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Emissions estimates of carbon tetrachloride for 1992–2014 in China☆

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ABSTRACT

Discrepancies in emission estimates of carbon tetrachloride (CCl_4, CTC), between bottom-up and top-down methods, have been shown since the 1990s at both the global and regional scale. This study estimates the emissions of China from 1992 to 2014 based on emission functions and aggregated activity information given reasonable uncertainties. The results show that emissions increase from 7.3 Gg/yr (5.6–9.1 Gg/yr at 95% confidential interval) to 14.0 (9.1–19.5) Gg/yr with a growth rate of 6.7 (1.9–11.4) %/yr during 1992–2002 and then decrease to a minimum of 4.3 (1.9–8.0) Gg/yr in 2011. More than 54% of the emissions during 1992–2009 are from the process agents sector. The estimates are comparable with those of other studies and those in this study based on observations during 2011–2014 using the interspecies correlation method. China's contribution to global emissions increases from 7.5% to 19.5% during 1992–2009, but the contribution is reduced to 9.9% and 8.0% in 2010 and 2011, respectively, indicating the effectiveness of compliance with the Montreal Protocol and its subsequent Amendments and Adjustments, whereby CTC emissions are phased-out. The results of this study are beneficial for narrowing the gap between bottom-up estimates and top-down emission calculations of CTC in China.

1. Introduction

The greenhouse gas carbon tetrachloride (CCl_4, CTC) is a primary, anthropogenic ozone depleting substance (ODS) whose production and consumption for emissive uses are regulated under the Montreal Protocol (MP) and its subsequent Amendments and Adjustments. It has an estimated total lifetime that varies from 26 years (Carpenter et al., 2014) to 33 years (SPARC, 2016), an ozone depletion potential (ODP) of 0.72, and a 100-year global warming potential (GWP) of 1730 (Harris et al., 2014).

Historically, CTC produced from chloromethane production facilities has been consumed mainly as a solvent and process agent, and as a feedstock for the production of chlorofluorocarbons (CFCs) and their substitutes. It is now used only as a feedstock, in addition to other less essential applications, including process agent and laboratory and analytical applications (Carpenter et al., 2014; MEPC, 2009; UNEP, 2015a).

Although it is important to control and regulate CTC during production and consumption, in compliance with the MP as a de facto means of emissions control, estimates of emissions are an important component of estimates of halogen loading to the atmosphere (Vollmer et al., 2009). Thus, accurate emission estimates will be beneficial. However, estimated emissions of CTC based on lifetime and precisely observed atmospheric abundances (i.e., top-down estimates) have not been in accord with those estimates based on reported production and consumption (i.e., bottom-up estimates) (Carpenter et al., 2014; SPARC, 2016). This discrepancy exists globally, and also occurs in China. The first bottom-up emission estimate of CTC for China, from 1995 to 2024, is reported by Wan et al. (2009), but that study is non-comprehensive because it covers only the use of solvent and process agents. Other relevant studies adopt interspecies correlation (ISC) techniques using CO or HCFC-22 as a tracer to estimate CTC emissions, e.g., Palmer et al. (2003), 17.6 ± 4.4 Gg/yr for 2001; Yao et al. (2010), 4.7 Gg/yr for 2007; and Wang et al. (2014), 4.4 ± 3.4 Gg/yr for 2010. Thus, the latter estimates are 197% ± 49%, 62%, 587% ± 453% of the emission estimates for 2001, 2007 and 2010 that are 8.9 Gg/yr, 7.6 Gg/yr and 0.75 Gg/yr in Wan et al. (2009), respectively. Another study combines observations at Shangdianzi, located in the North China Plain, with an inverse modeling approach and estimates emissions of 15^{+7}_{-5} Gg/yr during the period October 2006 to March 2008 (Vollmer et al., 2009), in which the best estimate (15 Gg/yr) is 197% of the estimate for 2007 (7.6 Gg/yr) in Wan et al. (2009). The

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discrepancy between the bottom-up inventory and top-down estimates of CTC emissions for China remains unresolved.

In addition, because of the low density of long-term surface observations in China, achieving a better understanding of the contribution of China's CTC emissions to total global emissions has remained difficult (Carpenter et al., 2014; Vollmer et al., 2009). Therefore, a comprehensive and reliable CTC inventory for China is needed for quantification of global CTC emissions.

