Behavior of the atmospheric sulphur dioxide (SO_2) at Cachoeira Paulista – SP, through the data obtained by the Brewer Spectrophotometer

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Abstract

For a better comprehension of the atmospheric chemistry, it is necessary to understand the behavior of the trace gases and aerosols, since the atmospheric chemical and radiative properties depend upon them. But the behavior of some of these species is not well studied and characterized. An example is sulphur, that both in the gaseous as in the aerosol phase have great environmental impact. With this purpose, a study to evaluate the behavior of the sulphur dioxide, an acid rain and sulfate aerosol precursor, and whose the main natural source are the volcanic eruptions will be shown. The ground-based observations presented in this study were made in the city of Cachoeira Paulista (22.6ºS, 45ºW), in the countryside of the State of São Paulo, through the acquisition of the gas total column measured by the Brewer Spectrophotometer of the National Institute for Space Research – INPE, as part of a doctorate thesis that will focus the data along South America.

Introduction

The study of the changes in the atmospheric SO_2 concentration is important because this gas has effects in the atmospheric chemistry and in the radiation field, with climatic consequences. In this case, the climate and atmosphere research requires continuous SO_2 observations (Fioletov et al., 1998). SO_2 is emitted in the atmosphere as a result of natural phenomena as well as anthropogenic activities, such as fossil fuel combustion, oxidation of soil organic material, volcanic eruptions and biomass burning. In a global scale, most of the SO_2 is produced by volcanoes and by the oxidation of sulphur gases produced by plant decomposition. The coal burning is the biggest anthropogenic source of SO_2, responsible for about 50% of the annual emissions, and the oil burning for 25 to 30% (Baird, 2002). According to Rocha et al. (2004), the residence time of SO_2 in the atmosphere varies from 1 to 4 days. SO_2 from anthropogenic activities was recognized as being the major source of sulfuric acid and sulfate aerosol over the continents (Thornton et al., 1999). In regions where the air pollution is small, the SO_2 concentration is lower than 2 DU, whereas in polluted regions this value reaches 4 to 6 DU (Fioletov et al., 1998), and in extreme cases reaching 20 DU or higher, as it is the case in volcanic eruptions events (De Backer and De Muer, 1991).

SO_2 near the ground, when in higher concentrations, have a direct effect on human health, which leads to respiratory diseases, difficulty in breathing, and premature deaths in some extreme cases, and inhibit plant growth. SO_2, when oxidized in the troposphere, form sulfuric acid (H_2SO_4) which is mostly deposited as acid rain. SO_2 also plays an important role in cloud formation physics, leading to clouds of high reflectivity. In the stratosphere SO_2 is also oxidized and combines with water to form sulfate aerosols (Bekki, 1995). These aerosols scatter solar radiation and absorb long-wave radiation, causing heating in the stratospheric region and net cooling at the Earth's surface (Georgoulias et al., 2009).

Cappelani e Bieli (1994) state that SO_2 in the air vertical column is concentrated in the low troposphere, mainly trapped in the mixture layer. De Backer and De Muer (1992) say that, occasionally, higher amounts of SO_2 in the stratosphere, resulting from volcanic eruptions, may be observed. However, the conclusions presented in these authors work show that, in general, almost every SO_2 in the vertical is found in the lower troposphere.

Several methods have been developed for measuring not only near surface concentrations but also the total atmospheric content using ground-based instruments (Georgoulias et al, 2009). The Brewer spectrophotometer was developed in the beginning of the 1980s to precisely measure ozone (O_3) (Kerr et al., 1981), and also measures sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and spectral irradiance in the ultraviolet band. This instrument is widely used by the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) to measure the O_3 columns. Today, there are more than 180 instruments installed around the globe (Fioletov et al., 2005).

