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Surface ozone concentrations and local cloud cover at an urban, tropical site in the Southern Hemisphere

Abel Antônio Silva [a,*], Luciano Machado Tomaz [b]

[a] Instituto de Estudos Avançados, Rod. dos Tamoios km 5.5, Torrão de Ouro II, São José dos Campos, SP, CEP 12228-001, Brazil
[b] PUC Minas, Av. Dom José Gaspar 500, Belo Horizonte, MG, CEP 30535-901, Brazil

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ABSTRACT

Surface ozone plays a key role in the photochemistry of the low troposphere, being associated with health and environmental problems. It results from a pool of reactions involving natural and anthropogenic pollutants, solar radiation, and the atmospheric condition. In this study, 12-months of recent measurements of surface ozone concentration (SOC) are presented for an urban, tropical site in Brazil. An analysis of the SOC dependence on the local cloud cover is introduced. Daily maxima of the one-hour averaged data (1-h SOC) ranged from 8.7 to 96.1 ppbv and averaged 38.1 ± 13.7 ppbv, while the monthly averages of the daily maxima of 1-h SOC varied from 24.5 ± 8.8 ppbv in early fall to 46.7 ± 9.3 ppbv in late winter.

1. Introduction

Apparently, the recovery of the ozone layer is in progress since the mid 1990's as a result of the Montreal Protocol ban on ozone depleting substances. The reduction in the year-round stratospheric ozone produced by ozone depleting substances over Brazilian latitudes was generally below 2.0%/decade, which represents a non-statistically significant value (Silva, 2007). On the other hand, the need of the human society for economic growth pushes the use of technologies that lead to increasing levels of pollution, which includes surface ozone. This is one of the key issues for the coming decades according to the Intergovernmental Panel on Climate Change (2007).

A natural catalytic cycle based on the nitrates produces ozone through the photolysis of NO_2 and destroy it through the reaction with NO. However, surface ozone is also a secondary pollutant, often resulting from anthropogenic sources. Highs in surface ozone concentration (SOC) – or, alternatively, ozone mixing ratio – come out in the presence of solar radiation ($\lambda < 420$ nm) and primary pollutants like the volatile organic compounds (VOCs) from natural and anthropogenic sources, and carbon monoxide (CO) and the nitrates from power plants based on fossil fuel and car exhausts (Atkinson, 2000). Meteorological and geophysical conditions (temperature, humidity, cloud cover, precipitation, aerosols, smoke plumes, and winds) also play important roles in the determination of SOC (Camalier et al., 2007; Duncan et al., 2008; Flynn et al., 2010; Kim and Newchurch, 1998). Surface ozone is a toxic and powerful oxidant that leads to deleterious effects on materials and life (Bell et al., 2004; Lippmann, 1991; McConnell et al., 2002; Pandrangi and Morrison, 2008; Tilton, 1989). The limits for human exposure to SOC vary worldwide depending on local legislation (Beig et al., 2008; Duncan et al., 2008; Meleux et al., 2007; Shan et al., 2008), which are generally based on the World Health Organization recommendations (WHO, 1987). In Brazil, a resolution (No. 03 of June 28 of 1990, www.mma.gov.br/port/conama/res/res90/res0390.html) of the Conselho Nacional do Meio Ambiente (CONAMA) states an hourly averaged limit of 160 μg m^{-3}, which must not be exceeded more than once a year. This limit is equivalent to 90 ppbv if temperature and atmospheric pressure are 23 °C and 913 hPa respectively.

Since SOC depends on the incidence of solar radiation, a seasonal behavior is likely to be found in SOC measurements. The solar elevation and temperature affect the photolysis efficiency and chemical reaction speed, respectively, in the complex atmospheric mechanism of surface ozone production. Moreover, clouds and aerosols produce variations in the incidence of solar radiation that affect SOC. Precipitation is the largest significant cause of reduction in SOC because it washes the pollutants out of the atmosphere in addition to reducing the incidence of solar radiation. The typical SOC amounts for a site depend on local factors like weather, climate, geography, and economy robustness. In addition, air transportation of pollutants from distant places also represents an important source of SOC and SOC formation (Duncan et al., 2008; Kim and Newchurch, 1998). Pristine sites or

* Corresponding author. Tel.: +55 12 3947 5502; fax: +55 12 3944 1177.
E-mail address: abel@ieav.cta.br (A.A. Silva).

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sites far from large urban polluted areas have shown maximum average SOC around 35 parts-per-billion by volume (ppbv) in Antarctica (Legrand et al., 2009), 70 ppbv in wild life parks like Yosemite National Park (Burley and Ray, 2007), 80 ppbv in Crete Island (Kouvarakis et al., 2000), or ranging from 15 to 70 ppbv in low polluted sites at mid and high latitudes (Oltmans et al.; 1998). On the other hand, in metropolitan areas the maxima of average SOC generally peak over 90 ppbv several times a year (Beig et al., 2008; Civerolo et al., 2007; Mazzeo et al., 2005; Meleux et al., 2007; Shan et al., 2008; Velasco et al., 2008).

Series of SOC measurements worldwide are generally from mid and high latitudes, especially from networks operating in the Northern Hemisphere. Only a few of them refer to the low latitudes of the Southern Hemisphere. Since an increase in SOC is foreseen for the coming decades (IPCC, 2007), there is a demand for improving and spreading field campaigns for SOC measurements. In this study, 12-months of recent SOC measurements are presented for a station in a metropolitan center of the southeastern region of Brazil. An analysis of the measurements in relation to both cloud cover and precipitation determined by an automatic sky imager is presented. A comparison with data from other Brazilian stations is provided too.

