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RESIDUAL EMISSIONS OF CFC-11 AND CFC-12 IN THE SÃO PAULO METROPOLITAN AREA

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ABSTRACT. A study of atmospheric chlorofluorocarbons CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) was performed in the *Metropolitan Region of São Paulo – MRSP* (23.5°S; 46.6°W) during 2002. For the quantitative determination of the CFC concentration, a gas chromatograph with electron capture detector (ECD) was optimized with relative precision of 1.0%. In the MRSP, the observations of CFC-12 showed that there are large spatial and temporal variations in their concentrations (540.1 to 1395.8 pptv), while the CFC-11 concentrations did not show any statistically significant variation. Daily samplings were performed in June, July, August, September, November and December and showed that the emissions of CFC-12 were concentrated on weekdays (Monday to Friday), relating the emissions of this gas with its use in air conditioning and refrigeration systems of commercial and industrial buildings. The spatial variation observed in monthly campaigns in MRSP (April, May, June, July, August and September) and their matching with the predominant local wind direction evidencing the existence of a source region of CFC-12, located in the central area of the city. These results are indicative that emissions of CFC-12 are still significant. The monitoring of the mixing ratios of these gases in large cities like São Paulo can add to evaluate how the countries are following the Montreal Protocol, which restricts the production and trading of CFCs in developing countries, and schedule their banishment to 2010.

Keywords: Chlorofluorocarbons, urban emission, atmospheric pollution, seasonal cycle, Montreal protocol.

RESUMO. Este trabalho apresenta um estudo das concentrações atmosféricas dos clorofluorcarbonos CCl_3F (CFC-11) e CCl_2F_2 (CFC-12) na *Região Metropolitana de São Paulo* – RMSP (23,5°S; 46,6°O) durante o ano de 2002. Para a determinação quantitativa da concentração dos CFCs foi utilizado um cromatógrafo a gás equipado com um detector de captura eletrônica (DCE) otimizado para a análise dos CFCs 11 e 12 com precisão relativa de 1,0%. Na RMSP, as observações de CFC-12 mostraram a existência de grande variação espacial e temporal em suas concentrações (de 540,1 até 1395,8 pptv), enquanto as concentrações de CFC-11 não apresentaram qualquer variação estatística significativa. Amostragens diárias realizadas nos meses de junho, julho, agosto, setembro, novembro e dezembro mostraram que as emissões de CFC-12 estavam concentradas nos dias úteis, relacionando-as assim com seu uso em sistemas de ar condicionado e refrigeração do setor comercial e industrial. A variação espacial observada em campanhas de amostragem mensais (abril, maio, junho, julho, agosto e setembro) na RMSP, e seu cruzamento com a direção predominante do vento local durante o dia de coleta foi indicativa da existência de regiões de emissão específicas de CFC-12, localizada na área central da cidade. Estes resultados são indicativos de que emissões de CFC-12 ainda são significantes. O monitoramento das concentrações destes gases em áreas metropolitanas como São Paulo pode ajudar a avaliar o cumprimento da programação de restrição, do banimento da produção e da comercialização dos CFCs nos países em desenvolvimento acordada no Protocolo de Montreal.

Palavras-chave: Clorofluorcarbonos, emissões urbanas, poluição atmosférica, ciclo sazonal, protocolo de Montreal.

