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Toward resolving the budget discrepancy of ozone-depleting carbon tetrachloride (CCl_4): an analysis of top-down emissions from China

Sunyoung Park^{1,2}, Shanlan Li^{2,3}, Jens Mühle⁴, Simon O'Doherty⁵, Ray F. Weiss⁴, Xuekun Fang⁶, Stefan Reimann⁷, and Ronald G. Prinn⁶

¹Department of Oceanography Kyungpook National University, Daegu 41566, Republic of Korea

²Kyungpook Institute of Oceanography Kyungpook National University, Daegu 41566, Republic of Korea

³Climate Research Division, National Institute of Meteorological Sciences, Seogwipo, Korea

⁴Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA

⁵School of Chemistry, University of Bristol, Bristol, UK

⁶Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

⁷Empa, Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland

Correspondence: Sunyoung Park (sparky@knu.ac.kr)

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Abstract. Carbon tetrachloride (CCl_4) is a first-generation ozone-depleting substance, and its emissive use and production were globally banned by the Montreal Protocol with a 2010 phase-out; however, production and consumption for non-dispersive use as a chemical feedstock and as a process agent are still allowed. This study uses the high frequency and magnitude of CCl_4 pollution events from an 8-year real-time atmospheric measurement record obtained at Gosan station (a regional background monitoring site in East Asia) to present evidence of significant unreported emissions of CCl_4 . Top-down emissions of CCl_4 amounting to $23.6 \pm 7.1 \text{ Gg yr}^{-1}$ from 2011 to 2015 are estimated for China, in contrast to the most recently reported, post-2010, Chinese bottom-up emissions of $4.3\text{--}5.2 \text{ Gg yr}^{-1}$. The missing emissions ($\sim 19 \text{ Gg yr}^{-1}$) for China contribute to approximately 54 % of global CCl_4 emissions. It is also shown that $89\% \pm 6\%$ of CCl_4 enhancements observed at Gosan are related to CCl_4 emissions from the production of CH_3Cl , CH_2Cl_2 , CHCl_3 and C_2Cl_4 and its usage as a feedstock and process agent in chemical manufacturing industries. Specific sources and processes are identified using statistical methods, and it is considered highly unlikely that CCl_4 is emitted by dispersive uses such as old landfills, contaminated soils and solvent usage. It is thus crucial to implement technical improvements

and better regulation strategies to reduce evaporative losses of CCl_4 occurring at the factory and/or process levels.

1 Introduction

Carbon tetrachloride (CCl_4) is a long-lived greenhouse gas and an ozone-depleting substance. Its emissive use, production and consumption are regulated under the Montreal Protocol on Substances that Deplete the Ozone Layer and its Amendments (MP). After reaching a peak in the early 1990s, the atmospheric abundance of CCl_4 has been decreasing at a rate of $-4.9 \pm 0.7 \text{ ppt Cl yr}^{-1}$ (Carpenter et al., 2014) due to the phase-out of CCl_4 use in MP non-Article 5 (developed) countries by 1995. MP Article 5 (developing) countries, including China, were required to cease CCl_4 production and consumption for dispersive applications by 2010. However, CCl_4 production and consumption for non-dispersive use (e.g., as chemical feedstock and as a process agent) continues to be allowed, and thus CCl_4 is still produced and consumed alongside the increasing production of non-ODS chemicals (Carpenter et al., 2014). At present, the global bottom-up CCl_4 emissions derived from reporting countries are $3\text{--}8 \text{ Gg yr}^{-1}$ for 2007–2013 (Carpenter et al., 2014; Liang et al., 2016).

The recent Stratosphere–Troposphere Processes and their Role in Climate (SPARC) report (Liang et al., 2016) updated bottom-up anthropogenic CCl₄ emissions to at most 25 Gg yr^{−1} in 2014, based on reconsideration of industrial production processes plus usage (15 Gg yr^{−1}), and the upper-limit estimate of 10 Gg yr^{−1} for the potential escape from legacy sites and unreported inadvertent emissions (Sherry et al., 2017).

To verify these bottom-up estimates, independent top-down CCl₄ emission studies have used the total lifetime of CCl₄ with atmospheric observations (i.e., the observed decline rate of CCl₄ concentrations) and atmospheric transport models to derive top-down emission estimates. Using the most current estimates for the lifetime of CCl₄ in the atmosphere, soil and ocean (Liang et al., 2016; Rhew and Hoppel, 2016; Butler et al., 2016), global top-down emissions to the atmosphere were calculated as 40 ± 15 Gg yr^{−1} from 2007 to 2014 (Liang et al., 2016). A recent top-down study based on the observed temporal trend and interhemispheric gradient of atmospheric CCl₄ (Liang et al., 2014) consistently derived global CCl₄ emissions of 30 ± 5 Gg yr^{−1} from 2000 to 2012 when using the newly determined relative strength of oceanic sink versus soil loss (Liang et al., 2016). Therefore, the best estimate of global emissions from top-down methods is 35 ± 16 Gg yr^{−1}, which is significantly higher than reported emissions of 3 Gg yr^{−1}, even when considering large uncertainties relating to soil and ocean CCl₄ sinks (and how those sinks might change over time). Although the revised bottom-up estimate of 25 Gg yr^{−1} mentioned above contributes considerably to closing the gap between bottom-up and top-down emission estimates, this new bottom-up value is still lower than the average SPARC-merged top-down emission estimate of 35 ± 16 Gg yr^{−1} (though the uncertainty is large). The discrepancy between bottom-up and top-down emission estimates implies the existence of unidentified sources and/or unreported industrial emissions.

