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Tropospheric NO_2 Monitoring Using the Multi-Axis Differential Optical Absorption Spectroscopy in Urban Area

Marilia Mitidieri Fernandes de Oliveira[1], Nelson Francisco Favilla Ebecken[1], Jorge Luiz Fernandes de Oliveira[2], & José Maria de Castro Jr.[3]

[1] Center of Technology, Federal University of Rio de Janeiro, Civil Engineering Program-COPPE/UFRJ, Rio de Janeiro, Brazil

[2] Geography Postgraduate Program, Geoscience Institute, Fluminense Federal University, Niterói, Brazil

[3] Defense and Civil Security Postgraduate Program, Fluminense Federal University, Niterói, Brazil

Correspondence: Marilia Mitidieri Fernandes de Oliveira, Center of Technology, Civil Engineering Program, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil. Tel: 55-(21)-9-8587-9634. E-mail: marilia@coc.ufrj.br

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Abstract

Spectroscopic methods have played an important role in the study of chemical and physical processes related to the composition of the atmosphere and the differential optical absorption spectroscopy (DOAS) has been one of the most powerful methods to measure a wide range of trace gases. The pollutants are identified by their respective ranges of wavelengths that must be previously known. A Passive Differential Optical Absorption Spectroscopy system that uses the ultraviolet region from 400 to 480 nm of the solar radiation is presented. In this research diurnal variation of NO_2 was remotely measured by means of MAX-DOAS system which uses multiple viewing angles to monitor pollutant concentrations in urban area at the city of Rio de Janeiro. The instrument was placed on the roof of a building oriented to the center of the city. Tropospheric NO_2 amounts are retrieved from the measured spectra using the DOAS technique. In this paper we give a general description of the procedure and present the results from measurements during four days in winter 2017 associated with the prevailing meteorological aspects. These days were characterized by mostly sunny and dry conditions, no convection, periods of medium clouds and clear sky. The tropospheric NO_2 slant column densities values are presented and the results are consistent for all three used elevation angles (5º, 10º, and 15º). The results demonstrate the capability and the potential of the MAX-DOAS technique to derive information on spatial distribution of NO_2 in an urban environment.

Keywords: Atmospheric Optics, DOAS Technique, Spectroscopy, Urban Pollution

1. Introduction

Air pollution is associated mainly to the processes of growth, industrialization and urbanization, which has been increasing since the first half of the twentieth century. In the last sixty years, the indiscriminate use of natural resources, increased automotive fleet and poor or non-existent planning played an important role in the deterioration of air quality in major world urban centers. Emissions from mobile and stationary sources together industrial activities are somehow responsible for the presence of pollutants in the atmosphere (Fernandes, 2017). NO_2 emissions due to such sources are already known to be directly related to environmental and public health problems (Lee, Kim, & Lee, 2009). However, the main sources of NO_2 in urban areas are fossil fuel combustion and its concentration is large due to the spatial complexity of emission sources and the photochemical lifetimes of NOx species. Therefore, it is very important to understand better the temporal and spatial presence of NO_2, especially in urban area over both the source and surrounding area with a high population density which is certainly not an easy task (Lee, Gu, Kim, Hwang, & Jung, 2012; Psiloglou et al., 2013).

Physical factors that more influence the air quality are related to the sources location and meteorological variables that play an important role to the dilution, dispersion and transport of pollutants in the troposphere. Coastal regions are often the most favorable locations for industrial development, but the meteorological processes that occur in these areas can affect the transport and dispersion of air pollutants. The circulation of sea breeze (during the day)

or land breeze (at night) on the regional scale (100 km) is caused by the difference in temperature between the sea surface and the continent, and it may affect the local pollutant concentration (Luhar & Hurley, 2004). The surface wind field was analyzed by Takashima et al. (2015) over Fukuoka (Japan), indicating that the NO_2 inhomogeneity is strongly related to vertical/horizontal transport of high concentrations from the city center, as well as to horizontal transport from the ocean through a land-sea breeze.

Efficiency in air quality control is related to the systematic observation of quality patterns established by environmental agencies. However, observing these patterns is not an easy task, involving a high cost in the network installation of monitoring stations and depending on the pollutants to be monitored, their maintenance and data analysis become even more complex (Wartenberg, 2009; Jin, Andersson, & Zhang, 2016).

The chemical modeling of the atmosphere depends on several components and therefore there is a need for more effective techniques for air pollution monitoring and control. Spectroscopic methods have played an important role in the study of chemical and physical processes related to the composition of the atmosphere. Among various spectroscopic techniques, the differential optical absorption spectroscopy (DOAS) has been one of the most powerful methods to measure a wide range of trace gases (Noxon, 1975; Platt, Perner, & Pätz, 1979; Noxon et al., 1983; Stutz & Platt, 1996). In principle to determine the concentration of a trace gas it would be necessary to quantify the other factors that influence the intensity. Since certain trace gases exhibit narrowband absorption structures, DOAS technique aims to separate broad and narrow band of spectral structures in an absorption spectrum in order to isolate the small gas absorptions in the UV and visible spectral region (Platt & Stutz 2008). The broad spectrum is then used as a new spectrum of intensity and the Lambert-Beer law can again be applied to narrow band absorptions that can be written as Equation (1):

$$I(\lambda) = I_0\ (\lambda)\ \cdot \exp(-\sigma(\lambda) \cdot c \cdot L) \quad (1)$$

where:

$I_0(\lambda)$ is the initial intensity of a light beam emitted by a source of radiation;

$I(\lambda)$ is the radiation intensity of the beam after passing through a layer of thickness L, where the absorber is present at a uniform concentration of c;

$\sigma(\lambda)$ is the absorption cross-section at wavelength λ characteristic of any species. The average trace gas concentration, c, can be calculated from the measured ratio $I_0(\lambda)/I(\lambda)$.

