Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-220
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 March 2018

Atmospheric Chemistry and Physics
Discussions

Toward resolving the mysterious budget discrepancy of ozone-depleting CCl_4: An analysis of top-down emissions from China

Sunyoung Park[1,2], Shanlan Li[2,3], Jens Mühle[4], Simon O'Doherty[5], Ray F. Weiss[4], Xuekun Fang[6], Stefan Reimann[7], Ronald G. Prinn[6]

[1]Department of Oceanography Kyungpook National University, Daegu 41566, Republic of Korea
[2]Kyungpook Institute of Oceanography Kyungpook National University, Daegu 41566, Republic of Korea
[3]Climate Research Division, National Institute of Meteorological Sciences, Seogwipo, Korea
[4]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA
[5]School of Chemistry, University of Bristol, Bristol, UK
[6]Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[7]Empa, Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland

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

Abstract. Emissive production and use of carbon tetrachloride (CCl_4), one of the first-generation ozone-depleting substances, have been banned by the Montreal Protocol with the 2010 phase-out for developing countries, but production and consumption for non-dispersive use as a chemical feedstock and as process agent are still allowed. Here, we present evidence that significant unreported emissions of CCl_4 still persist, based on the high frequency and magnitude of CCl_4 pollution events observed in the 8-year real time atmospheric measurement record at Gosan station, a regional background monitoring site in East Asia. From this we estimate top-down emissions of CCl_4 amounting to 23.6±7.1 Gg yr^{-1} from 2011 to 2015 for China, in contrast to the 4.3–5.2 Gg yr^{-1} reported as the most up-to-date post-2010 Chinese bottom-up emissions. The missing emissions (~19 Gg yr^{-1}) for China are highly significant, contributing about 54 % of global CCl_4 emissions. We show that 89±6 % of the CCl_4 enhancements observed at Gosan can be accounted for by fugitive emissions of CCl_4 occurring at the factory level during the production of CH_3Cl, CH_2Cl_2, $CHCl_3$ and C_2Cl_4 (PCE) and feedstock and solvent use in chemical manufacturing industries. Thus, it is crucial to implement technical improvements and better regulation strategies to reduce the evaporative losses of CCl_4 occurring at the factory and/or process level.

1. Introduction

Carbon tetrachloride (CCl_4) is a long-lived greenhouse gas and an ozone-depleting substance. Its emissive 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±0.7 ppt Cl yr^{-1} (Carpenter et al., 2014) due to the phase-out of CCl_4 use in MP non-Article-5 (developed) countries. MP Article-5 (developing) countries, including China, were required to cease CCl_4 production and consumption for dispersive applications by 2010. Because CCl_4 production and consumption for non-dispersive use (e.g., as chemical feedstock and as a process agent) is allowed, CCl_4 continues to be 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 (0–8) Gg yr^{-1} for 2007–2013 (Carpenter et al., 2014; Liang et al., 2016).

To verify these reported bottom-up estimates, independent CCl_4 emission studies have used atmospheric observations and atmospheric transport models to derive "top-down" estimates. Using the most up-to-date estimates of CCl_4 lifetimes in the atmosphere, soils, and ocean (Liang et al., 2014, Rhew et al., 2008; Butler et al., 2016), the global top-down emissions to the atmosphere were calculated to be 40±15 Gg yr^{-1}. The top-down emissions estimate is significantly higher than the reported emissions, even taking into account the large uncertainties on the soil and ocean CCl_4 sinks and how those sinks might change over time. A recent top-down study using a 3-D atmospheric transport model estimated mean global emissions of 30±5 Gg yr^{-1} in 2000–2012 based on the observed temporal trend and inter-hemispheric gradient of atmospheric CCl_4 (Liang et al., 2014). The large discrepancy between bottom-up and top-down emission estimates implies the existence of unidentified sources and/or unreported anthropogenic emissions. Thus, the recent SPARC report (Liang et al., 2016) updated anthropogenic CCl_4 emissions to at most 25 Gg yr^{-1} in 2014 based on re-consideration of industrial production processes, usage, and potential escape (Sherry et al., 2017). These new bottom-up values contribute considerably to closing the gap between bottom-up and top-down emission estimates. However, the revised bottom-up estimate of 25 Gg yr^{-1} is still lower than the average SPARC-merged top-down emission estimate of 35±16 Gg yr^{-1}. Additionally, quantification of regional/country-scale and industry-based CCl_4 emissions, which is crucial for establishing practical and effective regulation strategies, remains incomplete.

In an effort to resolve the apparent CCl_4 budget discrepancy, this study presents a regional emissions estimate of CCl_4 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 particular, recent studies based on atmospheric monitoring have consistently reported a significant increase in the emissions of most halocarbons in East Asia (Vollmer et al., 2009, Kim et al., 2010, Li et al., 2011). Top-down estimates of Chinese emissions for CCl_4 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 by these studies were quite variable: 17.6±4.4 Gg yr^{-1} in 2001 (Palmer et al., 2003), 18.0±4.5 Gg yr^{-1} in 2007 (Vollmer et al., 2009) and 4.4±3.4 Gg yr^{-1} in 2010 (Wang et al., 2014). These studies were carried out before the complete phase-out of CCl_4 production for emissive applications in China went into effect in 2010. Most recently, Bie et al. (2017) published an updated estimate of post-2010 bottom-up emissions for China made by starting from a previous bottom-up estimate of zero emission (Wan et al., 2009) and including the conversion of C_2Cl_4 emissions to CCl_4 as well as a source of CCl_4 from coal combustion smog. These recent estimates were 4.3 (1.9–8.0) Gg yr^{-1} in 2011 and 5.2 (2.4–8.8) Gg yr^{-1} in 2014.

