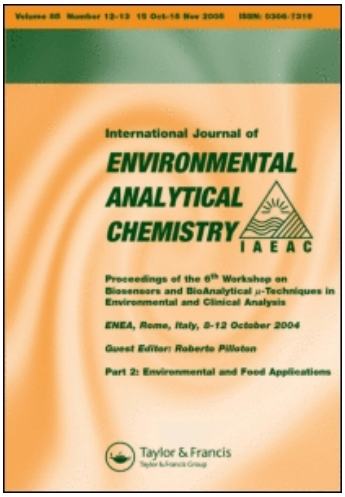

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Trends of Atmospheric CCl 3 F, CCl 2 F 2 and CCl 2 FCClF 2 in Shanghai (China)

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TRENDS OF ATMOSPHERIC CCl_3F, CCl_2F_2 AND CCl_2FCClF_2 IN SHANGHAI (CHINA)

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Atmospheric concentrations of CCl_3F (CFC-11), CCl_2F_2 (CFC-12), and CCl_2FCClF_2 (CFC-113) in troposphere in Shanghai, China (31°1N) have been routinely monitored by using gas chromatography with electron capture detector from November 1997 to December 2000. The observation shows that there is a slowly declining trend of the three compounds. On the other hand, a comparison has been drawn between the concentrations observed and the ones calculated by 2-box model on the basis of the global statistical data of CFCs production and emission. Our observation agrees with the calculations. It shows that production and emission of chlorofluorocarbons (CFCs) in China are still at a low level and gradually decreasing.

Keywords: CFC; Troposphere; Temporal trend

INTRODUCTION

Based on previous studies of anthropogenic chlorine-(Cl) and bromine-(Br) containing gases with the depletion of stratospheric ozone-(O_3), the link between the long-term build-up of chlorine as well as bromine and the decline of ozone in the upper stratosphere has been firmly established[1–5]. Accordingly, complete compliance with the adjusted and amended Montreal Protocol on substances that deplete the ozone layer in both developed and developing countries is essential for the recovery of ozone levels[4]. Although production of ozone-destroying gases has been curtailed under the protocols, the largest geographical size of the ozone hole has been observed in September 2000 on record and the ozone depleted earlier than ever[6]. Thus, the responsibility to restore ozone levels resting largely on developing countries has been highlighted, since developed countries have phased out the production of CFCs by the year 1996. Under the terms of the protocol, developing countries should complete the phasing out of ozone-depleting chemicals by 2010[4].

CCl_3F (CFC-11), CCl_2F_2 (CFC-12), and $C_2Cl_3F_3$ (CFC-113) have been widely employed as solvents and as cooling and foam-blowing agents across the world during the last decades[5]. A recent report has shown that the chlorine from these

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three chemical compounds makes up 48% of the equivalent chlorine from persistent organic compounds in the atmosphere[7]. Thus, they are important species for estimation of the behavior of tropospheric chlorine in the global atmosphere. Global monitoring networks such as those in ALE, GAGE, AGAGE, NOAA and CMDL have been established since early 1980's[3, 8]. China, one of the largest developing countries in the world, is trying its best to control and eliminate its CFC-production and consumption to fulfill earlier projections outlined in the protocol. However, in China there are rare routine monitoring and model studies on atmospheric CFCs as the evidence of the compliance with the protocols. As an important economic and industrial center in China, as well as a main chlorofluorocarbons producer and consumer in locality, Shanghai's CFCs data can reasonably reflect the level of the production and emission of CFCs across the country, representing that of China in some degree. At this stage, we have successfully established a method of monitoring CFCs by using gas chromatography with ECD. Routine analysis of the tropospheric CFCs in Shanghai starts in November 1997. Here the original monitoring concentration data is reported: the trends of atmospheric CCl_3F, CCl_2F_2 and $C_2Cl_3F_3$ in Shanghai from November 1997 to December 2000. We believe this study is important for understanding the CFCs phase-out processes in China.

EXPERIMENTAL

The gas chromatographic analytical system has been described earlier[9, 10]. In brief, the system consists of two parts: a sample introducing and cryotrapped system and a temperature-programmed gas chromatograph with an electron-capture detector (Shimadzu GC-14B). The former consists of a stainless steel vacuum line, a dehydration trap, and a U-shaped pre-concentration trap (SS tube packed with Flusin GH, glass beads).