Regional studies of episodic enhancements of CCl₄ above atmospheric background concentrations observed in several regions using inverse model techniques have suggested emissive fluxes of 0.11 ± 0.04 Gg yr^{−1} in 2009–2012 from Australia (Fraser et al., 2014), 15 (10–22) Gg yr^{−1} in 2007 from East Asia (Vollmer et al., 2009), 4 (2–6.5) Gg yr^{−1} in 2008–2012 from the USA (Hu et al., 2016) and 2.3 ± 0.8 Gg yr^{−1} in 2006–2014 from western Europe (Graziosi et al., 2016). The summed emissions were estimated to total 21 ± 8 Gg yr^{−1} (Liang et al., 2016), with the most significant contribution belonging to East Asia. As the sum of regional emissions quantified to date has not accounted for global top-down emissions, an improved quantification of regional-/country-scale and industry-based CCl₄ emissions is required to gain a better insight into the causes of the discrepancy between the regional sums and the global top-down estimate. This would improve our understanding of the unidentified and/or unreported industrial emission sources and would help to establish practical and effective regulation strategies.

With the aim of resolving the apparent CCl₄ budget discrepancy, this study presents an estimate of regional CCl₄ emissions from China, one of the MP Article 5 countries in East Asia. Due to its recent and ongoing strong industrial growth, current emissions and changes in emission patterns are of special interest. In addition, recent studies based on atmospheric monitoring have consistently reported a significant increase in the emissions of most halocarbons in China (Vollmer et al., 2009; Kim et al., 2010; Li et al., 2011). Top-down estimates of Chinese emissions for CCl₄ have been made in previous studies using a Lagrangian inverse model based on ground-based monitoring data (Vollmer et al., 2009) and an interspecies correlation method based on aircraft observations (Palmer et al., 2003; Wang et al., 2014). The estimates made in these studies were quite variable, with 17.6 ± 4.4 Gg yr^{−1} in 2001 (Palmer et al., 2003), 15 (10–22) Gg yr^{−1} in 2007 (Vollmer et al., 2009) and 4.4 ± 3.4 Gg yr^{−1} in 2010 (Wang et al., 2014), and these studies were conducted before the complete phase-out of CCl₄ production for emissive applications in China came into effect in 2010. Most recently, Bie et al. (2017) published post-2010 bottom-up emission estimates for China of 4.3 (1.9–8.0) Gg yr^{−1} in 2011 and 5.2 (2.4–8.8) Gg yr^{−1} in 2014, which updated the previous zero-emissions estimate (Wan et al., 2009) by including the conversion of C₂Cl₄ emissions to CCl₄ as well as the source of CCl₄ from coal combustion smog.

In this study, we present an 8-year record of continuous, high frequency, high-precision, atmospheric CCl₄ concentrations measured at the Gosan station (33° N, 126° E) on Jeju Island, Korea for 2008–2015. Using a tracer–tracer correlation method (Li et al., 2011) based on a top-down interpretation of atmospheric observations, we estimate yearly emission rates of CCl₄ for China and examine changes in these rates following the scheduled phase-out for CCl₄ in 2010. Gosan station monitors air masses arriving from a variety of different regions (Kim et al., 2012), and the emission footprints of these cover an area from north-eastern China down to south of the Yangtze River, which is the most industrialized region in China. We also analyze the measurements of 17 other anthropogenic compounds to identify key industrial sources of CCl₄ emissions and their potential locations using a positive matrix factorization model in combination with trajectory statistics (Li et al., 2014).

2 Data overview

2.1 Measurements of CCl₄ at Gosan

Gosan station (GSN) is located on the remote south-western tip of Jeju Island, which lies to the south of the Korean peninsula (72 m a.s.l.) and is well situated for monitoring long-range air mass transport from surrounding regions (Fig. S1 in the Supplement). Wind patterns at GSN are typical of the