The equation above is the basis of most absorption spectroscopic applications in the laboratory. The intensities are determined by measurements in the light beam where L is known a priori. It can be achieved by removing the absorbers from the path of light, but in the atmosphere this becomes impossible since the multiple factors that influence the intensity represent a challenge. Thus, the Lambert-Beer law for the open atmosphere becomes more difficult to apply. This would involve the removal of the absorbent gas from the atmosphere. The solution lies in the measurement of so-called "differential" absorption, i.e. the difference between absorptions at two different wavelengths by comparing the intensity of direct sunlight at two wavelengths λ_1 and λ_2 with different sections of absorption (Platt & Stutz, 2008) Equation (2) and (3).

$$\sigma_1 = \sigma(\lambda_1) \quad (2)$$

$$\sigma_2 = \sigma(\lambda_2) \quad (3)$$

DOAS technique uses the narrow bands of molecular absorption to identify and retrieve the tropospheric and stratospheric trace gas concentrations (Shutz & Platt, 1996). An important advantage over other techniques is low cost and time reduction especially when sunlight is used as a source, known as passive DOAS system (Mejía, Vázquez, Isakina, García, & Iglesias, 2013). The two most important sources are the sun and the moon. The instrument collects the scattered sunlight on UV-VIS range absorption measurement. The pollutants absorption lines in the DOAS technique interfere with each other and it is necessary to carry out a preprocessing of the measured spectra. The pollutants are identified by their respective ranges of wavelengths that must be previously known.

Various techniques have been utilized to identify the temporal and vertical characteristics of NO_2 in urban areas such as: LIDAR (Light Detection And Ranging), an active remote-sensing technique (Rothe, Brinkmann, & Walther, 1974; Edner., Ragnarson, Spännare, & Svanberg, 1993; Gondal & Mastromarino, 2000; Volten et al., 2009); Topographic Target Light scattering Differential Optical Absorption Spectroscopy (ToTaL-DOAS) used to derive temporal variations in the spatial distribution of trace gas volume mixing ratios (Frins, Platt, & Wagner, 2008; Louban, Píriz, Platt, & Frins, 2008; Lee et al., 2012) and Multi-Axis DOAS system with multiple view

angles to monitor rapid changes in tropospheric and stratospheric trace gas concentrations (Leser, Hönninger, & Platt, 2003; Hönninger, Leser, Sebastian, & Platt, 2004; Leigh, Corlett, Friess, & Monks, 2006; Wagner, Ibrahim, Shaiganfar, & Platt, 2010). Other types of DOAS are used in experiments, such as a mobile mini DOAS (Johansson et al., 2009) to measure the flow from a source and quantify the total emissions of NO_2 and SO_2 by passing under a plume, checking the wind field influence on the transport of pollutants. Mejia et al. (2013) developed a portable DOAS system for in situ measurements and real time. This system has been applied in the retrieval of SO_2 columns emitted either by anthropogenic or natural sources.

The urban area of the city of Rio de Janeiro is part of the metropolitan region of Rio de Janeiro (MRRJ) and is inserted into the space of the second economic center of the country, with a high degree of urbanization and industrialization. The air quality in this region is, in general, strongly influenced by meteorological variables mainly due to the proximity of the Guanabara Bay (GB).

The aim of this research is to analyze the measurements collected by a DOAS system that is operating at the Geoscience Institute of Fluminense Federal University at the city of Niterói, state of Rio de Janeiro. The telescope is directed to the center of Rio de Janeiro in order to retrieve the trace gas NO_2 in a remote site located away from the instrument during 2017 winter period (26 to 29 June) in relation to the prevailing meteorological conditions. These four days were characterized by mostly sunny and dry conditions, no deep convection, periods of medium clouds and clear sky. In addition, the prevailing wind blew southeast during this period. Thus, this paper presents the results of passive MAX-DOAS measurement of the NO_2 over the urban area at Rio de Janeiro, showing the capability and the potential of this technique to derive information on vertical distribution of pollutants in an urban environment related to the local meteorological conditions, where the air quality tends to worse if not taken measures to reduce the impact of them.

2. Material and Methods

2.1 Study Area

The area of interest is the city center of Rio de Janeiro and its surrounding environment used by road and waterway transportation, entering or leaving the city through GB. The cities of Rio de Janeiro and Niterói are very close, separated only by GB in the geographic coordinates of 22º 54 '13" S / 43º 12' 35" W. They are located in the southeastern coastal of Brazil in the MRRJ where is inserted the bay (Figure 1). The MRRJ is densely populated and industrialized where meteorological systems influence the air quality, recirculating pollutants in the region. Rio de Janeiro has two major airports; the International airport and one for domestic flights, both are near the GB. In addition, the city has a large port situated on the GB. The highest exposure levels of air pollution are found in ports and near them because most of the world fleet is positioned in these areas. Oliveira et al. (2016 & 2016) verified the pollutant trajectories emitted by these two airports and by the port, using the Brazilian Regional Atmospheric Modelling System (BRAMS) to generate wind fields in the MRRJ. This model captured the influence of mesoscale systems, type breeze, showing the dependence of the trajectories related to the season and time of day. Therefore, it is very important to monitor air quality in a city or region, which helps in decision making processes. But to manage the air quality of a region is necessary to know the meteorological, geographical and socioeconomic variables, as well as the chemistry of the troposphere.