The relatively low concentration levels of atmospheric CFCs make it necessary to pre-concentrate the air samples prior to gas chromatographic separation. The sample will first flow through the dehydration trap, which is soaked in the mixture of alcohol and dry ice ($-78^{\circ}C$), to eliminate water vapor. Then under a low pressure, the sample will flow through the pre-concentration trap, which is soaked in liquid nitrogen ($-196^{\circ}C$). Compounds of interest were quantitatively trapped onto the adsorbent[10] at liquid nitrogen temperature. Thirty to forty milliliters of air sample was used in an analytical run, and the procedures of dehydration and pre-concentration were about 5 min. When the adsorption tube was heated at $80^{\circ}C$, the substances were desorbed and carried into the gas chromatograph at a flow rate of $30\,ml\,min^{-1}$ by the carrier as (N_2, 99.999%).

The gas chromatographic column was a $3\,m \times 1/8'$ o.d. stainless steel (316 SUS), packed with Silicone DC-550 on Chromosorb WAW (DMCS 20%) 80–100 mesh. The following temperature programme was used: 2 min at $15^{\circ}C$, then $0.5^{\circ}C\,min^{-1}$ up to $30^{\circ}C$. High purity nitrogen (> 99.999%), which was purified by oxygen trap and molecular sieve, was used as a carrier gas. The detector temperature was $250^{\circ}C$. The standard deviation of the analysis was less than 1.5%, and the international calibration was done between Fudan University and the University of Tokyo [10]. A typical chromatogram of chlorofluorocarbons (CFC-11, CFC-12 and CFC-113) is shown in Fig. 1.

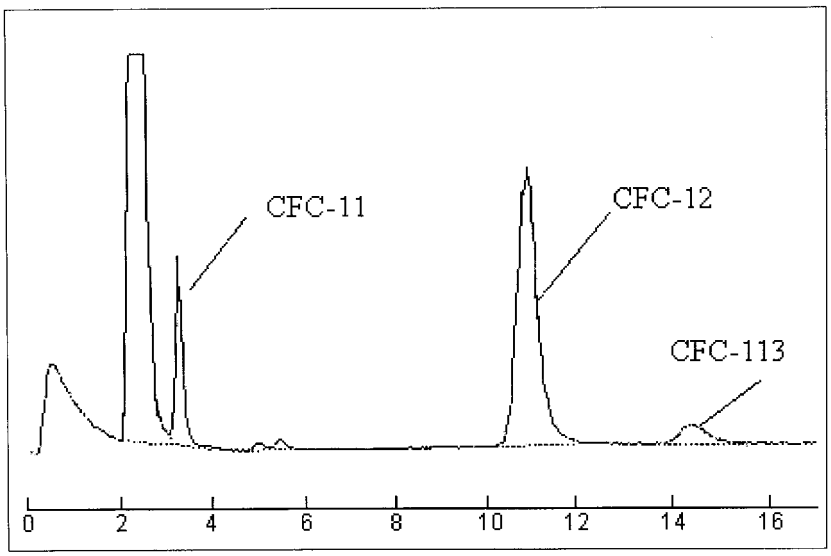

FIGURE 1 Typical ECD gas chromatograms of a tropospheric air sample. Sample: 32 ml background air, collected at Bailong harbor (121°3E, 31°1N) in Shanghai suburb on Mar. 31, 1998.

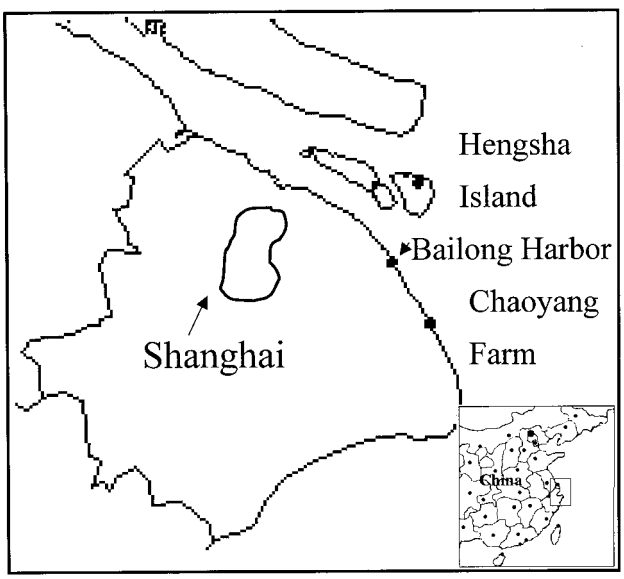

FIGURE 2 Sampling site in Shanghai.

Because CFCs' concentrations at Bailong harbor was the least influenced after comparison made at three places at seashore, which are Bailong harbor, Chaoyang farm, and Hengsha island, Bailong harbor (31°1N, 121°3E) was chosen as our sample collecting site (shown in Fig. 2). It is about 30 km away from the center of Shanghai. We believe CFCs' concentrations at Bailong harbor can represent their mean atmospheric abundance of Shanghai.