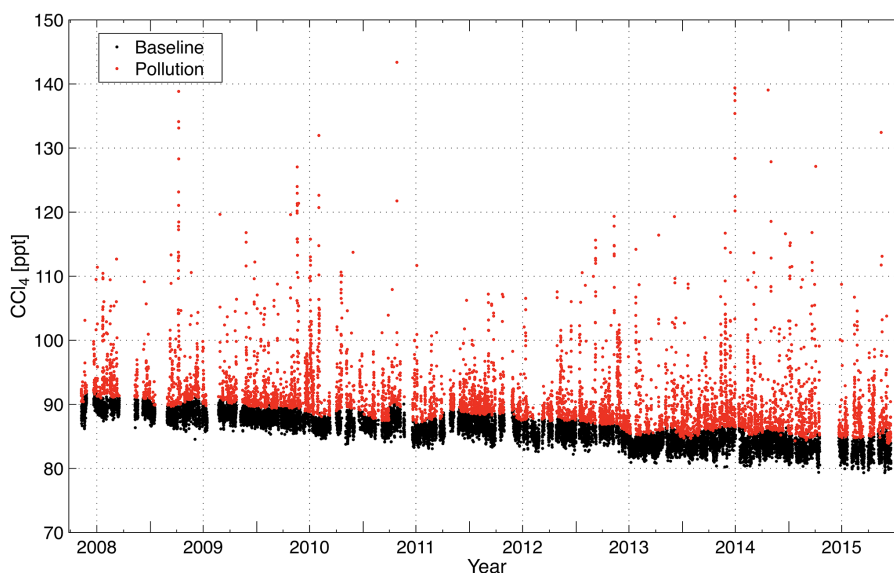


Figure 1. Atmospheric CCl_4 concentrations observed from 2008 to 2015 at Gosan station (GSN, 33°N , 126°E) on Jeju Island, Korea. Pollution events (identified as significant enhancements in concentrations from background levels shown in black) are denoted by red dots.

Asian monsoon, with strong predominant north-westerly and north-easterly continental outflows of polluted air from fall through to spring, clean continental air flowing directly from northern Siberia in winter and pristine maritime air from the Pacific in summer (Fig. S2). High-precision and high-frequency measurements of 40 halogenated compounds including CCl_4 were made continuously every 2 h from 2008 to 2015 using a gas chromatography-mass spectrometer (GC-MS) coupled with an online cryogenic preconcentration system (Medusa) (Miller et al., 2008) as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) program. Precisions (1σ) derived from repeated analysis ($n = 12$) of a working standard of ambient air were better than 1 % of background atmospheric concentrations for all compounds, e.g., ± 0.8 ppt (1σ) for 85.2 ppt of CCl_4 . The measurements are mostly on calibration scales developed at the Scripps Institution of Oceanography (SIO).

2.2 Results

The 8-year observational record of CCl_4 analyzed in this study is shown in Fig. 1. It is apparent that pollution events (red dots) with significant enhancements above background levels (black dots) occurred frequently, resulting in daily variations of observed concentrations with relative standard deviations (RSDs) of 4 %–20 % (in contrast to the RSDs of 0.1 %–1.5 % shown in all the remote stations that operated under the AGAGE program). These results clearly imply that CCl_4 emissions are emanating from East Asia. The background concentrations at GSN were determined using the statistical method detailed in O'Doherty et al. (2001), and they agree well with those observed at the Mace Head station (53°N , 10°W) in Ireland (which is representative of a

remote background monitoring station in the Northern Hemisphere) and are declining at a similar rate to the global trend (Fig. S4). The magnitude of pollution data analyzed in this study was defined as the observed enhancements (red dots in Fig. 1) in concentration units above the baseline values (i.e., background values representing regional clean conditions without regional/local pollution events, black dots) to exclude the influence of trends and/or variability in background levels from the analysis.

3 Potential source regions of CCl_4 in East Asia

A statistical analysis combining enhanced concentrations (above-baseline concentrations) of CCl_4 from 2008 to 2015, with corresponding back trajectories, enabled identification of the regional distribution of potential CCl_4 emission sources. The statistical method (see Trajectory Statistics in the Supplement) was first introduced in 1994 (Seibert et al., 1994) and has previously been applied to analyses relating to halogenated compounds (e.g., Li et al., 2014; Reimann et al., 2004).

An elevated concentration at an observation site is proportionally related to both the average concentration in each grid cell over which the corresponding air mass has traveled and the air mass trajectory residence time in the grid cell. This allows the method to compute a residence-time-weighted mean concentration for each grid cell by simply superimposing the back trajectory domain on the grid matrix. We used 6-day kinematic backward trajectories arriving at a 500 m altitude above the measurement site that were calculated using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the NOAA Air Re-

sources Laboratory (ARL) based on meteorological information from the Global Data Assimilation System (GDAS) model with a $1^\circ \times 1^\circ$ grid cell (Li et al., 2014). The residence times were calculated using the methods of Poirot and Wishinski (1986). To eliminate low confidence level areas, we applied a point filter that removed grid cells that had less than 12 overpassing trajectories (Reimann et al., 2004).

The resulting map of potential source areas for CCl_4 in East Asia (Fig. 2) shows that emission sources are widely distributed in China, but they are particularly concentrated in north-eastern China and south-central China (approximately Shandong, Henan, Hubei and Guangdong provinces). These provinces include industrialized urban areas that conduct intensive industrial activities, such as chemical manufacturing (<http://eng.chinaiol.com/>, last access: 21 June 2018). It is of note that this statistical analysis has little sensitivity to emissions from southwestern China, due to the limits of the typical 5- to 6-day back-trajectory domain of the HYSPLIT model. Additionally, this method tends to underestimate the inherently sharp spatial gradients in the vicinity of emission hotspots, because its calculation scheme distributes the measured concentrations evenly throughout grid cells over which a trajectory has passed (Stohl, 1996). Nonetheless, it is clear that the CCl_4 emission sources from East Asia were predominantly located in China.

