# Atmospheric Short-Chain Chlorinated Paraffins in China, Japan, and South Korea

Qilu Li,[†] Jun Li,*[,†] Yan Wang,[†] Yue Xu,[†] Xiaohui Pan,[‡] Gan Zhang,[†] Chunling Luo,[†] Yuso Kobara,[§] Jae-Jak Nam,[∥] and Kevin C. Jones[†,⊥]

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

[‡]Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

[§]National Institute for Agro-Environmental Sciences, Tsukuba, Ibaraki 305-8604, Japan

[∥]Certification and Business Team, Foundation of Ag. Tech Commercialization and Transfer (FACT), 211-2 Seodun-dong Gwonseon-gu, Suwon 441-857, Republic of Korea

[⊥]Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, U.K.

**S** *Supporting Information*

**ABSTRACT:** This study presents the first investigation of concentrations and congener group patterns of atmospheric short-chain chlorinated paraffins (SCCPs) throughout East Asia. Based on an absorption rate calibration experiment, a spatial survey of SCCPs was performed using passive air samplers in China, Japan, and South Korea during two separate periods in 2008. The atmospheric concentrations of SCCPs in China were clearly greater than those in Japan and South Korea, both of which exceed the levels determined for other regions of the world. $C_{10}$ components were the most abundant type of SCCPs in China, whereas $C_{11}$ components were dominant in Japan and South Korea. With respect to the total chlorine content, $Cl_6$ and $Cl_5$ were the predominant compounds in China and Japan; however, $Cl_6$ and $Cl_7$ were predominant in South Korea. A similar pattern was also found for remote sites within China, Japan, and South Korea, respectively. Together with the back-trajectories calculated for the remote sites, the results indicate that the SCCPs in the air of East Asia were mainly influenced by local sources due to their relatively low long-range atmospheric transport potential compared to other POPs.
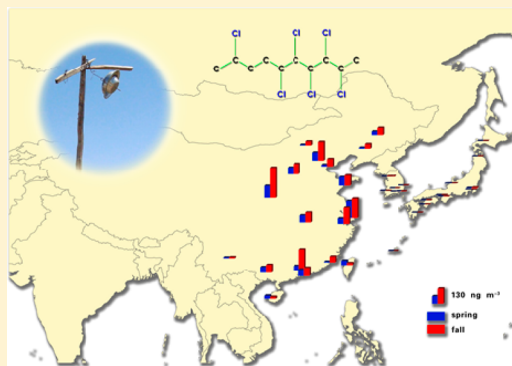
## INTRODUCTION

Chlorinated paraffins (CPs) are chlorinated derivatives of n-alkanes and include complex mixtures of homologues and isomers. CPs can be classified as short-chain chlorinated paraffins (SCCPs, $C_{10}$–$C_{13}$), medium-chain chlorinated paraffins (MCCPs, $C_{14}$–$C_{17}$), or long-chain chlorinated paraffins (LCCPs, $C > 17$) according to their carbon chain length[1] and have been manufactured as lubricants and metal cutting fluids (71% of the total use), flame retardants in the rubber industry (10%), paints (9%), sealing materials (5%), and for other uses (5% leather and textiles) since the 1930s.[2] The annual worldwide production of CPs is on the order of hundreds of thousands of tons. As a result, CPs have been routinely detected in various environmental matrices such as air, aquatic systems, soils, sediments, and biota.[3-10] SCCPs have drawn concern in the past decade due to their persistence, their higher level of toxicity, and their greatest potential for long-range atmospheric transport (higher vapor pressure) relative to other CP mixtures.[11] SCCPs have also been reviewed as a candidate POP by the Stockholm Convention

in 2009. However, studies of atmospheric SCCPs have been limited to Europe, North America, and the Arctic.[3,12,13]

East Asia is one of the most prosperous areas of the world. However, rapid economic development and industrialization in this region have resulted in a series of environmental problems. Several studies conducted in this region have focused on classically studied persistent organic chemicals, such as PAHs, OCPs, PCBs, and PBDEs,[14-16] suggesting that East Asia has become one of hot spots of global POPs pollution.[17] Although East Asia, and China in particular, is the largest producer and consumer of SCCPs in the world,[18] there have been relatively few studies of SCCPs in the environment in this region. Recently, a small number of studies have reported the distributions of SCCPs in a wastewater treatment plant [19] as well as sediments and soil[8,20-22] and have examined dietary exposure to humans.[23] However, these studies were confined to

the meso- and microscale. Prior to this present study, research has not been performed to investigate the large-scale distribution of atmospheric SCCPs in the region.