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INTRODUCTION

The chlorofluorocarbons (CFCs) were synthesized in the 1930s, and due their chemical properties were intensively used for refrigeration, air conditioning, production of aerosols and foams. During the major part of the twentieth century there was a large increase of use of two main CFCs: CCl_3F (CFC-11) and CCl_2F_2 (CFC-12), which led to the continuous increase in their concentrations observed in the atmosphere in the years 70-80 (Montzka et al., 1996; Montzka et al., 1999; Elkins et al., 1993). These gases are inert in the troposphere, being slowly transported to the stratosphere by turbulent and diffusive processes. In this region, they can be dissociated by solar ultraviolet radiation, releasing chlorine atoms, which can destroy the ozone molecule (Molina & Rowland, 1974; Stolarski & Cicerone, 1974). Besides this participation in the ozone chemistry in the stratosphere, CFCs have a potential to provide significant radiative warming to the troposphere (Ramanathan, 1975). Their relative role in climate forcing increased rapidly during the 1980s because of the large increases in their atmospheric concentrations, reaching a relative contribution of about 12% during the 1990s (Krupa, 1997). After the Montreal Protocol, their concentrations stop to increase, and the CFC-11 concentrations began to decrease. Their relative contribution for both to the radiative forcing are recently estimate in 8% (CMDL, 2005).

Because of the important role of the CFCs in ozone depletion, the production and trade are presently controlled by the Montreal Protocol and subsequent amendments, which called for the elimination of their production by 1996 in the developed countries. After the Protocol, a decrease of the global tropospheric mixing ratio of CFC-11 was observed at the Climate Monitoring and Diagnostics Laboratory/National Oceanic and Atmospheric Administration (CMDL/NOAA) stations, with a global average mixing ratio of 255 pptv (parts per trillion by volume) in 2004, with an annual decrease rate of –2.6 pptv/year (CMDL, 2005). For CFC-12, the global mixing ratio begun to stabilize since 1998, and the global mixing ratio average was near 535 pptv, in 2004. The global atmospheric growth rate for 2002-2003 was virtually zero (0.10 ± 0.09 pptv yr^{-1}), although the in situ analyses suggest that the CFC-12 concentrations in the atmosphere have begun to decline (CMDL, 2005).

Tropospheric mixing ratio trends have been extracted from time series at remote sites (like the CMDL/NOAA stations) where the air masses are well mixed and there are no sources or sinks of these gases. Trends observed in the background data showed indications of changes in global-scale emissions (Montzka et al., 1996; Montzka et al., 1999; Elkins et al., 1993), but provide little information about regional and national releases to the atmosphere. Measurements in urban areas have shown spatial and temporal variations in many scales, from seasonal to hourly and daily variations linked with emissions and transport. Ho et al. (1998) and Hurst et al. (1998) showed that measurements at sites near to source regions are sensitive indicators of changes in their regional pattern emissions.

In this work we present a study of CFC-11 and CFC-12 mixing ratios in urban air in the Metropolitan Region of São Paulo (MRSP – 23.5°S; 46.6°W), Brazil, during the year 2002. The urban area comprises 8051 km^2 and is situated in a plain that is bounded by elevations to the north (Serra da Cantareira, with altitude of 1200m) and west/south (Serra do Mar, with altitude of 800m) and by two water reservoirs at south. The estimate for the population of the metropolitan region is approximately 17 million, distributed in an urbanized area of 1742 km^2. The Metropolitan Region of São Paulo represents 0.1% of the Brazilian territory and is the third major urban conglomerate in world. It has 7.4 million vehicles, about 60,000 industries and has 1/6 of the Brazilian Gross Domestic Product (GDP) (CETESB, 2006). The daily and spatial variations for both gases were evaluated to investigate the existence of residual emissions. These data are also compared with those obtained in a continuous monitoring site placed in Barra de Maxaranguape. It is a remote sampling station near Natal (6°S; 35°W), which is used as a control site to monitoring trace gases, since it is not influenced by anthropogenic activity (Alvalá & Kirchhoff, 1998).

