Observations of CFC-11 and CFC-12 in remote and urban areas in Brazil

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Abstract

This work presents a study of atmospheric chlorofluorocarbons CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) in the lower troposphere of remote regions in Brazil (Barra de Maxaranguape - 6ºS; 35ºW; Campo Grande - 20.5ºS; 54.6ºW and Maringá - 23.4ºS; 51.9ºW), and daily variations in an urbanized area (São Paulo-23.5ºS; 46.6ºW). For quantitative determination of CFCs mixing ratios, a gas chromatograph equipped with electron capture detector (ECD) was optimized. Surface data for both CFCs showed no latitudinal variation. The annual averages for 2002 were: Barra de Maxaranguape, CFC-11: 259.2 $\pm$ 4.1 pptv and CFC-12: 544.4 $\pm$ 3.5 pptv; Campo Grande, CFC-11: 257.6 $\pm$ 2.2 pptv and CFC-12: 543.7 $\pm$ 3.2 pptv; Maringá, CFC-11: 257.2 $\pm$ 2.4 pptv and CFC-12: 544.5 $\pm$ 3.6 pptv. The observed CFC-12 concentrations at the three remote locations presented a little seasonal variation with minimum in June/July. In Barra de Maxaranguape the CFC-11 concentration showed a decreasing trend, with a rate of about 8,3 pptv/year, while the CFC-12 concentration did not show any annual variation. The mixing ratios of CFC-12 in the urban areas showed a large spatial and temporal variation ranging from 551.1 pptv to 1,059.0 pptv, indicating that there are releases in the urban areas

Introduction

Chlorofluorocarbons (CFCs) were intensively used for refrigeration, production of aerosols and foams. Human use of halocarbons has led to a steady increase in the concentrations of these compounds in the atmosphere in the years 70-80[1,2,3]. Because of their role in ozone depletion, their production and trade are presently controlled by the Montreal Protocol and subsequent amendments, which called for the elimination their production by 1996. Decreasing of the tropospheric mixing ratios of the CFC-11 and in the global growth rate of CFC-12 mixing ratio attest the compliance with the Montreal Protocol[1,2].

Tropospheric mixing ratios trends are extracted from time series at remote sites where the air masses are well mixed and there are not sources or sinks of the analyzed gases. Trends in background data are giving indications of changes in global-scale emissions[1,2,3], but provide little information about regional and national atmospheric releases. Mixing ratios determined from measurements at sites near to source regions are sensitive indicators of changes in their regional emissions[4].

In this work we present a study of CFC-11 and CFC-12 mixing ratios in remote areas to provide information about their mixing ratios in different regions, and an estimative of the CFCs trends. The daily variations in an urbanized area (São Paulo) for both gases are evaluated in two different seasons.

Method

The sites where samples were collected are showing in the Figure 01 by the red boxes.

Figure 1 – Localization of the sites of sample collection.

The CFCs mixing ratios were determined by the gas chromatography technique with an ECD. Routine analysis of the tropospheric CFCs 11 and 12 in Barra de Maxaranguape starts in August 2001 (in Maringá and Campo Grande, the analysis starts in December 2001). The samples were collected in stainless steel canisters. The frequency of sample collection was two or three times per week and were collected in pairs. To study the CFCs variation in São Paulo, daily samples were collected over two periods (June/July/August and November/December) in the São Paulo metropolitan area.

Results

The monthly average of CFC-11 mixing ratios at Barra de Maxaranguape, Campo Grande and Maringá are presented in Figure 02. Also are showed the 3-month running average, in red. In Barra de Maxaranguape was observed a trend of decrease of about 8.3 pptv/year in the CFC-11 mixing ratios (annual average for 2001: 264.7±4.7 pptv; and for 2002: of 259.2±4.1 pptv), in agree with the annual average reported by NOAA/CMDL[5]. In the other two sample sites (Campo Grande and Maringá) the CFC-11 mixing ratios were constant over the observed period (2002 annual average: 257.6±2.2 pptv and 257.2±2.4 pptv, respectively), with a possible result from some continental contribution.

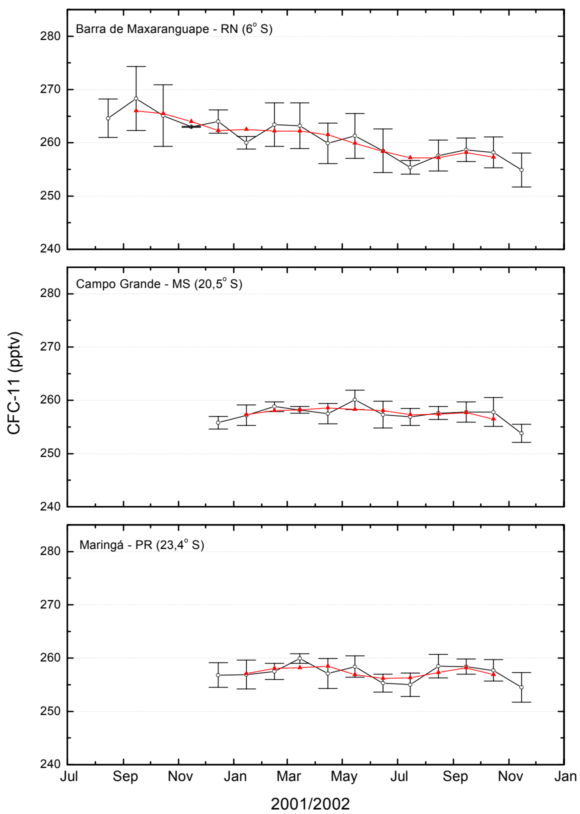

Figure 02 – Monthly averages and 3-month running average (in red) of CFC-11 mixing ratios over Barra de Maxaranguape, Campo Grande and Maringá.

