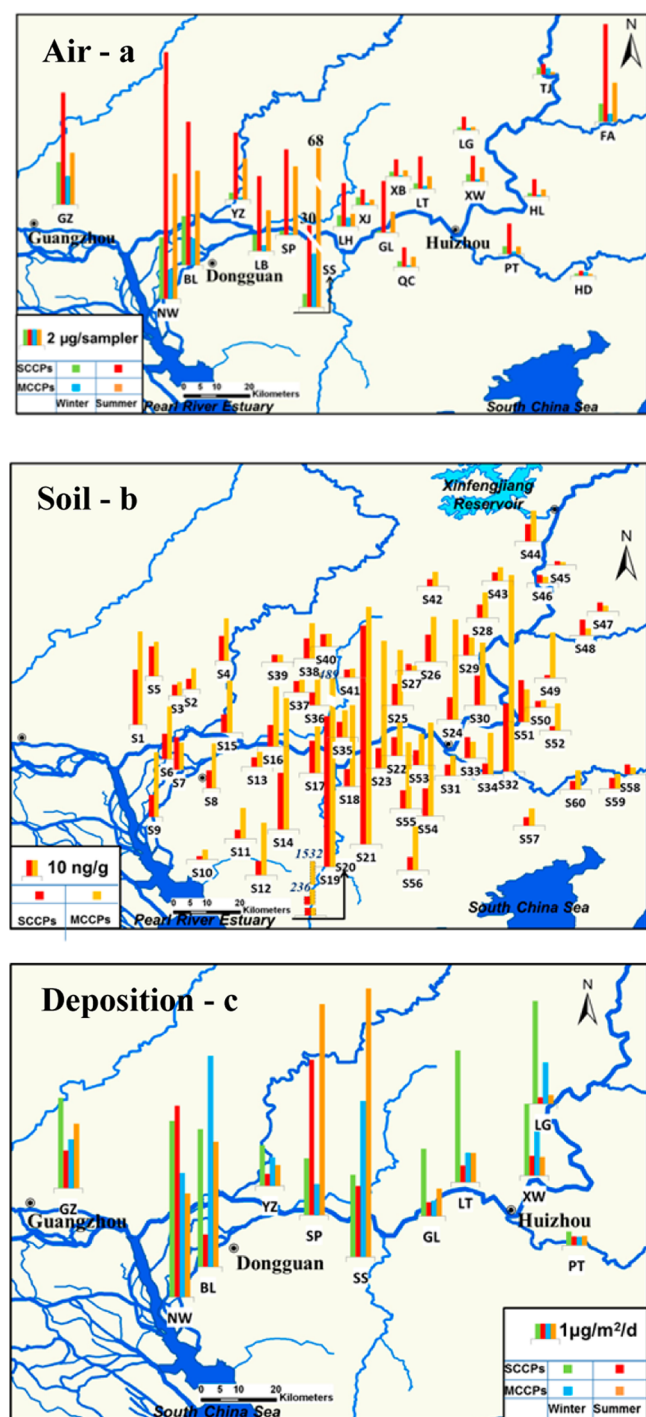


Figure 2. Distribution of concentrations of SCCPs and MCCPs in soil, air, and deposition samples.