EXPERIMENTAL METHODS

The air samplings were performed above 2 meters from the surface using stainless steel internally polished cans of 0.8 liters. The canisters were cleaned before sampling by evacuating to 10^{-2} mbar, heated at 100°C, during one hour, as mentioned by Alvalá & Kirchhoff (1998) and Alvalá et al. (2004). To observe and prevent the occurrence of contaminations, the canisters had been full with nitrogen and analyzed once a month. To make the samples, the ambient air was pumped up to 30 psi with a Metal Bellows Corp MB158 pump. The CFCs mixing ratios were determined using a commercial Varian gas chromatograph (Varian CG 3800) with an electron capture detector (ECD). Two stainless steel columns of 1/8" diameter were used; the first column, for backflush, 1.5 m long and the second, for analyses, 3.0 m long, both packed with Porasil B. The columns were operated at 120°C, and the detector at 350°C. The sample injection was carried

through a sampler loop of 2.2 mL volume using a mixture of 5% of methane balanced in argon as carrier gas, with high purity grade. The CFCs mixing ratios were determinate by comparison between the samples peak areas and the peak areas of a NOAA-made standard (264.7 ± 5.3 pptv and 550.5 ± 11.0 pptv for CFC-11 and CFC-12, respectively). The relative precision for analysis of the four injections of each sample was 1% or better for both gases. The limit of detection was establishing by use the double of the peak-to-peak noise level. For the CFC-11 and CFC-12, the limit of detection was 1,4 pptv and 1,0 pptv, respectively.

In Barra do Maxaranguape (6°S; 35°W) there is a systematic sampling that started in August 2001, with a frequency of two or three times per week. The samplings were performed in pairs (two canisters) in a sequential way. This site receives air masses from the South Atlantic, which normally travel over the ocean for many days without any direct contact with anthropogenic sources, and has been used for study of many trace gases (Alvalá & Kirchhoff, 1998; Kirchhoff et al., 2003).

Two different schemes of sampling were performed in the MRSP to evaluate the emissions of CFC-11 and CFC-12: a) to study the spatial distribution of emissions, samples were obtained in six points around the city center (University of São Paulo – USP, Ibirapuera Park – IBI, Ipiranga Park – PIN, Tietê Ecological Park – PET, Anhembi Park – PAN and Toronto's City Park – PCT). These samples were obtained once a month from April to October. All samples were obtained between 10:00 and 14:00 (local time) using only one canister per sampling site; b) to evaluate week and seasonal variations in the emissions, daily samples were obtained at the USP site at two periods of 2002 (June/July/August and November/December). All sample sites were, at least, 100 m away from the main avenues to avoid direct influence of the heavy traffic and the sampling were made only in days with clear sky and low possibility of rain. Fig. 1 presents a map of the Metropolitan Region of São Paulo with the sampling sites.

RESULTS

The mixing ratios for CFC-11, obtained at the points showed in Fig. 1, in the seven campaigns are presented in Fig. 2. The monthly averages (and one standard deviation) obtained in the Barra de Maxaranguape site is also plotted (solid and dot horizontal lines, respectively), for comparison. The overall average mixing ratio observed in this urban area (264.4 ± 6.8 pptv) was just a few pptv higher than the average observed in Barra de Maxaranguape in the same period (258.5 ± 1.8 pptv). This result shows that the emissions of CFC-11 in the MRSP were small and represent a source whose amplitude was inside the variation of the measurements. The spatial variation shows that small emissions still occurs and their sources were not fixed, since the highest mixing ratios of each month had occurred in different places without relation with wind direction. These results show also that the emissions of CFC-11 were probably linked with leakages or purges, and not with systematic use on industries. The same pattern of mixing ratios for CFC-11 was observed by Wang et al. (1998), in Taipei City, Taiwan.