4 Using observed interspecies correlations to estimate country-based, top-down CCl_4 emissions in China

To identify pollution events solely related to Chinese emissions, we classified an event as “Chinese” if the 6-day kinematic back trajectories arriving at GSN had entered the boundary layer (as defined by HYSPLIT) only within the Chinese domain, which was defined as a regional grid of $100\text{--}124^\circ \text{E}$ and $21\text{--}45^\circ \text{N}$ (Fig. S5a). This analysis classified 29 % of all observed CCl_4 pollution events from 2008 to 2015 (Fig. S5b) as Chinese. An additional 46 % were affected by Chinese domain plus another country; however, these blended air masses were excluded from the determination of Chinese emissions.

For the Chinese emissions estimate of CCl_4 , we use an interspecies correlation method, analogously to many recent emission studies (e.g., Kim et al., 2010; Li et al., 2011; Palmer et al., 2003; Wang et al., 2014). In this method, the emission rate of a co-measured compound of interest can be inferred based on its compact empirical correlation with a reference compound with a country-scale emission that has been independently well defined. This empirical ratio approach provides a simple yet comprehensive method for estimating regional emissions of almost all halogenated compounds measured at GSN, and it minimizes the uncertainties inherent in more complex modeling schemes. This method is particularly useful for compounds such as CCl_4 , where the associated bottom-up inventories indicate close to zero emis-

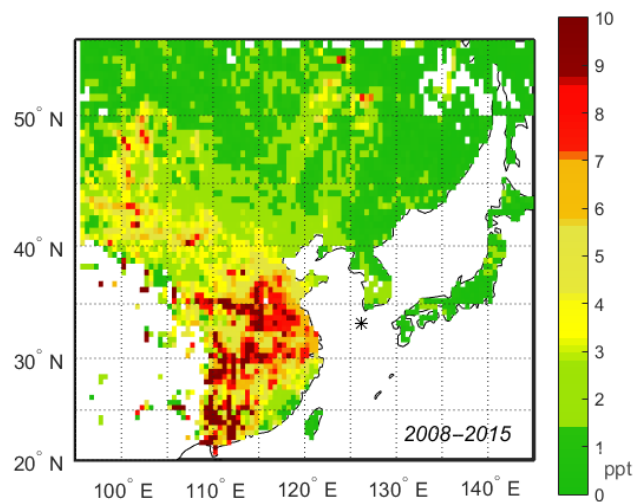


Figure 2. Distribution of potential source regions calculated from trajectory statistics for enhancement data of CCl_4 observed from 2008 to 2015. The color code (in ppt) denotes a residence-time-weighted mean concentration for each grid cell. The resulting map of potential source areas for CCl_4 shows that emission sources are widely distributed over China. The site of Gosan station is indicated by an asterisk (*).

sions and/or clearly have large errors, which thus makes it difficult to adequately define the prior emissions required for inverse modeling. However, the ratio method is restricted by its core assumptions: that the emissions of the reference and target compounds are co-located (or at least well mixed) until they reach the measurement site, and that the reference emissions are well known. The interspecies ratios we observed at GSN showed statistically significant correlations for many compounds on a national scale (Li et al., 2011), suggesting that overall these core assumptions were satisfied in this study.

An adequate reference compound should be a widely used industrial species with high national emission rates, thereby allowing for robust and compact correlations with many other species and low uncertainties in its own emission estimate. The reference compound was chosen by examining the observed relationships of CCl_4 enhancements above baseline versus the enhancements above baseline for 25 other halocarbons in air masses classified as Chinese. We found that the $\Delta\text{CCl}_4/\Delta\text{HCFC-22}$ ratio ($0.13 \text{ ppt ppt}^{-1}$) showed one of the most significant correlations ($R^2 = 0.72$, $p < 0.01$) (Fig. S6). Furthermore, given that China has been the largest producer and consumer of HCFCs since 2003, and that production of HCFC-22 accounts for more than 80 % of all Chinese HCFC production (UNEP, 2009), HCFC-22 is the best-suited reference compound for use with China. Additionally, strong Chinese HCFC-22 emissions have been determined from atmospheric observations and inverse modeling in previous studies (Kim et al., 2010; Li et al., 2011; Stohl et al., 2010; An et al., 2012; Fang et

al., 2012), with estimates ranging from 46 to 146 Gg yr⁻¹ over the period 2007–2009. Our estimates of annual HCFC-22 emissions in China for 2008–2015 were independently derived from atmospheric measurements at GSN using an inverse technique based on FLEXible PARTicle dispersion model (FLEXPART) Lagrangian transport model analysis (Stohl et al., 2010; Fang et al., 2014) and ranged from 89 Gg yr⁻¹ in 2011 to 144 Gg yr⁻¹ in 2015. The uncertainty in the top-down estimates was 30 %, which mainly related to an assumed uncertainty of ± 50 % in annual prior emissions used for the inversion calculation (Fig. S7).

