

Table 1. Events of the Antarctic ozone hole influence over Southern Space Observatory with corresponding reduction of ozone.

Events days	Ozone (DU)	Reduction (%)
28/09/2008	275.2	6.9
12/10/2008	267.8	8.1
26/10/2008	266.5	8.5
05/09/2009	261.2	11.6
06/09/2009	249.9	15.5
01/10/2009	270.2	7.3
Average	265.1 \pm 8.8	9.7 \pm 3.3

Results

Climatological averages of ozone total column measured by Brewer Spectrophotometer at Southern Space Observatory from 1992 to 2009 were $295,6 \pm 10,2$ DU for September and $291,5 \pm 8,9$ DU for October. The days of 2008 and 2009 with ozone total column lower than these climatological averages minus 1.5 times the standard deviation was analyzed according to the methodology described above. The examples of 26 October 2008 and 05 September 2009 are shown in Figure 1 and Figure 2, respectively, where an increase of absolute potential vorticity at the level of 620 K (a), the backward trajectories of air masses poor of ozone (b) and OMI data (c) are represented showing the influence of Antarctic Ozone Hole over South of Brazil. Considering only the days with decreased ozone measured at Southern Space Observatory, increased absolute potential vorticity shown at GRADS maps and HYSPLIT backward trajectories indicating the origin of polar air masses, it was observed 3 events in 2008 and 2 events in 2009 presented at Table 1,

with an average decreased about $9.7 \pm 3.3\%$ when compared with climatological means.

Conclusion

The analysis of all days with decrease of ozone total column at Southern Space Observatory showed the influence of Antarctic Ozone Hole over South of Brazil. 3 events in 2008 and 2 events in 2009, with an average decreased about $9.7 \pm 3.3\%$ when compared with climatological means, were observed.

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ATMOSPHERIC SO₂ MEASUREMENTS AT THE BRAZILIAN ANTARCTIC STATION

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Abstract: For a better comprehension of the atmospheric chemical and radiative properties, it is necessary to understand the behaviour of trace gases and aerosols; some of these gas types have not been deeply studied. Sulphur dioxide (SO₂) is found in the troposphere, as a result of both natural and anthropogenic emissions. To study the behaviour of this gas in the Antarctic continent, the data collected by the Brewer Spectrophotometer installed in the Brazilian Antarctic Station Comandante Ferraz (62° 05' S and 58° 24' W) was used. With this ground-based instrument, the total column of SO₂ was measured from the beginning of springtime, to the start of summer, during the years 2003 to 2009. It was possible to observe that the total columns of SO₂ did not show any differences in the time of the development of the ozone hole, as compared to other periods. The main sources of anthropogenic SO₂ pollution in this region are the generation of energy, the operations with ships, and the burning of garbage, being a punctual impact. The natural generation of SO₂ in this region is mainly related to the conversion of DMS (dimethyl sulfide) emitted by the ocean. In a few days, the SO₂ total column exceeded the values considered normal for remote regions (>2 UD), and these high concentrations must have their sources identified and monitored.

Keywords: atmospheric chemistry, sulfur dioxide, Brewer Spectrophotometer

Introduction

Antarctica is the coldest, windiest, and driest continent on Earth, with a remote location far from the major centres of population. Yet as one of the two heat sinks in the global climate system it plays a crucial role in the general circulation of the atmosphere and has a profound effect on the atmospheric and oceanic conditions across the Southern Hemisphere (Turner, 2003).

The study of the changes in the atmospheric SO₂ 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 SO₂ observations (Fioletov *et al.*, 1998). SO₂ is emitted in the atmosphere as

a result of natural phenomena as well as anthropogenic activities, such as fossil fuel combustion, volcanic eruptions, biomass burning and the oxidation of organic materials in soil and of dimethyl sulfide (DMS) over oceans. The sulfur dioxide (SO₂) found in the Antarctic region is mostly originated from DMS. SO₂ also plays an important role in cloud formation physics, leading to clouds of high reflectivity. In the stratosphere SO₂ 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 (Georgoulas *et al.*, 2009).