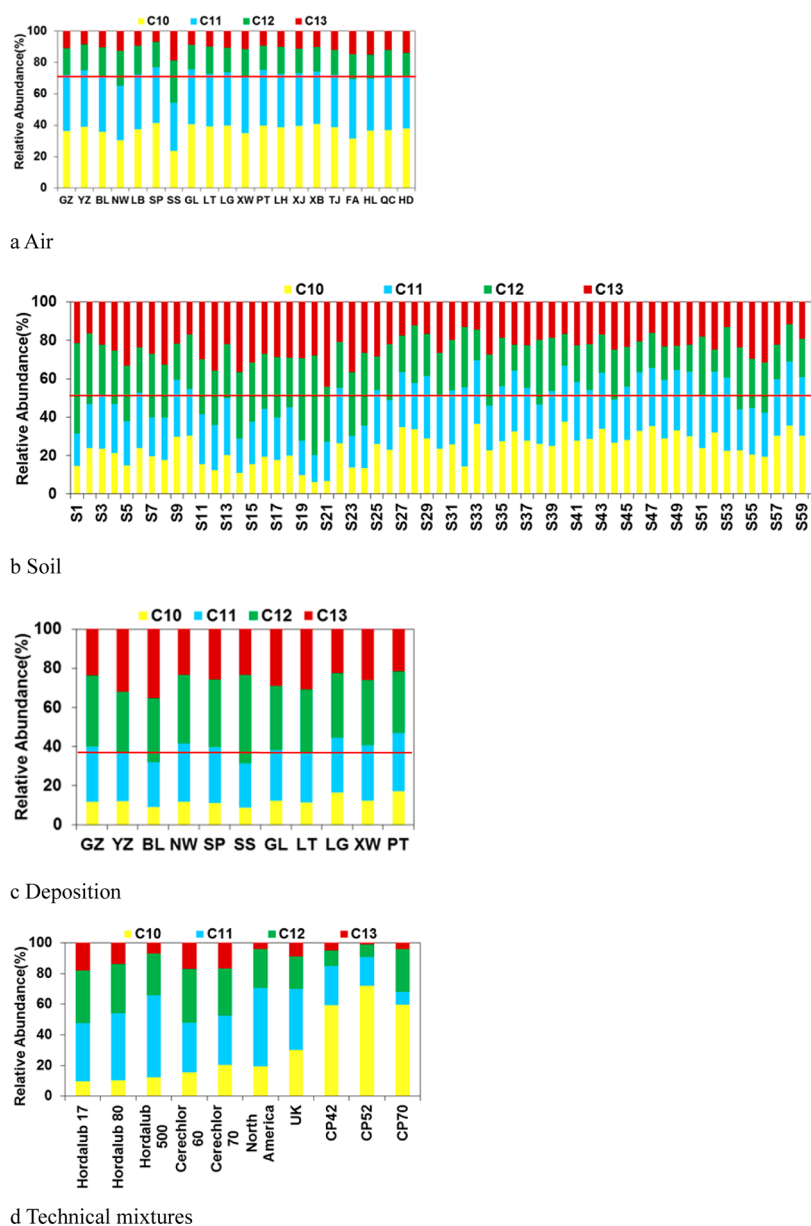


Figure 3. Site-specific composition profiles of SCCPs in air (a), soils (b), deposition (c), and technical mixtures (data from refs 23, 35, and 40) (d). (The red lines are the average abundance values for C_{10–11}. Hordalub mixtures were from Germany; cerechlor mixtures were from England, and CP mixtures were from China.)

China. For MCCPs, the patterns in the air looked almost identical at all sites with 14 carbons and 6–7 chlorines being the dominant congeners (Figure S3a, Supporting Information), consistent with other studies.^{33,40–42}

Concentrations of CPs in Soils. CP concentrations in soils ranged from 1.9 to 236 ng/g with an average of 18.3 ± 35.2 ng/g for SCCPs and from 2.1 to 1530 ng/g with an average of 59.3 ± 204 ng/g for MCCPs (Figure 2b). The M/S ratios in soils were 2.4 ± 2.1 with most ratios above 1 except for samples from rural areas (S47, 0.6; S48, 0.5; and S58, 0.7). The high M/S ratios also indicated a shift to the use of formulations containing more MCCPs in the PRD. Chen et al.¹⁵ also suggested a shift to more use of MCCPs in recent years. Wide spatial variation of CP concentrations revealed that the gradient decreasing trend of CPs from more to less industrialized areas was also found in soils (Figure 2b). Proximity to industrial point sources is the main reason for this spatial distribution.

Similarly to the air samples, most of the highly contaminated sites (e.g., S20, S19, and S21) were in the area of Dongguan City; contrarily, the less contaminated soils were in Huizhou City. Besides the influence of industrial sources, environmental conditions and soil parameters (e.g., land use type, soil texture, and organic matter content) may also influence the spatial variation of organic pollutants.²⁹ However, no significant correlation was observed between total organic carbon (TOC) and CP concentrations in soils (Supporting Information 2).

As presented in Figures 3b and S2b, Supporting Information, C_{10–12} Cl_{6–7} were the dominant groups in soil samples for SCCPs. Congeners with more carbon and/or chlorine atoms (C_{12–13} Cl_{8–10}) also exhibited higher concentrations in Dongguan (e.g., S19 and S20), compared to the rural areas in Huizhou (e.g., S58) for the relative lower volatility and less transport ability.³⁹ The SCCP homologue patterns in soils were