Next, we used empirical correlations between observed enhancements of CCl₄ and HCFC-22 ($\Delta\text{CCl}_4/\Delta\text{HCFC-22}$; annual slopes shown in Fig. S8) to estimate CCl₄ emission rates. The interspecies slopes were determined based on observed enhancements obtained by subtracting regional background values from the original observations to avoid potential underestimation of the slopes due to the high density of low background values (following Palmer et al., 2003). Estimated uncertainties for our CCl₄ emission estimates comprise the emissions uncertainty of HCFC-22 and an uncertainty associated with the $\Delta\text{HCFC-22}/\Delta\text{CCl}_4$ slope, which was calculated using the Williamson–York linear least-squares fitting method (Cantrell, 2008), considering measurement errors of both HCFC-22 and CCl₄.

Figure 3 provides the annual CCl₄ emissions in China for the years 2008–2015, which were calculated based on our interspecies correlation method, and also shows a comparison between our results and previous estimates of CCl₄ emissions from China. The CCl₄ emission rate of 16.8 ± 5.6 Gg yr⁻¹ in 2008 found in this study is consistent with 2001 (Palmer et al., 2003) and 2007 (Vollmer et al., 2009) top-down emissions estimates of 17.6 ± 4.4 Gg yr⁻¹ and 15 (10–22) Gg yr⁻¹. To obtain those results, Palmer et al. (2003) used observed correlations of CCl₄ with CO as a tracer to investigate CCl₄ emissions in aircraft observations of the Asian plume over a 2-month period (March to April) in 2001, and Vollmer et al. (2009) estimated the 2007 emissions using an inverse model based on atmospheric measurements taken from late 2006 to early 2008 at an inland station (Shangdianzi, 40° N, 117° E) located in the North China Plain. Wang et al. (2014) obtained aircraft measurements over the Shandong Peninsula on 22 July and 27 October 2010 and from March to May in 2011, and estimated CCl₄ emission in 2010 based on observed correlations of CCl₄ with both CO and HCFC-22. However, the estimates from these two different tracers differed by ~ 100 % (8.8 Gg yr⁻¹ versus 4.4 Gg yr⁻¹) and were much lower than the two previous results of Palmer et al. (2003) and Vollmer et al. (2009) and our 2010 estimate of 32.7 ± 5.1 Gg yr⁻¹. Although the cause of this discrepancy is unclear, it is considered that it could be related to the low numbers of observations obtained in the aircraft campaigns and to difficulties defining regional background values and extracting pollution signals from the aircraft data. It is also possible that the results mostly rep-

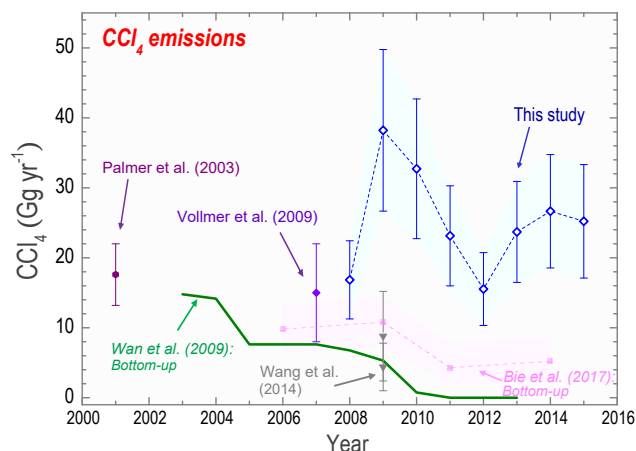


Figure 3. CCl₄ emissions in China as determined by an interspecies correlation method. A comparison between our results and previous estimates for Chinese emissions is also shown. Note that emissions reached a maximum in 2009–2010 in concurrence with the scheduled phase-out of CCl₄ by 2010, but the average annual emission rate of 23.6 ± 7.1 Gg yr⁻¹ for the years 2011–2015 is still substantial.

resent emissions from northern China. Extrapolating them to the entire country using data from northern China would lead to an underestimate of emissions, as most industrial activities occur in the south-central and eastern parts of China.