Figure 3 presents the mixing ratios for CFC-12 obtained in RMSP from April to October 2002. Monthly averages and one standard deviation for the Barra de Maxaranguape site are also presented (solid and dotted horizontal lines, respectively). Distinct from the CFC-11, the observations of the CFC-12 showed higher mixing ratios compared to the Barra de Maxaranguape averages, with values ranging from 540.1 pptv to 1395.8 pptv, with a large spatial variation. The overall average for MRSP was 635.2 ± 149.9 pptv, approximately 17% higher than the observed for Barra de Maxaranguape point, which had an average mixing ratio of 544.0 ± 2.0 pptv in the May-October period. The large standard deviation in the MRSP was due to the large variability observed in the mixing ratios in different locations for each month. Wang et al. (1998) obtained variations of about 15.5% in their samplings, reflecting a large spatial variation also. The highest values (in the points PCT in July and PIN and PIB in August) were observed in the places which the local wind was arriving from the city center in that time, which reveals the existence of a more intense source in the central zone. This central source was confirmed when the other points were considered, which showed lower mixing ratios. As in the central zone there is a high density of old commercial buildings, some of them with old system of air conditioning that are still using CFC-12. The use, maintenance and leakages of these equipments could account for the emissions observed in our measurements.

The lowest mixing ratios of CFC-12 were obtained in the point PET, which is located in the east region of the city, about 15 km away from the city center and inside an ecological park, with a less influence of the urban sources. The average mixing ratio for this point was 555.3 ± 4.7 pptv, with a low variability compared with the other points, and the individual mixing ratios were near to that observed in the Barra de Maxaranguape point (544.0 ± 2.0 pptv).

Two campaigns using the USP site were performed to study a possible weekly and seasonal variation in the emissions of the chlorofluorocarbons, with one daily sampling. The first period