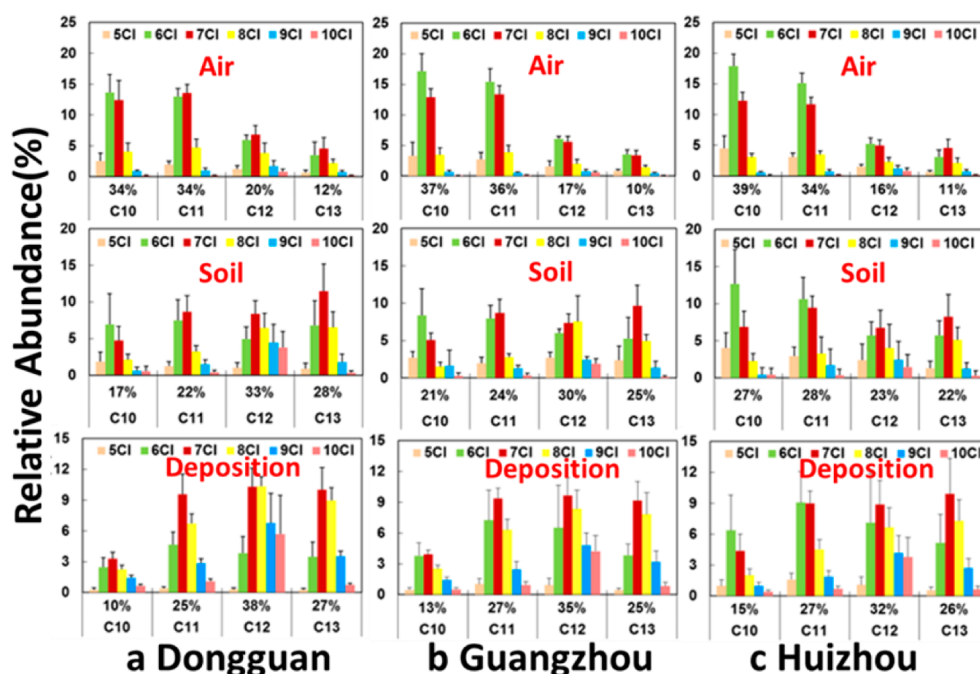


Figure 4. Congener group abundance profile of SCCPs based on the average values within the same cities.

different from those in the commercial CP mixtures;^{23,35,40} however, there were also substantial spatial differences observed. Figure 3b showed that C₁₀ had accounted for 10–40% and a similar variation was seen for C₁₃. If soil pollution was only due to atmospheric emissions and consequent deposition, then the profiles would probably present more similarities to the air samples. Instead, the difference between soil and air samples in respect to the SCCPs burden suggested that soil pollution in the studied areas may be a result of direct discharges from different sources. Contrarily, the MCCP profiles between air and soil samples show some similarities, with C₁₄ Cl_{6–8} being the most frequently detected congeners (Figure S3b, Supporting Information). Previous studies in China reported that CP concentrations in soils close to e-waste dismantling areas⁴³ and wastewater irrigated areas¹³ and in sediments from the PRD¹⁵ and Liaohe River²³ exhibited higher concentrations than the average concentrations in our present study but were comparable to the concentrations observed in heavily polluted sites.

Atmospheric Deposition Fluxes of CPs. The atmospheric deposition fluxes of SCCPs and MCCPs were in the range of 1.0–12.5 $\mu\text{g}/(\text{m}^2 \text{ d})$ and 0.6–15.2 $\mu\text{g}/(\text{m}^2 \text{ d})$ in winter and 0.5–13.6 $\mu\text{g}/(\text{m}^2 \text{ d})$ and 0.7–19.1 $\mu\text{g}/(\text{m}^2 \text{ d})$ in summer, respectively (Figure 2c). The M/S ratios in deposition samples were 0.7 ± 0.5 in winter and 1.8 ± 1.1 in summer. Similar to the spatial variation of air and soils, the atmospheric deposition flux of CPs also decreased from more industrialized to less industrialized areas (Figure 2c). Samples from Dongguan City (e.g., site NW and SS) showed higher CP fluxes than those from Huizhou City.

Atmospheric deposition of CPs also presented seasonal variation. However, the trends were different between the rural areas and source areas. For the rural areas like site LG and XW, deposition fluxes were mostly higher in winter than in summer, which was opposite to the trend observed for the passive air samples. Since high temperatures can enhance the volatilization of CPs resulting in decreased concentrations in the particle

phase, the lower deposition fluxes in summer suggest that the atmospheric deposition of CPs is mainly controlled by the CPs adsorbed on the particle phase. Moreover, the summer period that is characterized by heavy rains presented lower deposition fluxes suggesting that deposition process of CPs was mainly dominated by the dry deposition, which can be confirmed by the low solubility of CPs in water.⁴⁴ For the possible source areas (e.g., site NW, SP, SS, GL), the deposition rates were higher in summer, because the deposition flux may have been dominated by episodic incidences of releases to the environment from regional point sources rather than by temperature or other meteorological factor dependent transport processes.³⁶

The M/S ratios in deposition samples showed a strong seasonal signal, being higher in summer (except site NW, a possible SCCP source area). Since the deposition flux of CPs was considered to be dominated by the particle deposition, the higher temperatures probably increase the escapability of SCCPs from particle to the gaseous phase, resulting in higher MCCP deposition and consequently higher ratios.

As presented in Figures 3c, S2c, and S3c, Supporting Information, C_{11–12} Cl_{6–8} and C₁₄ Cl_{7–8} were the dominant groups in deposition samples for SCCPs and MCCPs, respectively. The composition of “heavy” congeners was higher in the possible source areas (SS) compared to the rural areas (PT). For the fractionation during the environment processes, the SCCP homologue patterns in the deposition samples were different from commercial CP mixtures as well.