The MRRJ relief is relatively flat but characterized by the presence of mountainous regions with altitudes between 1024 and 887 meters. These mountains lie approximately in the direction of W-E, enclosing low areas interspersed by small and isolated hills. These lowlands are called Baixada Fluminense, having an estuarine-lacustrine system with extensive coastal mangroves. This system forms a single expanse of water during floods, including multiple rivers. The orientation and altitude of the region influence the direction and speed of surface winds, facilitating or hindering the dilution and dispersion of gases and particles at various points. A high number of stationary and mobile sources are factors that affect the local air quality and, consequently, the population's health (Oliveira, 2004).

The study area is under influence by the South Atlantic semi-stationary subtropical anticyclone system, a large-scale circulation pattern. The high levels of air pollution depend on the region and topography relative to the general circulation of the atmosphere. This atmospheric system determines the air quality in MRRJ according to its positioning along the Brazilian coastline, presenting a well-defined seasonal movement. Other important systems that affect the region are the mesoscale meteorological systems known as breezes. These wind systems are affected by local topography and the differential heating of the surface, favoring or harming the places where they move. The breezes are generated due to the differential heating between the GB and the continent, recirculating pollutants in MRRJ (Oliveira, 2004). Usually the sea breeze follows the south-north direction, carrying pollutants into the metropolitan area during the day. Otherwise the land breeze follows the north-south

direction, carrying pollutants to densely urbanized regions at night. The topography of the MRRJ with the hills located parallel to the coastline acts as a physical barrier to the winds from the sea, blocking the ventilation in areas located further inland. At the regional scale, the breeze circulation due to the temperature difference between the sea surface and the continent can change air quality by recirculation of pollutants (Luhar & Hurley, 2004). Therefore it is important to take into account these meteorological factors in order to minimize the effects caused by the possible trajectories related to them, which have a direct response in urban air quality.

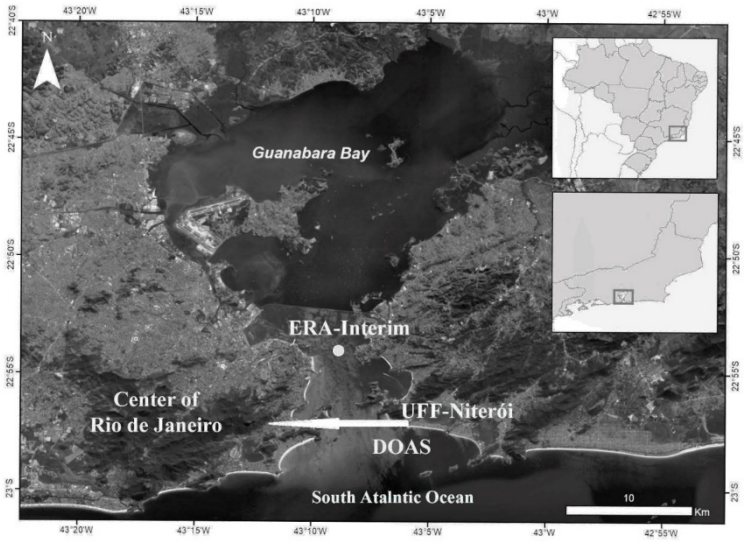

Figure 1. Map of the site where is installed the DOAS system (terrace of Geosciences Institute of the Fluminense Federal University in the city of Niterói). It is oriented to the center of Rio de Janeiro. Geographic coordinates of the ERA-Interim point over the GB:.22º 53’ S /43º 08’ W

Source: Adapted from Google image (May, 2019).

2.2 Troposferic Trace Gas Retrieval Observed by Ground-Based MAX-DOAS

The presence of tropospheric trace gases could be detected using the MAX-DOAS technique, which has become a widely and successfully used for this purpose (Leser et al., 2003; Wittrock et al., 2004; Hönninger, Von Friedeburg, & Platt, 2004; Hönninger, Leser, Sebastian, & Platt, 2004; Sinreich, Frieß, Wagner, & Platt, 2005; Heckel et al., 2005; Frins, Bobrowski, Platt, & Wagner, 2006; Theys et al., 2007; Wagner et al., 2004, 2007, Wagner, Deutschmann, & Platt, 2009; Irie et al., 2008). The instruments observe scattered sun light under different viewing angles, providing high sensitivity to tropospheric trace gases. The assumption that the same air parcels are present in different elevation and relative azimuth angles is important for the accurate analysis of tropospheric species. The precise analysis of tropospheric trace gases is closely related to the assumption that the air parcels present at different angles of elevation and azimuth have the same physical characteristics. However, this assumption may be violated, since species may be located at high altitudes above the measurement point with the instrument and be detected at different horizontal distances, depending on the viewing geometry. Another factor to consider is the sequence of the elevation angles used in the measurement with MAX-DOAS, as the air masses in the site may change due to prevailing wind conditions, and the column densities recorded at the different elevation angles can belong to different air masses (Wagner et al., 2010). Nevertheless, these aspects are usually neglected using the MAX-DOAS method at fixed locations because generally the highest trace gas concentrations are close to the surface and they are rather small when comparing the horizontal distances of the air masses with the different elevation angles, As the temporal resolution of observations is normally of the order of minutes, the distances which the air masses move between successive observations are usually small. A more accurate analysis of tropospheric species must be careful to perform the measurements with different elevation angles and azimuth in the same air mass. However, as air masses can change according to prevailing wind conditions, Records at different elevation angles may belong to different air masses. But, in an atmospheric condition with a wind speed about 2 m /s, the air masses will have a rather slow trajectory compared to the typical lengths of the absorption path of observations in the troposphere. (Wagner, 2010).