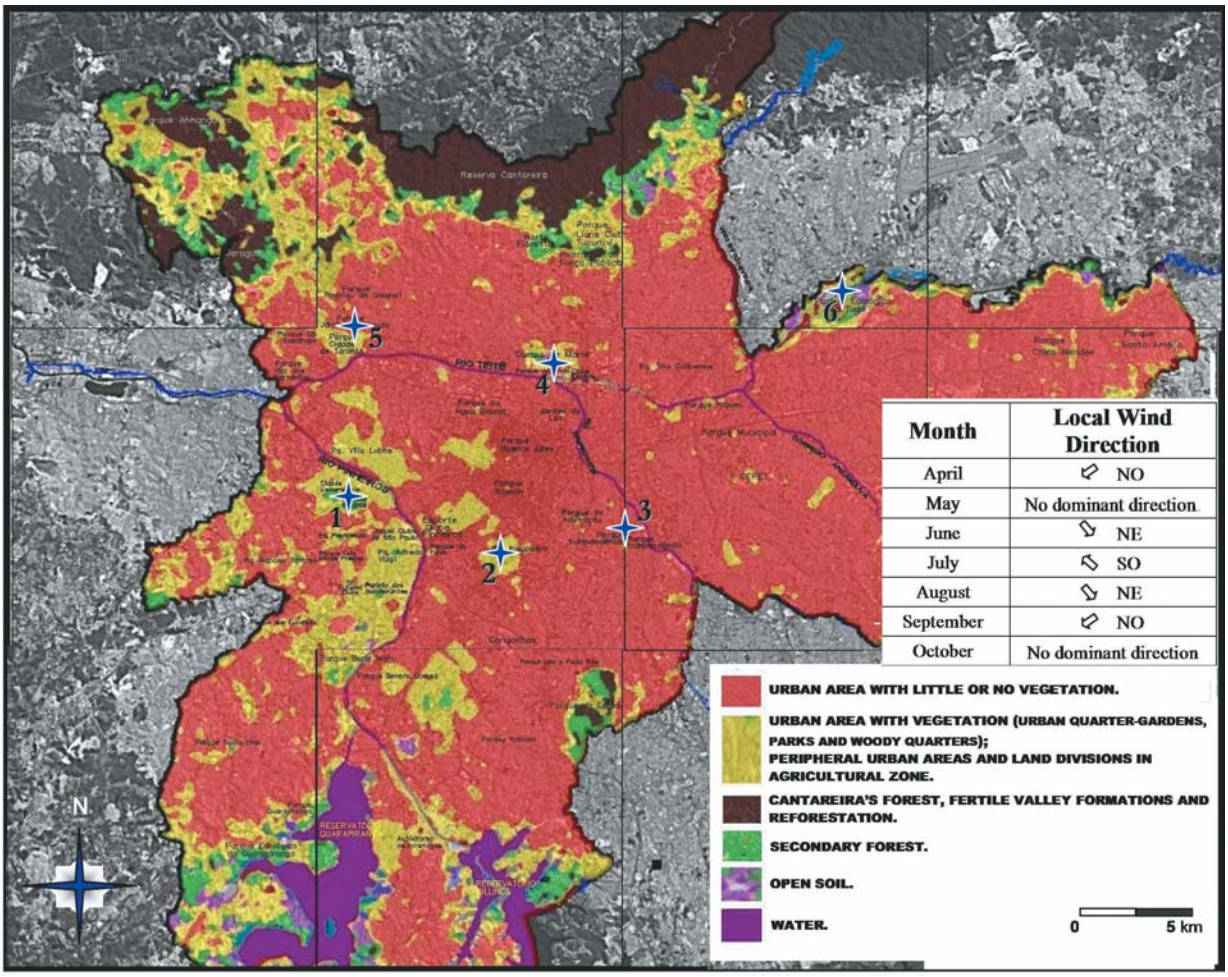

Figure 1 – Diagram of the São Paulo Metropolitan area, with the six sampling sites (stars): 1-USP (University of São Paulo), 2-PIB (Ibirapuera Park), 3-PIN (Ipiranga Park), 4-PAN (Anhembi Park), 5-PCT (Toronto's City Park) and 6-PET (Tietê Ecological Park). Also are showed the predominant wind direction.

was from June to August 2002 (winter, 23 samples), and the second in the months of November and December 2002 (spring, 19 samples). The Figure 4 presents the daily average mixing ratios for CFC-11 (Figure 4a) and CFC-12 (Figure 4b) for both periods with one standard deviation (error bar). The distribution of the samples was: six on Tuesday, Wednesday, Thursday and Friday, and seven samples on Saturday, Sunday and Monday. The average mixing ratio observed in Barra de Maxaranguape at the same period was represented by the dot line, and the shadow area represents one standard deviation.

The daily average mixing ratios observed for the CFC-11 obtained in the spring (261.9 ± 6.7 pptv) and the winter (262.2 ± 5.2 pptv) presented the same pattern, with the higher values occurring during the weekdays and the highest individual value observed on Wednesday (281.1 pptv). Although the daily mixing ratios of CFC-11 obtained in MRSP for both periods presented a remarkable spread, a comparison of these averages with Barra de Maxaranguape data (4a) showed that they are not statistically different and did not reveal any seasonal behavior. These results show that the CFC-11 releases were small, resulting in an average concentration near that observed in Barra de Maxaranguape, which was used as our background reference.

The daily mixing ratio of CFC-12 obtained at USP site showed large variations during the weekdays with smaller average mixing ratios and spread in the weekend (Saturday and Sunday), as can be observed in Fig. 4b. The same pattern was reported by Ho et al. (1998) in New York City study. This probable weekly cycle can be associated to industrial and commercial activities in the MRSP due the use of CFC-12 in the old refrigeration systems, as revealed in the monthly sampling. Although a seasonal pat-

