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The changing ambient mixing ratios of long-lived halocarbons under Montreal Protocol in China

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ABSTRACT

The varying trend of long-lived halocarbons demands close attention of their atmospheric climate impact. Chlorofluorocarbons (CFCs) were phased out in 2008 under the Montreal Protocol in China, and nowadays, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are the main substitutes. Since 2000, studies on CFCs, HCFCs, and HFCs, with respect to their ambient mixing ratios and emissions, were intensively performed over China. CFCs declined evidently, while HCFCs and HFCs greatly increased in China due to the successful phase-out of CFCs under the Montreal Protocol. In the Pearl River Delta (PRD) region, the most developed region in China, the increasing and decreasing rates of CFC-11, CFC-12, HCFC-22, and HCFC-141b since 2000 were -3.6 ± 0.5 pptv/yr, -11.7 ± 3.3 pptv/yr, 17.9 ± 4.9 pptv/yr and 7.2 ± 2.0 pptv/yr, respectively. The increase of HCFC-141b in northern China was 1.1 ± 0.6 pptv/yr, much lower than the PRD region. The overall increase of HFC-134a in China was 5.6 ± 0.2 pptv/yr. These rates were significantly higher than those for their corresponding background averages in the northern hemisphere. Other HFCs excluding HFC-134a were of great global warming potentials, but their ambient mixing ratios were reportedly limited in China. The emission ratios between HCFC-22 and CFC-12, and HFC-134a and HCFC-22 were used as the measurements, showing virtual replacement occurring in China. The rapidly increasing contribution of HFCs to climate risk in China requires further observation.

1. Introduction

Chlorofluorocarbons (CFCs), formerly the dominant coolants, refrigerants, blowing agents and propellants, have been completely phased out since 2008 in China; regulated hydrochlorofluorocarbons (HCFCs) and unregulated hydrofluorocarbons (HFCs) are now the main alternatives (Wan et al., 2009; Fang et al., 2016; Li et al., 2016). Unfortunately, these are not environmentally friendly in regards to ozone depletion in the atmosphere (Kim et al., 2011), the greenhouse effect (Hodnebrog et al., 2013), or toxic product (Tsai, 2005) and more (Burkholder et al., 2015).

CFCs and HCFCs are ozone depletion substances (ODSs) that cause the degradation of the stratospheric ozone layer through the release of reactive chlorine. To quantify the effect of various ODSs on the ozone layer, ozone depletion potentials (ODPs) were introduced as a simple measure. The ODP is defined as the integrated change in total ozone per unit mass emission of a specific ODS relative to the integrated change in total ozone per unit mass emission of CFC-11 (WMO, 2014). As shown in Table 1, HFCs were chosen to replace CFCs and HCFCs mainly because of their nearly zero ODPs.

However, ozone-friendly HFCs, like CFCs and HCFCs, are greenhouse gases (GHGs) that absorb radiation and warm the atmosphere (IPCC/TEPA, 2005). Their effect on global warming is non-negligible. The global warming potentials (GWPs) are a measure of the future radiative effect of a substance emission relative to an emission of the same amount of CO_2 integrated over a chosen time horizon (GWP 100 over 100 years) (Hodnebrog et al., 2013). HFC-23 appeared to be the strongest GHG, with a GWP 100 of 12400 among the halocarbons under discussion (Table 1).

To evaluate future alternatives, their possible toxic products, such as ground-level ozone (measured by Photochemical Ozone Creation Potentials, POCPs, or the Maximum Incremental Reactivity, MIR), trifluoroacetic acid (TFA), and CF_4 (persistent GHG),

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Table 1
Summary of characteristics of main CFCs, HCFCs and HFCs and potential substitutes present in the atmosphere.

Halocarbons	Formula	Main Usage	Lifetime[a] (yrs)	ODP[b]	GWP100[c]	POCP [d]
CFC-11	CCl_3F	Blowing agent	52 (45)	1.0	4660	–
CFC-12	CCl_2F_2	Refrigeration, air-conditioning system	102 (100)	0.82	10200	–
CFC-113	CCl_2FCClF_2	Cleaning solvents	93 (85)	0.85	5820	–
CFC-114	$CClF_2CClF_2$	low-temperature refrigeration	189 (190)	0.58	8590	–
HCFC-22	$CHClF_2$	Refrigeration, air-conditioning system	11.9 (11.9)	0.04	1760	0.1
HCFC-141b	CH_3CCl_2F	Blowing agent	9.4 (9.2)	0.12	782	0.1
HCFC-142b	CH_3CClF_2	Blowing agent	18 (17.2)	0.06	1980	0.1
HCFO-1233zd(E)	trans-CF_3CH= CHCl	Blowing agent	(0.07)	–	1	–
HFC-23	CHF_3	Coproduct from HCFC-22 production	228 (222)	$<3.9 \times 10^{-4}$*	12400	0
HFC-32	CH_2F_2	Room air conditioning	5.4 (5.2)	–	677	0.2
HFC-125	CHF_2CF_3	Room air conditioning	31 (28.2)	$<3 \times 10^{-5}$	3170	0
HFC-134a	CH_2FCF_3	Mobile air conditioning	14 (13.4)	$<1.5 \times 10^{-5}$*	1300	0.1
HFC-143a	CH_3CF_3	Refrigeration, air-conditioning system	51 (47.1)	–	4800	0
HFC-152a	CH_3CHF_2	Aerosol propellant	1.6 (1.5)	–	138	1
HFC-245fa	CHF_2CH2CF_3	Blowing agent	7.9 (7.7)	–	858	–
HFO-1234yf	CH_2=$CFCF_3$	Mobile air conditioning	0.03 (0.03)	0	<1	–