Based on a survey of CTC and chloromethane production plants and thorough investigation of CTC application fields, we adopt the bottom-up method to estimate China's CTC emission inventory. Approximately 0.03–0.25% of tetrachloroethylene (PCE) emissions convert to CTC (Singh et al., 1975; Franklin, 1994); due to considerable PCE consumption, and emissions of 60 Gg/yr in 2013 (Yang, 2013) and 44.9 ± 32.4 Gg/yr in 2010 (Wang et al., 2014), this emission source in China should also be considered. Additionally, CTC has been found in smog from coal combustion (Li et al., 2003). As China is the largest coal producer and consumer in the world, with production and consumption of more than 2.5 Tg/yr in 2008 (Lin and Liu, 2010), we consider this source as well. Because these two emission sources have not been included in bottom-up emission inventories previously (Carpenter et al., 2014; Wang et al., 2014; SPARC, 2016), they may contribute to addressing the discrepancy between bottom-up and top-down estimates. Hydrochloric acid (HCl) and chlorine water (Dong, 2008), instead of CTC, are applied to remove NCl_3 during the spraying cleaning process of chloralkali plants in China. In addition, there is little convincing evidence that other non-industrial CTC emission sources could substantially account for the discrepancy (Fraser et al., 2014; Hu et al., 2016), so we have not considered these sources (e.g., landfills, waste treatment or incineration facilities, and contaminated industrial sites) (SPARC, 2016). Furthermore, based on the CTC and HCFC-22 concentrations measured at a monitoring site, a campus station at Peking University (40.00° N, 116.30° E), in northern China during 2011–2014, CTC emissions are also estimated using the ISC method, with the updated HCFC-22 emissions (in the same period) of Li et al. (2016). We have estimated the historical emissions and compared the results with those of other studies from 1992 to 2014. The uncertainties in emission estimates are quantified using the Monte Carlo method.

2. Methodology

2.1. Bottom-up estimation of historical emissions during 1992–2014

The bottom-up CTC emission estimates refer to the General methodological issues for all ODS substitutes sub-source categories in Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (IPCC, 2000), and Methods to combine uncertainties in 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2006), and as well as the prompt emission factor in Wan et al.(2009). CTC emissions from 1992 to 2010 have been estimated in five fields in China (as shown in Fig. 1):

A. CFC production sector, in which CTC is used mainly as feedstock for CFC-11 and CFC-12 production;

B. Feedstock production sector, in which CTC is used as a raw material to produce non-ODS chemicals;

C. Process agents sector, where CTC has unique chemical and/or physical properties that facilitate intended chemical reactions and/or inhibit unintended chemical reactions;

D. Solvents sector, in which CTC has been produced for use as a cleaning agent or solvent, such as for electronic machinery, medical equipment, automobiles, precision instruments, etc.;

E. Chemical reagents in laboratory, for technological development and laboratory-based scientific research.

In addition, because CTC has been produced and consumed in China, leakage emissions from CTC production, storage and transport, ventilated to the atmosphere, cannot be neglected. From 2011 to 2014, CTC consumption is limited for applications in sectors C and E, with uncontrolled consumption in sector B. However, as CTC is still produced as an unavoidable byproduct of chloromethane production after 2010 in China, and as the annual production of chloromethane remains in millions of metric tons due to rapid growth (Xu, 2012), emission estimates from this sector should be of considerable concern. Additionally, we consider the emissions associated with the atmospheric conversion of PCE (Singh et al., 1975; Franklin, 1994), as well as the production and consumption of coal (Li et al., 2003; ODEQ, 1998). The annual total CTC emissions obtained by summing the results of each sector are calculated by Equation (1):

$$E_{CTC-(t)} = \left\{ \begin{array}{c} P_{CTC-(t)} \times EF_{CTC-Pro} + C_{CTC-CFCs-(t)} \times EF_{CFCs-Pro} + C_{Sol-(t-1)} \times (1 - EF_{Sol}) + C_{Sol-(t)} \times EF_{Sol}, 1992 \le t \le 2010 \\ P_{CM-(t)} \times \frac{R_{CM-CTC}}{1 - R_{CM-CTC}} \times EF_{CTC-Pro}, 2011 \le t \le 2014 \end{array} \right\} C_{Lab-(t-1)} \times (1 - EF_{Lab}) + C_{Lab-(t)} \times EF_{Lab} C_{non-ODS-(t)} \times EF_{non-ODS} + C_{CA-t} \times EF_{CA} C_{CTC-(t)} \times EF_{Loss} + E_{PCE-(t)} \times R_{PCE-CTC} P_{Coal-(t)} \times EF_{Coal-Pro} + C_{Coal-(t)} \times EF_{Coal-Con}, \quad (1)$$

where $E_{CTC-(t)}$ stands for the total CTC emissions in the year t; $P_{CTC-(t)}$ and $P_{CM-(t)}$ are the annual productions of CTC and chloromethane excluding CTC, respectively; $EF_{CTC-Pro}$ is the emission factor of CTC emission from productions of CTC and chloromethane;$C_{CTC-(t)}$ is the annual total CTC consumption; $C_{CTC-CFCs-(t)}$, $C_{non-ODS-(t)}$, C_{CA-t}, $C_{Sol-(t)}$, and $C_{Lab-(t)}$ are the CTC consumption of sectors A, B, C, D, and E, and hence $EF_{CFCs-Pro}, EF_{non-ODS}, EF_{CA}, EF_{Sol}$ and EF_{Lab} are the corresponding emission factors, respectively, EF_{Loss} is the loss ratio from storage and transport; and R_{CM-CTC} represents the proportion of CTC production among total chloromethane production. E_{PCE-t} is the annual emission of PCE in China, $R_{PCE-CTC}$ represents the conversion factor of CTC from PCE, and $P_{Coal-(t)}$ and $C_{Coal-(t)}$ are the annual production and consumption of coal in China, respectively. We have obtained the production and consumption information for coal during 1992–2014 from the *China Statistical Yearbook: 2015* (NBSC, 2015), as shown in Fig. S1 in the Supporting Information (SI). The activity information about PCE is estimated and discussed in detail in the SI.

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