In regions where the air pollution is small, the SO₂ 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 in the case of volcanic eruption events (De Muer & De Backer, 1992). Cappellani and Bieli (1994) state that SO₂ in the air vertical column is concentrated in the low troposphere, mainly trapped in the mixture layer. De Muer & De Backer (1992) say that, occasionally, higher amounts of SO₂ in the stratosphere, resulting from volcanic eruptions, may be observed. However, the conclusions presented by these authors work show that, in general, almost every SO₂ 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 (Georgoulas *et al.*, 2009). The Brewer spectrophotometer was developed at the beginning of the 1980s to precisely measure ozone (O₃) (Kerr *et al.*, 1981), and also measures sulphur dioxide (SO₂), nitrogen dioxide (NO₂) 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 O₃ columns. Today, there are more than 180 instruments installed around the globe (Fioletov *et al.*, 2005).

Materials and Methods

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 (O₃), sulphur dioxide (SO₂) and nitrogen dioxide (NO₂). 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 O₃, NO₂ and SO₂.

The Brewer spectrophotometer is totally automated and made up of three parts: tripod, tracker (a system that traces the sun) and the spectrophotometer itself. The instrument contains a microprocessor, responsible for the equipment's

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 O₃ and SO₂ absorption spectrum, which have a strong and variable absorption in this region: 306.3; 310; 313.5; 316.8; 320 nm.

The measurement of the total column of an atmospheric gas made by a ground based instrument is based on the principle of absorption of radiation that penetrates a quantity of matter. Surface based methods use radiance measurements of an external source, such as the Sun or the moon, after the radiation had been extinguished, as a result of atmospheric absorption, molecular scattering and aerosol (particle) scattering, all of them dependant on the wavelength (Whitten & Prasad, 1985).

Data collection and treatment

The Ozone Laboratory, that belongs to the National Institute for Space Research, has a network of Brewer Spectrophotometers in South America. The data presented here was obtained in the Brazilian Antarctic Station Comandante Ferraz, from 2003 to 2009 through the Direct Sun method, using the direct solar beam as a radiation source. The data collected by the Brewer required reducing in order to be evaluated. This process is undertaken by an analysis program developed specially for the instrument - the Brewer Spectrophotometer B Data Files Analysis Program. This program reads 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 longer to be completed. For the analysis of the data collected for this research, techniques of Descriptive Statistics were used.

Results and Discussion

It is possible to notice a great variability in the data (Figure 1), including negative results, which are due to the Brewer SO₂ algorithm and must be considered corresponding to very low total columns. When the total column increases, on isolated days, it is not likely that this is

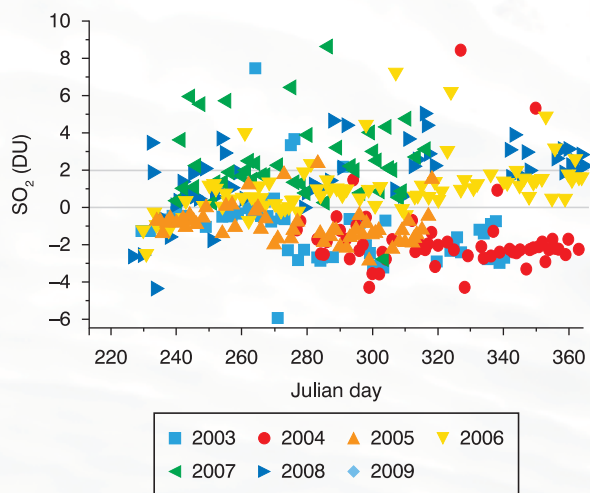


Figure 1. Daily average of the SO_2 total column for the Brazilian Antarctic Station from August to December, from 2003 to 2009.

Table 1. Annual average of the SO_2 total columns for the Brazilian Antarctic station.

Year	Average
2003	-0,9
2004	-1,7
2005	-0,9
2006	0,9
2007	2,5
2008	1,6
2009	3,0

associated with an increase of SO_2 in the stratosphere, unless when this is related to volcanic eruptions, which is not the case in this study. In the Antarctic region, the main natural contribution to the maintenance of the SO_2 column (even in low concentrations) is the conversion of organic material from the soils, and the oxidation of DMS over the ocean.