In this study, we present high frequency, high precision 8-year real time records of atmospheric CCl_4 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 the atmospheric observations, we estimate yearly emission rates of CCl_4 for China and examine changes in those rates following the scheduled phase-out for CCl_4 in 2010. Gosan station is known to experience air masses arriving from a variety of different regions (Kim et al., 2012), such that their emissions footprints cover an area from north-eastern China down to south-eastern China below the Yangtze River, the most industrialized region in China. We also analyze the measurements of 17 other anthropogenic compounds to identify key industrial sources of CCl_4 emissions and their potential locations using a Positive Matrix Factorization model in combination with trajectory statistics (Li et al., 2014).

2. Data overview

Gosan station (GSN) is located on the remote south-western tip of Jeju Island, south of the Korean peninsula (72 m above sea level). This station is well situated to allow monitoring of long-range transport from the surrounding region. Wind patterns at GSN are typical of the Asian Monsoon, with strong predominant north-westerly and north-easterly continental outflows of polluted air from fall through spring, clean continental air flowing directly from northern Siberia in wintertime, and pristine maritime air from the Pacific in summer (Fig. S1). High-precision and high-frequency measurements of 40 halogenated compounds including CCl_4 were made continuously every two hours from 2008 to 2015 using a gas chromatography-mass spectrometer (GC-MS) coupled with an online cryogenic pre-concentration 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 are better than 1 % of background atmospheric concentrations for all the 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). 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) occur frequently, clearly implying ongoing emission of CCl_4 in East Asia. The background levels were determined using the statistical method detailed in O'Doherty et al. (2001). Note that the "background" concentrations at GSN agree well with the background concentrations observed at a remote background station in the Northern Hemisphere and are declining at a similar rate to the global trend (Fig. S3). 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 to exclude the influence of trends and/or variability in the background levels from the analysis.

A statistical analysis combining the enhanced concentrations (above-baseline concentrations) of CCl_4 from 2008 to 2015 with corresponding back trajectories allowed us to illustrate the regional distribution of potential CCl_4 emission sources. The statistical method (SI text) was introduced first in 1994 (Siebert et al., 2004) and has previously been applied to other halogenated compounds (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 travelled 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 500 m altitude above the measurement site calculated with the HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the NOAA Air Resources Laboratory (ARL) based on meteorological information from the Global Data Assimilation System (GDAS) model with a 1°×1° grid cell (Li et al., 2014). The residence times were calculated by the methods of Poirot and Wishinski (1986). To eliminate low confidence level areas, we applied a point filter that which removed grid cells that had less than 12 overpassing trajectories (Riemann et al., 2004). The resulting map of potential source areas for CCl_4 in East Asia (Fig. 2) shows that the emission sources are widely distributed in China, but are particularly concentrated in north eastern China and south-central China (approximately Shandong, Henan, Hubei, and Guangdong provinces). These provinces include industrialized urban areas containing intensive industrial activities such as chemical manufacturing. Note that this statistical analysis has little sensitivity to emissions from southwest 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 hot-spots, because its calculation scheme distributes the measured concentrations evenly throughout the grid cells over which a trajectory has passed (Stohl, 1996). Nonetheless, it is clear that the CCl_4 emission sources in East Asia were predominantly located in China.

To identify pollution events influenced solely by 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 100–124° E and 21–45° N (Fig. S4(a)). This analysis classified 29 % of all observed CCl_4 pollution events in 2008–2015 (Fig. S4(b)) as Chinese. An additional 46 % of all trajectories were affected by China plus another country. These blended air masses were excluded from the determination of Chinese emissions.

3. Using observed interspecies correlations to estimate country-based, top-down CCl_4 emissions

In this study, we use an interspecies correlation method to estimate emissions of CCl_4 from China, analogously to many recent emission studies (e.g., Kim et al., 2010; Li et al., 2011; Palmer at 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 whose country-scale emission has been well-defined independently. This empirical ratio approach provides a simple yet comprehensive method for estimating the regional emissions of almost all halogenated compounds measured at GSN and minimizes the uncertainties inherent in more complex modeling schemes. This method is particularly useful for compounds such as CCl_4 for which bottom-up inventories indicate close to zero emissions and/or clearly have large errors, which would make it difficult to define a 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 and that the reference emissions are well-known. The interspecies ratios we observed at GSN showed statistically significant correlations for many compounds at national scales (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, 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 enhancements of CCl_4 above baseline versus enhancements above baseline for 25 other halocarbons in air masses classified as Chinese. We found that the $\Delta CCl_4/\Delta$HCFC-22 ratio (0.13 ppt/ppt) showed one of the most significant correlation ($R^2 = 0.72$, $p < 0.01$) (Fig. S5). Furthermore, given that China has been the largest producer and consumer of HCFCs since 2003, and that the 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 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 FLEXPART Lagrangian transport model analysis (Stohl et al., 2010; Fang et al., 2014). These estimates ranged from 89 Gg yr^{-1} in 2011 to 144 Gg yr^{-1} in 2015. The uncertainty in the top-down estimates was 30 %, mainly due to an assumed uncertainty of ±50 % in the annual prior emissions used for the inversion calculation (Fig S6). Then the empirical correlations between the observed enhancements of CCl_4 and. HCFC-22 ($\Delta CCl_4/\Delta$HCFC-22; annual slopes shown in Fig. S7) were used to estimate the CCl_4 emission rates. The interspecies slopes were determined based on the observed enhancements obtained by subtracting the 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 on our CCl_4 emission estimates consist of the emissions uncertainty of HCFC-22 and an uncertainty associated with the ΔHCFC-22/ΔCCl_4 slope, which was calculated using the Williamson-York linear least-squares fitting method (Cantrell, 2008), taking into account the measurement errors of both HCFC-22 and CCl_4.