Several studies using this instrument were already made to better understand the behavior of O_3 in South America (Casiccia *et al.* (1995); Casiccia *et al.* (2003); Kirchhoff and Guarnieri (2002); Kirchhoff *et al.* (1993); Kirchhoff *et al.* (1995); Sahai *et al.* (2000)). However, there is a lack of studies concerning the SO_2 chemistry and the validation of the data obtained by Brewer spectrophotometers in previous campaigns. In this paper we present some results of the SO_2 total column measurements from a Brewer spectrophotometer at the city of Cachoeira Paulista (22.6ºS, 45ºW), in the countryside of São Paulo. The years of 2003 and 2005 were separately evaluated, since they have a more homogeneous time series, to find if there are any trends in the SO_2 concentrations. Longer

time series and other locations will be also evaluated and published later in a doctorate thesis.

Method

Brewer spectrophotometer

The Brewer spectrophotometer is a ground based instrument which makes measurements of solar radiation, allowing the measurement of the total column of the following atmospheric gases: ozone (O_3), sulphur dioxide (SO_2) and nitrogen dioxide (NO_2). It can also measure the solar global radiation in the band ultraviolet B (UVB). This instrument uses the Dobson unit (DU) to express the total columns of O_3, NO_2 and SO_2.

The Brewer spectrophotometer is totally automatized and composed by three parts: tripod, tracker (system that traces the sun) and the spectrophotometer itself. The instrument contains a microprocessor, responsible for the equipment internal operations. This microprocessor is connected to a computer that, through the Brewer software, controls the functioning of the instrument, and the data reduction and storage. The five wavelengths of operation are located in the ultraviolet band of the O_3 and SO_2 absorption spectrum, which have a strong and variable absorption in this region: 306.3; 310; 313.5; 316.8; 320nm.

The measurement of the total column of an atmospheric gas made by a ground based instrument is based in the principle of absorption of radiation incident over a quantity of matter. Methods based on the surface use radiance measurements of an external source, such as the Sun or the moon, after the radiation suffered extinction, as a result of atmospheric absorption, molecular scattering and aerosol (particles) scattering, all of them dependant on the wavelength (Whitten, 1985).

Since the amounts of SO_2 in the atmosphere are low, the measurements made by the Brewer need a high signal-noise relation to be valid, as in the event analyzed by Sahai et al. (1997), that studied the effects of SO_2 and O_3 over Brazil after the eruption of Mount Pinatubo, in June, 1991.

Data collection and treatment

The Ozone Laboratory, that belongs to the National Institute for Space Research, have a network of Brewer Spectrophotometers in South America (Figure 01). The one in Punta Arenas operated from 1991 to 2002, when the University of Magallanes acquired its own instrument. The data presented here were obtained in Cachoeira Paulista through the Direct Sun method, using the direct solar beam as a radiation source, in the years of 2003 and 2005. The data collected by the Brewer need to be reduced so they can be evaluated. This is made by an analysis program developed specially for the instrument – the Brewer Spectrophotometer B Data Files Analysis Program. This program read the Brewer files according to the calibration data of each instrument. Since each instrument has a distinct calibration, this stage of the data treatment takes a longer time to be done. To the analysis of the data collected for this research, techniques of Descriptive Statistics were used.

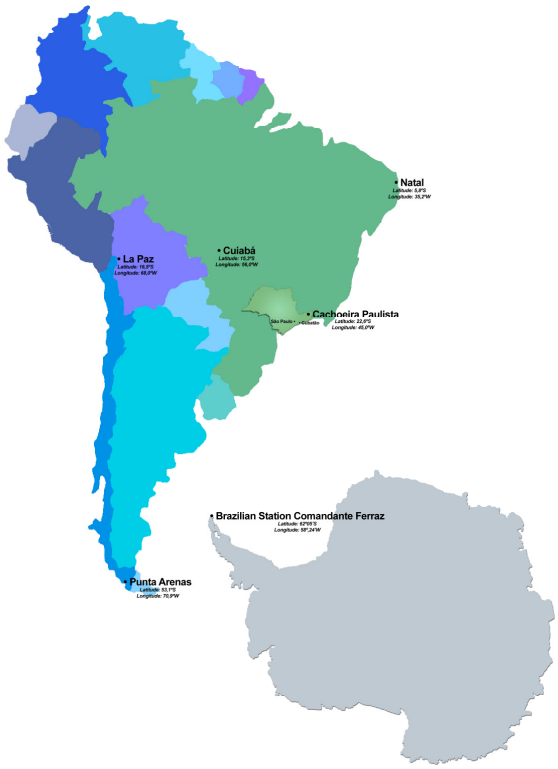

Figure 01 – Location of the Brewer spectrophotometers belonging to the network of the National Institute for Space Research.