[a] Global steady-state lifetimes took from the WMO (2014). Data in brackets from Hodnebrog et al. (2013).
[b] Semi-empirical ODP from WMO (2014). ODPs with * from Ravishankara et al. (1994).
[c] From Hodnebrog et al. (2013).
[d] From IPCC/TEPA (2005).

should also be considered (IPCC/TEPA, 2005; Jubb et al., 2015; Solomon et al., 2016). In the presence of sunlight and NO_x, volatile organic compounds (VOCs) take part in ground-level ozone formation, thereby contributing to regional and urban air quality deterioration and the adverse health effects. The ability of each VOC for ozone formation can be indexed in the reactivity scale, POCP, which is relative to the ozone formation produced by the unit mass of ethylene ($POCP_{ethylene} = 100$). CFCs, HCFCs, and HFCs usually had low POCPs (<1, Table 1) due to their low reactivity. The latest potential alternatives were unsaturated hydrochlorofluoroolefins (HCFOs) and hydrofluoroolefins (HFOs), such as HCFO-1233zd(E) and HFO-1234yf (Table 1). Due to their high reactivity and short lifetime, their GWP and ODP was expectedly low, but correspondingly, a high POCP.

Additionally, HCFCs, HFCs, and HFOs degradation was considered a main source for TFA, an toxic acid present in the atmosphere and hydrosphere (Solomon et al., 2016). While significant amounts of TFA were observed in both particulate and gas phases in Beijing in 2012–2013 (Wu et al., 2014b), its concentration in Beijing surface water increased 17-fold from 2002 to 2012 (Zhai et al., 2015). Recent laboratory work found a new source for CF_4 from the photolysis of trifluoroacetyl fluoride, a degradation product of several CFCs and HFCs now present in the atmosphere (Jubb et al., 2015).

As the largest Article 5 country under the Montreal Protocol, the emissions of CFCs, HCFCs and HFCs in China are of great concern. In the beginning of the 21st century, early field campaigns were conducted from a survey study by Barletta et al. (2006) over 45 Chinese cities. Simultaneously, Chan et al. (2006) and Chan and Chu (2007) studied the Pearl River Delta region, while Libo et al. (2001) focused on the Yangtze River Delta region. Intensive field campaigns in northern China started relatively late by Qin (2007) in 2005. The Pearl River Delta, Yangtze River Delta and the Beijing-Tianjin-Hebei (Jing-Jin-Ji in abbreviation) are the three most developed and densely populated megalopolises in China (Table 2). Since then, most studies were performed in these regions with respect to the ambient mixing ratios and emissions of CFCs, HCFCs and HFCs. Additionally, the aircraft missions of Transport and Chemical Evolution over the Pacific (TRACE-P) (Blake et al., 2003), and Chemical Transport Experiment – Phase B (INTEX-B) (Barletta et al., 2009), and shipborne observation over South Yellow Sea (SYS) (He et al., 2013) supplied further information on the pollution plumes originating in China.

Compared with the bottom-up inventory studies, the ambient mixing ratios of long-lived halocarbons provided more ocular clues on their emission patterns and the effect of controlling polices. Thorough efforts have been made to study pollution levels of long-lived halocarbons in China more widely under current regulations. Fang et al. (2012b) and Wang et al. (2014) surveyed the ambient mixing ratios of long-lived halocarbons over 46 Chinese cities in 2010 and produced top-down emission estimates. Zhang et al. (2014) made a grid campaign including 84 sites in the PRD region in 2008 and 2009 to identify the overlooked emission sources. Zhang et al. (2017) performed measurements in five background sites to determine the general pollution levels over China.

However, while replacing CFCs with HCFCs and further, HFCs, the total emission of long-lived halocarbons increased significantly as did the living condition demands of the human population. The influence of controlling policies in operation on the decreasing or increasing tendency of the ambient mixing ratios of different long-lived halocarbon were inexplicit.

Our paper aimed to link the historic observatory data to determine their tendency to increase or decrease. The ratios of HCFC-22 to CFC-12 and HFC-134a to HCFC-22 emissions were used to quantitatively measure the replacement progress in China compared to developed countries. Since CFCs were already banned in 2008 and HFCs started frozen in 2013, our efforts may help pinpoint the main risk China currently faces.

In section 2, existing regulations on CFCs and HCFCs emissions in China and proposed regulations on HFCs under the Montreal Protocol were summarized; the experimental methods and tracer relationship approach for emission estimates were also briefly introduced. In section 3, the spatiotemporal characteristics of CFCs, HCFCs, and HFCs and their corresponding emission patterns between 2000 and 2012 were discussed in detail. In section 4, we presented the emission estimates of long-lived halocarbons and considered the replacement of CFC-12 by HCFC-22 and HCFC-22 by HFC-134a. We relied mostly on estimates derived from datasets observed in China by the tracer species correlation (TSP) method or inverse modeling, as listed in Table 2. Other emission estimates formed from either bottom-up or top-down methods and based on global networks such as AGAGE and NIES would be discussed as references.