The annual CCl_4 emissions in China for the years 2008–2015 calculated based on our interspecies correlation method are given in Fig. 3. Figure 3 also shows a comparison of our results with previous estimates of CCl_4 emissions in China. The CCl_4 emission rate of 16.8 ± 5.6 Gg yr^{-1} in 2008 found in this study is consistent with the 2001 (Palmer et al., 2003) and 2007 (Vollmer et al., 2009) top-down emissions estimates of 17.6 ± 4.4 Gg yr^{-1} and 18.0 ± 4.5 Gg yr^{-1}, respectively. Palmer et al. (2003) used the observed correlations of CCl_4 with CO as a tracer to investigate CCl_4 emissions in aircraft observations of the Asian plume over a two-month period (March to April) in 2001. 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 July 22 and October 27 in 2010 and from March to May in 2011, and estimated CCl_4 emission in 2010 based on the observed correlations of CCl_4 with both CO and HCFC-22. The estimates from these two different tracers differed by ~100 % (8.8 vs. 4.4 Gg yr^{-1}) and were much lower than both the two previous results (Palmer et al., 2003; Vollmer et al., 2009) and our 2010 estimate of 32.7±5.1 Gg yr^{-1}. Although the cause of these discrepancies is not clear, it could be attributed to the low number of observations obtained in the aircraft campaigns and difficulties in defining the regional background values and extracting the pollution signals from the aircraft data. It is also possible that their results mostly represent emissions from northern China. Extrapolating 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} just before the scheduled phase-out of CCl_4 by 2010. The sudden large increase could be attributed to uncontrolled use/production leading to emissions of stored CCl_4 before the scheduled restrictions went into effect. Interestingly, this increase in our emission estimates was also consistent with the increase by about 20 Gg yr^{-1} in the total annual production of CCl_4 in China from 2008 to 2010. The production increase was mainly due to increase in feedstock production sector, i.e., raw material production for non-ODS chemicals (Bie et al., 2017). After perhaps a dip in 2012, our estimated emissions in 2013–2015 remain stable and similar to those in 2011, overall without statistically discernible differences between these years. Note that the average emission rate of 23.6±7.1 Gg yr^{-1} for the years 2011–2015 estimated in this study is significant, whereas post-2010 bottom-up emissions of CCl_4 in China have been reported to be near zero (Wan et al., 2009) and even the most up-to-date bottom-up estimates (Bie et al., 2017) indicate 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 fugitive emissions of CCl_4 from either non-regulated feedstock production/use or unrestricted applications as process agents for various chemical manufacturing industries are larger than anticipated.

4. Industrial source apportionment of atmospheric CCl_4 in East Asia

To identify the key industrial CCl_4 sources, we used the Positive Matrix Factorization (PMF) model (Li et al., 2014). In contrast to the previous analysis, here we included all events of CCl_4 enhancement observed at GSN thereby representing 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). PMF 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 SI text) and to resolve the number of “source factors” controlling the observations. A brief mathematical expression of the model is given by Eq. (1):

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

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-squared that measures how close the predicted concentrations are to the observed enhancements of 18 species including not only CCl_4, major CFCs, HCFCs, HFCs, PFCs, SF_6, carbonyl sulfide (COS), but also CH_3Cl, CH_2Cl_2, $CHCl_3$, and PCE to account for potential chemical intermediate release of CCl_4 during industry activities. The model’s R-squared values, as estimated from a correlation plot between the measured and 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 percent contributions of the factors to the observed enhancements of individual compounds are shown in Fig 4. The uncertainties were determined from the 1σ standard deviation of factor contributions from 5 sets of 20 runs (total 100 replications) (Relf et al., 2007).