To our knowledge, there is currently no other study to report atmospheric deposition fluxes of CPs. The surface deposition fluxes of SCCPs in the lake sediments with the flux of 0.001–0.402 $\mu\text{g}/(\text{m}^2 \text{ d})$ ⁴⁵ and 0.022–0.466 $\mu\text{g}/(\text{m}^2 \text{ d})$ ⁴⁶ were lower than those in the present study, since degradation processes may occur in the sediment.^{15,23}

Fate of CPs during Environment Processes. As a class of multiphase chemicals, the environmental fate of CPs is strongly influenced by the physicochemical properties of individual congeners. Light congeners (shorter carbon-chain

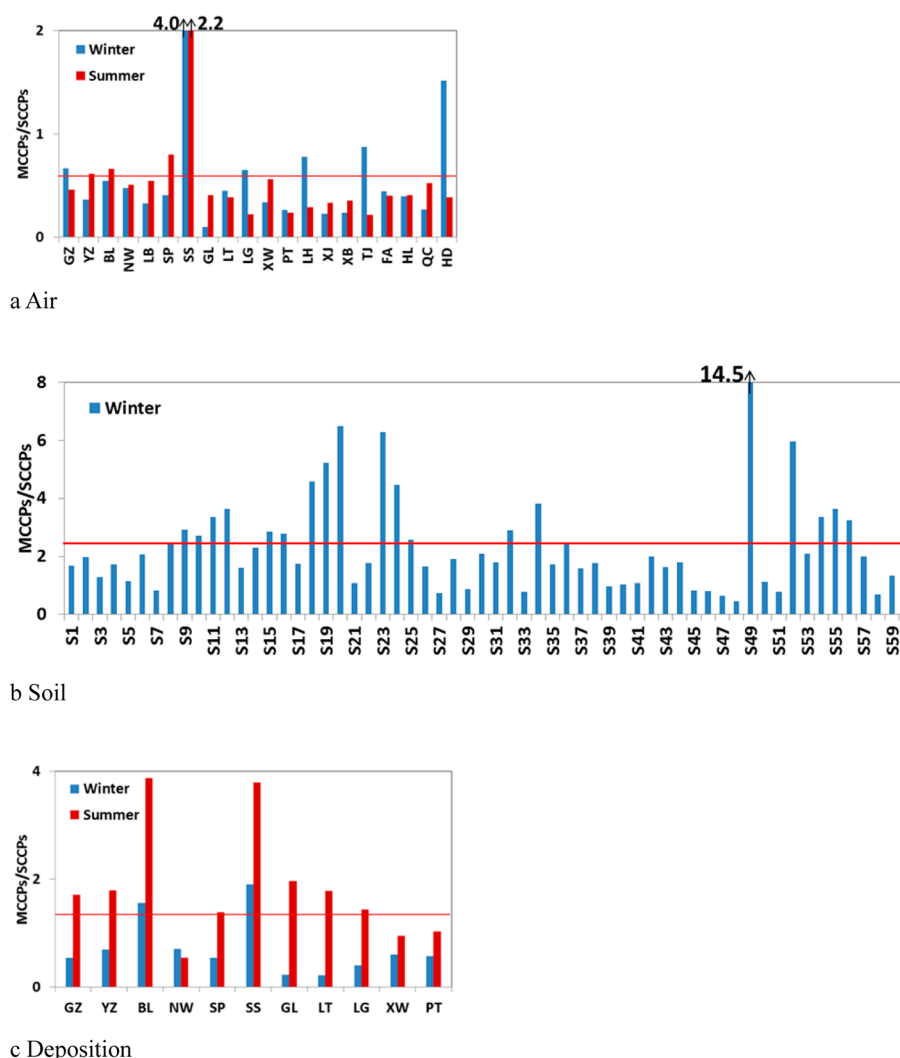


Figure 5. Spatial and seasonal distributions of ratios of MCCPs/SCCPs in air (a), soils (b), and deposition (c). (The red lines are the average values for MCCPs/SCCPs.)

and less chlorine atoms) with high volatility tend to be in the gaseous phase of air, while heavy congeners (longer-chain and higher chlorine atoms) with lower volatility tend to adsorb onto particles and can easily deposit to the surface soil. This theory is confirmed by the differences in the congener profiles in different matrixes found in the PRD (Figures 4 and S4, Supporting Information). Air samples showed a larger proportion of light congeners, while deposition samples had a higher percentage of heavy congeners. Soil samples are eclectic with comparable proportions of light and heavy congeners for soil acting as a reservoir for both particle and gaseous depositions. For MCCPs, though the profiles were almost identical, the compositions of light congeners were still higher in the air samples relative to soil and deposition samples (Figure S4, Supporting Information).