Results

The SO_2 total column found over Cachoeira Paulista agree with the ones found in regions with similar characteristics, that is, varying from times with little pollution, until some occasions with concentrations similar to polluted regions. The peaks along the year in this region might be related to the Presidente Dutra highway, since the city of Cachoeira Paulista, in the countryside of São Paulo, is located near the highway.

As previously mentioned, the SO_2 in the air vertical column is mainly concentrated near the surface. This indicates that in this location the main responsible for the gas concentration are the surface anthropogenic emissions, since that higher total columns generally suggests contributions from volcanic eruptions, that cannot be related to the region of Cachoeira Paulista, not even through transport in the stratosphere, at least in the studied period.

It is possible to notice a great daily variability in the time series for both years. The year of 2003 (Figure 2), with annual average of 2.6±1,0 DU, presented higher values than 2005 (Figure 4), that had a total column with an average of 1.8±0,6 DU. Georgoulias et al. (2009) found an average total column of 1.7±1,1 DU for Thessaloniki, Greece, result that agree with the data shown here. In

2005, the SO_2 total column remained more regular, but in both years it is possible to notice the increase in the total column from approximately the month of September, beginning of spring.

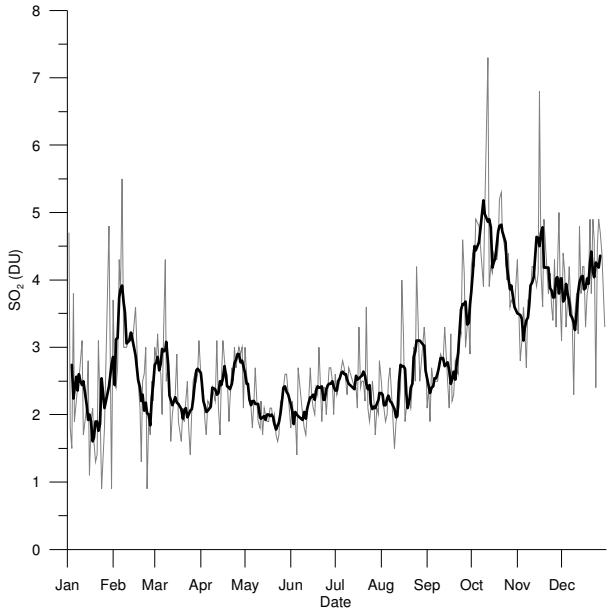

Figure 02 – Time series of the SO_2 total column, in Dobson Units, at Cachoeira Paulista – SP, in the year of 2003.

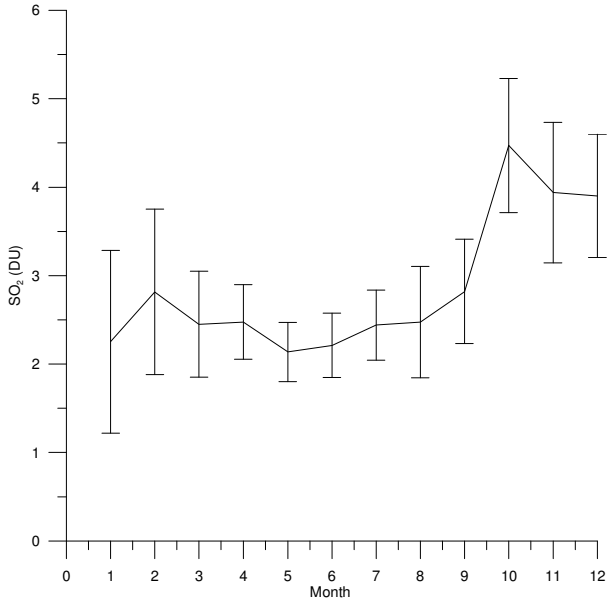

Figure 03 – Monthly means of the SO_2 total column, in Dobson Units, at Cachoeira Paulista – SP, in the year of 2003.

