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Analysis of 3-year observations of CFC-11, CFC-12 and CFC-113 from a semi-rural site in China

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ABSTRACT

In-situ measurements of atmospheric chlorofluorocarbons (CFCs) can be used to the assess their global and regional emissions and to check for compliance with phase-out schedules under Montreal protocol and its amendments. The atmospheric mixing ratios of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 ($CCl_2F–CClF_2$) have been measured by an automated in-situ GC-ECDs system at the regional Chinese Global Atmosphere Watch (GAW) station Shangdianzi (SDZ), from November 2006 to October 2009. The time series for these three principal CFCs showed large episodic events and background conditions occurred for approximately 30% (CFC-11), 52% (CFC-12) and 56% (CFC-113) of the measurements. The mean background mixing ratios for CFC-11, CFC-12 and CFC-113 were 244.8 ppt (parts per trillion, 10^{-12}, molar) 539.6 ppt and 76.8 ppt, respectively, for 2006–2009. The enhanced CFC mixing ratios compared to AGAGE sites such as Trinidad Head (THD), US and Mace Head (MHD), Ireland suggest regional influences even during background conditions at SDZ, which is much closer to highly-populated areas. Between 2006 and 2009 background CFCs exhibited downward trends at rates of −2.0 ppt yr^{-1} for CFC-11, −2.5 ppt yr^{-1} for CFC-12 and −0.7 ppt yr^{-1} for CFC-113. De-trended 3-year average background seasonal cycles displayed small fluctuations with peak-to-trough amplitudes of 1.0 ± 0.02 ppt (0.4%) for background CFC-11, 1.3 ± 2.1 ppt (0.3%) for CFC-12 and 0.2 ± 0.4 ppt (0.3%) for CFC-113. On the other hand, during pollution periods these CFCs showed much larger seasonal cycles of 11.2 ± 10.7 ppt (5%) for CFC-11, 7.5 ± 6.5 ppt (2%) for CFC-12 and 1.0 ± 1.2 ppt (1.2%) for CFC-113, with apparent winter minima and early summer maxima. This enhancement was attributed to prevailing wind directions from urban regions in summer and to enhanced anthropogenic sources during the warm season. In general, horizontal winds from northeast showed negative contribution to atmospheric CFCs loading, whereas South Western advection (urban sector: Beijing) had positive contributions.

1. Introduction

Chlorofluorocarbons (CFCs) used mainly as refrigerants, foam blowing agents, solvents and cleaning agents are sources of chlorine to the atmosphere, which can catalytically destroy stratospheric ozone (Molina and Rowland, 1974). Furthermore, they are strong infrared absorbers in the atmospheric window region and are very potent greenhouse gases (Daniel et al., 1995; Schneider et al., 2005). Attention has been focused on these substances since the 1970s because of their rapid increases in the Earth's atmosphere (Fraser et al., 1996; Montzka et al., 1999; Butler et al., 1999). In recent years their tropospheric abundances have declined (e.g. Cunnold et al., 1997; Prinn et al., 2000; Clerbaux et al., 2007), showing the positive effects of the Montreal Protocol and its amendments. The consumption and most of the production of CFCs have been phased out in developed countries in 1996, however, feedstock use and allowance to supply the needs of developing countries remains until global phase-out in 2010. Additionally, as global production of CFCs continues to decline in response to the protocol, the quantity of CFCs in existing products and equipment, referred to as "banks", has the potential to make an important contribution to future CFC emissions. The analysis of atmospheric

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CFC measurement data can be used to assess their global and regional emissions and check the compliance with phase-out schedules (e.g. Stohl et al., 2005, 2009; Reimann et al., 2005; Greally et al., 2007; Montzka et al., 2009).

China has been the world's leading consumer and producer of CFCs since 1996 (Hu et al., 2005; Wan et al., 2009). In the last decade the knowledge on VOCs in urban and remote Chinese environments has greatly increased. However, most studies were related to hydrocarbons and most studies related to halocarbons were performed only during campaigns focused on industrial and heavily populated urban areas, such as the Jing-Jin-Ji region, the North-China Plain, the Chang river delta region, the Pearl river delta region and the Taiwan region (Wang et al., 1998, 2000; Chang et al., 2001, 2008; Wu et al., 2001; Guo et al., 2004, 2009; Zhang et al., 2006, 2010, 2007a, 2007b; Barletta et al., 2006; Chan et al., 2006; Chan and Chu 2007; Lee and Chiou, 2007, 2008; Qin, 2007). In addition, Chinese CFC emissions have been discussed using TRACE-P and PEM-west B aircraft measurement data (Blake et al., 2003; Palmer et al., 2003). However, in-situ CFC observations in more remote areas of China, which capture both pollution pattern and long-term background trends and seasonality, have only been performed by Vollmer et al. (2009). Therefore, it is important to develop long-term CFCs in-situ measurement programs at a specific sampling site, which could represent the airflow from large-scale populated areas in China (e.g. the Jing-jin-ji region, having large CFC production and emissions) so as to observe effects on consumption and phase-out of CFCs under the Montreal Protocol and its amendments.