The factor shown in the first panel of Fig. 4 is characterized by 38±4 % of CCl_4 and 97±2 % of CH_3Cl, suggesting (a) advertent or inadvertent co-production and escape of CCl_4 during CH_3Cl generation in the chemical plants (see SI text for the chemical reactions), (b) fugitive emissions of CCl_4 being used as a chlorination feedstock for CH_3Cl production, and/or (c) CCl_4 and CH_3Cl being co-emitted in smog from coal combustion (Li et al., 2003). The latter case is the least likely given that COS, a major coal burning tracer, does not contribute to this factor. A recent study (Li et al., 2017) showed that the chemical industrial emissions of CH_3Cl in China (363±85 Gg yr^{-1} for 2008–2012) are comparable in magnitude to the known global total of anthropogenic CH_3Cl emissions from coal combustion and indoor biofuel use. The second source factor also accounts for a large fraction of CCl_4 (32±4 %) and shows high percentages for several compounds: 72±18 % of CH_2Cl_2, 59±11 % of $CHCl_3$, 39±10 % of CFC-11, and 51±12 % of HFC-23. Note that CH_2Cl_2, $CHCl_3$, and CFC-11 can all be produced as by-products of chlorination and are used as intermediates or solvents in chemical manufacturing, along with CCl_4. In addition, CCl_4 is a common feedstock for CH_2Cl_2 production (Liang et al., 2016) and is also used in CFC production (Wan et al., 2009). CCl_4 released as a by-product during the chlorination process is also readily converted back to $CHCl_3$ (Chen and Yang, 2013). $CHCl_3$ can be used as a feedstock for HCFC-22 production. This is consistent with this second factor also being distinguished by a high contribution of HFC-23, because HFC-23, of which the Chinese emissions account for ~70 % of total global emissions (Kim et al., 2010; Li et al., 2011), is a typical by-product of HCFC-22 generation (Fang et al., 2015). Thus, HFC-23 is emitted at factory level from the regions where chemical manufacturing industries are heavily located. Therefore, the fact that the observed enhancements of HFC-23, CCl_4, CH_2Cl_2, $CHCl_3$, and CFC-11 are grouped into the second factor by the PMF analysis implies that this factor most likely represents fugitive emissions of these compounds at the factory level during various chemical manufacturing processes in China. The third source factor is distinguished by 19±1 % of CCl_4 and 95±2 % of PCE and can possibly be explained by advertent or inadvertent co-production and escape of CCl_4 during industrial C_2Cl_4 production and/or fugitive emissions of CCl_4 being used as a chlorination feedstock for C_2Cl_4 production. The spatial distribution (Fig. S8) of the first three source factors derived from trajectory statistics (SI text) are similar, covering areas in and around Guangzhou of Guangdong, Wuhan of Hubei, Zhengzhou of Henan, and Xian of Shaanxi province. This is consistent with the PMF analysis, confirming that CCl_4 emissions from China are more strongly associated with industrial processes than with population density. The three emission sources accounting for 89±6 % of CCl_4 enhancements observed at GSN can be considered as dispersive emissions of CCl_4 at the factory level due to inadvertent by-production, feedstock usage for production of chlorinated compounds, and intermediate/solvent use for chemical processes. The fourth factor is characterized by high percentages of CF_4 (50±9 %) and COS (94±24 %). COS is mostly emitted from coal and biomass burning as well as various industrial processes including primary aluminum production (Blake et al., 2004). The aluminum production industry, particularly in China, is a well-known emission source of PFCs (Mühle et al., 2010). About 9±4 % of CCl_4 enhancements are attributed to this factor. The fifth source factor is characterized by high percentages of HFCs (89±1 % of HFC-125, 78±1.3 % of HFC-32, 52±1.4 % of HFC-143a, and 43±5 % of HFC-134a). These compounds are used in air conditioning and refrigeration applications and are predominantly produced in China (Fang et al., 2016). Their azeotropic blends, such as R-410A (50 % HFC-32, 50 % HFC-125 by weight), R404A (52 % HFC-143a, 44 % HFC-125 and 4 % HFC-134a), R-407C (23 % HFC-32, 52 % HFC-134a, 25 % HFC-125) and R-507A (50 % HFC-125 and 50 % HFC-143a), are also increasingly used in China (Fang et al., 2016). The small percentages of contributions of these fourth and fifth sources to CCl_4 enhancements are not statistically significant when considering the uncertainty range, but may suggest that CCl_4 is emitted to some extent by coal fired power plants located close to primary aluminum smelters and to production facilities for air-conditioning systems and refrigerant units. It is notable that the sixth, seventh, and eighth factors do not contribute to the observed CCl_4 enhancements. The description of the last three factors is given in the Supporting Information.

4. Conclusions

The 8-year record of atmospheric CCl_4 observations at GSN provides evidence for ongoing CCl_4 emissions in East Asia during 2008–2015. Based on these measurements, we present top-down emissions estimates for CCl_4 from China of 23.6±7.1 Gg yr^{-1} for the years 2011–2015, in contrast to the 4.3–5.2 Gg yr^{-1} given by the most up to date bottom-up emission inventory of post-2010 China. A factor analysis combining the observed concentration enhancements of 18 species was used to identify key industrial sources for CCl_4 emissions. Three major source categories accounting for 89±6 % of CCl_4 enhancements observed at GSN were identified as by-product/feedstock emissions from (1) CH_3Cl production plants and (2) PCE production plants, and (3) fugitive emissions from feedstock use for the production of other chlorinated compounds (e.g., CH_2Cl_2 and $CHCl_3$) and from solvent/process agent use. These sources are consistent with the bottom-up CCl_4 emissions pathways identified in SPARC (Liang et al., 2016): feedstock and process agent usage (Pathway A denoted in (Liang et al., 2016)) and CCl_4 production from CH_3Cl and PCE plants (Pathway B in (Liang et al., 2016)). However, our current analysis is limited in its ability to distinguish other potential pathways, such as industrial and domestic use of chlorine and legacy emissions from landfill and contaminated soils. SPARC estimated 2 Gg yr^{-1} of CCl_4 emissions for Pathway A and 13 Gg yr^{-1} for Pathway B, globally, with contributions from China of 0.7 and 6.6 Gg yr^{-1}, respectively. Our analysis shows that the relative contributions to the observed CCl_4 enhancements due to fugitive emissions from feedstock and process agent use (factor 2) and from CH_3Cl and PCE related emissions (factors 1 and 3 combined) are 32±4 % and 57±4 %, respectively. If we assume that the relative contributions of the two pathways correspond to the emission rates from the corresponding sources to the total Chinese emission rate (23.6±7.1 Gg yr^{-1} for the years 2011–2015), CCl_4 emissions associated with CH_3Cl and PCE plants are estimated to contribute 13±4 Gg yr^{-1}, which is two times larger than the SPARC bottom-up estimate for Pathway B in China. For the emissions from feedstock and process agent usage (Pathway A), the difference between the SPARC estimate of 0.7 Gg yr^{-1} and our estimate of ~7±2 Gg yr^{-1} is even more significant. Although this analysis has many uncertainties, it suggests that the emissions from feedstock and process agent usage could be even more severely underestimated than the emissions associated with CH_3Cl and PCE production plants. This seems plausible, as evaporative losses of CCl_4 during its use as feedstock and/or process agent and from storage reservoirs of factories are easily overlooked and very poorly constrained. Therefore, improvements in estimating bottom-up emissions of CCl_4, particularly at the factory and/or process level, are crucial to better understanding and evaluating ongoing global emissions of CCl_4.