Regional atmospheric observations are an important means to confirm regional sources of POPs, elucidate atmospheric transport processes and understand spatial and temporal trends. Atmospheric observations can be accomplished using active air samplers (AAS) or passive air samplers (PAS). The latter method has the advantage that large scale spatial surveys can be conducted economically and conveniently. This study was conducted as part of a passive air sampling program in Asia. Our group deployed a previously tested and commonly used design that uses polyurethane foam (PUF) disk passive sampling devices adapted for a range of persistent organic pollutants (POPs).[14] The primary objective of this study was to provide an overview of the levels, delineate the spatial distribution, and identify congener group profiles of SCCPs in key regions of East Asia (i.e., China, Japan, and South Korea). This study also sought to explore the differences in these parameters and the possible explanations for the observed trends in the survey data that occur among the three countries.

## ■ MATERIALS AND METHODS

**Air Sampling.** During August to October, 2008, the PUF disk samplers were deployed in a total of 37 urban and rural locations in China, Japan, and South Korea. Two separate deployments of ∼60 days were performed in 2008: spring (March to May) and fall (August to October). The samplers used in this study have been previously described.[14] Disks were precleaned by extraction with dichloromethane (DCM) and acetone (ACE) for 48 h at the Guangzhou Institute of Geochemistry and then transferred to the sampling locations in sealed, solvent-cleaned aluminum foil.

In China, a total of 18 samplers were successfully deployed in 16 urban and 2 rural sites; 12 samplers were deployed in Japan (10 urban and 2 rural), and 7 were deployed in South Korea (5 urban and 2 rural) (see Table S1). In the urban areas, the samplers were deployed in open areas 3 m above the ground. In the rural areas, the sampling sites were distant from local human activities or significant pollution sources. After the sampling events, the PUF disks were retrieved, resealed in their original solvent-cleaned aluminum foil at the sampling locations, returned to the laboratory, and stored at −20 °C until extraction.

**Sample Extraction and Purification.** Prior to Soxhlet extraction of the PUF disks with DCM for 24 h, $^{13}C_{10}$-trans-chlordane was added as a recovery standard. Activated copper was used to remove elemental sulfur. The extract was then concentrated and solvent-exchanged into hexane and cleaned on an 8 mm i.d. column packed with 50% sulfuric acid silica (6 cm) and anhydrous sodium sulfate from bottom to top. The 20 mL eluate was reduced to 0.5 mL under a gentle nitrogen stream and purified on an 8 mm i.d. alumina/silica column packed, from bottom to top, with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), and anhydrous sodium sulfate. Finally, the volume was reduced to 200 μL under a gentle nitrogen stream and solvent exchanged into 35 μL of iso-octane containing $^{13}C_8$-mirex as an internal standard.

**Rates of Passive Air Sampling of SCCPs.** Because studies on passive air sampling of atmospheric SCCPs are scarce, a calibration experiment of absorption rates was conducted to obtain the rate of SCCP uptake. The experiment was conducted on the roof of a library building, Guangzhou Institute of Geochemistry, Guangzhou. There were no impedimental buildings to influence air flow to the samplers and no obvious target emission source in the vicinity.

Based on the passive sampling theory of linear uptake (eq 1), the experiment was divided into two parts. (1) Passive air sampling. A total of ten groups of PASs were employed from August to November, 2008 (90 d), and each group included three parallel samplers. Each group of samplers was collected on the 5th, 10th, 15th, 20th, 30th, 40th, 50th, 60th, 75th, and 90th day. (2) Active air sampling. One active air sampler was operated simultaneously. Each sample was collected for 16 h d$^{-1}$ for 5 consecutive days (the sampling volume was approximately 300 m$^3$). The following equation was used

$$R_{PUF} = \frac{N_{PUF}}{C_A t} \tag{1}$$

where $R_{PUF}$ is the absorption rate of PUF disk, $N_{PUF}$ is the cumulative mass (ng sampler$^{-1}$), $C_A$ is the atmospheric concentration of SCCPs (ng m$^{-3}$), and $t$ is the passive sampling time (days). Finally, a series of sampling rates for different periods were calculated, and the average value was calculated as the mean absorption rate over 90 days.

Prior to sampling, the PUF disks were precleaned by extraction with DCM and ACE for 48 h. The glass fiber filters (GFF) (GF/A, 20.3 cm × 25.4 cm, Whatman) were baked at 450 °C for 12 h to remove any organic contaminants. After sampling, the PUF disks and GFFs were sealed in aluminum foil and stored in freezers (−20 °C) until analysis.

**Instrumental Analysis.** SCCPs ($C_{10}$–$C_{13}$ with $Cl_5$–$Cl_{10}$) were analyzed simultaneously by gas chromatography electron capture negative-ion low resolution mass spectrometry (GC-ECNI-LRMS) using a DB-5MS column (30 m length × 0.25 mm i.d., 0.25 μm film thickness). Methane and helium were used as the reagent and carrier gases, respectively, with constant flow rate of 1.0 mL min$^{-1}$. Sample volumes of 2 μL were injected in splitless mode with an injector temperature of 280 °C. The initial oven temperature was set at 120 °C for 1 min, was then increased by 15 °C min$^{-1}$ to 290 °C, and held for 15 min. The MSD and quadrupole temperatures were 200 and 150 °C, respectively. The two most abundant isotopes of the [M-Cl]$^-$ ions of SCCP congeners were monitored in a selected ion monitoring (SIM) mode (dwell time of 30 ms per ion). To improve the instrument sensitivity, all monitored ions of SCCPs were divided into two groups: $C_{10}$–$C_{12}$ and $C_{11}$–$C_{13}$. Therefore, two individual injections were executed for each sample.