The tropospheric profiles are mainly based on observations of low elevation angles (below 20º) and with higher vertical resolution near the surface (Höninger & Platt, 2002; Heckel et al., 2005). They can usually be performed only under cloudless conditions. There is usually retrieval from two steps. In the first step, the observed spectra are analyzed by producing trace gas concentrations integrated along the light pathways of the atmosphere, the so-called slant column density (SCD). SCDs from DOAS measurements can be expressed as follows:

$$SCD = SCD_{atmosphere} + SCD_{target} \quad (4)$$

where $SCD_{atmosphere}$ and SCD_{target} denote trace gas concentrations integrated over the light path length between the top of the atmosphere and the target, and between the target and the instrument, respectively (Lee et al., 2012). As the presence of air mass should be considered as a relevant aspect in DOAS measurements, the so-called air mass factor (AMF) should be applied, which is defined as the ratio of the (total) SCD and (total) VCD (Solomon, Schmeltekopf, & Sanders, 1987; Marquard, Wagner, & Platt, 2000) according to Equation 5:

$$VCD=SCD/AMF \quad (5)$$

where the AMF is usually derived from numerical simulations of the atmospheric radiative transfer, however for ground-based MAX-DOAS observations, in many cases (using e.g. elevation angles larger than ~ 10º and small aerosol extinction) it is possible to approximate the tropospheric AMF by a geometrical AMF (Wagner, 2010) according to Equation (6):

$$AMF_{trop} \approx \frac{1}{sen\ (\alpha)} \quad (6)$$

where α is the elevation angle.

In ground-based measurements, where the sun is used as the light source, the measured spectrum already contains absorption structures. These absorptions are called Fraunhofer (FR) lines. A FR spectrum is recorded with the detector directly to the sun to correct these absorptions. FR reference spectrum also contains atmospheric trace gas absorptions and the result of the DOAS analysis represents the difference between the slant columns of the measured spectrum and that of the FR reference spectrum. Due to the Raman scattering in the atmosphere, which describes the inelastic scattering of light through matter, Fraunhofer's lines are then filled. This effect is called the Ring effect (Grainger & Ring, 1962) and needs to be corrected during the DOAS evaluation (Leigh et al., 2006).

MAX-DOAS instruments observe scattered sunlight from various viewing directions and while the sensitivity to stratospheric trace gas absorptions is almost independent on the viewing direction, the sensitivity for tropospheric trace gases depends strongly on the elevation angle; and to a lesser degree also on the relative azimuth angle, i.e. the difference of the azimuth angles of the telescope and the sun (Hönninger & Platt, 2002; Leser et al., 2003; Fietkau et al., 2007; Theys et al., 2007) Elevations below 20 degrees above the horizon (Figure 2) have greater sensitivity to tropospheric trace gases because the highest concentration of photons is found in the lowest layer of the atmosphere, leading to a more tropospheric absorption path horizontally (Leigh et al., 2006).

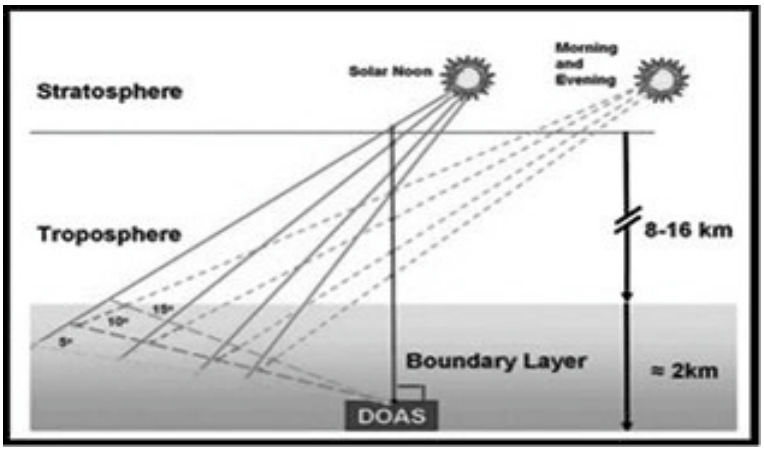

Figure 2. Ground-based MAX-DOAS setup for NO_2 measurements: Spectra are recorded from 5º, 10º and 15º above the horizon as well as from zenith direction (90º). The arrows indicate photon paths through the atmosphere and into the telescope. The intersections are the main photon paths (wide arrows) for the 3 elevation

angles and the upper limit of a trace gas layer near the surface. Thus the sensitivity for absorbers in the boundary layer increases strongly for the low elevation angles

Adapted from Leigh et al. (2006).

2.3 MAX-DOAS Dataset

This research focuses on diffuse light measurements, where only scattered light, due to the Mie and Rayleigh scattering, is recorded by a detector (spectrometer). The object of study is limited to the atmosphere layer known as the Planetary Boundary Layer (from the surface to approximately 2km of altitude-PBL) within the troposphere, which has the highest concentration of trace gases. Therefore, a MAX-DOAS system has been developed to measure four successive elevation angle sequences (5º, 10º, 15º, 90º) tested in urban conditions (central area of the city of Rio de Janeiro) to measure the quantity of NO_2 in the PBL. The quantity of molecules/cm^2 along the atmospheric light paths called SCD was retrieved and analyzed under different viewing directions, using the software DOASIS (Kraus, 2006). The acquisition of the spectra of the atmosphere, at these elevation angles, was done at the beginning of each full hour from 8:00 to 16:00 (local time). Firstly, this routine starts by subtracting the background from the recorded spectrum and a program was developed to control the telescope and capture the spectra in an hourly and automatic manner at different viewing angles. According to the literature, in the process of evaluating, it is necessary to prepare the measured data by taking the dark current (electronic detector) and offset influences (non-zero values even when no lighting is coming, also related to electronic detector) from the spectra. Thus, dark current and offset signals are removed from measured dataset. The spectra taken at 90º around noon (Fraunhofer) on each day are used as reference spectra (FR) that contain information on trace gas absorption that occurred between the top of the atmosphere and the target (viewing angle).