POPs can be fractionated during their transport toward sink areas (e.g., poles) because they migrate at different velocities.⁴⁷ Light congeners have stronger tendency to pass to the vapor phase and can undergo atmospheric transport by air masses, while heavier congeners, bound on particles, are more likely to deposit to adjacent areas. Therefore, atmospheric transport is an important pathway for the movement of light contaminants from sources to distant regions,⁴⁸ while atmospheric deposition

is the main process contributing to air-to-soil transport of heavy contaminants to regions in the proximity of sources.²⁰ A fractionation was also discovered for CP congeners in the PRD, especially for SCCPs, with a trend toward increasing levels of light congeners (e.g., C_{10–11} Cl_{5–6}) and decreasing levels of heavy congeners (e.g., C_{12–13} Cl_{7–10}) from the industrialized Dongguan and Guangzhou to the rural Huizhou City (based on the average abundance within the same city, Figures 4 and S4, Supporting Information). Besides the fractionation within the same category, fractionation was also observed between MCCPs and SCCPs during atmospheric transport. MCCPs tend to bind on particles and are harder to transport compared to SCCPs. It resulted in a higher ratio of M/S near the sources of MCCPs (e.g., S19, S20, S49, S52, and SS) and in a lower ratio in the rural area (e.g., S47, S48, S58, and PT) or close to SCCPs sources, like site NW (Figure 5). This hypothesis can be confirmed by the different CP concentrations in those areas (Figure 2) and the significant correlations between M/S and log₁₀MCCPs in three matrixes (Figure S5, Supporting Information). Therefore, the site-specific usage or the point sources of SCCPs and MCCPs can probably be reflected by the M/S ratio. Similar observation with “light” congeners enriched

in the low industrial activity areas was also obtained in the sediments from the PRD.¹⁵

Meanwhile, the differences in the congener profiles between samples and commercial mixtures (Figure S6, Supporting Information)^{15,23,35} also suggested that CPs released from industrial activities may undergo certain complex environmental processes (e.g., partition, dechlorination, fractionation, and degradation) before they reach different matrixes. Since CP toxicity is inversely related to the chain length with short-chain congeners being more toxic,^{49–51} light congeners may pose more risks to the remote regions, while heavy congeners remain in the regions close to the known sources, causing a long-term environmental impact.

Estimated Contributions of Gaseous and Particle Transport of CPs to Soils. Significant correlations were found between SCCP and MCCP concentrations as well as between SCCP and MCCP chlorine contents in three matrixes (Table S3, Supporting Information). Since commercial products of CPs in China are mixtures of both SCCPs and MCCPs, the significant correlations suggested that sources of SCCPs and MCCPs in the PRD may be similar: gaseous and particle transport from industrial activities. The CP composition is very complex with thousands of structural isomers, and it is very difficult to discover the contributions of atmospheric transport and deposition to the soil contamination for each CP congener. For such reason, the percentages of individual congener in air and deposition matrixes were employed to estimate the contributions of gaseous exchange (mainly related to air) and particle deposition (mainly related to deposition) to burden of CPs in the PRD soils. Assuming the transport was only controlled by exchange and deposition processes, the contributions can be calculated using the following equation:

$$k_a R_a + k_d R_d = R_s \quad (1)$$

where R_a , R_d , and R_s are proportions of individual CP congener to the total CPs in air, deposition, and soil, respectively, k_a is the contribution ratio of air contamination to soil burden for individual CP congener, k_d is the contribution ratio of deposition contamination to soil burden, and $k_d = 1 - k_a$ (assuming the transport was only controlled by air exchange and deposition). $k_a \gg 0.5$ implies that CP congeners in soils mainly originate from gaseous exchange from air, while $k_a \ll 0.5$ suggests that they are mostly from atmospheric deposition. The uncertainties of CP measurements in different media were all assumed to be 25%,²⁹ while the uncertainties of spatial variation for air, soil, and deposition were 15%, 15%, and 10%, respectively. Thus, the uncertainty of contribution ratio was 50%, suggesting both deposition and gaseous exchange contribute to the pollution in soil when k_a is close to 0.5 ± 0.25 .

The estimated contributions of air and atmospheric deposition to CP soil burden in different cities were presented in Tables S4 and S5 and Figure S7, Supporting Information. Both gaseous exchange and deposition contribute to the SCCPs in soils. Gas exchange from air may be the main transport pathway for light congeners to soil, while particle associated deposition may be the main pathway for heavy congeners. Spatially, the contribution of gaseous exchange was enriched in the rural area relative to the industrialized area. For MCCPs, the spatial trend was even obvious with deposition dominating in the highly industrialized Dongguan City and gaseous transport dominating in rural Huizhou City. Though degradation, revolatilization, and partition occurring for certain congeners in soil may more or less vary the composition

resulting in the uncertainty of contribution ratio, this result can still illustrate, to some extent, the roles of gaseous exchange and atmospheric particle deposition that play in CP transport.