Data used in this study are available from https://agage.mit.edu/ and from data repositories referenced therein.

Acknowledgments: This research was supported by the National Strategic Project-Fine particle of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT), the Ministry of Environment (ME), and the Ministry of Health and Welfare (MOHW) (No. NRF-2017M3D8A1092225). We acknowledge the support of our colleagues from the Advanced Global Atmospheric Gases Experiment (AGAGE). The operation of the Mace Head AGAGE station, the MIT theory and inverse modeling and SIO calibration activities are supported by the National Aeronautics and Space Administration (NASA, USA) (grants NAG5-12669, NNX07AE89G, NNX11AF17G and NNX16AC98G to MIT; grants NAG5-4023, NNX07AE87G, NNX07AF09G, NNX11AF15G, NNX11AF16G, NNX16AC96G and NNX16AC97G to SIO). AGAGE stations operated by the University of Bristol were funded by the UK Department of Business, Energy and Industrial Strategy (formerly the Department of Energy and Climate Change) through contract TRN 34/08/2010, NASA contract NNX16AC98G through MIT and NOAA contract RA-133R-15-CN-0008.

References

An, X.Q., Henne, S., Yao, B., Vollmer, M.K., Zhou, L.X., Li Y.: Estimating emissions of HCFC-22 and CFC-11 in China by atmospheric observations and inverse modeling, Sci. China Chem, 55, 10, 2233–2241, https://doi.org/10.1007/s11426-012-4624-8, 2012.

Bie P., Fang X., Li Z., Hu J.: Emissions estimates of carbon tetrachloride for 1992-2014 in China, Environ. Poll., 224, 670–678, https://doi.org/10.1016/j.envpol.2017.02.051, 2017.

Blake, N.J., Streets, D.G., Woo, J.H., Simpson, I.J., Green, J., Meinardi, S., Kita, K., Atlas, E., Fuelberg, H.E., Sachse, G., Avery, M A., Vay, S.A., Talbot, R.W., Dibb, J.E., Bandy, A.R., Thornton, D.C., Rowland, F. S., Blake, D.R.: Carbonyl sulfide and carbon disulfide: Large-scale distributions over the western Pacific and emissions from Asia during TRACE-P, J. Geophys. Res., 109 (D15), https://doi.org/10.1029/2003JD004259, 2004.

Butler, J. H., Yvon-Lewis, S. A., Lobert, J. M., King, D. B., Montzka, S. A., Bullister, J. L., Koropalov, V., Elkins, J. W., Hall, B. D., Hu, L., and Liu, Y.: A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl_4) to the ocean, Atmos. Chem. Phys., 16, 10899–10910, https://doi.org/10.5194/acp-16-10899-2016, 2016.

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477–5487, https://doi.org/10.5194/acp-8-5477-2008, 2008.

Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewis, S. A.: Ozone-Depleting Substances (ODSs) and other gases of interest to the Montreal Protocol, in: Scientific Assessment of Ozone Depletion: 2014. Global Ozone Research and monitoring Project – Report N. 55, World Meteorological Organization, Geneva, Switzerland, 2014.

Chen, Z.L., Yang B.: Study on the conversion technology of carbon tetrachloride, Organo-Fluorine Ind., 1, 48–53 (In Chinese with English Abstract), 2013

Choi E., Heo J.B., Yi S.M.: Apportioning and locating nonmethane hydrocarbon sources to a background site in Korea, Environ. Sci. Technol., 44, 15, 5849–5854, https://doi.org/10.1021/es903634e, 2010.

Fang, X., Wu, J., Su, S., Han, J., Wu, Y., Shi, Y., Wan, D., Sun, X., Zhang, J., Hu, J.: Estimates of major anthropogenic halocarbon emissions from China based on interspecies correlations, Atmos. Environ., 62, 26–33, https://doi.org/10.1016/j.atmosenv.2012.08.010, 2012.

Fang, X., Thompson, R. L., Saito, T., Yokouchi, Y., Kim, J., Li, S., Kim, K. R., Park, S., Graziosi, F., and Stohl, A.: Sulfur hexafluoride (SF6) emissions in East Asia determined by inverse modeling, Atmos. Chem. Phys., 14, 4779–4791, https://doi.org/10.5194/acp-14-4779-2014, 2014.

Fang, X., Stohl, A., Yokouchi, Y., Kim, J., Li, S., Saito, T., Park, S., Hu, J.: Multiannual top-down estimate of HFC-23 emissions in East Asia, Environ. Sci. Tech., 49, 7, 4345–4353, https://doi.org/10.1021/es505669j, 2015.