In this research we chose to use the NO_2 cross-section obtained from the literature downloaded from www.iup.uni-Bremen. The spectrum obtained in this way cannot be used directly, since it is obtained with unknown resolution and, therefore, it is necessary to convolve the cross-section with the function of USB2000 related to the spectrometer used in the present research. A germicidal lamp was used in the convolution of the measured spectra and the cross-section so that both would have the same wavelength ranges related to each pixel value (Mejìa et al., 2013). The NO_2 absorption cross-section, FR, and the Ring spectrum are simultaneously fitted in the wavelength interval of 400 and 480nm (spectral region). A polynomial of degree 5 was calculated to fit this part of the spectrum by means of a least squares fitting routine (Stutz & Platt, 1996). The output of the spectral analysis is the measured SCD, the integrated trace gas quantifies along the light path through the atmosphere.

Measurements were taken from 8:00 to 16:00 on June 26, 27, 28, and 29, 2017 with the telescope toward the city center, passing through the GB. Thereby, pollutants also originated due to maritime and aircraft transports occurring in this bay could be retrieved (Oliveira, Ebecken, Oliveira, & Aires, 2016); Oliveira, Ebecken, Oliveira, Aires, & Castro Jr, 2016). Week days were chosen because the emission of gases is greater. During the measurement period the wind was relatively calm, blowing from the northeast with mean values of 2.4 ms^{-1}; the air temperature was 23°C. Wind data were obtained from ERA-Interim (Dee et al., 2011) for the month of June 2017. It is a global atmospheric reanalysis dataset produced by the European Centre for Medium-Range Weather Forecasts (ECMWF) from 1979, continuously updated in real time. The point with geographic coordinates of 22º 53’ S 43º 08’ W is near the study region.

2.4 Instrumentation

The MAX-DOAS instrument consists of three main elements: the input optics, the imaging spectrometer, and a CCD-based detection system. Figure 3 shows a schematic of the DOAS system used to measure trace gas absorption in the open atmosphere developed in this research. Light emitted by a source (in this case, by the Sun) passes through a volume of air with absorbers, being captured at the end of the optical path. As light travels through the atmosphere, its intensity is reduced by absorption of a specific trace gas.

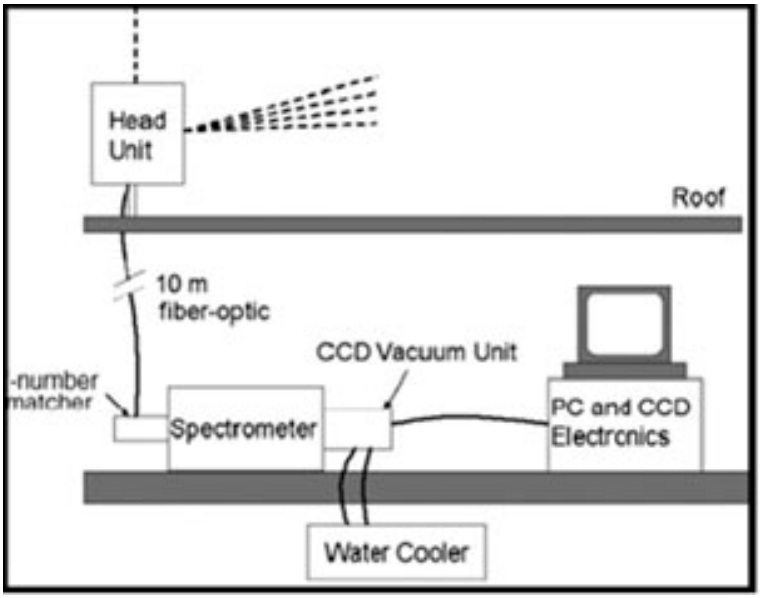

Figure 3. Schematic representation of instrumentation used in DOAS measurements

Source: Leigh et al. (2006).