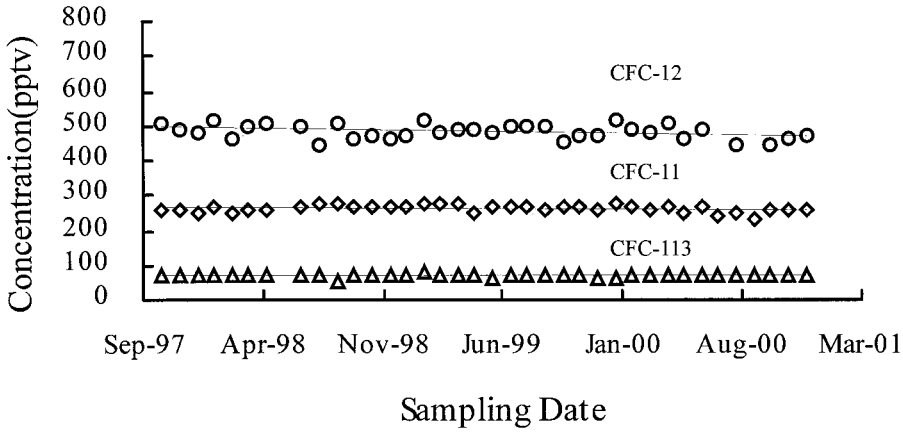

FIGURE 3 Observed atmospheric concentrations of CFC-11, CFC-12 and CFC-113 in Bailong harbor from November 1997 to December 2000. Solid lines represent observed trends to monthly data in routine measurements. Clean air sample in Hokkaido, Japan on Aug. 14, 1997 was used as a standard as well as ambient air sample at Bailong harbor, Shanghai on Apr. 21, 1998 has been used after the former run out. Time on the x axis corresponds to the first day when samples were obtained in the month.

The frequency of sample collection was three or four times per month at the site. Three flasks of air sample were collected and analyzed within one week each time. Every flask of sample was analyzed three times, and the concentration datum of the sample was the mean value of the results. The weekly mean is the average concentration of the three flasks, while the monthly means of compounds of interest are shown in Fig. 3.

RESULTS AND DISCUSSION

Although the background atmospheric concentrations of chlorofluorocarbons are governed by global totals of their emission, transient concentrations respond to local and regional release[11]. Thus, the local concentrations of CFCs are greatly influenced by regional emissions and the meteorological conditions (mainly wind speed and wind direction), and their decrease rate largely depends on their atmospheric lifetimes and the rapidity with which their emissions are curtailed[3]. Considering the geographical location and synoptic weather conditions, the abundance of CFC-11, CFC-12, CFC-113 in Shanghai has been analyzed and obtained, and the data is representative.

The trends of the three main chlorofluorocarbons (CFC-11, CFC-12 and CFC-113) are shown in Fig. 3. A gradually declining trend of CFC-11, CFC-12 and CFC-113 has been observed, respectively. Considering the long atmospheric lifetime of CFC-11, CFC-12 and CFC-113, the rapidity of the anthropogenic chlorocarbons decrease rate could be significantly influenced by their emission[12]. The atmospheric lifetimes of the three chemical compounds are shown in Table I. The observation about the descending trends of CFCs in Shanghai shows that both the production and emission in China have slowly declined. It proves for the compliance with the protocol from China. Accordingly, both the annual production and consumption of total ozone-

TABLE I Atmospheric chlorofluorocarbons (CFCs) characteristics. Values are in parentheses

Compound	*Chemical Formula*	*Atmospheric Lifetime (yr)*[11]
CFC-12	CF_2Cl_2	102
CFC-11	$CFCl_3$	50
CFC-113	$C_2F_3Cl_3$	85