**Identification and Quantification Method.** Because SCCPs contain thousands of homologues and possess similar mass spectrometric fragments, the analysis of complex mixtures SCCPs may be complicated by mass overlap when using LRMS. An improved quantification procedure, based on a linear correlation between the total response factors of SCCP standard mixtures and their chlorine contents, was described by Reth et al.[24] This method compensates for the differences in the response factors between the reference SCCP mixtures and the SCCP pattern present in environmental samples.

In this study, three SCCP (51.5, 55.5, and 63%Cl) mixtures from Dr. Ehrenstorfer GmbH were used to establish a reasonably linear correlation between the chlorine content and the total response factor. The identification of the SCCP congener groups was performed by comparing the retention

11949

dx.doi.org/10.1021/es302321n | Environ. Sci. Technol. 2012, 46, 11948−11954

**Table 1. Summary of Measured SCCP Concentrations (ng m⁻³) in East Asia and Other Regions**

| | min | max | mean | sd | median | sampling type | detection method | reference |
|---|---|---|---|---|---|---|---|---|
| East Asia (2008) | 0.28 | 517 | 67.6 | 104 | 11.2 | PAS, PUF disk | ECNI/GCMS | this study |
| China (2008) | 13.5 | 517 | 137 | 114 | 116 | PAS, PUF disk | ECNI/GCMS | this study |
| Japan (2008) | 0.28 | 14.2 | 2.26 | 3.06 | 1.19 | PAS, PUF disk | ECNI/GCMS | this study |
| South Korea (2008) | 0.60 | 8.96 | 2.06 | 2.36 | 1.12 | PAS, PUF disk | ECNI/GCMS | this study |
| Canada, Egbert (1990) | 0.065 | 0.924 | 0.543 | - | - | Hi-Vol, GFF+PUF | ECNI/HRMS | [1] |
| Canada, Alert (1992) | <0.001 | 0.0085 | - | - | - | Hi-Vol, GFF+PUF | ECNI/HRMS | [35] |
| Canada, Alert (1994−1995) | 0.00107 | 0.00725 | - | - | - | - | - | [36] |
| UK, Lancaster (1997) | 0.0054 | 1.085 | 0.320 | 0.320 | - | Hi-Vol, GFF+PUF | ECNI/HRMS | [27] |
| UK, Lancaster (1997−1998) | - | - | 0.099 | 0.101 | - | - | - | [3] |
| Norway, Svalbard (1999) | 0.009 | 0.057 | - | - | - | Hi-Vol, GFF+PUF | ECNI/HRMS | [13] |
| Ontario Lake (1999) | - | - | 0.249 | - | - | - | - | [26] |
| Bear Island (2000) | 1.8 | 10.6 | | - | - | Hi-Vol, GFF+PUF | ECNI/HRMS | [37] |
| UK, Lancaster (2003) | <0.185 | 3.430 | 1.130 | - | - | Hi-Vol, GFF+PUF | ECNI/HRMS | [4] |
| UK[a] (2003) | 220 | 9100 | 1600 | - | - | PAS, PUF disk | ECNI/HRMS | [4] |
| China, East River (2010) | 4.4 | 129 | 31.4 | 28.3 | 20.0 | PAS, PUF disk | ECNI/HRMS | [38] |

[a]ng sample⁻¹.

time, signal shape, and correcting isotope ratio. The congener group abundance profiles were obtained by correcting the relative integrated signals for the isotopic abundance and response factors. The calculated chlorine contents were approximately 58.1−62.2% for the SCCPs.

**Quality Assurance and Quality Control.** Field and method blanks consisted of pre-extracted PUF disks that were extracted and analyzed in the same manner as the samples. Three samples spiked with 5 $\mu$g of SCCP standards and 10 ng of $^{13}C_{10}$-trans-chlordane were simultaneously analyzed. The method detection limit (MDL) was defined as the mean of the blanks plus 3 times the standard deviation and was estimated to be 0.18 ng m⁻³ for SCCPs. The recoveries of SCCP and $^{13}C$-trans-chlordane standards from spiked samples were in the range of 83.2−95.7% and 79.5−92.8%, respectively. The recoveries of $^{13}C$-trans-chlordane from all of the atmospheric samples were 71.6−103%. The quantitative results were corrected using the blanks but not the surrogate recoveries. Similarly, to ensure the reliability of the passive air sampling rate experiments, a field blank of passive and active break through were deployed. The active air sampler was continuously calibrated using a flow calibration system during the entire period.