Fang, X., Velders, G.J.M., Ravishankara, A. R., Molina, M.J., Hu, J., Prinn, R.G.: Hydrofluorocarbon (HFC) emissions in China: An inventory for 2005–2013 and projections to 2050, Environ. Sci. Tech., 50, 4, 2027–2034, https://doi.org/10.1021/acs.est.5b04376, 2016.

Guo, H., Ding, A. J., Wang, T., Simpson, I. J., Blake, D. R., Barletta, B., Meinardi, S., Rowland, F. S., Saunders, S. M., Fu, T. M., Hung, W. T., Li, Y. S.: Source origins, modeled profiles, and apportionments of halogenated hydrocarbons in the greater Pearl River Delta region, southern China, J. Geophys. Res.: Atmos., 114, D11302, 2156–2202, http://doi.org/10.1029/2008JD011448, 2009.

Kim, J., Li S., Kim K.R., Stohl A., Muhle J., Kim S.K., Park M.K., Kang D.J., Lee G., Harth C.M., Salameh P.K., Weiss R.F.: Regional atmospheric emissions determined from measurements at Jeju Island, Korea: Halogenated compounds from China, Geophys. Res. Lett., 37, L12801, https://doi.org/10.1029/2010GL043263, 2010.

Kim, J., Li, S., Mühle, J., Stohl, A., Kim, S.K., Park, S., Park, M.K., Weiss, R.F., Kim, K.R.: Overview of the findings from measurements of halogenated compounds at Gosan (Jeju Island, Korea) quantifying emissions in East Asia, Environ. Sci., 9, 1, 71–80, https://doi.org/101080/194315X.2012.696548, 2012.

Lanz, V. A., Henne, S., Staehelin, J., Hueglin, C., Vollmer, M. K., Steinbacher, M., Buchmann, B., and Reimann, S.: Statistical analysis of anthropogenic non-methane VOC variability at a European background location (Jungfraujoch, Switzerland), Atmos. Chem. Phys., 9, 3445–3459, https://doi.org/10.5194/acp-9-3445-2009, 2009.

Li, S., Kim, J., Kim, K.R.: Emissions of halogenated compounds in East Asia determined from measurements at Jeju Island, Korea, Environ. Sci. Technol., 45, 13, 5668–5675, https://doi.org/10.1021/es104124k, 2011.

Li, S., Kim, J., Park, S., Kim, S.K., Park, M.K., Mühle, J., Lee, G., Lee, M., Jo, C.O., Kim, K.R.: Source identification and apportionment of halogenated compounds observed at a remote site in East Asia, Environ. Sci. Tech., 48, 1, 491–498, https://doi.org/10.1021/es402776w, 2014.

Li, X., Wang, S., Duan, L., Hao, J.: Characterization of non-methane hydrocarbons emitted from open burning of wheat straw and corn stover in China, Environ. Res. Lett., 4, 044015, 2009.

Jiaxi, L., Junzhi, W., Hong, L., Zhu, R., Qi, L., Songguang, L.: The production and release of CFCs from coal combustion, Acta Geolog. Sinica, 77, 1, 1755–67241, http://doi.org/10.1111/j.1755-6724.2003.tb00113.x, 2003.

Li, S., Park, MK., Jo, C.O., Park, S.J.: Emission estimates of methyl chloride from industrial sources in China based on high frequency atmospheric observations, J. Atmos. Chem. 74, 2, 227–243, https://doi.org/10.1007/s10874-016-9354-4, 2017.

Liang, Q., Newman, P.A., Daniel, J.S., Reimann, S., Hall, B.D., Dutton, G., Kuijpers L.J.M.: Constraining the carbon tetrachloride (CCl_4) budget using its global trend and inter-hemispheric gradient, Geophys. Res. Lett., 41, 5307–5315, doi:10.1002/2014GL060754, 2014.

Liang, Q. Newman, P.A., Reimann, S. (Eds.), SPARC Report on the Mystery of Carbon Tetrachloride. SPARC Report No. 7, WCRP-13/2016, 2016.

Miller, B.R., Weiss, R.F., Salameh, P.K., Tanhua, T., Greally, B.R., Mühle, J., Simmonds, P.G.: Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Anal. Chem., 80, 5, 1536–1545, https://doi.org/10.1021/ac702084k, 2008.

Mühle, J., Ganesan, A. L., Miller, B. R., Salameh, P. K., Harth, C. M., Greally, B. R., Rigby, M., Porter, L. W., Steele, L. P., Trudinger, C. M., Krummel, P. B., O'Doherty, S., Fraser, P. J., Simmonds, P. G., Prinn, R. G., and Weiss, R. F.: Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane, Atmos. Chem. Phys., 10, 5145–5164, https://doi.org/10.5194/acp-10-5145-2010, 2010.

O'Doherty, S., Simmonds, P. G., Cunnold, D. M., Wang, H. J., Sturrock, G. A., Fraser, P. J., Ryall, D., Derwent, R. G., Weiss, R. F., Salameh, P., Miller, B. R., Prinn, R. G.: In situ chloroform measurements at Advanced Global Atmospheric Gases Experiment atmospheric research stations from 1994 to 1998, J. Geophys. Res.: Atmos., 106, D17, 20429–20444, https://doi.org/10.1029/2000JD900792, 2001.

Paatero, P., Tapper, U.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environ., 5, 111–126, https://doi.org/10.1002/env.3170050203, 1994.

Palmer P.I., Jacob, D.J., Mickley, L.J. Blake, D.R., Sachse, G.W., Fuelberg, H.E., Kiley, C.M.: Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data, J. Geophys. Res., 108, 4753, D24, https://doi.org/10.1029/2003JD003591, 2003.