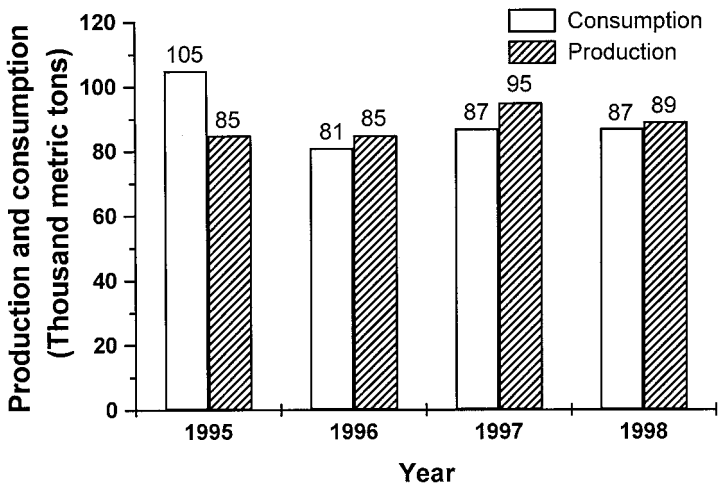

FIGURE 4 Annual production and consumption of the total ozone-depletion compounds in China. The left columns represent the consumption, while the right columns represent the production. All the data are reported by the National Environmental Protection Agency in China at the 11th Meeting of the Montreal Protocol Parties on Substances that Deplete the Ozone Layer (China). Time on the *x* axis corresponds to 1 January of indicated year.

depleting compounds in China shown in Fig. 4 have revealed that they are unsteadily but slowly decreasing[13].

The trends of CFC-11 and CFC-113 observed here agree with those measurements reported previously by other research groups, such as ALE/GAGE/AGAGE or NOAA/CMDL[3, 7]. In accordance with the increasing abundance of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as substitutes for the CFCs[4], the production and emission of CFCs have also declined worldwide further. However, the trend of CFC-12 observed in Shanghai is different from those described before. The discrepancy of newly obtained results and those reported previously may have been caused by two reasons: one is the different calibration and analytical methods since samples have been analyzed not only by using electron capture–gas chromatography[3, 8], but also by gas chromatography–mass spectrometry[3], while the other reason is the different release and meteorological conditions in localities.

Recent reports have shown that the sum of all CFCs reported to AFEAS in 1999 is only 4% of the total in the peak year 1988 as shown in Fig. 5. The global production of CFC-11, CFC-12 and CFC-113 in 1999 has decreased by 12%, 18% and 37%, respectively, from 1998. Further, production of CFCs and HCFCs reported by AFEAS,

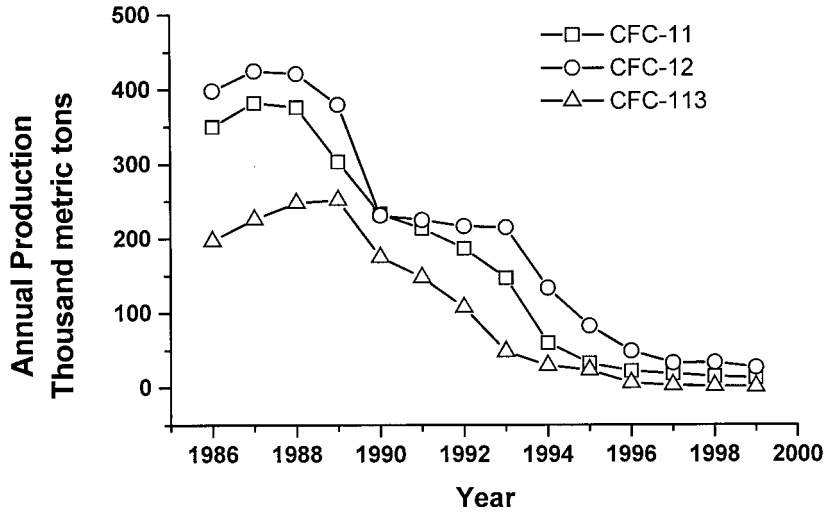

FIGURE 5 Reported Global Productions of CFC-11, CFC-12 and CFC-113 from AFEAS. The sum of all CFCs reported to AFEAS in 1999, estimated to represent about 30% of global CFC production by comparison with UNEP totals, is only 4% of the total in the peak year 1988. Time on the x axis is corresponding to 1 January of indicated year.

weighted according to the ozone depletion potential (ODP) of each compound, has been reduced by more than 93% from 1998[14]. Although China is not an AFEAS survey but a member of the Montreal Protocol, it has made efforts to make progress in eliminating ozone-depleting compounds. The slowly decreasing trends of CFC-11, CFC-12 and CFC-113 measured by our group provide evidence for China's phase-out of halocarbons.