## RESULTS AND DISCUSSION

**Absorption Rate of Passive Air Sampling.** In the present study, the SCCP absorption rate was 4.2 m³ d⁻¹ based on the aforementioned PUF calibration experiment. Active air sampling (AAS) events were used to calibrate the absorption rate of the PAS. The mean particle fraction of total SCCP was 14.6%. It was relatively higher than that reported by Wang et al.[25] during July in Beijing, China (6%) and by Barber et al.[4] observed from April to May, 2003 in Northern England (9%). The details of the discussions were given in the Supporting Information (SI). As shown in Figure S1, the SCCP contents of the PUF disks used for passive air sampling showed a linear increase over time, thereby indicating that SCCP absorption did not saturate the PUF disks during the sampling period. Therefore, the PUF concentrations can be used to calculate the uptake rate. In addition, the absorption rate showed a slight fluctuation that was affected by the instantaneous levels of SCCPs in the ambient atmosphere (Figure S1). In summary, it

was necessary to obtain the apparent absorption rate by averaging the sampling rates of each specified time interval.

Compared to the only known study of the air-sampling rate of SCCPs using PAS,[4] which reported a value of 17 m³ d⁻¹, there was a considerable difference between the results, even though both data sets were calibrated using active air sampler. This discrepancy may have been caused by the following three factors. First, the selected concentrations used for the calibrations based on active air sampling were different in the two studies. Barber et al.[4] only selected the mean concentrations from the initial period as the mean concentrations of the entire absorption phase. In contrast, our study chose to use the average values of the entire sampling period, which were much closer to the true atmospheric concentrations. Secondly, the concentration of SCCPs in air reported by Barber et al. was most likely affected by a point source during the sampling period, which may augment the absorption capacity of the PUF and increase the uptake rate. Finally, SCCPs tend to adsorb onto the particle phase. However, the previous study only applied a concentration of the SCCPs in the gas phase to calculate the absorption rate, which also contributed to the higher absorption rate of SCCPs.

**Concentrations and Composition.** The total concentrations of SCCPs in the atmosphere ranged from 0.28 to 517 ng m⁻³ based on the SCCP adsorption rate (4.2 m³ d⁻¹), which was obtained according to the aforementioned PUF calibration studies. Table 1 presents a summary of the data derived from the present experiments and previous studies throughout the world. Further details on each sampling site and the duration of the two seasons are available in the SI (Table S1). The concentrations ranged from 13.5 to 517, 0.28−14.2, and 0.60−8.96 ng m⁻³ in China, Japan, and South Korea, respectively. The level of SCCPs in China was the highest of those three countries of East Asia. There was no significant difference between the results from Japan and South Korea. [18] Table 1 also shows a comparison of our research with previous studies on atmospheric SCCPs; it can be inferred that the atmospheric levels of SCCPs in East Asia clearly exceed those of Europe and North America.

The chemical distribution patterns in the study area and three individual countries are shown in Figure 1. Overall, the composition of the carbon chains were dominated by $C_{11}$ and $C_{10}$, accounting for 38.2% ± 5.48% and 35.6% ± 10.3% of the
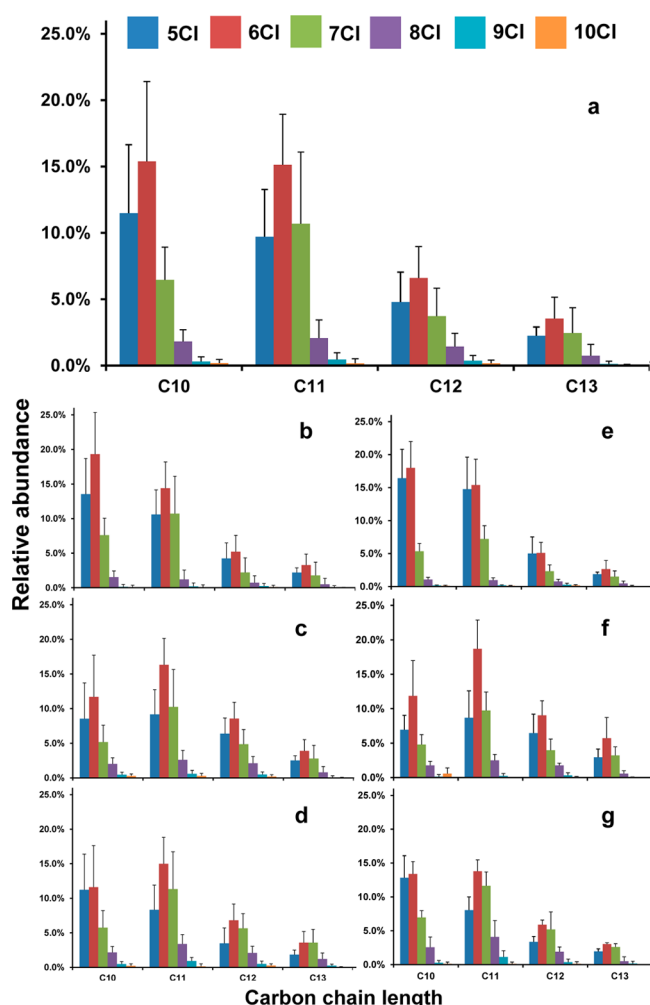
**Figure 1.** Average proportions of SCCP congener group profiles throughout East Asia. a, East Asia; b, all samples from China; c, all samples from Japan; d, all samples from South Korea; e, two rural sites in China; f, two rural sites in Japan; g, two rural sites in South Korea.