Our estimates show that Chinese emissions increased sharply before reaching a maximum in 2009–2010 (with a range of 38.2 ± 5.5 to 32.7 ± 5.1 Gg yr⁻¹) immediately prior to the scheduled phase-out of CCl₄ by 2010. The sudden large increase could be attributed to uncontrolled use or production leading to emissions of stored CCl₄ before the scheduled restrictions came into effect. Interestingly, this increase in our emission estimates was also consistent with the increase of about 20 Gg yr⁻¹ in the total annual production of CCl₄ in China from 2008 to 2010, which was mainly related to an increase in the feedstock production sector, i.e., raw material production for non-ODS chemicals (Bie et al., 2017). After a dip in 2012, our estimated emissions in 2013–2015 remain stable and are similar overall to those in 2011, with no statistically discernible differences between these years. It is of note that the average emission rate estimated in this study of 23.6 ± 7.1 Gg yr⁻¹ for the years 2011–2015 is significant, as post-2010 bottom-up emissions of CCl₄ in China have been reported as near zero (Wan et al., 2009), and even the most up-to-date bottom-up estimates (Bie et al., 2017) have indicated emissions of only 4.3 (1.9–8.0) Gg yr⁻¹ in 2011 and 5.2 (2.4–8.8) Gg yr⁻¹ in 2014. These discrepancies between bottom-up and top-down emission estimates may suggest that emissions of CCl₄ from either non-regulated feedstock and process agent use or unreported non-feedstock emissions from the production of chloromethanes (CH₃Cl, CH₂Cl₂, CHCl₃) and PCE (C₂Cl₄) are larger than expected.

5 Industrial source apportionment of atmospheric CCl₄ in East Asia

The positive matrix factorization (PMF) model was used to characterize key industrial CCl₄ sources based solely on atmospheric observations (Paatero and Tapper, 1994). We included all CCl₄ enhancement events observed at GSN, thereby representing a better characterization of emission sources throughout East Asia and not just in China. The PMF model has been widely used to identify and apportion sources of atmospheric pollutants (Guo et al., 2009; Lanz et al., 2009; Li et al., 2009; Choi et al., 2010) and is an optimization method that uses a weighted least squares regression to obtain a best fit to the measured concentration enhancements of chemical species (details in the text of the Supplement) and to resolve the number of source factors controlling the observations. A brief mathematical expression of the model is given by Eq. (1):

$$x_{ik} = \sum_{j=1}^p g_{ij} f_{jk} + e_{ik} \quad (i = 1, 2, \dots, m; j = 1, 2, \dots, p; k = 1, 2, \dots, n), \quad (1)$$

where x_{ik} represents enhanced concentrations in the time series of the i th compound at the k th sampling time; g_{ij} is the concentration fraction of the i th compound from the j th source; f_{jk} is the enhanced concentration from the j th source contributing to the observation at the k th time, which is given in ppt; e_{ik} is the model residual for the i th compound concentration measured in the k th sampling time; and p is the total number of independent sources (i.e., the number of factors) (Paatero and Tapper, 1994). The number of source factors is an optimal value determined based on the R^2 that measures how close the predicted concentrations are to the observed enhancements of 18 species (including not only CCl₄, major CFCs, HCFCs, HFCs, PFCs, SF₆, carbonyl sulfide (COS), but also CH₃Cl, CH₂Cl₂, CHCl₃ and PCE) to account for the potential chemical intermediate release of CCl₄ during industrial activities. The model's R-squared values, as estimated from a correlation plot between the measured and PMF model-predicted concentrations, showed that an eight-source model is most appropriate, suggesting eight potential source categories for those 18 species. Each source factor is defined based on the source profile (i.e., relative abundances of individual species). The percentage contributions of factors to the observed enhancements of individual compounds are shown in Fig. 4. Uncertainties were determined from the 1σ standard deviation of factor contributions from 5 sets of 20 runs (total 100 replications) (Reff et al., 2007).

Factor (A) shown in Fig. 4 is characterized by $38\% \pm 4\%$ of CCl₄ and $97\% \pm 2\%$ of CH₃Cl, suggesting inadvertent or inadvertent co-production and escape of CCl₄ during chloromethane generation in chemical plants (see Supplement text for chemical reactions). CCl₄ and CH₃Cl co-