In this study, 3-year in-situ observations of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 ($CCl_2F{-}CClF_2$) have been performed at the regional Chinese Global Atmosphere Watch (GAW) station Shangdianzi (SDZ), from November 2006 to October 2009. Mixing ratios, seasonal variations and trends are presented and characterized for both "background" and "non-background" conditions. Additionally, the impacts of local surface horizontal advection on the observed CFCs mixing ratios have been investigated.

2. Site

Shangdianzi (SDZ, 40°39′N, 117°07′E, 286.5 m asl) is one of the regional stations of the World Meteorological Organization (WMO)/GAW, located in a mountainous area approximately 100 km northeast of urban Beijing in the North China Plain (Fig. 1). In a relatively large-scale area of 30 km around the site, there are a few small villages with sparse population and thus insignificant local anthropogenic emissions. The area surrounding the station essentially grows shrubs, maintaining its natural environment of vegetation along with small agricultural activities. Biomass burning in winter is the main activity that could significantly affect the local air quality.

The prevailing winds have been studied by Lin et al. (2008) to be southwest and northeast and are caused by the valley topography. Also, the previous study (Vollmer et al., 2009) showed that pollution events at the SDZ site are mainly influenced by air masses from Beijing and other urban areas in the Jing-jin-ji region. Clean air masses often arrive at the site via Siberia, Mongolia, and the Chinese province Inner Mongolia, carrying relatively clean regional air with atmospheric background conditions well representative of the northern hemisphere (Vollmer et al., 2009; Prinn et al., 2000). Because of its semi-remote location, the site experiences both background conditions and pollution events.

3. Instrument and methods

An automated system for the measurement of atmospheric halocarbons was installed at SDZ in October 2006, consisting of a gas chromatograph (Agilent 6890N) equipped with 2 electron capture detectors (ECDs) and a custom-built sample preparation system (SPS) (Vollmer et al., 2009). Ambient air is drawn from a 10 m tall tower which is 60 m distant from the station laboratory through a continuously flushed sampling tube (10 mm OD Synflex-1300 tube) from where it is diverted into the SPS by means of a membrane pump (KNF-86). Air samples are taken every 80 min. The three CFCs discussed here are all measured on one ECD channel using two separate injections. A 2 ml sample loop is directed through a molecular sieve (MS) 5 A column (4 m, 1/8″ OD) located in an auxiliary oven at 90 °C and allows for the separation of CFC-12 from other substances. After CFC-12 is detected in the ECD, the sample deriving from the second loop (10 ml) and passed through a Silicon SP-2100 pre-column (32 cm, 3/16″ OD) and a main column (300 cm, 3/16″ OD) is switched in line with the ECD for the analysis of CFC-11 and CFC-113 and some other compounds (Vollmer et al., 2009). Each

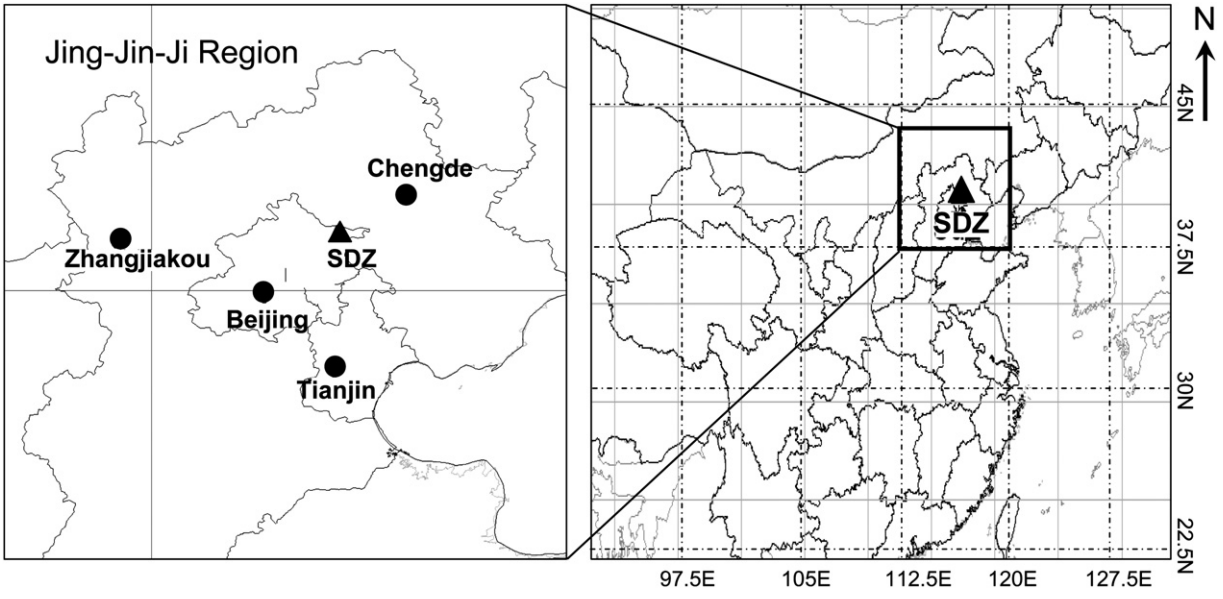

Fig. 1. Maps showing location of the Shangdianzi station (black triangle).