total, respectively. The percentages of $C_{11}$ in the samples from China, Japan, and South Korea were consistently high (37.2% ± 6.64%, 39.2% ± 4.21%, and 39.2% ± 3.58%, respectively), although the relatively elevated $C_{10}$ proportion can be attributed to the high percentages of $C_{10}$ in samples from China (42.2% ± 8.98%). $C_{10}$ components were the major contributors to the SCCPs in the atmosphere of China (Figure 1b). The predominance of $C_{10}$ components was consistent with the SCCP congener group profiles of the three major industrial CP products manufactured in China (i.e., CP-42, CP-52, and CP-70).[21] The predominant homologue group in all samples from Japan and South Korea was $C_{11}$ (Figure 1c and d). Regarding the chlorine content, the dominant number of chlorine atoms are $Cl_6$ and $Cl_5$, accounting for 40.7% ± 5.56% and 28.2% ± 8.05% of the total, respectively. It is worth mentioning that $Cl_6$ and $Cl_7$ were the dominant groups in South Korea, although $Cl_6$ and $Cl_5$ were the dominant groups in China and Japan. The composition in Japan and South Korea was similar with that at Ontario Lake, Canada,[26] but significantly different with a report for Lancaster, UK,[27] where $C_{12}$ was dominant. One obvious explanation is that the differences in the national homologue patterns reflect the commercially produced SCCP mixtures of each country.

**Spatial Distribution and Seasonal Variations.** The spatial distribution of SCCPs concentrations in air throughout East Asia are shown in Figures 2 and 3. As expected, there is a concentration decline from urban to rural areas. On average, the atmospheric concentration of SCCPs in China was much higher than those in Japan and South Korea. The highest total concentration of atmospheric SCCPs occurred in Xi'an (CNU8) in the fall, whereas the lowest value was detected in the fall samples from Gifu (JAU6).

In China, the concentrations of SCCPs at the sites located in the Southeast Coastal region (CNU3 Beijing, CNU11 Shanghai, CNU12 Hangzhou, and CNU16 Guangzhou) and individual heavy industry sites in the Midwest (such as CNU8 Xi'an) were clearly higher than at other sites. This result is consistent with the regional distribution of SCCP production[28] and usage in China.[19,20] The concentrations of SCCPs at the two rural sites (CNR5 Huade and CNR18 Jianfeng Mountain) were significantly lower than those at the urban sites. Temporally, the air concentrations in fall were usually higher than those in spring (also see Figure 2). Regarding the compound compositions, the percentages of $C_{10}$−$C_{11}$ and $Cl_6$−$Cl_7$ in fall were generally significantly higher than in the spring samples. This trend is not surprising given that high SCCP emissions appear to be directly related to high temperature. It is notable that there were no significant temporal variations between the two seasons in CNU6 Qingdao and CNU10 Shanghai, indicating that these two sites may be influenced by sustained sources of SCCPs.

Geographically, the concentrations of SCCPs in Japan and South Korea were uniform (Figure 3). Only a few sites were found to have relatively high levels (JAU4 Tokyo, JAU7 Osaka, JAU9 Matsuyama, SKU2 Seoul, and SKU3 Incheon). Considering that these sites are situated in the main industrial belt of each country,[18] this phenomenon suggests that releases from industrial regions may be a primary source of SCCPs in the atmosphere. Significant seasonal variations were not observed (Figure 3), including changes in either the atmospheric concentrations or the relative abundance of each compound, with the exception of a small number of sites (JAR2 Kuroishi, SKU2 Seoul, SKU3 Incheon, and SKU4 Wonju).

**Levels and Compositions at Remote Sites.** Six rural samples were collected in the present study: CNR5 Huade, CNR18 Jianfeng Mountain, JAR2 Kuroishi, JAR11 Miyazaki, SKR1 Yeonggwang, and SKR5 Geochang. Generally, discrepancies between the results from remote sites were similar to the overall trend in the corresponding country, reflecting the aforementioned regional differences. The total SCCP concentrations at these remote sites were distinct with an average of 43.7 ± 24.6 ng m$^{-3}$ in China that was clearly higher than in Japan and South Korea (0.70 ± 0.23 and 0.87 ± 0.19 ng m$^{-3}$, respectively). Notably, the levels are far greater than those recorded in the Arctic region (Table 1). Similarly, the patterns of SCCP compositions in remote sites were consistent within each country (see Figure 1e−g).