It was possible to observe an increase in the average total SO_2 column over the years for each annual period evaluated (Table 1). From 2006, the average turned positive. This coincides with the beginning of the construction of the expansion of the station, which may indicate an increase in the emission of pollutants. As the Antarctic region is a remote location, total columns above 2 DU can already be

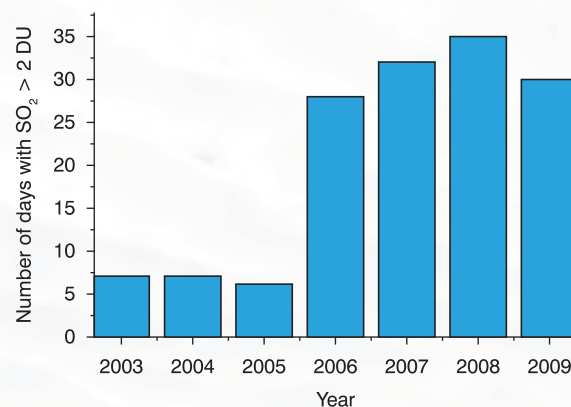


Figure 2. Number of days with SO_2 total column higher than 2 Dobson Units DU for the period studied.

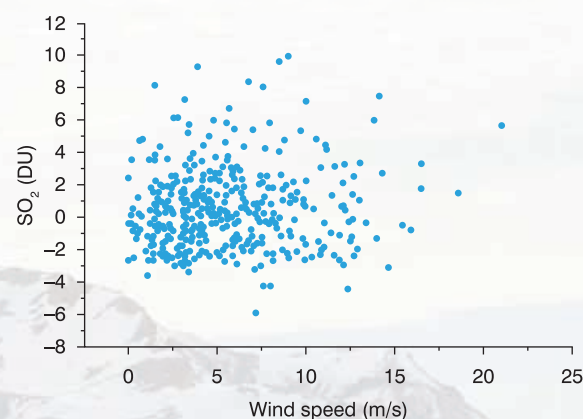


Figure 3. Correlation between the SO_2 total column and Wind speed for the studied period.

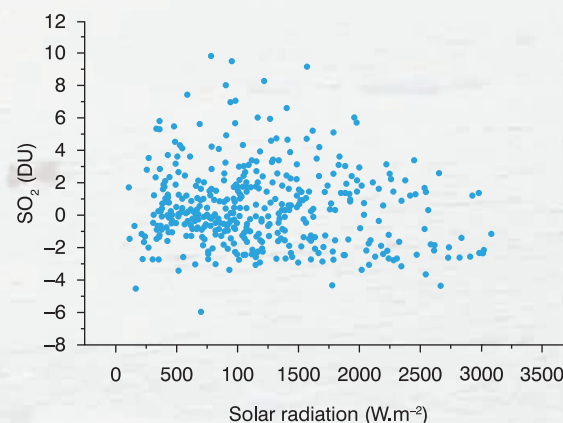


Figure 4. Correlation between the SO_2 total column and solar radiation for the studied period.

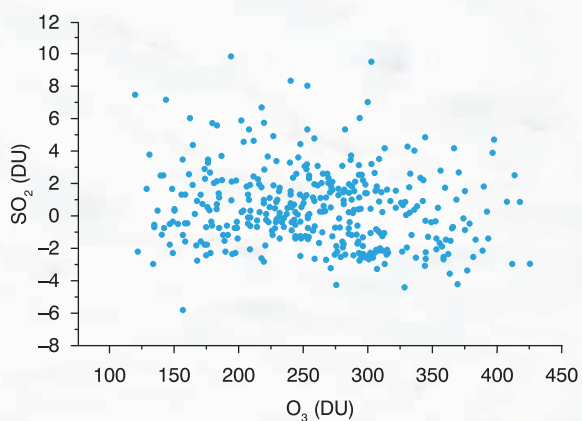


Figure 5. Correlation between the SO_2 total column and the O_3 total column for the studied period.

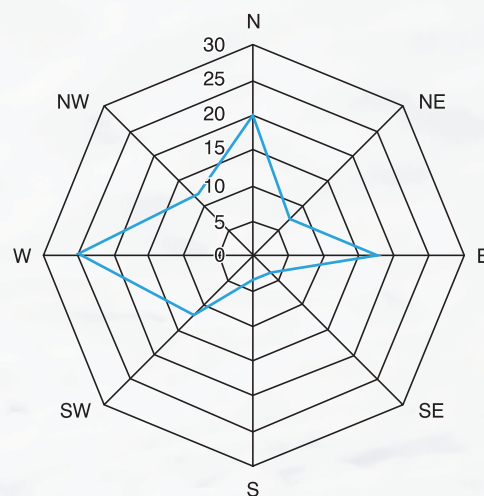


Figure 6. Predominant Wind direction for the days with SO_2 higher than 2 Dobson Units.