■ ASSOCIATED CONTENT

§ Supporting Information

Detailed information for materials and methods, for TOC in soils; tables for isotopes of SCCP and MCCP congeners used for quantification and identification (Table S1), for the mixed standards of SCCPs and MCCPs (Table S2), and for estimated contributions of air and deposition to CP soil burden (Table S4, S5); figures for the dependence of the total response factor on the degree of chlorination for the mixed standards (Figure S1), for the site-specific composition profiles of SCCPs (Figure S2) and MCCPs (Figure S3), and for the congener group abundance profile of CP commercial mixtures (Figure S4) and MCCPs (Figure S5). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Santos, F. J.; Parera, J.; Galceran, M. T. Analysis of polychlorinated n-alkanes in environmental samples. *Anal. Bioanal. Chem.* **2006**, 386 (4), 837–857.
- (2) Bayen, S.; Obbard, J. P.; Thomas, G. O. Chlorinated paraffins: A review of analysis and environmental occurrence. *Environ. Int.* **2006**, 32 (7), 915–929.
- (3) Barber, J. L.; Sweetman, A. J.; Thomas, G. O.; Braekevelt, E.; Stern, G. A.; Jones, K. C. Spatial and temporal variability in air concentrations of short-chain (C_{10} – C_{13}) and medium-chain (C_{14} – C_{17}) chlorinated n-alkanes measured in the UK atmosphere. *Environ. Sci. Technol.* **2005**, 39 (12), 4407–4415.
- (4) Feo, M. L.; Eljarrat, E.; Barcelo, D. Occurrence, fate and analysis of polychlorinated n-alkanes in the environment. *Trends Anal. Chem.* **2009**, 28 (6), 778–791.
- (5) Poremski, H. J.; Wiandt, S.; Knacker, T. Chlorinated paraffins - a further POP to consider? *Organohalogen Compd.* **2001**, 52, 397–400.
- (6) Li, Q.; Li, J.; Wang, Y.; Xu, Y.; Pan, X.; Zhang, G.; Luo, C.; Kobara, Y.; Jae-Jak, N.; Jones, K. Atmospheric short-chain chlorinated paraffins in China, Japan, and South Korea. *Environ. Sci. Technol.* **2012**, 46 (21), 11948–11954.
- (7) OSPAR. *Background Document on Short Chain Chlorinated Paraffins*; OSPAR Commission: London, U.K., 2001.
- (8) Stern, G. A.; Tomy, G. An overview of the environmental levels and distribution of polychlorinated paraffins. *Organohalogen Compd.* **2000**, 47, 135–138.
- (9) Tomy, G. T.; Muir, D. C. G.; Stern, G. A.; Westmore, J. B. Levels of C_{10} – C_{13} polychloro-n-alkanes in marine mammals from the Arctic and the St. Lawrence River estuary. *Environ. Sci. Technol.* **2000**, 34 (9), 1615–1619.
- (10) Fisk, A. T.; Tomy, G. T.; Cymbalisty, C. D.; Muir, D. C. G. Dietary accumulation and quantitative structure-activity relationships

for depuration and biotransformation of short (C_{10}), medium (C_{14}), and long (C_{18}) carbon-chain polychlorinated alkanes by juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **2000**, *19* (6), 1508–1516.

(11) Muir, D.; Braekevelt, E.; Tomy, G.; Whittle, M. Medium chain chlorinated paraffins in Great Lakes food webs. *Organohalogen Compd.* **2003**, *64*, 166–169.

(12) Houde, M.; Muir, D. C. G.; Tomy, G. T.; Whittle, D. M.; Teixeira, C.; Moore, S. Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. *Environ. Sci. Technol.* **2008**, *42* (10), 3893–3899.

(13) Zeng, L.; Wang, T.; Han, W.; Yuan, B.; Liu, Q.; Wang, Y.; Jiang, G. Spatial and vertical distribution of short chain chlorinated paraffins in soils from wastewater irrigated farmlands. *Environ. Sci. Technol.* **2011**, *45* (6), 2100–2106.

(14) Castells, P.; Parera, J.; Santos, F. J.; Galceran, M. T. Occurrence of polychlorinated naphthalenes, polychlorinated biphenyls and short-chain chlorinated paraffins in marine sediments from Barcelona (Spain). *Chemosphere* **2008**, *70* (9), 1552–1562.

(15) Chen, M. Y.; Luo, X. J.; Zhang, X. L.; He, M. J.; Chen, S. J.; Mai, B. X. Chlorinated paraffins in sediments from the Pearl River Delta, South China: Spatial and temporal distributions and implication for processes. *Environ. Sci. Technol.* **2011**, *45* (23), 9936–9943.

(16) Koh, I. O.; Wolfgang, R. B.; Thiemann, W. H. P. Analysis of chlorinated paraffins in cutting fluids and sealing materials by carbon skeleton reaction gas chromatography. *Chemosphere* **2002**, *47* (2), 219–227.

