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ESTIMATION OF COLUMN DENSITIES OF SO2, NO2, O3 AND NH3 TROPOSPHERIC TRACES GASES BY MAX-DOAS MEASUREMENTS IN BAMAKO CITY (MALI)

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ABSTRACT

This study concerns the estimation of column densities of four tropospheric trace gases, SO2, NO2, O3, and NH3 by MAX-DOAS measurement techniques in Bamako city in Mali during two measurement campaigns. The estimated column densities are the slant column density (SCD), and the vertical column density (VCD). In-situ measurements of the absorbance (optical density) of trace gases from solar radiation, at several angles of elevation between horizontal (0°) and zenith (90°), were performed by Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS). The results during the two MAX-DOAS measurement campaigns indicate that the gas NO2 presents the higher values of SCD and VCD; and respectively the gases NO2, O3, and NH3, the values of and VCD values for NO2. The higher values of daily variations of SCD are 15.70 E+17 for the gas NO2; 9.37 E+17 for SO2; 6.29 E+17 for the gas O3; and 2.34 E+17 for NH3. The higher values of daily of SCD by observation angles are obtained at the angle 50º and they are 9.25 E+17 for the gas NO2; 5.66 E+17 for SO2; 3.26 E+17 for O3; and 1.48 E+17 for the gas NH3. The higher values of daily variations of VCD are 10.86 E+17 for NO2; 7.66 E+17 for the gas SO2; 4.42 E+17 for O3; and 1.62 E+17 for the gas NH3. The higher values of VCD by observation angles are also obtained at the angle 50º and they are 1.21 E+18 for the gas NO2; 7.41 E+17 for SO2; 4.74 E+17 for O3; and 1.94 E+17 for the gas NH3.

INTRODUCTION

In recent years, multiaxial differential optical absorption spectroscopy (MAX-DOAS) is one of the passive sensing techniques from the ground, the most used to determine traces of atmospheric gases such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2), nitrous acid (HONO), ozone (O_3), bromine oxide (BrO) and aerosols (Irie *et al*., 2011; Vlemmix *et al*., 2015; *et al*., 2016). The principle uses diffuse sunlight from different oblique viewing angles, allows for the determination of slant column densities (SCD) and estimates of vertical column densities (VCD) of tropospheric gas traces (Wagner *et al*. , 2010, Irie *et al*., 2011;Vlemmix *et al*., 2015, Dix *et al*., 2016 and Stutz *et al*., 2017). The sensitivity of tropospheric gas traces depends on elevation angles. In the first step, the measured spectra are analyzed to determine the integrated concentrations of gas traces along the atmospheric light pathways, called the slant column density (SCD) (Pinardi *et al*., 2013; Lübcke *et al*., 2016) and in the second step, the set of SCDs of gas traces observed in different directions is converted to Vertical Column Density (VCD) (Wagner *et al*., 2010, 2013, 2016). For the determination of vertical column density (VCD) gas traces, Air Mass Factors (AMF) are taken into account to perform the analysis. Air mass factors (AMF) vary with the length of the light path, which is mainly due to changes in aerosol radiation extinction in the lower troposphere, as well as changes in the position of the sun (Wagner *et al*., 2013, Stutz *et al*., 2017). This study is based two on in situ measurement campaigns from 21 March to 2 April 2017 and from 13 to 25 July 2017. These two campaigns concerned the measurement of the absorbance of tropospheric trace gases SO_2, NO_2, O_3 and NH_3 by the MAX-DOAS technique on the Badalabougou Hill, in the city of Bamako (Mali). We have named those two measurement campaigns as the two MAX-DOAS measurement campaigns.

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Study site, Instrumentation and Methodology

Geographical Location of the Study site

The city of Bamako is at latitude 12°39 ' North, at longitude 8° West and the elevation above sea level is 338 m. Bamako city is, both the political and economic capital of Mali, in West Africa. Bamako city area is esteemed to 2,992 km^2, located on both banks of the Niger River, called "Djoliba". The city of Bamako, the largest and most populous of the country with 3.337.122 inhabitant, has a higher density, or 1.115 inhabitants per km^2. A railway line linking Bamako to Dakar (Senegal) has contributed to the economy of both countries at a significant cost. There is a road network to reach other parts of the country and an international airport in Sénou, located 15 km from the city center. Thousands of taxis, minibuses commonly referred to as "Sotrama", hundreds of thousands of two-wheeled and three-wheeled vehicles and other special machines are the main elements of the city's urban transportation means and are increasing more of the city's automobile fleets. Three (03) large bridges connect the two banks of the river are: the bridge of Martyrs (former bridge Vincent Auriol before the independence of the country in 1960, then became the bridge of Badalabougou); Saudi Arabia's King Fahd Bridge built in 1992 and the Sino-Malian Friendship Bridge built in 2010. The city of Bamako is becoming increasingly polluted due to its rapid population growth, considerable intensification of the socio-economic activities carried out there.