2. Materials and methods

2.1. Site description

Belo Horizonte (BH, Brazil) is the 3rd largest Brazilian metropolitan area. Fig. 1 and Table 1 show geographical and demographic data for BH (IBGE, 2011). Commercial and industrial activities are predominant in the region, where the mining industry and high technology enterprises represent the main activities. As a municipality, BH has a fleet over 1.2 million vehicles fueled with gasoline, ethanol, gasoline–ethanol mix, diesel, biodiesel, and natural gas. Despite its renewed fleet of electronic injection engines coupled with catalytic exhaust converters, BH faces a significant production of gases and particle matter launched into the atmosphere by traffic. In terms of environment, BH is in a hilly area settled between the Savanna (Cerrado, to the west and north) and the remains of the Atlantic forest (Mata Atlântica, to the east and south) about 400 km away from the Atlantic Ocean in the southeastern region of Brazil. The site features a tropical climate of altitude. Smoke and aerosol plumes from events of biomass burning outside the site are blown into it during the dry season in May–September when humidity falls below 20%. Rainy season is in the November–March period. Seasons can be split up into: December, January, and February for summer; March, April, and May for fall; June, July, and August for winter; and September, October, and November for spring. The site's annual amount of accumulated precipitation is ≈ 1450 mm with predominance of easterly winds. Table 2 shows seasonal averages for solar elevation, temperature, atmospheric pressure, and wind speed around 16:00 h Universal Time (UT), or 13:00 h local time (noon time). The averages of the three meteorological parameters over 12-months in 2009–2010 were 23.0 ± 2.9 °C (1σ), 913.1 ± 2.9 hPa, and 1.8 ± 1.1 m/s, respectively. Note that, the averages of solar elevation and temperature are related to each other and increase in the order winter, fall, spring, and summer.

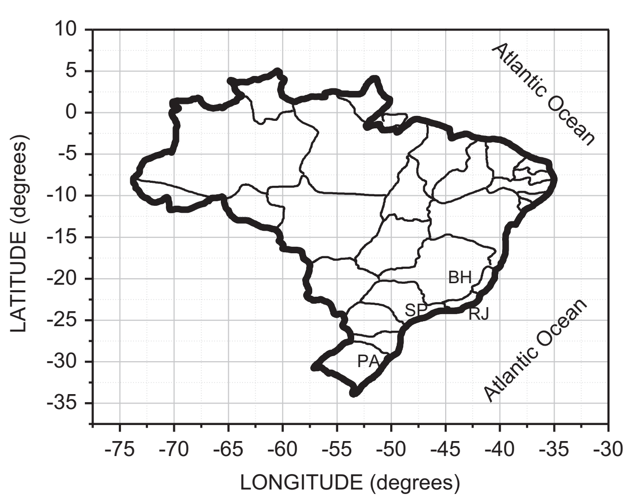

Fig. 1. Geographical positioning of Porto Alegre (PA), Belo Horizonte (BH), Rio de Janeiro (RJ), and São Paulo (SP) in Brazil.

In this study, a station for SOC measurements was set up by the Laboratório de Luz Ultravioleta (LLUV, www.dfq.pucminas.br/PUV/index.html) at the campus of the Pontifícia Universidade Católica de Minas Gerais (PUC Minas). It will be called the LLUV station. The campus is settled on the top of a hill (911 m asl) in a crowded neighborhood. Small buildings are found among green areas that compose 43% of the local surface, and over 20,000 people can be found here on weekdays. The highest contribution of antrhopogenic gases to SOC comes likely from the hundreds of thousands of vehicles crossing daily 3 large roads in the vicinity (less than 2 km away) of the campus.

2.2. Instruments

All instruments at the LLUV station were set up within a 250 m^2 grassy area surrounded by small buildings at least 100 m from parking spaces.

2.2.1. The Surface Ozone Monitor Model 202

The Surface Ozone Monitor Model 202 (M202, 2B Technologies Inc., Bolder, USA) is a portable, lightweight monitor for ozone concentration measurements. It is based on the absorption by ozone molecules of the radiation of 254 nm from a low-pressure mercury lamp. Air samples are pumped into M202 through a Teflon membrane filter for particle matter retention. A solenoid valve alternately switches air directly to a chamber or to an ozone scrubber then to the chamber. The difference in light absorption between these two samples gives the ozone concentration using the Beer–Lambert Law. Pressure and temperature inside the chamber are monitored to provide measurements in ppbv units,

Table 1
Geographical and demographic aspects for the Brazilian cities of Porto Alegre (PA), Belo Horizonte (BH), Rio de Janeiro (RJ), and São Paulo (SP).

City	Lat. (°) S	Long. (°) W	Altitude (m asl)	Area (km^2)	Inhabitants (millions)	Car fleet (millions)
PA	30.03	51.23	3	497	1.4	0.62
BH	19.92	43.94	858	331	2.4	1.2
RJ	22.90	43.21	2	1200	6.3	1.8
SP	23.55	46.64	760	1523	11.2	5.8

Table 2
Seasonal averages ± 1 standard deviation for solar elevation, temperature, atmospheric pressure and wind speed around 16:00 UT (noontime) in BH.

Season	Solar elevation (°)	T (°C)	p (hPa)	v (m/s)
Summer	86.1 ± 2.9	25.6 ± 1.4	911.3 ± 2.4	1.9 ± 1.4
Fall	61.0 ± 8.9	22.8 ± 1.9	912.2 ± 2.2	1.5 ± 0.7
Winter	50.9 ± 4.6	19.4 ± 1.8	911.7 ± 2.3	1.9 ± 0.9
Spring	78.4 ± 8.9	24.4 ± 2.2	915.8 ± 2.0	2.0 ± 1.2