Poirot, R.L., Wishinski, P.R.: Visibility, sulfate and air-mass history associated with the summertime aerosol in northern Vermont, Atmos. Environ, 20, 7, 1457−1469, https://doi.org/10.1016/0004-6981(86)90018-1, 1986.

Reff, A., Eberly, S.I., Bhave, P.V.: Receptor modeling of ambient particulate matter data using positive matrix factorization: review of existing methods, J. Air & Waste Manage. Assoc., 57, 2, 146–154, https://doi.org/10.1080/10473289.2007.10465319, 2012.

Reimann S., Schaub, D., Stemmler, K., Folini, D., Hill, M., Hofer, P., Buchmann, B., Simmonds, P.G., Greally, B.R., O'Doherty, S.: Halogenated greenhouse gases at the Swiss High Alpine Site of Jungfraujoch (3580 m asl): Continuous measurements and their use for regional European source allocation, J. Geophys. Res., 109, D05307J, https://doi.org/10.1080/10473289.2007.10465319109, 2004.

Rhew, R.C., Miller, B.R., Weiss, R.F.: Chloroform, carbon tetrachloride and methyl chloroform fluxes in southern California ecosystems, Atmos. Environ., 42, 30, 7135–7140, https://doi.org/10.1016/j.atmosenv.2008.05.038, 2008.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D.T., Schwikowski, M.: Trajectory analysis of aerosol measurements at high Apline sites, in: Transport and transformation of pollutants in the troposphere, Borrell, P.M., T. Cvitaš, W. Seiler (Eds.), Academic Publishing, Den Haag, 689–693, 2008.

Sherry, D., McCulloch, A., Liang, Q., Reimann, S., Newman, P.A.: Current sources of carbon tetrachloride in our atmosphere, Environ. Res. Lett., 13, 2, https://doi.org/10.1088/1748-9326/aa9c87, 2018.

Stohl, A.: Trajectory statistics: A new method to establish source receptor relationships of air pollutants and its application to the transport of particulate sulfate in Europe, Atmos. Environ., 30, 4, 579−587, https://doi.org/10.1016/1352-2310(95)00314-2, 1995.

Stohl, A., Kim, J., Li, S., O'Doherty, S., Mühle, J., Salameh, P. K., Saito, T., Vollmer, M. K., Wan, D., Weiss, R. F., Yao, B., Yokouchi, Y., and Zhou, L. X.: Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling, Atmos. Chem. Phys., 10, 3545–3560, https://doi.org/10.5194/acp-10-3545-2010, 2010.

Vollmer, M. K., Zhou, L. X., Greally, B. R., Henne, S., Yao, B., Reimann, S., Stordal, F., Cunnold, D. M., Zhang, X. C., Maione, M., Zhang, F., Huang, J., Simmonds, P. G., Emissions of ozone-depleting halocarbons from China, Geophys. Res. Lett., 36, 15, http://dx.doi.org/10.1029/2009GL038659, 2009.

Wang, C., Shao, M., Huang, D., Sihua, L., Zeng, L., Hu, M., Zhang, Q.: Estimating halocarbon emissions using measured ratio relative to tracers in China, Atmos. Environ., 89, 816–826, https://doi.org/10.1016/j.atmosenv.2014.03.025, 2014.

Wan, D., Xu, J., Zhang, J., Tong, X., Hu, J.: Historical and projected emissions of major halocarbons in China, Atmos. Environ., 43, 36, 5822–5829, https://doi.org/10.1016/j.atmosenv.2009.07.052, 2009.

United Nations Environment Programme (UNEP 2009) Ozone Secretariat Data Access Centre; http://ozone.unep.org/reporting/, last access: 11 February 2018.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-220
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 March 2018

Figure Captions

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 the background levels shown in black) are denoted by red dots.

Figure 2. Distribution of potential source regions calculated from trajectory statistics for the 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 the emission sources are widely distributed over China. The site of Gosan station is indicated by an asterisk (*).

Figure 3. CCl_4 emissions in China as determined by an inter-species correlation method. A comparison of our results with previous estimates for Chinese emissions is also shown. Note that the emissions reached a maximum in 2009–2010 in concurrence with the scheduled phase-out of CCl_4 by 2010, and the average annual emission rate of 23.6±7.1 Gg yr^{-1} for the years 2011–2015 are still substantial.

Figure 4. Source profiles derived from PMF analysis for 18 compounds, including CCl_4, CFCs, HCFCs, HFCs, PFCs, SF_6, COS, CH_3Cl, CH_2Cl_2, $CHCl_3$, and C_2Cl_4. 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.

Figure 1.