The average back-trajectories at 500 m AGL (above ground level) during the sampling period at the six sites are presented in Figures S2−4. At the rural sites of Japan and South Korea, portions of the air mass back-trajectories passed through China. However, both the atmospheric levels and congener patterns were in complete accordance with the characteristics of each nation. This phenomenon demonstrates that SCCPs were mainly influenced by local sources, even though other POPs in the atmospheres of Japan and South Korea have been shown to
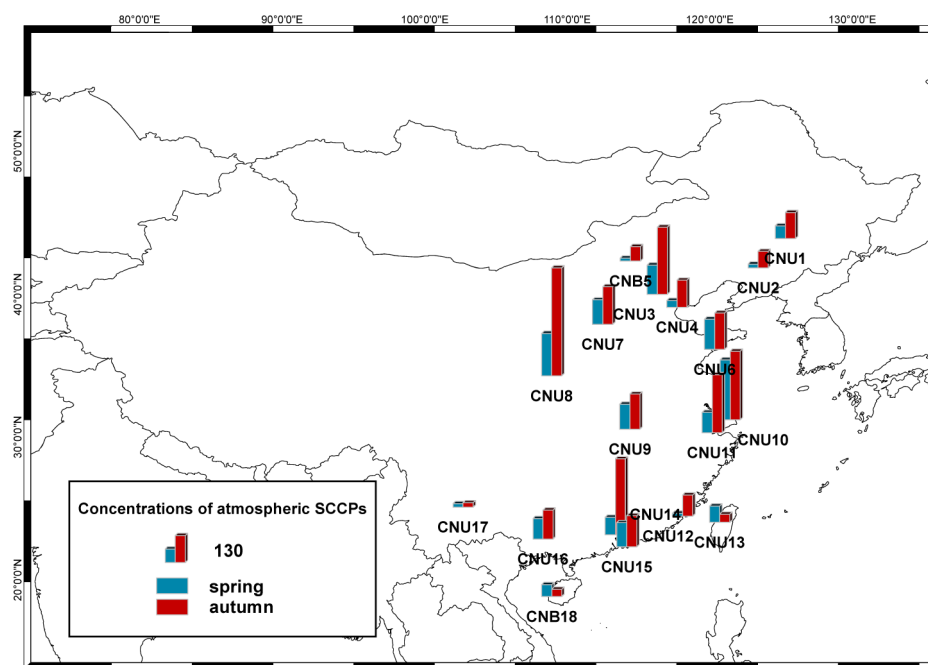
**Figure 2.** Spatial distributions and seasonal variations of atmospheric SCCP concentrations in China (ng m$^{-3}$).
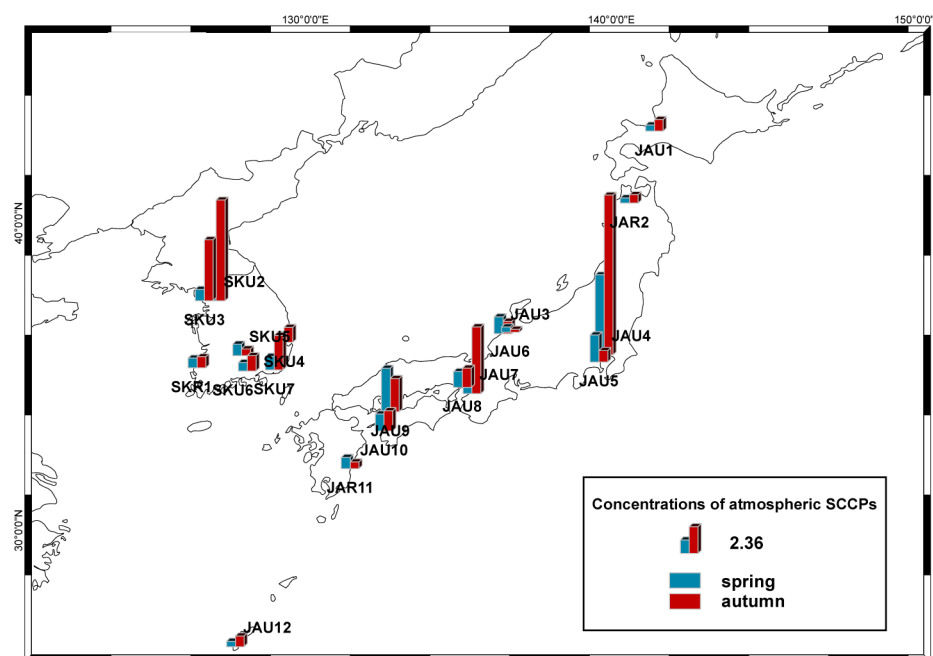