The input optics for the MAX-DOAS system comprises one telescope that collect scattered solar radiation from four viewing angles. This system was built at the Laser Spectroscopy Laboratory at the Physics Institute of the Fluminense Federal University (UFF) with support from Foundation for Research Support of the State of Rio de Janeiro (FAPERJ) from May to September 2015. To record the spectrum of scattered sunlight in the troposphere, an acrylic box with 50 cm x 30 cm x 50 cm was constructed, coated with aluminum foil to protect a telescope with 80mm in length with diameter of 20mm, connected to an optical fiber of 10m in length with two quartz windows for light input with a convex lens. A deflector of 40mm was placed before the convex lens to prevent scattered light from entering. The aluminum blanket was an alternative used to avoid heating inside the box (Figure 4). The nature of the plane–convex lens assembly combined with the antireflective entrance windows produces a constrained field of view. This telescope is especially suitable for light collimation from a distant source. The collimated light is guided to the spectrometer connected to the optical fiber input. The spectra measurement was performed using a spectrometer (USB 2000, Ocean Optics) with a diffraction grating of 2400 lines/mm with 90mm x 65mm x 35mm, type Asymmetric crossed Czerny-Turner. The light is scattered through a grid on the spectrometer and focused on the Sony ILX511 CCD detector that records the light spectrum with 1nm, and an optical resolution of ~0.3 nm. This set was equipped with a diffraction grating of 650 lines/mm, covering a spectral band of 198-891 nm. The spectrometer has a spectral resolution of 2048 pixels and a spectral range of 200 to 850 nm, being powered from a USB cable and controlled by DOASIS software (DOAS Intelligent System). It is a free program provided by the Institute of Environmental Physics University of Heidelberg Germany developed by Stefan Kraus, intended for acquisition and analysis of spectra. This software is used to measure the number of molecules per square centimeter (molec/cm^2) of trace gases present in the air column over the region, measuring specific UV/VIS band absorption structures of the solar spectrum. The reference and measured spectra of NO_2 columns by the passive DOAS technique used for the determination content was done using the 400 to 480nm wavelength range. The instrumental was mounted on the roof of the Institute of Geoscience at the UFF (22º53’00’’S, 43°06’10’’W) to 21 meters of height, which ensures unobstructed viewing geometries on the respective axes. The viewing angles used in this experiment are 5°, 10°, 15°, and 90° (zenith) elevation above the horizon with the telescope pointing directly to the west approximately 20km away from the center of Rio de Janeiro.

Figure 4. Components of the MAX-DOAS system: (A) and (B) telescope to obtain the spectra, (C) acrylic box with view of the quartz window and (D) box installed on the terrace of the Institute of Geosciences, (E) Ocean Optics-USB 2000 with physical dimensions of 90 mm x 65 mm x 35 mm, type Asymmetric crossed Czerny-Turner, (F) computer-spectrometer-fiber optics mounted in Institute laboratory

3. Results and Discussion

The area of interest is the center of Rio de Janeiro, as well as, the nearby environment, where emissions from mobile and stationary sources play an important role in the deterioration of air quality in this urban center due to various means of transportation that circulate throughout the city. The MAX-DOAS station is located on the urban areas boundary of the GB, where several industries operate in the industrial area north-west of the MRRJ. The industrial activities mainly of petroleum such as an oil refinery and vehicle operations in the industrial area lead to significant emissions of trace gases. In the urban central area, traffic and other anthropogenic emissions emit significant amounts of NO_2.

The routine of measurements followed by the measurement of target and the sequence was repeated during the day between the morning and the afternoon with hourly exposure time. Hourly SCDs of NO_2 were obtained with the software DOASIS from four days winter period (26 to 29 of June 2017). The temporal evolution of the measured is shown in Figure 5 with notable peaks occurring at 12:00 h local time. Measurements at 5º elevation angle show well defined peaks at times of intense traffic on days 26, 27 and 28 (Monday, Tuesday and Wednesday, respectively). The rush hour is starting earlier and ending later in the city of Rio de Janeiro with three peaks of vehicles in circulation, between 7:00 and 9:00 hours, noon and between 16:00 and 17:30 hours.

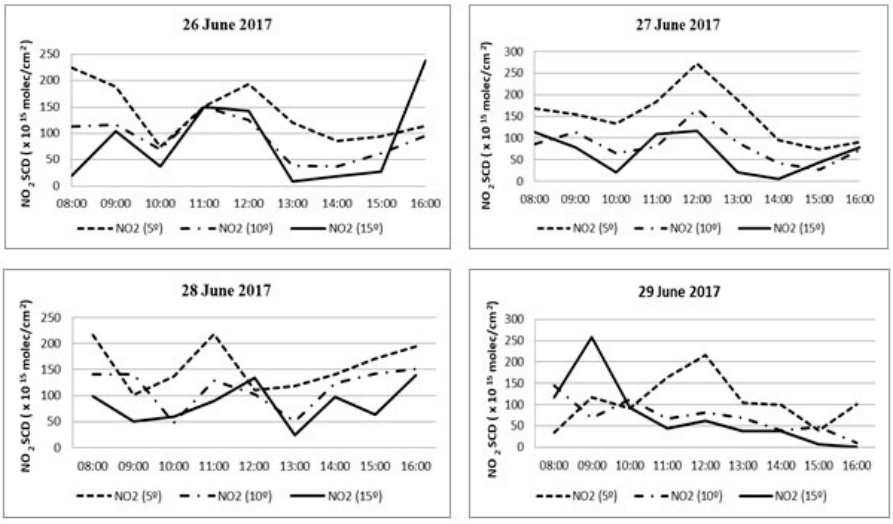

Figure 5. Slant-column densities of NO_2 calculated from spectra originating from target measurements on 26 to 29 June 2017. Results for all three elevation angles are shown

In Table 1 are presented mean and standard deviation values (molec/cm^2) of NO_2 measured for the three different viewing angles. The software DOASIS estimated some statistical parameters for the whole period of interest; however in the table below only the mean and the standard deviation (SD) of the samples within the selected range were shown.