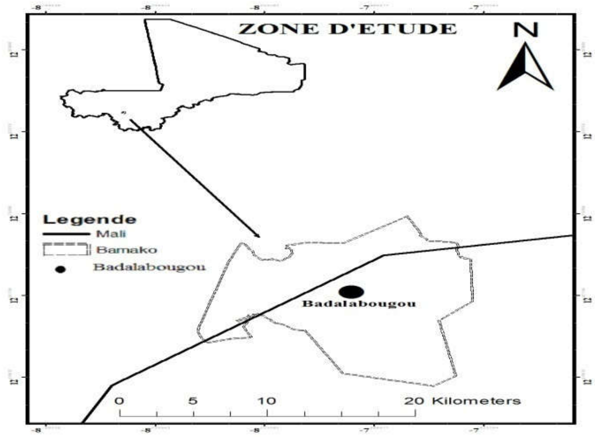


Figure 1 The figure shows the location of the measurement site in Bamako city (Mali).

Instrumentation

The instrumentation of the MAX-DAOS technique for our study consists of: a Newton LXD75 telescope with a diameter of 203 mm and a focal length of 800 mm, a CCD (Charge Coupled Device) spectrometer of the Ocean Optics USB2000+ type, an optical fiber (Ocean Optics) 2 m long and a laptop with Spectrasuite software for data collection. In addition, a database of atmospheric gas trace absorption cross sections, available on the website: http://satellite.mic.de/spectral_atlas/cross_sections/, "MPI-Mainz-UV-VIS Spectral Atlas" of Gaseous Molecules ". The device of MAX-DOAS is mounted on the second floor of building block "B" at the Faculty of Sciences and Techniques (FST), on the hill of Badalabougou in the city of Bamako (Mali) and was marked on the various events following the sequence of elevation angles selected: 10°, 20°, 30°, 40°, 50°, 60°, 70°, 80° and 90° during the two MAX-DOAS measurement campaigns considered. The duration of an individual measurement was between 40 and 75 seconds. For data gathering, we connect the telescope to the Ocean Optics USB2000+ CCD spectrometer (2048 individual pixels) with a spectral resolution of 0.7 nm over a spectral range of 180-1046 nm, using a fiber optical and spectrometer to the laptop via the USB cable, the latter is equipped with Spectrasuite software that allows controlling the acquisition parameters and storing the data for subsequent analysis (see Figure 2).

Figure 2 Photo of the MAX-DOAS measurement device on the roof of the FST "Block B" building.

METHODOLOGY

Law of Beer-Lambert

The MAX-DOAS technique is based on the Beer-Lambert law which is given follows:

$$\mathbf{I(\lambda) = I_0(\lambda).e^{-\sigma(\lambda).C.L}} \quad (1)$$

Where $I_0(\lambda)$ indicates the intensity of the solar radiation extraterrestrial solar radiation of the atmosphere; $I(\lambda)$ is the intensity of the radiation in the surface of earth; L is an optical path; C denotes the average molecular concentration of considered trace gases at a given wavelength (λ); and $\sigma(\lambda)$ denotes the effective absorption section of the trace gas at a given wavelength.

Measurements of Overall Absorbance

We used the zenith spectrum as the reference spectrum in this study, for the analysis of all the measurements during the two MAX-DOAS measurement campaigns.

For absorbance measurements using MAX-DOAS technique we have used Spectrasuite software to acquired.

- checking that the software is in mode (S) (scope: display of the raw spectrum);
- recording the dark spectrum $D(\lambda)$ (dark spectrum) by clicking on the icon (black) after closing the telescope, It is automatically eliminated by clicking on the icon;
- adjusting the integration time according to the light intensity, so as to use the best system dynamics without saturation;
- Save the reference spectrum $S_{ref}(\lambda)$ by clicking on the icon (yellow) in Spectrasuite interface after opening and pointing the telescope towards the sun. Thus, the system

is then ready for any absorption measurement. Just point to the events in the air and click on interface (A) of Spectrasuite interface, so that the software automatically gives the measurements of the global absorbance A(λ), given by the following formula:

$$A(\lambda) = -\log_{10}[S(\lambda)-D(\lambda)]/[S_{ref}(\lambda)-D(\lambda)] \quad (2)$$

Where A(λ) is the absorbance and S(λ) is the current spectrum. Global absorbance is given in ultraviolet, visible and near infrared spectral bands of atmospheric gases.