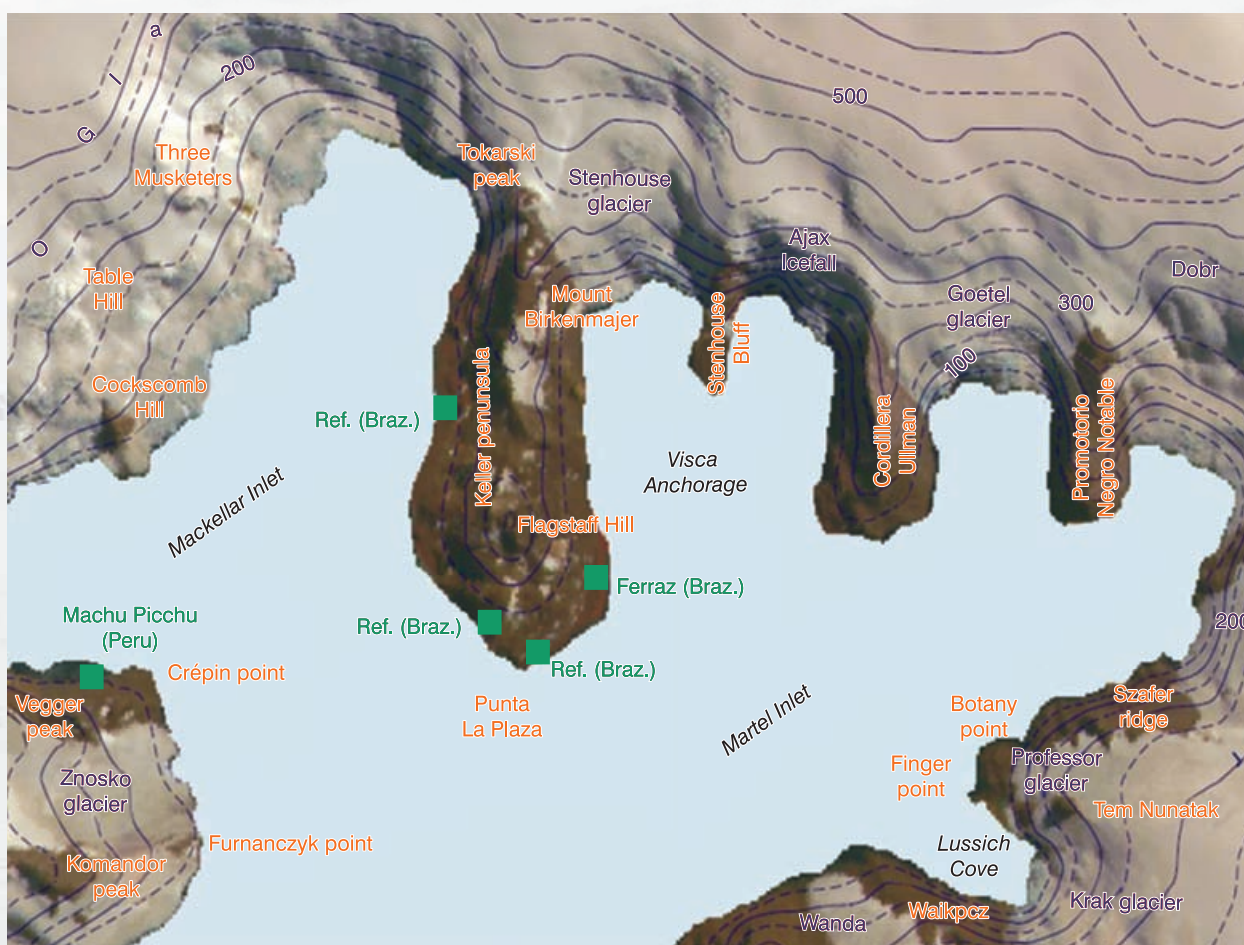


Figure 7. Map of the King George Island, showing the main stations. Adapted from http://hs.pangaea.de/Images/Maps/King_George_Island/King_George_Island_Map.pdf.