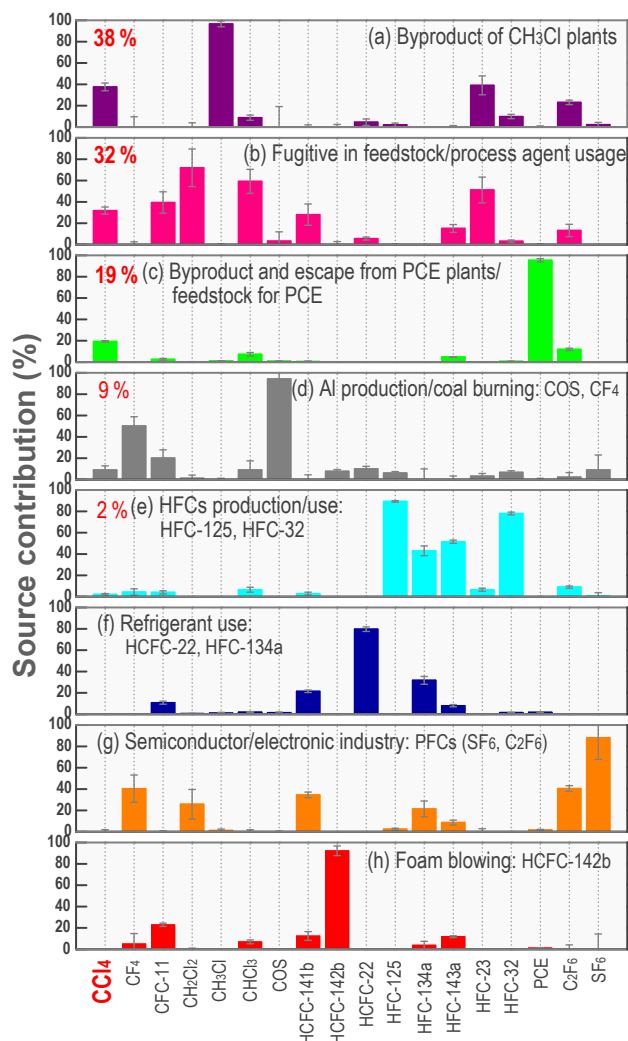


Figure 4. Source profiles derived from PMF analysis for 18 compounds, including CCl₄, CFCs, HCFCs, HFCs, PFCs, SF₆, COS, CH₃Cl, CH₂Cl₂, CHCl₃ and C₂Cl₄. The PMF analysis is performed on the time series of enhanced concentrations. The y axis shows the percentage of all observed enhancements associated with each factor (with 1σ standard deviation) such that the vertical sum for each species listed on the x axis is 100.

emitted in smog from coal combustion (Li et al., 2017) are less likely to be the source of this factor because COS, which is a major coal burning tracer, does not contribute to this factor. Source factor (B) is largely related to fugitive emissions in feedstock and process agent use of various compounds; it accounts for a large fraction of CCl₄ ($32\% \pm 4\%$) and shows high percentages for several compounds: $72\% \pm 18\%$ of CH₂Cl₂, $59\% \pm 11\%$ of CHCl₃, $39\% \pm 10\%$ of CFC-11 and $51\% \pm 12\%$ of HFC-23. It is of note that CH₂Cl₂ and CHCl₃ can be produced as byproducts of chlorination along with CCl₄ and are used as intermediates or solvents in chemical manufacturing. CCl₄ is a feedstock for PCE, HFC, methyl chloride and divinyl acid chloride production (Liang

et al., 2016) and is also used in CFC production (Zhang et al., 2010; Sherry et al., 2018). In addition, CHCl₃ can be used as a feedstock for HCFC-22 production (Montzka et al., 2011), which is consistent with factor (B) also being distinguished by a high contribution of HFC-23: Chinese emissions of HFC-23 account for ~ 70 % of total global emissions (Kim et al., 2010; Li et al., 2011) and it is a typical byproduct of HCFC-22 generation (Fang et al., 2015). HFC-23 is thus emitted at factory level in regions where chemical manufacturing industries are heavily collocated. Overall, the fact that observed enhancements of HFC-23, CCl₄, CH₂Cl₂, CHCl₃ and CFC-11 are grouped together into factor (B) in the PMF analysis implies that this factor most likely represents fugitive emissions of these compounds occurring at factory level during various chemical manufacturing processes in China. Source factor (C) is distinguished by $19\% \pm 1\%$ of CCl₄ and $95\% \pm 2\%$ of PCE; it can be explained by inadvertent or inadvertent co-production and escape of CCl₄ during industrial C₂Cl₄ production and in part by fugitive emissions of CCl₄ used as a chlorination feedstock for C₂Cl₄ production.

The spatial distributions (Fig. S9) of source factors (A)–(C) derived from trajectory statistics (text of Supplement) are similar and cover areas in and around Guangzhou of Guangdong, Wuhan of Hubei, Zhengzhou of Henan and Xian of Shaanxi province. These distributions are consistent with the results of PMF analysis, which confirms that CCl₄ emissions from China are more strongly associated with industrial processes than with population density. Our results are also consistent with those of a previous study on halocarbon observations in the Pearl River Delta region of Guangdong (Zhang et al., 2010), which used a source profile analysis to reveal that CFCs and CCl₄ emissions from an industrial source related to chemical (i.e., refrigerant) production increased by 1.4–2.0 times from 2001–2002 to 2007, even though there were no significant changes in the atmospheric mixing ratios of these compounds for the 6 years. These results imply an increased use of CCl₄ in chemical production. The three emission source factors (A–C), which account for $89\% \pm 6\%$ of CCl₄ enhancements observed at GSN, are thus considered to be mostly escaped CCl₄ emissions at factory level relating to an inadvertent byproduct, feedstock usage for production of chlorinated compounds, and process agent use for chemical processes.

Other factors of PMF analysis relate to (D) primary aluminum production (Blake et al., 2004), (E) HFC production/applications, (F) refrigerant consumption, (G) processes in the semiconductor and electronics industry, and (H) foam blowing agent use, and can mostly be summarized as being distributed emissions. However, the percentage contributions of these other source factors to CCl₄ enhancements are not statistically significant when considering the uncertainty range. The smallest contribution to CCl₄ of the sources characterized as general consumption and legacy release could suggest that CCl₄ emissions from old landfills, contaminated

soil and solvent usage have become less significant. A detailed description of factors D–H is provided in the Supplement.

