Atmospheric Environment 160 (2017) 55–69

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Ambient mixing ratios of atmospheric halogenated compounds at five background stations in China

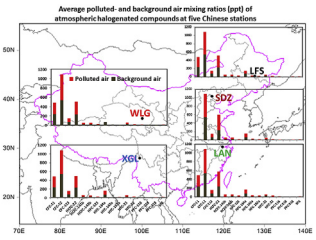
Gen Zhang [a], Bo Yao [b, *], Martin K. Vollmer [c], Stephen A. Montzka [d], Jens Mühle [e], Ray F. Weiss [e], Simon O'Doherty [f], Yi Li [a], Shuangxi Fang [b], Stefan Reimann [c]

[a] State Key Laboratory of Severe Weather & Key Laboratory of Atmospheric Chemistry of China Meteorological Administration (CMA), Chinese Academy of Meteorological Sciences (CAMS), Beijing 100081, China
[b] Meoteorological Observation Centre (MOC), China Meteorological Administration (CMA), Beijing, 100081, China
[c] Empa, Swiss Federal Laboratories for Materials Science and Technology, Dubendorf, 8600, Switzerland
[d] Global Monitoring Division (GMD), Earth System Research Laboratory (ESRL), National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
[e] Scripps Institution of Oceanography, University of California, San Diego, La Jolla 92093, CA, USA
[f] Atmospheric Chemistry Research Group, University of Bristol, Bristol, BS8 1TS, UK

HIGHLIGHTS

- Atmospheric halogenated compounds were measured at five stations in China.
- Mixing ratios were distinguished as in polluted and background air, respectively.
- Background mixing ratios were comparable with those at two AGAGE stations.
- In China, background CFCs are declining while increased for other compounds.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form
10 April 2017
Accepted 11 April 2017
Available online 14 April 2017

Keywords:
CFCs
HCFCs
HFCs
PFCs
SF_6
Ambient mixing ratios

ABSTRACT

High precision measurements of three chlorofluorocarbons (CFCs), three hydrochlorofluorocarbons (HCFCs), six hydrofluorocarbons (HFCs), three perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6) were made at five Chinese background stations from January 2011 to December 2012. Their station means in the background air were 239.5 ± 0.69 parts-per-trillion dry-air mole fraction mixing ratios (ppt) for CFC-11, 536.5 ± 1.49 ppt for CFC-12, 74.66 ± 0.09 ppt for CFC-113, 232.1 ± 4.77 ppt for HCFC-22, 23.78 ± 0.29 ppt for HCFC-141b, 22.92 ± 0.42 ppt for HCFC-142b, 11.75 ± 0.43 ppt for HFC-125, 71.32 ± 1.35 ppt for HFC-134a, 13.62 ± 0.43 ppt for HFC-143a, 9.10 ± 1.26 ppt for HFC-152a, 25.45 ± 0.1 ppt for HFC-23, 7.28 ± 0.48 ppt for HFC-32, 4.32 ± 0.03 ppt for PFC-116, 0.63 ± 0.04 ppt for PFC-218, 1.36 ± 0.01 ppt for PFC-318, and 7.67 ± 0.03 ppt for SF_6, respectively, which were comparable with those measured at the two Northern Hemisphere (NH) AGAGE stations: Mace Head, Ireland (MHD) and Trinidad Head, California, USA (THD). Compared with our results for earlier years from in-situ measurement at SDZ, background-air mixing ratios of CFCs are now declining, while those for HCFCs, HFCs, PFCs, and SF_6 are still increasing. The ratios of the number of sampling events in which measured mixing ratios were elevated above background (pollution events) relative to the total sample frequency (POL/SUM) for CFCs, HCFCs, and HFCs were found to be station dependent, generally LAN > SDZ > LFS > XGL > WLG. The enhancement (△, polluted mixing ratios minus background mixing ratios) generally show distinct patterns, with HCFCs (40.7–175.4 ppt) > HFCs (15.8–66.3 ppt)> CFCs (15.8

* Corresponding author.
E-mail address: yaob@cma.gov.cn (B. Yao).

http://dx.doi.org/10.1016/j.atmosenv.2017.04.017

−33.8 ppt)> PFCs (0.1−0.9 ppt) at five stations, especially for HCFC-22 ranging from 36.9 ppt to 138.2 ppt. Combining with the molecular weights, our findings imply biggest emissions of HCFCs in the regions around these Chinese sites compared to HFCs and CFCs, while the smallest of PFCs, consistent with CFCs being phased out and replaced with HCFCs in China. In addition, relative emission strengths (emission was expressed by mole fractions) of these halocarbons in China were inferred as HCFC-22 > HCFC-141b > HFC-134a > HCFC-142b for the Yangtze River Delta (YRD) and as HCFC-22 > HCFC-142b > HCFC-141b ≈ HFC-134a in the North China Plain (NCP).