Table 1. Mean and SD (SCD x 10^5 molec/cm^2) of NO_2 measured in the period 26 to 29 June 2017

Local time	5º (mean)	SD	10º (mean)	SD	15º (meam)	SD
08:00	193	0,067	127	0,047	107	0,059
09:00	136	0,062	115	0,053	91	0,066
10:00	113	0,043	67	0,061	49	0,093
11:00	174	0,039	104	0,078	100	0,116
12:00	205	0,036	114	0,064	126	0,113
13:00	120	0,035	59	0,076	23	0,097
14:00	97	0,035	41	0,054	28	0,078
15:00	84	0,083	55	0,048	36	0,053
16:00	108	0,202	84	0,182	109	0,195

Figure 6 shows the frequency distribution of NO_2 hourly slant column densities, measured from 26 to 29 June 2017 for 5º, 10º and 15º viewing angles. High values of SCD were retrieved especially for the 5º viewing angle which could be attributed to the optical path directed to the lower layers of the atmosphere near to the ground where the highest concentrations of trace gases occur. Whereas the lower concentrations with higher frequencies are observed for the 15º angle, confirming the general declining trend in the upper layers of the atmosphere.

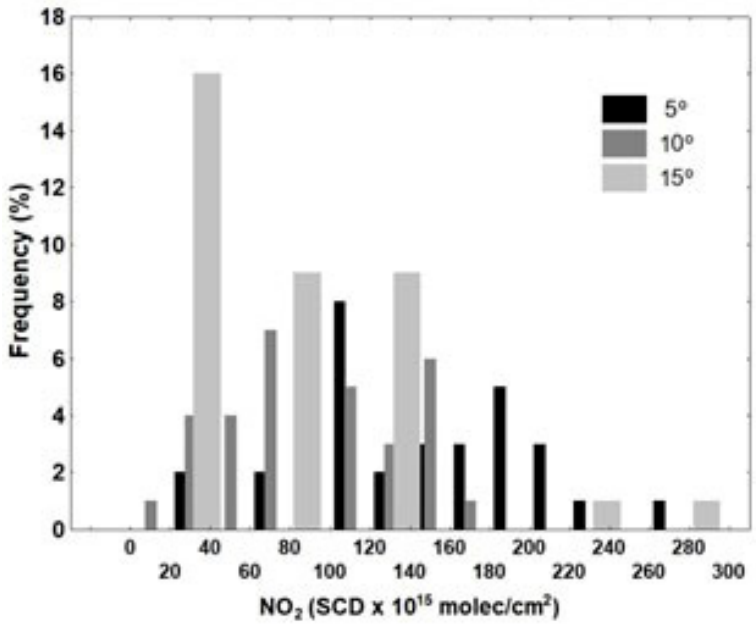

Figure 6. Frequency distribution of NO_2 hourly slant column quantities from 26 to 29 June 2017

Equation (5) and (6) are used to derive the tropospheric NO_2 VCDs. The values for the measurements at 5º, 10º and 15º elevation angles are shown in Figure 7.

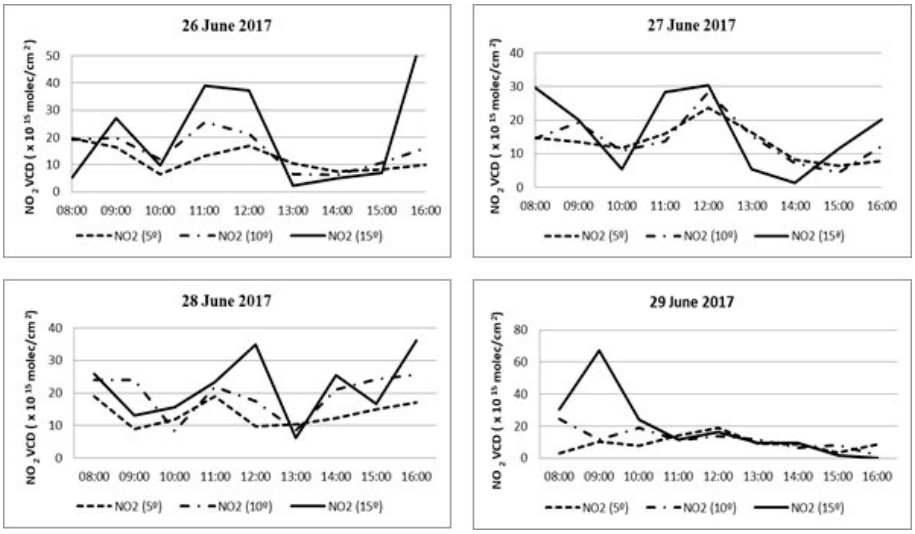

Figure 7. The tropospheric VCDs of NO_2 calculated according Eq. 5 from observations at different elevation angles

The three sets of data relating to the elevation angles show good agreement with the SCDs obtained with the DOASIS software. The general uncertainties of measurement, such as signal to noise observations, cross section errors, and errors caused by approximations can be neglected. The results in agreement of the VCDs derived from the different elevation angles indicate that these errors are small for our measurements.

The densely populated and industrialized city of Rio de Janeiro has affected air quality as the urban air of the city of Los Angeles, surrounded on its southwest by the North Pacific Ocean, and on all other sides by mountains. In the MRRJ, the land breeze carries the pollutants towards the ocean and the sea breeze towards the continent. Because its action is restricted to the hours of greater economic activity, the sea breeze is undoubtedly the main natural mechanism of transportation of pollutants to the most densely populated areas of the city of Rio de Janeiro.

Wind speed and direction play a significant role in dilution photochemical reactive pollutants. Normally, during night period the wind is weaker than during the day favoring the concentration of pollutants. But the period of the measurements occurred during the day and as shown the Figure 8, the wind speed remained low during the four days with values around 2m/s.