**Figure 3.** Spatial distributions and seasonal variations of atmospheric SCCP concentrations in Japan and South Korea (ng m$^{-3}$).

be affected by sources in China to a certain extent.[29,30] The calculated characteristic travel distances (CTD) of SCCPs, calculated using the OECD software tool, were approximately 600−900 km.[31] This relatively low long-range atmospheric transport potential could explain the observations of this present study. Furthermore, it is worth noting that the seasonal variation was related to air mass flow directions in the two remote sites of China (Figure S2). At CN5, the back-trajectories, combined with the fact that the SCCP concentration in spring was significantly lower than in the fall, indicated that the airflow originating from the central region of China (41%) in the fall affect this site. However, at CN18, the situation was reversed: when the air mass mainly passed through the southeastern coastal region of China (23%) from March to May, the total SCCP concentration was clearly higher than during August to October, when the air mass originated from southern China, Southeast Asia, and the East China Sea.

**Probable Explanation for the Differences Observed in the Three Countries.** As mentioned above, the statistical analyses showed clear differences among the three countries with respect to either the total concentrations or composition of SCCPs, which can be attributed to the following two factors.

*Production and Usage.* The production and industrial usage of SCCPs was generally believed to be the main source of environment contaminants.[19,32] According to a previous report, China has become the largest producer of CPs in the world

with a production level of 600,000 tons per year since 2006.[18] Japan is also a producer of SCCPs, although the level of production in Japan has been far less than in China at only approximately 500 tons per year.[18] South Korea has no records of SCCP production, although it imported approximately 156 tons of SCCPs in 2002 (http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.5-INF-18.English.pdf). These differences in usage level may be a major reason for the high atmospheric concentrations observed in China. Additionally, the results of the correlation analysis corroborated this conclusion based on a different perspective. In China for example, the $C_{10}$ to $C_{13}$ components of the atmospheric SCCPs (see Table S3) were significant correlated ($p < 0.01$); this result is not only consistent with the actual reported SCCP industrial production levels, which do not strictly distinguish between carbon chains but also reflect the composition of the homologues detected in China.

*Differential Application Patterns.* According to previous studies, differential usage patterns of SCCPs would result in disparate emission rates and ultimately lead to different contaminant levels. Studies by the European Union[33] and World Economic Organizations[34] also indicated that when SCCPs are used as metalworking fluids, the atmospheric emissions factor was 8%, which was much larger than that of consumer goods additives (0.0029%). Although metal working industry have voluntarily phased out the use of SCCPs since 2007.[23] The site with the highest measured level of SCCPs (JAU4 Tokyo) was located in a region of significant SCCP usage, i.e., the Kanto industrial region, where SCCPs have been mainly used as metal working fluids. In contrast, a relatively low concentration was detected at JA8 Kobe, which is located in another major area of SCCPs usage (materials additives), i.e., the Kansai region.[18] Together with the spatial distribution of atmospheric SCCPs (Figure 3), these results indicate that the pattern of SCCP usage in Japan,[18] to a certain extent, may have an effect on the atmospheric concentrations in this country.

## ASSOCIATED CONTENT

**ⓈSupporting Information**

Location of the sampling sites, sampling duration, correlation of SCCP congeners in the atmosphere of China, and detailed information on the back-trajectories of each rural site are available at the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

**Corresponding Author**

*Phone: (86) 20 85291508. Fax: (86) 20 85290706. E-mail: junli@gig.ac.cn.

**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

## REFERENCES

(1) Tomy, G. T.; Fisk, A. T.; Westmore, J. B.; Muir, D. C. Environmental chemistry and toxicology of polychlorinated n-alkanes. *Rev. Environ. Contam. Toxicol.* **1998**, *158*, 53−128.

(2) Štejnarová, P.; Coelhan, M.; Kostrhounová, R.; Parlar, H.; Holoubek, I. Analysis of short chain chlorinated paraffins in sediment samples from the Czech Republic by short-column GC/ECNI-MS. *Chemosphere* **2005**, *58* (3), 253−262.

(3) 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.

(4) 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.

(5) Fridén, 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.

(6) Castells, P.; Santos, F. J.; Galceran, M. T. Solid-phase microextraction for the analysis of short-chain chlorinated paraffins in water samples. *J. Chromatogr., A* **2003**, *984* (1), 1−8.

(7) 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.

(8) 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.

(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) 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.

(11) Reth, M.; Zencak, Z.; Oehme, M. First study of congener group patterns and concentrations of short- and medium-chain chlorinated paraffins in fish from the North and Baltic Sea. *Chemosphere* **2005**, *58* (7), 847−854.

(12) Harner, T.; Kylin, H.; Bidleman, T. F.; Halsall, C.; Strachan, W. M. J.; Barrie, L. A.; Fellin, P. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in Arctic air. *Environ. Sci. Technol.* **1998**, *32* (21), 3257−3265.