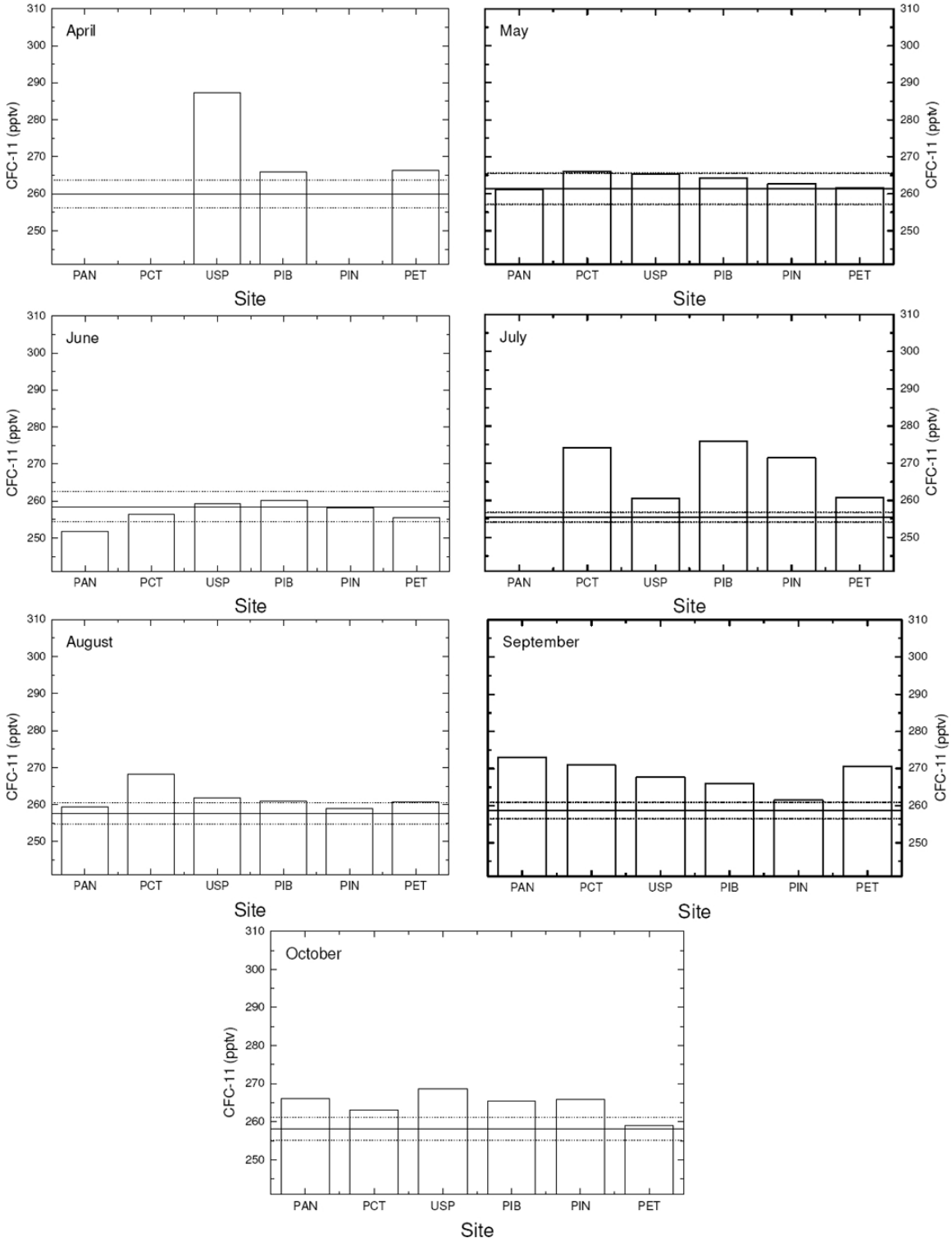

Figure 2 – CFC-11 mixing ratios over the six sampling sites (bars) and in Maxaranguape (horizontal line), from April to October 2002.