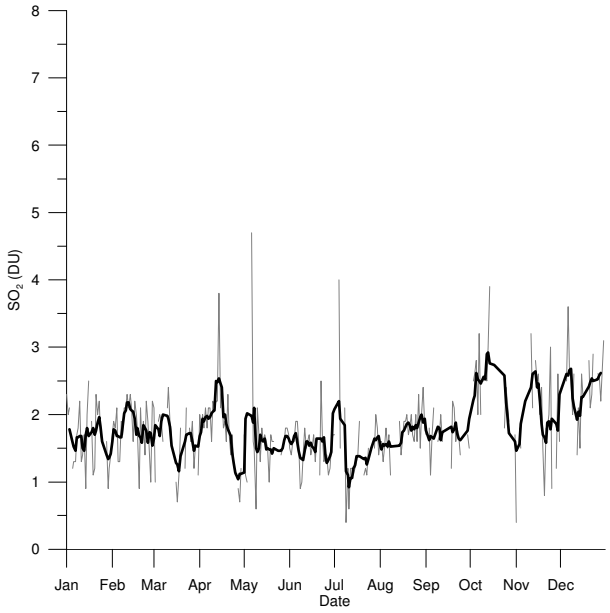

Figure 04 – Time series of the SO_2 total column, in Dobson Units, at Cachoeira Paulista – SP, in the year of 2005.

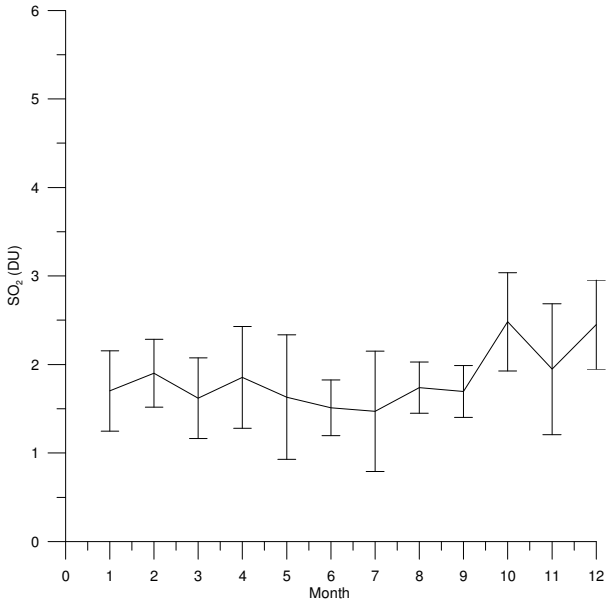

Figure 05 – Monthly means of the SO_2 total column, in Dobson Units, at Cachoeira Paulista – SP, in the year of 2005.

Since the years of 2003 and 2005 were the only with a full 12-month set of data, they were used in this analysis. In the monthly means (Figures 03 and 05), it is possible to notice a small secondary peak in the month of February, and increase in the total column in the second semester, approximately in the beginning of spring. The origin of these peaks is not totally understood, and might be related to the wind direction at the time of the peaks.

Conclusions

Based on the data presented here, it is possible to conclude that the city of Cachoeira Paulista, concerning the SO_2 concentration, might be considered polluted in some periods of the year, especially in the second semester, possibly because of the proximity with the Presidente Dutra highway, with an average annual total column of 2.2 DU.
It is important to stress that this study is part of a larger one, in which the SO_2 total columns in several latitudes of South America will be evaluated, to establish the behavior of the gas in the whole continent, identifying the differences among the several studied sites. Studies like this one are important for they establish a dataset that is essential to the assimilation of meteorological models and in air pollution studies. The results presented here are a part of the doctorate thesis of the first author.

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