(13) Borgen, A. R.; Schlabach, M.; Gundersen, H. Polychlorinated alkanes in arctic air. *Organohalogen Compd.* **2000**, *47*, 272−274.

(14) Jaward, F. M.; Zhang, G.; Nam, J. J.; Sweetman, A. J.; Obbard, J. P.; Kobara, Y.; Jones, K. C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* **2005**, *39* (22), 8638−8645.

(15) Li, Y. F.; Cai, D. J.; Shan, Z. J.; Zhu, Z. L. Gridded usage inventories of technical hexachlorocyclohexane and lindane for China with 1/6° latitude by 1/4° longitude resolution. *Arch. Environ. Contam. Toxicol.* **2001**, *41* (3), 261−266.

(16) Zhang, Y.; Tao, S. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos. Environ.* **2009**, *43* (4), 812−819.

(17) Pozo, K.; Harner, T.; Wania, F.; Muir, D. C. G.; Jones, K. C.; Barrie, L. A. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environ. Sci. Technol.* **2006**, *40* (16), 4867−4873.

(18) Fiedler, H. Short-Chain Chlorinated Paraffins: Production,Use and International Regulations. In *Chlorinated Paraffins*; de Boer, J., Ed.; Springer Press: Berlin, Heidelberg, 2010.

(19) Zeng, L.; Wang, T.; Ruan, T.; Liu, Q.; Wang, Y.; Jiang, G. Levels and distribution patterns of short chain chlorinated paraffins in sewage sludge of wastewater treatment plants in China. *Environ. Pollut.* **2012**, *160* (0), 88−94.

(20) 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.

(21) 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 Liaohe River Basin, P. R. China. *Environ. Sci. Technol.* **2012**, *46* (7), 3771−3778.

(22) 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.

(23) 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.

(24) 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.

(25) Wang, T.; Han, S.; Yuan, B.; Zeng, L.; Li, Y.; Wang, Y.; Jiang, G. Summer−winter concentrations and gas-particle partitioning of short chain chlorinated paraffins in the atmosphere of an urban setting. *Environ. Pollut.* **2012**, *171* (0), 38−45.

(26) Muir, D.; et al. Short Chain Chlorinated Paraffins: Are They Persistent and Bioaccumulative? In *Persistent, Bioaccumulative, and Toxic Chemicals II*; Robert, L. L., Bo, J., Donald, M., Myrto, P., Eds.;American Chemical Society Press: Washington, DC, 2000; Vol. 773, pp 184−202.

(27) 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.

(28) Tang, E. T.; Yao, L. Q. Industry status of chlorinated paraffin and its development trends. *China Chlor-Alkali* **2005**, *2*, 1−3.

(29) Lee, S.-J.; Park, H.; Choi, S.-D.; Lee, J.-M.; Chang, Y.-S. Assessment of variations in atmospheric PCDD/Fs by Asian dust in Southeastern Korea. *Atmos. Environ.* **2007**, *41* (28), 5876−5886.

(30) Primbs, T.; Simonich, S.; Schmedding, D.; Wilson, G.; Jaffe, D.; Takami, A.; Kato, S.; Hatakeyama, S.; Kajii, Y. Atmospheric outflow of anthropogenic semivolatile organic compounds from East Asia in spring 2004. *Environ. Sci. Technol.* **2007**, *41* (10), 3551−3558.

(31) Wegmann, F.; Cavin, L.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. The OECD software tool for screening chemicals for persistence and long-range transport potential. *Environ. Modell. Software* **2009**, *24* (2), 228−237.

(32) Přibylová, P.; Klánová, J.; Holoubek, I. Screening of short- and medium-chain chlorinated paraffins in selected riverine sediments and sludge from the Czech Republic. *Environ. Pollut.* **2006**, *144* (1), 248−254.

(33) *Technical guidance document in support of commission directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No 1488/94 on risk assessment for existing substances*; Office for Official Publications of the European Communities: Brussels, Luxembourg, 1996.

(34) *Emission scenario document on plastics additives*; OECD Environment Health and Safety Publications series on emission scenario documents No. 3; Environment Directorate, Organisation for Economic Co-operation and Development, Paris, 2004.

(35) 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

(36) Bidleman, T.; Alaee, M.; Stern, G. *New persistent chemicals in the Arctic environment*; Indian and Northern Affairs Canada: Ottawa, Ontario, 2001.

(37) 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.

(38) Wang, Y. Polychlorinated naphthalenes and chlorinated paraffins in the atmosphere and soil in Dongjiang River catchment, South China. Ph.D. Dissertation, Guangzhou Institute of Geochemistry, Guangzhou, 2010.

11954

dx.doi.org/10.1021/es302321n | *Environ. Sci. Technol.* 2012, 46, 11948−11954