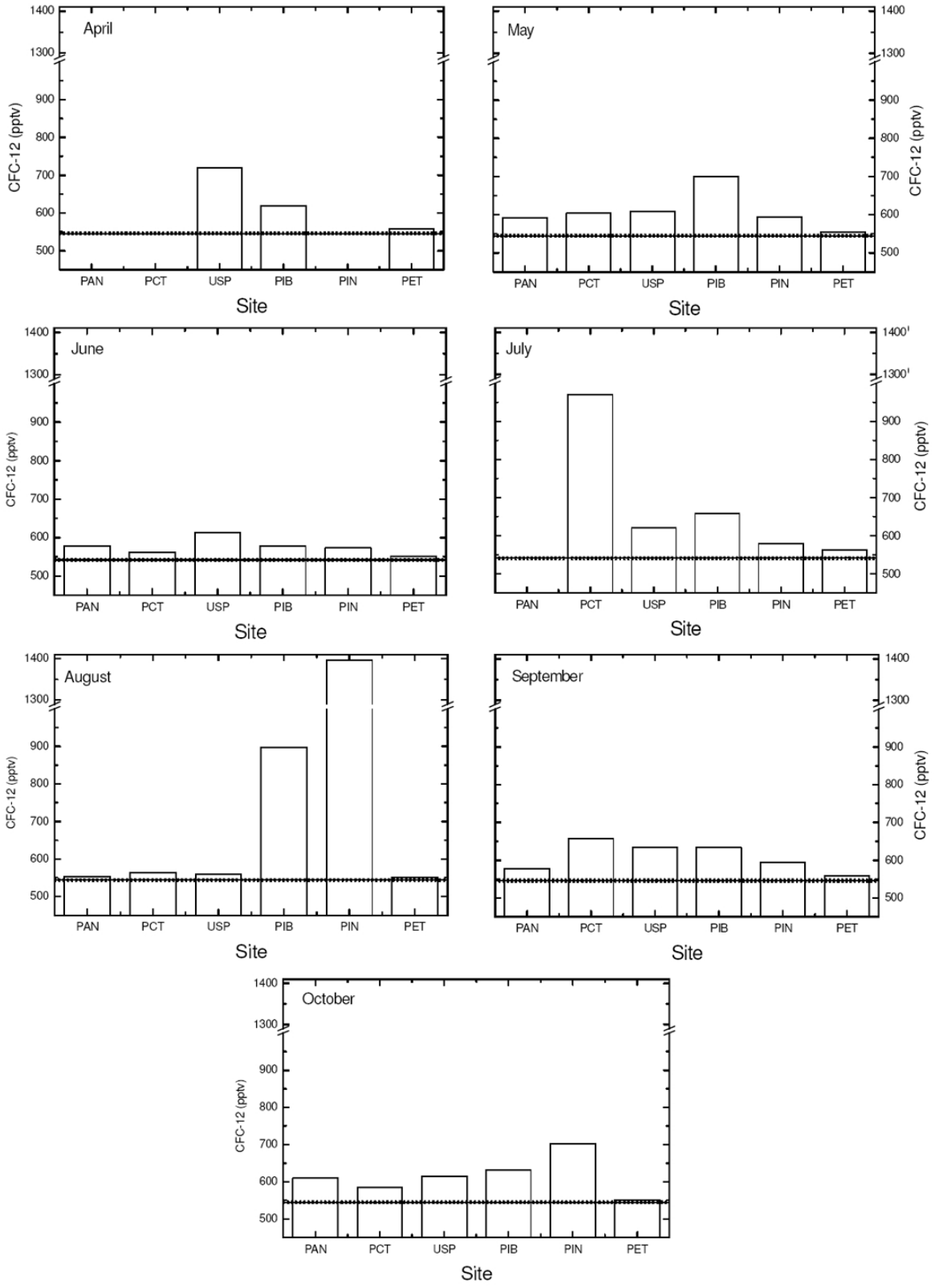

Figure 3 – CFC-12 mixing ratios over the six sampling sites (bars) and in Maxaranguape (horizontal line), from April to October 2002.