(17) Friden, U. E.; McLachlan, M. S.; Berger, U. Chlorinated paraffins in indoor air and dust: Concentrations, congener patterns, and human exposure. *Environ. Int.* **2011**, *37* (7), 1169–1174.

(18) Harada, K. H.; Takasuga, T.; Hitomi, T.; Wang, P.; Matsukami, H.; Koizumi, A. Dietary exposure to short-chain chlorinated paraffins has increased in Beijing, China. *Environ. Sci. Technol.* **2011**, *45* (16), 7019–7027.

(19) Lead, W. A.; Steinnes, E.; Jones, K. C. Atmospheric deposition of PCBs to moss (*Hylocomium splendens*) in Norway between 1977 and 1990. *Environ. Sci. Technol.* **1996**, *30* (2), 524–530.

(20) Cousins, I. T.; Beck, A. J.; Jones, K. C. A review of the processes involved in the exchange of semi-volatile organic compounds (SVOC) across the air-soil interface. *Sci. Total Environ.* **1999**, *228* (1), 5–24.

(21) Harner, T.; Mackay, D.; Jones, K. C. Model of the long-term exchange of PCBs between soil and the atmosphere in the southern UK. *Environ. Sci. Technol.* **1995**, *29* (5), 1200–1209.

(22) Gigliotti, C. L.; Totten, L. A.; Offenberg, J. H.; Dachs, J.; Reinfelder, J. R.; Nelson, E. D.; Glenn, T. R.; Eisenreich, S. J. Atmospheric concentrations and deposition of polycyclic aromatic hydrocarbons to the Mid-Atlantic East Coast Region. *Environ. Sci. Technol.* **2005**, *39* (15), 5550–5559.

(23) Gao, Y.; Zhang, H.; Su, F.; Tian, Y.; Chen, J. Environmental occurrence and distribution of short chain chlorinated paraffins in sediments and soils from the Liaohai River basin, P. R. China. *Environ. Sci. Technol.* **2012**, *46* (7), 3771–3778.

(24) Zeng, L. X.; Wang, T.; Wang, P.; Liu, Q.; Han, S. L.; Yuan, B.; Zhu, N. L.; Wang, Y. W.; Jiang, G. B. Distribution and trophic transfer of short-chain chlorinated paraffins in an aquatic ecosystem receiving effluents from a sewage treatment plant. *Environ. Sci. Technol.* **2011**, *45*, 5529–5535.

(25) De Boer, J.; El-Sayed Ali, T.; Fiedler, H.; Legler, J.; Muir, D. C.; Nikiforov, V. A.; Tomy, G. T.; Tsunemi, K. Chlorinated Paraffins. In *The Handbook of Environmental Chemistry*; Springer-Verlag Berlin: Berlin/Heidelberg, 2010; Vol. 10.

(26) Li, J.; Zhang, G.; Guo, L.; Xu, W.; Li, X.; Lee, C. S. L.; Ding, A.; Wang, T. Organochlorine pesticides in the atmosphere of Guangzhou and Hong Kong: Regional sources and long-range atmospheric transport. *Atmos. Environ.* **2007**, *41* (18), 3889–3903.

(27) Lang, C.; Tao, S.; Zhang, G.; Fu, J.; Simonich, S. Outflow of polycyclic aromatic hydrocarbons from Guangdong, Southern China. *Environ. Sci. Technol.* **2007**, *41* (24), 8370–8375.

(28) Wang, Y.; Li, Q.; Xu, Y.; Luo, C.; Liu, X.; Li, J.; Zhang, G. Improved correction method for using passive air samplers to assess the distribution of PCNs in Dongjiang River basin of the Pearl River Delta, South China. *Atmos. Environ.* **2012**, *54*, 700–705.

(29) Wang, Y.; Cheng, Z.; Li, J.; Luo, C.; Xu, Y.; Li, Q.; Liu, X.; Zhang, G. Polychlorinated naphthalenes (PCNs) in the surface soils of the Pearl River Delta, South China: Distribution, sources, and air-soil exchange. *Environ. Pollut.* **2012**, *170*, 1–7.

(30) Wang, Y.; Li, J.; Liu, X.; Cheng, Z.; Zhang, R.; Zhang, G. Atmospheric deposition of polychlorinated naphthalenes in Dongjiang River basin of Guangdong province. *Chin. J. Environ. Sci.* **2012**, *33* (1), 20–25.

(31) Reth, M.; Zencak, Z.; Oehme, M. New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. *J. Chromatogr., A* **2005**, *1081* (2), 225–231.

(32) Reth, M.; Oehme, M. Limitations of low resolution mass spectrometry in the electron capture negative ionization mode for the analysis of short- and medium-chain chlorinated paraffins. *Anal. Bioanal. Chem.* **2004**, *378* (7), 1741–1747.