The Figure 03 shows the monthly averages of CFC-12 mixing ratio in Barra de Maxaranguape, Campo Grande and Maringá and 3-month running average. The 2001 average at Barra de Maxaranguape was 546.3±2.9 pptv and 244.4±3.5 pptv in 2002. The mixing ratio of CFC-12 did not show a latitudinal variation, and the annual averages at Campo Grande and Maringá were 543.7±3.2 pptv and 544.5±3.6 pptv, respectively. These results are compatible with the reported by NOAA/CMDL[5], and denote the equilibrium of the CFC-12 sources and sinks.

To study the mixing ratios variations in an urban area, we collected daily samples on a winter period (June/July/August) and on a summer period (November/December) in São Paulo. The daily average of all samples collected in São Paulo are showed in Figure 04.

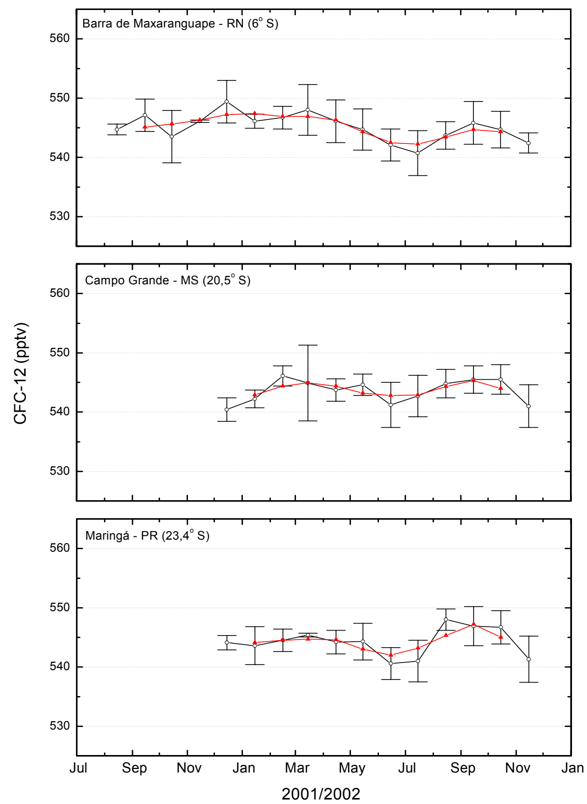

Figure 03 – Monthly averages and 3-month running average (in red) of CFC-12 mixing ratios over Barra de Maxaranguape, Campo Grande and Maringá.

Daily CFC-11 variations are small, and there are no a clearly week variation. The average to CFC-11 mixing ratio were 264.1±12.0 pptv and 261.9±6.6 pptv on winter and summer, respectively. This is indicating that the sources of CFC-11 are very weak in the urban area.

The daily CFC-12 mixing ratio showed large variations with the smaller mixing ratios occurring in the weekend (Saturday and Sunday). This weekly cycle can be associated to industrial and commercial activities in the São Paulo metropolitan area and with the probable use of CFC-12 in the refrigeration systems.

The CFC-12 average for winter and summer were 604.0±61.8 pptv and 614.4±107.4 pptv, respectively. These large variations observed in CFC-12 averages indicate that there are some releases of this gas in São Paulo, with a higher frequency in summer.

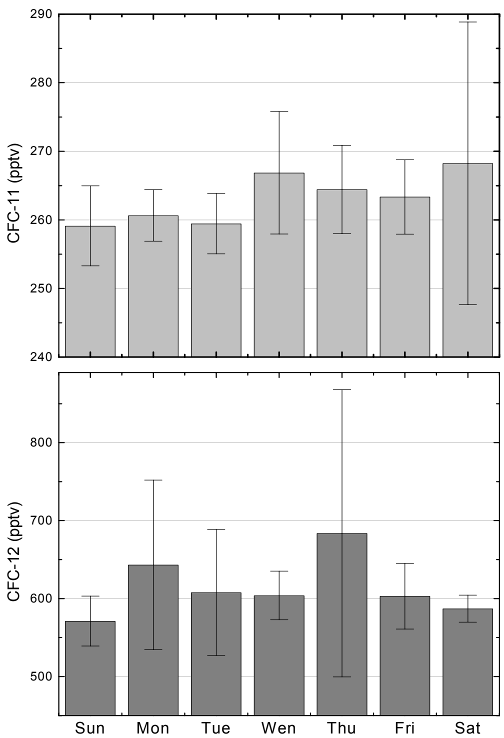

Figure 04 – Daily averages of CFC-11 (top) and CFC-12 (bottom) mixing ratios over São Paulo.

Conclusions

The monitoring of CFC-11 in Barra de Maxaranguape showed that its mixing ratios are decreasing, while CFC-12 mixing ratios are about constant. The sampling performed in Campo Grande and Maringá did not show a latitudinal variation, and the CFCs mixing ratios at these sites are about constant over the observed period. These agree with the restrictions outlined in the Montreal Protocol and its subsequent adjustments.

In urban areas, the variations observed in CFC-12 mixing ratio showed clearly the existence of many sources. These emissions can be from CFC-12 storage in olds refrigeration systems and foams.

References

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Acknowledgments

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