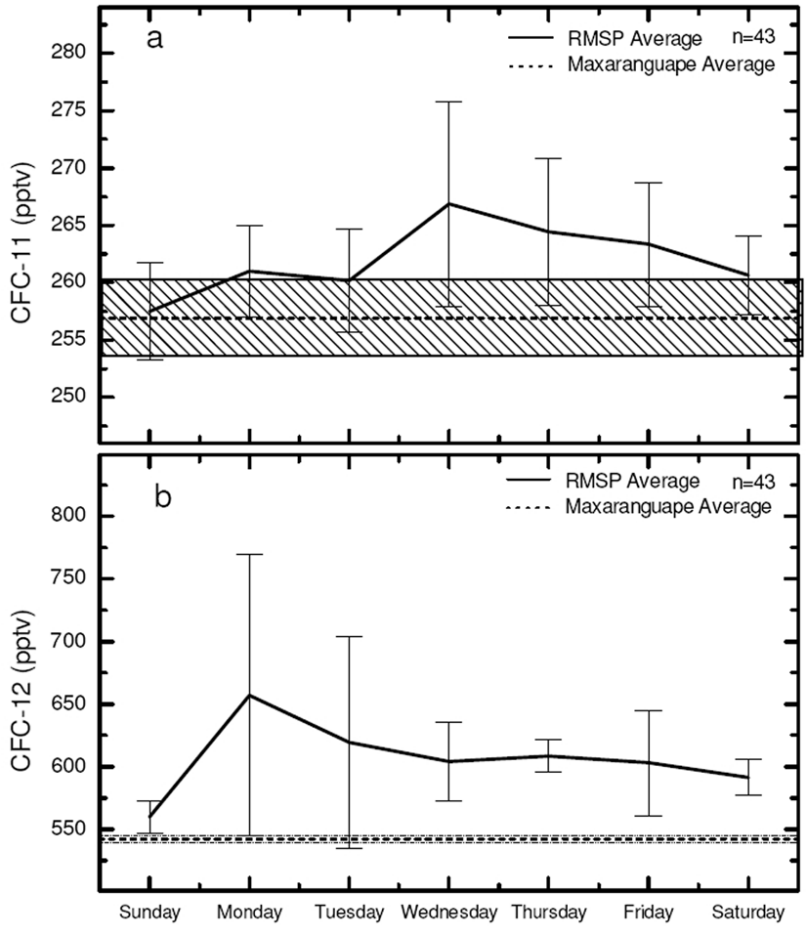

Figure 4 – Daily averages of CFC-11 (a) and CFC-12 (b) mixing ratios over São Paulo, obtained at USP site during year 2002.

tern can not be observed for CFC-12, the highest mixing ratios and average (613.0 ± 74.9 pptv) occurred in winter. Differently from the observed in the CFC-11, the daily average mixing ratios of the CFC-12 were higher than the spread obtained in Maxaranguape site. The overall average for both periods shows that there is a variable, but continuous release of CFC-12 to the atmosphere in the MRSP.

CONCLUSIONS

This work add new information to our understanding of the residual emissions of CFCs 11 and 12 from the Metropolitan Region of São Paulo, one of the largest urban area of developing countries, where the production and trade of these gases are restrict under Article 5(1) of the Montreal Protocol. Two kinds of sampling schedule were performed to study spatial and temporal variations of the mixing ratios of CFC-11 and CFC-12 in the MRSP. Correlations between CFC-11 and CFC-12 concentrations and meteorological parameters were investigated, but only the wind direction showed an influence in CFC-12 concentration. When confronted with dataset of Barra de Maxaranguape (a remote site and considered as our background), the CFC-11 data showed small temporal and spatial variations, with mixing ratios near those observed in the background site, revealing that still there are sources, but they must be weak and sparse.

Distinct from CFC-11, the CFC-12 mixing ratios presented large spatial and temporal variations (including a possible weekly cycle). A comparison with the background data showed that emissions of CFC-12 to the atmosphere are still significant, and could be associated with the use of this gas in old refrigeration systems. The monitoring of the concentration of these gases in large cities like São Paulo in the next years can contribute to evaluate how these countries are following the Montreal Protocol and will clarify the results observed in this work concerning the trends of their concentrations.

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