(33) Iozza, S.; Muller, C. E.; Schmid, P.; Bogdal, C.; Oehme, M. Historical profiles of chlorinated paraffins and polychlorinated biphenyls in a dated sediment core from Lake Thun (Switzerland). *Environ. Sci. Technol.* **2008**, *42* (4), 1045–1050.

(34) Tomy, G. T. The mass spectrometric characterization of polychlorinated n-alkanes and the methodology for their analysis in the environment, Ph.D. Dissertation, University of Manitoba, Canada, 1997.

(35) Peters, A. J.; Tomy, G. T.; Stern, G. A.; Jones, K. C. Polychlorinated alkanes in the atmosphere of the United Kingdom and Canada - Analytical methodology and evidence of the potential for long-range transport. *Organohalogen Compd.* **1998**, *35*, 439–442.

(36) Peters, A. J.; Tomy, G. T.; Jones, K. C.; Coleman, P.; Stern, G. A. Occurrence of C_{10} - C_{13} polychlorinated n-alkanes in the atmosphere of the United Kingdom. *Atmos. Environ.* **2000**, *34* (19), 3085–3090.

(37) Borgen, A. R.; Schlabach, M.; Gundersen, H. Polychlorinated alkanes in Arctic air. *Organohalogen Compd.* **2000**, *47*, 272–274.

(38) Borgen, A. R.; Schlabach, M.; Kallenborn, R.; Christensen, G.; Skotvold, T. Polychlorinated alkanes in ambient air from Bear Island. *Organohalogen Compd.* **2002**, *59*, 303–306.

(39) Drouillard, K. G.; Tomy, G. T.; Muir, D. C. G.; Friesen, K. J. Volatility of chlorinated n-alkanes (C_{10} - C_{12}): Vapor pressures and Henry's law constants. *Environ. Toxicol. Chem.* **1998**, *17* (7), 1252–1260.

(40) Reth, M.; Ciric, A.; Christensen, G. N.; Heimstad, E. S.; Oehme, M. Short- and medium-chain chlorinated paraffins in biota from the European Arctic - Differences in homologue group patterns. *Sci. Total Environ.* **2006**, *367* (1), 252–260.

(41) Tomy, G. T.; Stern, G. A. Analysis of C_{14} - C_{17} polychloro-n-alkanes in environmental matrixes by accelerated solvent extraction-high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry. *Anal. Chem.* **1999**, *71* (21), 4860–4865.

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

(43) Yuan, B.; Wang, Y. W.; Fu, J. J.; Jiang, G. B. Evaluation of the pollution levels of short chain chlorinated paraffins in soil collected from an e-waste dismantling area in China. *Organohalogen Compd.* **2009**, *71*, 3079–3081.

(44) Drouillard, K. G.; Hiebert, T.; Tran, P.; Tomy, G. T.; Muir, D. C. G.; Friesen, K. J. Estimating the aqueous solubilities of individual chlorinated n-alkanes (C_{10} - C_{12}) from measurements of chlorinated alkane mixtures. *Environ. Toxicol. Chem.* **1998**, *17* (7), 1261–1267.

(45) Tomy, G. T.; Stern, G. A.; Lockhart, W. L.; Muir, D. C. G. Occurrence of C_{10} - C_{13} polychlorinated n-alkanes in Canadian midlatitude and arctic lake sediments. *Environ. Sci. Technol.* **1999**, *33* (17), 2858–2863.

- (46) Marvin, C. H.; Painter, S.; Tomy, G. T.; Stern, G. A.; Braekevelt, E.; Muir, D. C. G. Spatial and temporal trends in short-chain chlorinated paraffins in Lake Ontario sediments. *Environ. Sci. Technol.* **2003**, *37* (20), 4561–4568.
- (47) Wania, F.; Mackay, D. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio* **1993**, *22* (1), 10–18.
- (48) Harner, T.; Bidleman, T. F. Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. *Environ. Sci. Technol.* **1998**, *32* (10), 1494–1502.
- (49) Madeley, J. R.; Birtley, R. D. N. Chlorinated paraffins and the environment. 2. Aquatic and avian toxicology. *Environ. Sci. Technol.* **1980**, *14* (10), 1215–1221.
- (50) Cooley, H. M.; Fisk, A. T.; Wiens, S. C.; Tomy, G. T.; Evans, R. E.; Muir, D. C. G. Examination of the behavior and liver and thyroid histology of juvenile rainbow trout (*Oncorhynchus mykiss*) exposed to high dietary concentrations of C₁₀-, C₁₁-, C₁₂- and C₁₄-polychlorinated n-alkanes. *Aquat. Toxicol.* **2001**, *54* (1–2), 81–99.
- (51) Ali, T. E.-S.; Legler, J. Overview of the Mammalian and Environmental Toxicity of Chlorinated Paraffins. In *Chlorinated Paraffins*; Boer, J., Ed.; Springer: Berlin, Heidelberg: 2010; pp 135–154.