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Changes in the levels and variability of halocarbons and the compliance with the Montreal Protocol from an urban view

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HIGHLIGHTS

- The variability of 7 halocarbons in Taipei was re-examined after 14 years.
- The reduced variability implies that the emissions have been largely curbed.
- Average concentrations of ODS in Taipei have approximated background levels.

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ABSTRACT

Ambient levels and variability of major atmospheric halocarbons, i.e. CFC-12, CFC-11, CFC-113, CCl_4, CH_3CCl_3, C_2HCl_3, and C_2Cl_4 in a major metropolis (Taipei, Taiwan) were re-investigated after fourteen years by flask sampling in 2012. Our data indicates that the variability expressed as standard deviations (SD) of CFC-113 and CCl_4 remained small (2.0 ppt and 1.9 ppt, respectively) for the 10th–90th percentile range in both sampling periods; whereas the variability of CFC-12, CFC-11, C_2HCl_3, and C_2Cl_4 measured in 2012 became noticeably smaller than observed in 1998, suggesting their emissions were reduced over time. By comparing with the background data of a global network (NOAA/ESRL/GMD baseline observatories), the ambient levels and distribution of these major halocarbons in Taipei approximated those at a background site (Mauna Loa) in 2012, suggesting that the fingerprint of the major halocarbons in a used-to-be prominent source area has gradually approached to that of the background atmosphere.

1. Introduction

Chlorofluorocarbons (CFCs) have been released from Earth's surface over the past several decades, resulting in ozone depletion due to their long atmospheric lifetimes and potent catalytic properties in the stratosphere (Molina and Rowland, 1974; Carpenter et al., 2014). These entirely man-made species also strongly absorb long-wavelength infrared radiation emitted from Earth's surface and by the atmosphere, allowing them to become the third largest contributor among long-lived greenhouse gases to the radiative forcing of the global climate next to carbon dioxide and methane (Ramanathan, 1975; Wuebbles et al., 1999; IPCC, 2013; Butler and Montzka, 2015). After implementation of the 1987 Montreal Protocol and its subsequent amendments (UNEP, 1987, 1992), production of these ozone-depleting substances (ODS) was largely restricted or phased out in most developed (non-A5) and developing (A5) nations. As a result of a significant reduction in emissions on the global scale, the tropospheric concentrations of CFCs and some other synthetic halocarbons, such as methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4), no longer increase and all have declined for at least a decade, as reported by long-term background monitoring networks (Prinn et al., 2005; Rigby et al., 2013; Carpenter et al., 2014). Their inter-hemisphere gradients also

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shrank drastically (Prinn et al., 2000). Furthermore, the radiative forcing from CFCs showed a negative trend since 1990–2000s (IPCC, 2013; Rigby et al., 2014). Other halocarbons such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), which are considered to be low-ozone-depleting-potential or as ozone-safe substitutes, gradually replaced CFCs in the application demands for refrigeration, air-conditioning, aerosol propulsion, and thermal-insulating foam production. Though the threats of ozone depletion are diminishing, the net forcing of halocarbons and related compounds still remains positive and is increasing due to the steeply increasing concentrations of the CFC replacements (HCFCs and HFCs) and other fully fluorinated halogens (e.g. PFCs, SF_6, and NF_3) in the post-Montreal Protocol era (Weiss et al., 2008; Rigby et al., 2010, 2014; Daniel et al., 2011; Li et al., 2011; Laube et al., 2012; IPCC, 2013).

Even though attention has shifted to the CFC-replacements in the last decade, the remaining atmospheric CFC abundance, which was responsible for about 76% of synthetic halocarbon radiative forcing in 2012 (Rigby et al., 2014), still outweighs the combined replacements. Moreover, despite background monitoring showing various degrees of decline for the Montreal Protocol-restricted halocarbons, the decline rates are still important from the perspectives of ozone layer recovery and the radiative forcing produced by the ODS (Weatherhead and Andersen, 2006; IPCC, 2013). As a result, it is always useful to periodically scrutinize CFC emissions to affirm the effectiveness of the regulatory phase-out policies.