1. Introduction

Halogenated organic compounds, including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, and hydrofluorocarbons (HFCs), are important industrial substances with a wide variety of applications such as refrigeration, foam blowing, fire extinguishing, air conditioning, and chemical solvents (Midgley and McCulloch, 1999). They have received attention due to the stratospheric ozone depletion properties of CFCs, HCFCs, halons, and other chlorinated or brominated compounds. Furthermore, many of them are also potent greenhouse gases (GHGs) (Myhre et al., 2013). The consumption and production of CFCs were phased-out in developed countries in 1996 by the fully adjusted and amended Montreal Protocol (MP) (UNEP, 2008). To facilitate the phase-out of CFCs, HCFCs with reduced ozone depletion potentials (ODPs) were introduced as temporary substitutes until 2030 in developing countries (UNEP, 2007). As substitutes for CFCs and HCFCs, the consumption of HFCs was expected to increase both in developed and developing countries for many applications (Velders et al., 2012). While HFCs only indirectly contribute to stratospheric ozone-depletion (Hurwitz et al., 2015), they are also greenhouse gases (GHGs) that contribute to the Earth's anthropogenic radiative forcing (Ciais et al., 2013), with their global warming potentials (GWPs) ranging from 138 to 12,400 for a 100 yr time horizon (Myhre et al., 2013). Many fluorinated compounds with high GWPs, including perfluorocarbons (PFCs), have been increasingly used since the 1980s in semiconductor and other electronics manufacturing processes such as chamber cleaning and dry etching agents, and PFCs are also by-products of aluminum production (Mühle et al., 2010; Ivy et al., 2012). In addition, sulfur hexafluoride (SF_6) is emitted mainly from electrical power distribution equipment. Hence, emissions of HFCs, PFCs and SF_6 are controlled under the Kyoto Protocol (KP) of the United Nations Framework Convention on Climate Change (UNFCCC).

As an Article 5 (A5) parties under the Montreal Protocol, China's timetable of phasing out ozone depleting substances (ODSs) lags the non-A5 parties by 10−15 years, but the common final global phase-out for HCFCs will be in 2030 (UNEP, 2003, 2007). With the support from the Multilateral Fund for Implementation of the MP, China has implemented a strategy to accelerate the phase-out of primary ODSs, and recent studies show that the Chinese emission of most first generation ODSs have declined (Kim et al., 2010; Li et al., 2011; Vollmer et al., 2009; Wan et al., 2009). Nevertheless, as of 2016 China is still allowed to produce and consume HCFCs to replace the first generation ODSs (UNEP, 2008), and this has led to increased banks of HCFCs. In the last decade, most measurements of CFCs, HCFCs, and HFCs in China were performed during campaigns focused on cities or industrialized areas (Barletta et al., 2006; Chan et al., 2006; Chan and Chu, 2007; Chang et al., 2001, 2008; Guo et al., 2004, 2009; Lee and Chiou, 2007, 2008; Qin, 2007; Wang et al., 1998, 2000; Li et al., 2016; Wu et al., 2001; Zhang et al., 2006a,b, 2007a, 2007b, 2010a, 2010b). However, halocarbon observations at background stations in China, which measure both polluted air and regional background air, have been performed with in-situ instrumentation only at the Shangdianzi station (SDZ), which represents the typical characteristics of the North China Plain (NCP) region (An et al., 2012; Vollmer et al., 2009; Yao et al., 2012a,b, 2014; Zhang et al., 2010a,b). In addition, previous observations in China have focused on one or two categories of halogenated compounds (CFCs, HCFCs, HFCs, or PFCs). Comprehensive air monitoring throughout China is essential for providing an indication of the effectiveness of the MP and KP for reducing Chinese emissions of these chemicals in a manner independent of inventory-based emission based on reporting of their production and sales.

In this study, we measured weekly canister samples collected at five Chinese stations from January 2011 to December 2012 and discussed the mixing ratios of five categories of halogenated compounds: CFCs (CFC-11 (CCl_3F), −12 (CCl_2F_2), and −113 ($CClFCClF_2$), HCFCs (HCFC-22 ($CHClF_2$), −141b (CH_3CCl_2F), −142b (CH_3CClF_2)), HFCs (HFC-125 (CHF_2CF_3), HFC-134a (CH_2FCF_3), HFC-143a (CH_3CF_3), HFC-152a (CH_3CHF_2), HFC-23 (CHF_3), and HFC-32 (CH_2F_2)), PFCs (PFC-116 (C_2F_6), PFC-218 (C_3F_8) and PFC-318 (c-C_3F_8)) and sulfur hexafluoride (SF_6). These include the first reported atmospheric mixing ratios of HFC-143a and PFC-318 in China, which are both important species among the halogenated organic compounds and are also GHGs with their respective GWPs of 5896 and 10,300 for a 100 yr time horizon (Myhre et al., 2013).

2. Site description

The five sampling stations shown in Fig. 1 and listed in Table 1

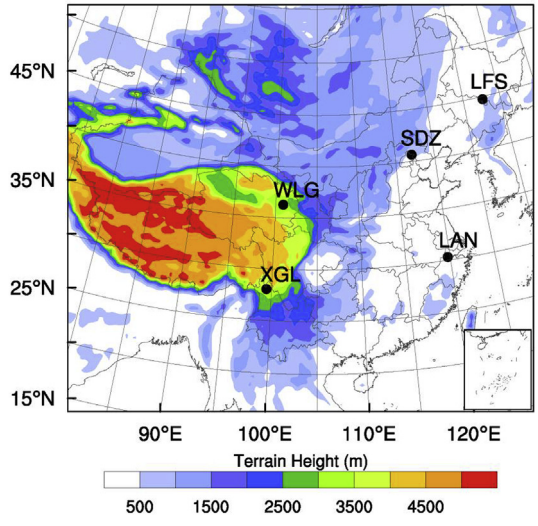


Fig. 1. Locations of the five Chinese background stations used in this study.