6 Conclusions

An 8-year record of atmospheric CCl₄ observations obtained at GSN provided evidence of ongoing CCl₄ emissions from East Asia during 2008–2015. Based on these measurements, this paper presents a top-down CCl₄ emissions estimate from China of 23.6 ± 7.1 Gg yr^{−1} for the years 2011–2015, which is different to a bottom-up estimate of 4.3–5.2 Gg yr^{−1} given by most current bottom-up emission inventories for post-2010 China.

Liang et al. (2016) estimated global top-down emissions as 35 ± 16 Gg yr^{−1}, which was an average estimate based on the estimate of 40 ± 15 Gg yr^{−1} for the new 33-year total lifetime of CCl₄ and an independent top-down method using the observed interhemispheric gradient in atmospheric concentrations, which yielded 30 ± 5 Gg yr^{−1}. The SPARC sum of regional emissions was estimated as 21 ± 8 Gg yr^{−1}, of which Chinese emissions of 15 (10–22) Gg yr^{−1} contributed $71\% \pm 33\%$ to the total amount, but this result is still lower than the aggregated top-down values. However, if we employ the higher emission estimate of 23.6 ± 7.1 Gg yr^{−1} obtained for China in this study, the summed regional estimate would be 30 ± 10 Gg yr^{−1}, which is largely in agreement with the best global emissions estimate of 35 ± 16 Gg yr^{−1} determined by Liang et al. (2016).

A factor analysis combining the observed concentration enhancements of 18 species was used to identify key industrial sources for CCl₄ emissions and link our atmospheric observation-based top-down identification of potential sources with bottom-up inventory-based estimates (e.g., Liang et al., 2016; Sherry et al., 2018). Three major source categories accounting for $89\% \pm 6\%$ of CCl₄ enhancements observed at GSN were identified as being related to inadvertent or inadvertent co-production and escape of CCl₄ from CH₃Cl production plants (factor A), escape during industrial PCE production (factor C), fugitive emissions (factor B) from feedstock use for the production of other chlorinated compounds (e.g., CHCl₃) and process agent use and possibly from other uses of chloromethanes in chemical manufacturing. These sources are largely consistent with the bottom-up CCl₄ emission pathways identified in SPARC (Liang et al., 2016). The SPARC estimate of global CCl₄ emissions from chloromethanes and PCE/CCl₄ plants (pathway B from Liang et al., 2016 and Sherry et al., 2018) was 13 Gg yr^{−1}, as the most significant source. Fugitive feedstock and process agent emissions, denoted by pathway A by Liang et al. (2016) and Sherry et al. (2018), were estimated as ~ 2 Gg yr^{−1}. The emission contributions from China to pathways B and A were 6.6 and 0.7 Gg yr^{−1}, respectively (Liang et al., 2016; Sherry et al., 2018).

If we assume that emission rates from sources correspond to the relative contributions of corresponding source factors to the total Chinese emission rate ($23.6 \pm 7.1 \text{ Gg yr}^{-1}$ for the years 2011–2015), source factors (A) (CCl₄ emissions from chloromethane plants) and (C) (emissions from PCE plants) amount to $13 \pm 4 \text{ Gg yr}^{-1}$ for China. This is as high as the global bottom-up number of 13 Gg yr^{-1} for pathway B emissions and more than 50 % higher than the Chinese estimate of 6.6 Gg yr^{-1} . This could represent the possibility that the ratio of CCl₄ emissions from these processes into the atmosphere is higher than previously assumed, although factor (C) could include the influence of fugitive emissions of CCl₄ when using as a chlorination feedstock for PCE production. Furthermore, source factor (B) (fugitive feedstock/process agent emissions) is estimated at $\sim 7 \pm 2 \text{ Gg yr}^{-1}$ from China alone, which again contrasts with the Chinese estimate of $\sim 0.7 \text{ Gg yr}^{-1}$ and even with the lower global estimate of only 2 Gg yr^{-1} for pathway A from Liang et al. (2016) and Sherry et al. (2018). Although the analysis provided here may contain uncertainties, it appears that the SPARC industry-based bottom-up emissions are underestimated. Therefore, improvements in estimating industry bottom-up emissions of CCl₄, particularly at the factory and/or process levels, are crucial for gaining a better understanding and evaluation of ongoing global emissions of CCl₄.

Data availability. Data used in this study are available from the AGAGE (Advanced Global Atmospheric Gases Experiment) database (http://agage.eas.gatech.edu/data_archive/agage/gc-ms-medusa/, last access: July 2018).

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Author contributions. SP and SL carried out the measurements of CCl₄ and other halogenated compounds at Gosan and analyzed the results. SP supported the Gosan observations, interpreted the data and wrote the manuscript. JM and RFW supported the calibration and long-term precision for the observations of halogenated compounds at Gosan. SR designed the study and interpreted the analyzed results. SOD provided the in situ measurement data from Mace Head. XF performed an inverse model and provided the HCFC-22 emission estimates. RGP supported the AGAGE observations.

Competing interests. The authors declare that they have no conflict of interest.

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