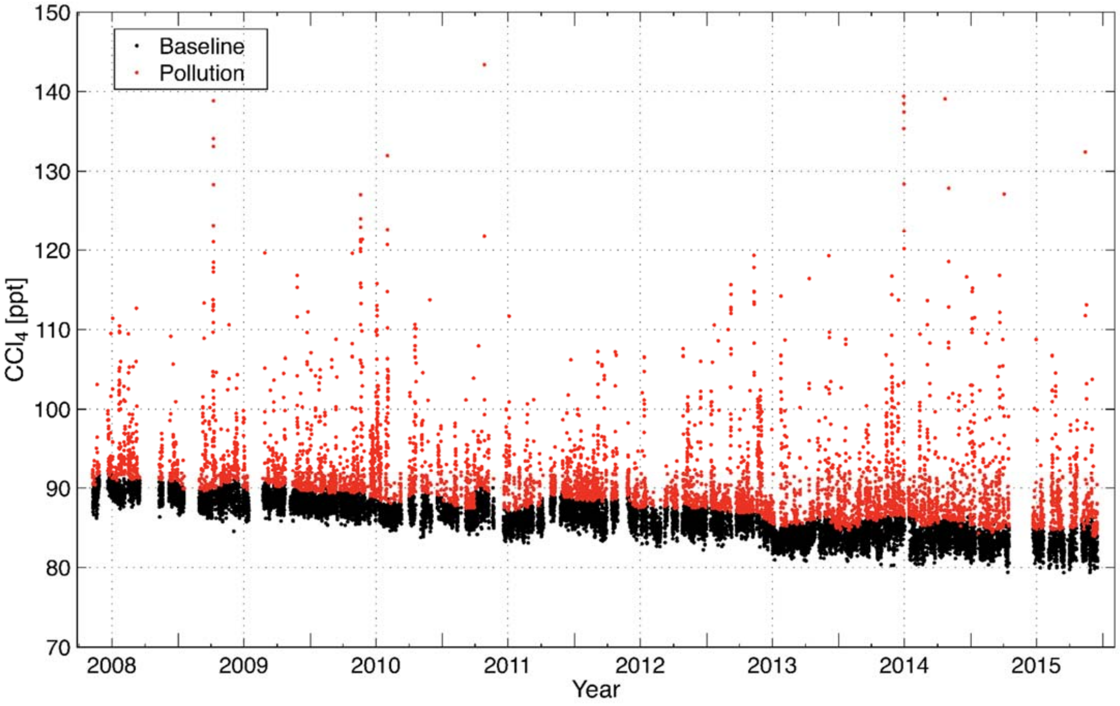

Baseline
Pollution
150
140
130
120
110
100
90
80
70
CCl_4 [ppt]
2008
2009
2010
2011
2012
2013
2014
2015
Year

Figure 2.

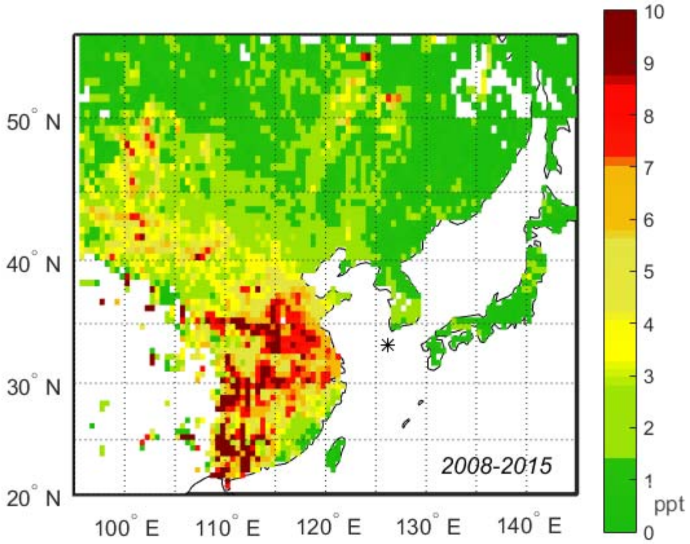
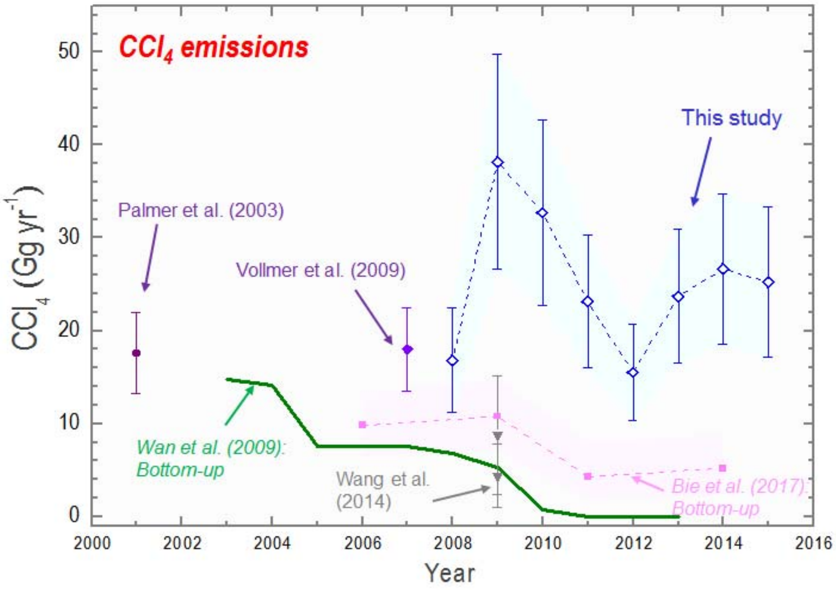

50° N
40° N
30° N
20° N
100° E
110° E
120° E
130° E
140° E
2008-2015
10
9
8
7
6
5
4
3
2
1
ppt
0

Figure 3.


CCl_4 emissions
CCl_4 (Gg yr^{-1})
0
10
20
30
40
50
Year
2000
2002
2004
2006
2008
2010
2012
2014
2016
This study
Palmer et al. (2003)
Vollmer et al. (2009)
Wan et al. (2009): Bottom-up
Wang et al. (2014)
Bie et al. (2017): Bottom-up

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-220
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 March 2018

Figure 4.