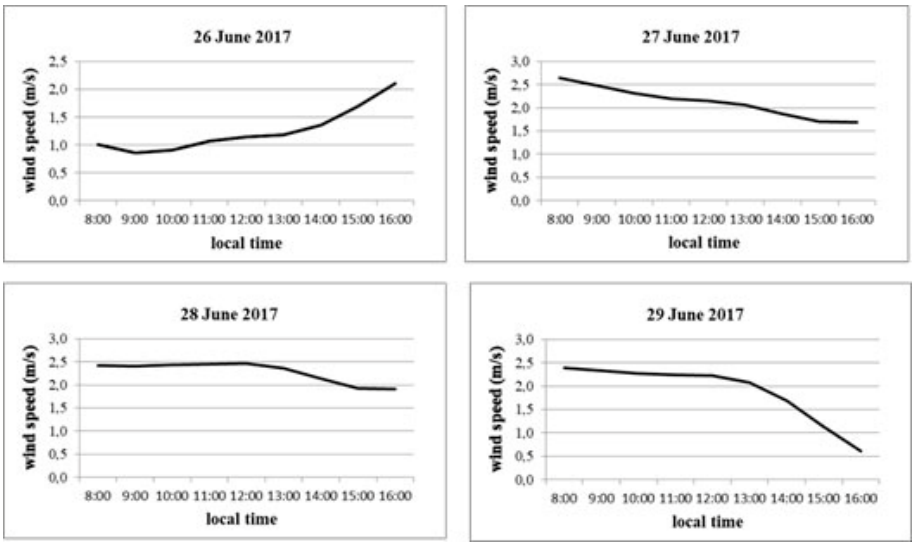

Figure 8. Mean diurnal variation of the wind speed

The mean wind speed (in m/s) per direction in June 2017 is also presented by the wind rose, indicating the dominant wind (Figure 9). The prevailing wind directions are the south–east during the examined period, which are associated with the influence by the South Atlantic semi-stationary subtropical anticyclone system, a large-scale circulation pattern and the mesoscale meteorological systems as breezes. These wind systems are generated due to the differential heating between the GB and the continent and follows the south-north direction carrying pollutants into the metropolitan area during the day. But during the night, the land breeze follows the north-south direction carrying pollutants to regions of the coast.

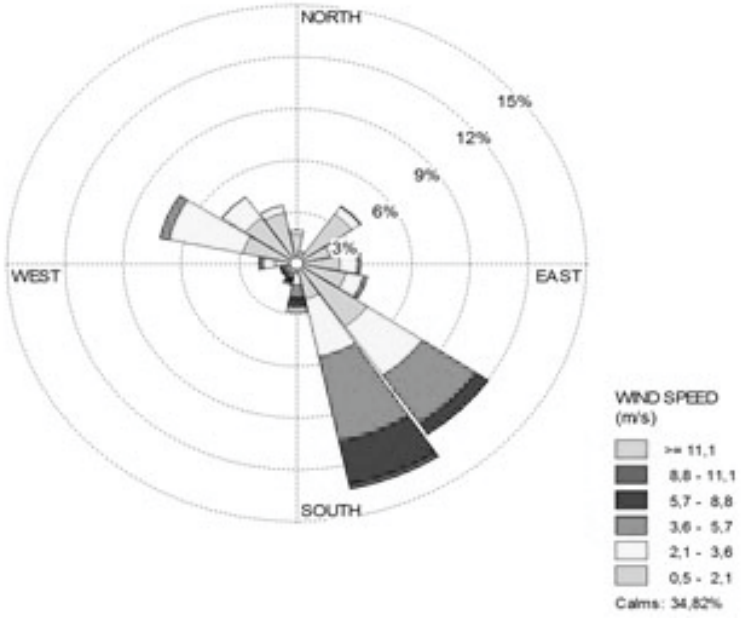

Figure 9. Wind rose of mean wind speeds per direction in m/s in June 2017

4. Conclusion

Emissions monitoring is very important to control air quality in major urban centers. We describe a passive DOAS system to determine NO_2 polluting columns that could be applied to develop some models of pollutants distribution considering the source, the dispersion and the wind conditions. The direct measurement of the pollutant columns provides useful information to evaluate the pollution level in real time. To retrieve the information from the spectra, a multi-axis DOAS system has been developed in this work to measure three successive elevation angle sequences (5º, 10º, 15º) and has been tested in central area of the city of Rio de Janeiro to measure the columns of NO_2 in the boundary layer, fitting the spectra in the wavelength interval of 400 and 480 nm. The measurements were performed from 26 to 29 June 2017 during the week from Monday to Thursday due to favorable weather conditions for trace gas concentration emitted from the mobile sources. A telescope attached to a spectrometer was used in order to point at the target (center of Rio de Janeiro) and the acquisition time was selected at daylight hours due to the highest traffic flow in this period.

MAX-DOAS allowed us, through the successive elevation angle measurements, monitoring the NO_2 trace gas for the distance between the instrument and the area of interest and therefore to exploit the potential of observations even in cases of small tropospheric trace gases in homogenous distributions and as expected higher SCDs are obtained for smaller elevation angles. The tropospheric NO_2 VCDs values calculated from Eq. 5 are consistent for all three used elevation angles, indicating that in this case the mathematical approach is appropriate.

Considering the relief, the weak winds, the high buildings and the intense traffic in the center of the city of Rio de Janeiro, the dispersion of NO_2 is reduced mainly in the winter, when the weather conditions are more adequate to keep the polluting columns in the city. An analysis of the surface wind field indicates that the observed variations in the NO_2 columns may be related to low dispersion through the breeze system (ocean and GB), since the winds remained weak during the period.

Our observations show that continuous trace gas measurements by MAX-DOAS are a useful tool for understanding the transport of air pollution in urban areas. This technique allows for fast measurements of gas emissions even on large distributed sources and increases the accuracy of pollutant emission inventories.

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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