In order to compare this observation with the global varying abundance of CFCs, the mean mixing ratios of CFCs in the Northern Hemispheric troposphere has been calculated with 2-box model[15–16] by using emission data reported to AFEAS[14] from 1930 to 1999. Here, the differential equations for the mean annual change in the mixing ratios for both hemispheres are shown in Eq. (1) and (2):

$$\frac{dCn}{dt} = \frac{2 \times \gamma_n \times f}{Na} E - \frac{Cn}{\tau} - \frac{(Cn - Cs)}{\tau_{ns}} \tag{1}$$

$$\frac{dCs}{dt} = \frac{2 \times (1 - \gamma_n) \times f}{Na} E - \frac{Cs}{\tau} + \frac{(Cn - Cs)}{\tau_{ns}} \tag{2}$$

where Cn and Cs represent the mean troposphere mixing ratio in the Northern Hemisphere and that in the Southern Hemisphere respectively; γ_n is the ratio of the emissions in the Northern Hemisphere to the total emissions (~ 0.95)[16]; f is the fraction of total atmospheric CFC in the troposphere divided by the fraction of the total atmospheric mass of the troposphere (f has a latitudinal dependence), Na is the total mass of the atmosphere; E is the emission rate; τ is the mean atmospheric lifetime; τ_{ns} is the mean inter hemispheric exchange time (2.3 years)[15]. The calculated result has been illustrated in Fig. 6.

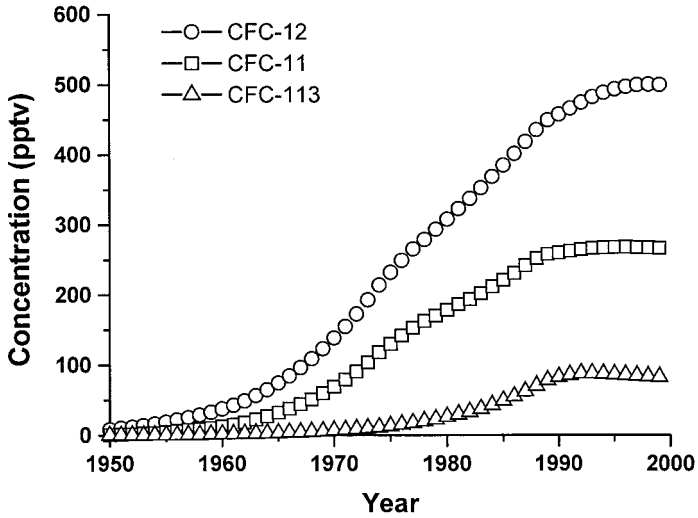

FIGURE 6 The estimated concentrations of CFC-12, CFC-11 and CFC-113 based on the statistical data of production and emission by a 2-box model calculation in the Northern Hemisphere respectively. Calculated concentrations are on the basis of the reported data to AFEAS from 1950 to 1999, and expected date appearing on the x axis corresponds to 1 January of indicated year. Model calculations for interhemispheric exchange time τ_{ns} is used as 2.3 years with mean atmospheric lifetime in Table I.

Dramatic growth rates of CFC-11, CFC-12 and CFC-113 in the Northern Hemisphere since 1970 are observed as shown in Fig. 6. Because the total combined abundance of ozone-depleting compounds in the lower atmosphere peaked in about 1994 and is now gradually falling[4], the concentrations of CFC-11 and CFC-113 have slightly decreased since 1994, while the growth rate of CFC-12 has become zero since 1997. This calculated result agrees with our observed data, i.e., the leisurely declining trends of CFCs in China. The abundance of tropospheric Cl observed in the Northern Hemisphere are more sensitive to emission changes, and they can essentially define future accumulation rates in the Southern Hemisphere and in the global mean[3]. This result suggests that both production and emission of CFCs in China have made small contribution to the abundance of global tropospheric chlorine. It supports that China has controlled its production and emission outlined in the Protocols in time. Further, it is possible that these chemicals will achieve zero emission if there is enough time, because CFCs are still being emitted from the "bank" in those equipments in use.

Model studies have predicted that tropospheric Cl will reach a zenith at about 3500–4000 ppt in the mid-1990s if behavior of exceeding limits outlined in the Copenhagen Amendments does not exist, and the atmospheric abundance of troposphere Cl will begin to decrease[5]. Though the annual production has declined, prominent decline of CFC-11, CFC-12 and CFC-113 in troposphere concentrations requires more time because of their long atmospheric lifetime. In addition, much uncertainty has remained regarding the timing and magnitude of peak chlorine loading of the atmosphere. They come from the noncompliance with the protocols, the uncertainty of the magnitude of CFC and HCFC used, and the illicit trades in CFCs worldwide. This is a challenge for both developed and developing countries. In this case, it is

strongly recommended that long time measurement, as well as the strictness adherence to restrictions be outlined in the revised protocols.

CONCLUSIONS

The trends of atmospheric concentrations of three man-made chlorofluorocarbons (CFC-11, CFC-12 and CFC-113) have been observed in Shanghai by using gas chromatography with ECD. The observation agrees with calculated trends by using 2-box model in the Northern Hemisphere based on the statistical data. The results show production and emission of CFCs in China are still at a low level and its atmospheric concentrations are now slowly declining.

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