Taiwan is not party to the Montreal Protocol, but has voluntarily strived to comply with the control measures set to the non-A5 countries since the mandate was ratified (Tsai, 2006). In addition to stringent domestic regulations to phase out ODS, field measurements have also been conducted to provide feedback to the regulatory agency for effectiveness assessment. For instance, both random and on-site measurements in urban or industrial areas were used to assess the effectiveness of the abatement of CFC emissions (Wang et al., 2000; Chang et al., 2001; Zhang et al., 2010, 2014). Li et al. (2011) utilized interspecies correlation to suggest the successful phase-out of CFCs and their growing replacement with HCFCs and HFCs in Taiwan based on in-situ measurements during the period 2007–2008. On site in-situ measurements conducted in Taipei in 2005 also suggested minimal emissions of CFC-12, CFC-11, and CFC-113 (Chang et al., 2008). While the on-site in-situ measurements are a useful means to examine emissions manifested as "noise" or variability in concentrations, the concentration variability revealed from the random sampling over large populated source areas can further complement the in-situ data in divulging spatial emission conditions (Hurst et al., 1998; Wang et al., 1998; Chen et al., 1999). As a result, Taipei, the largest and the most economically viable metropolitan area in Taiwan, served as the test ground for re-assessment of the variability of these primary CFCs in 2012. The analytical technique and sampling approach were kept as similar as possible to the first inspection of this kind conducted in 1998, 14 years ago, in order to minimize bias. By comparing the variability of the change in the concentrations, the overall emission status for the compliance with the Montreal Protocol for the major ODS over time can be better understood.

2. Experimental

Two sample collections were conducted in August 1998 and February 2012 in Taipei. Fig. 1 illustrates the sampling sites in the Taipei basin. To avoid over-influence from nearby point sources, sampling was carried out in open fields such as parks and schoolyards, and was as evenly and randomly distributed as possible. The sampling locations, time of day, and the analytical methods in 1998 and 2012 were almost identical. Spatial distributions of the seven target halocarbons (CFC-12, CFC-11, CFC-113, CCl_4, CH_3CCl_3, C_2HCl_3, and C_2Cl_4) in the metropolis were then interpolated or extrapolated from the randomly distributed sampling sites. Two time periods (i.e., 5:00–6:15 A.M. and 5:45–7:00 P.M.) were chosen to pose a contrast, with the early morning as a city baseline when traffic, business, and domestic activities were minimal, and the evening hours when conditions were busy and brisk. The sampling days in 1998 and 2012 were deliberately selected for calm weather with low wind speeds less than 1 ms^{-1}, which is in favor of registering any release from nearby point sources during sampling and can minimize seasonal disturbance arising from the synoptic weather conditions. Air samples were collected in 2-L stainless steel canisters purchased from University of California, Irvine (UCI) (Blake et al., 1992).

2.1. 1998 collection

In the 1998 study, 56 and 53 samples were collected between 5:45 and 6:15 A.M. and between 5:45 and 6:15 P.M., respectively. The ambient temperatures were 24.6–26.9 °C and 28.7–31.3 °C during the morning and evening sampling period, respectively. Air samples were analyzed by a gas chromatograph equipped with electron capture detection (GC/ECD, Varian 3400 CX). A PC-controlled automated valve system with an online cryo-trap was built to enrich the target halocarbons. A 300 mL aliquot of air was drawn consistently from the canister to the system for sample preconcentration, which was performed by a cryo-trap made of a piece of stainless steel tubing (1/8 in. × 10 cm) packed with glass beads. During cryo-trapping, the trap was cooled by purging liquid nitrogen (LN_2) to the setpoint of -170 °C into the trap housing. During injection, the stainless steel trap was short-circuited by a high electrical DC current (30 A; 4 V) for thermal desorption of the analytes into GC. A DB-1 column (J&W Scientific, 60 m × 0.32 mm × 1.0 μm) was used for separation. The reproducibility of this system was evaluated with a replicate precision of about 1–2% for the seven halocarbons. Details of this automated system can be found in literature (Wang et al., 1999). Pressurized air (~700 kPa) filled in a 30-L Aculife-treated cylinder (Scott Specialty Gases, San Bernardino, CA) was used as the reference mixture, with its absolute calibration scales for the target gases aligned to those used in UCI (Wang et al., 1995).

2.2. 2012 collection

In the 2012 study, 52 and 53 samples were collected between 5:00 and 6:00 A.M. and between 6:00 and 7:00 P.M., respectively. The ambient temperatures were 18.0–21.5 °C and 20.0–23.8 °C during the morning and evening sampling period, respectively. Canister air samples were analyzed by an automated GC–MS system (3800-GC and Saturn 2200-MS, Varian), which is a laboratory version of the one described in our previous study (Wang et al., 2012). The pre-concentration and chromatographic techniques for enriching and separating the halocarbons were similar to those applied in the 1998 study. The GC oven was cooled with LN_2 and maintained at -15 °C for 1 min initially, ramped to 0 °C at 7.5 °C min^{-1}, ramped to 140 °C at 5 °C min^{-1}, ramped to 180 °C at 20 °C min^{-1}, and finally maintained at 180 °C for a further 15 min. Internal standards were blended with each sample aliquot to back-correct the analytical drift to safeguard stability. Precision was assessed to be less than 1.5% for the seven target halocarbons. Calibration of C_2HCl_3 was made with a commercial standard (Linde SPECTRA Environmental Gases, USA), which exhibited a difference within 10% from the UCI standard. A tertiary standard purchased from National Oceanic and Atmospheric Administration/Earth System Research Laboratory/Global Monitoring Division