According to the Beer-Lambert law, the absorbance A(λ) at a given wavelength can be defined by:

$$A(\lambda) = \sigma(\lambda).C.L \quad (3)$$

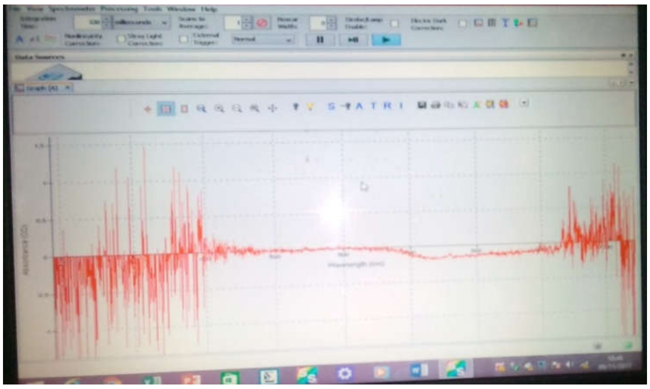


Figure 3 Viewing the display of parameters by the Spectrasuite software

Determination of the Slant Column Density (SCD)

The Slant Column Density (SCD) is obtained by making the ratio of the absorbance A by the effective cross section σ of the trace of gas considered at a wavelength by the following formula:

$$SCD(\lambda) = \frac{A(\lambda)}{\sigma(\lambda)} \quad (4)$$

Determination of the Vertical Column Density (VCD)

The resulting stray Slant Column Density (SCD) of the gas traces is converted to Vertical Column Density (VCD). In the determination of VCD, the air mass factor (AMF) is considered, it is defined as the ratio of the SCD and VCD, so we have:

$$VCD = \frac{SCD}{AMF} \quad (5)$$

The air mass factor is usually derived from numerical simulations of atmospheric radiative transfer (Wagner *et al*., 2010). It is possible to geometrically determine the tropospheric air mass factor (AMF) (Brinksma *et al*., 2008, Wagner *et al*., 2010) by the following formula:

$$AMF \approx \frac{1}{\sin(\alpha)} \quad (6)$$

Where α is the viewing angle of the telescope (angle between the horizontal and the telescope position). Equation (5) becomes for us the basis for the determination of VCD of trace gases tropospheric by observations of MAX-DOAS.

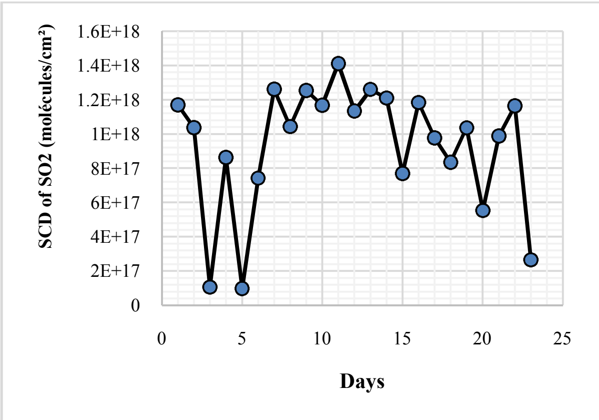
RESULTS AND DISCUSSIONS

In this part all variations are from daily averages during the two MAX-DOAS measurement campaigns (from 21rst March to 2nd April and from 13th to 25th July 2017). In this study we have considered four atmospheric gases which are SO_2, NO_2, O_3, and NH_3 in the column of atmosphere over Bamako city. Those gases are in trace quantities in the atmosphere and are ranging as green gases effect. The observed variations in this study are daily variations of slant column density (SCD), and the vertical column density (VCD) of those four atmospheric trace gases over Bamako city. The variations of SCD, and VCD concerned daily variations following an interval of 25 days, and following observation angles with an interval of 10º from 10º to 90º. The units of SCD and VCD are molecules per square centimeter (molecules/cm^2).

Daily Variations of the Slant Column Density (SCD) of the Four Gases

The daily variations of slant column density (SCD) of the four considered atmospheric gases, SO_2, NO_2, O_3, and NH_3 are represented in the below figure (figure 4).

For the gas SO_2, the daily variations of SCD are approximately between the values 1.50 E + 17 and 1.40 E +18. The daily variations of SCD for NO_2 are approximately from the value 7.00 E +17 to the value 3.60 E + 18. For O_3 gas, the daily variations are approximately between the values 1.90 E +17 and 1.00 E + 18. The daily variations of SCD for NH_3 approximately from the value of 4.80 E +16 to the value 4.50 E + 17. Those results indicate that the gas NO_2 presents the higher values of the daily variations of SCD of all those four atmospheric gases. After SO_2, O_3, and NH_3 respectively have also consistent values of the daily variations of SCD during the two MAX-DOAS measurement campaigns.



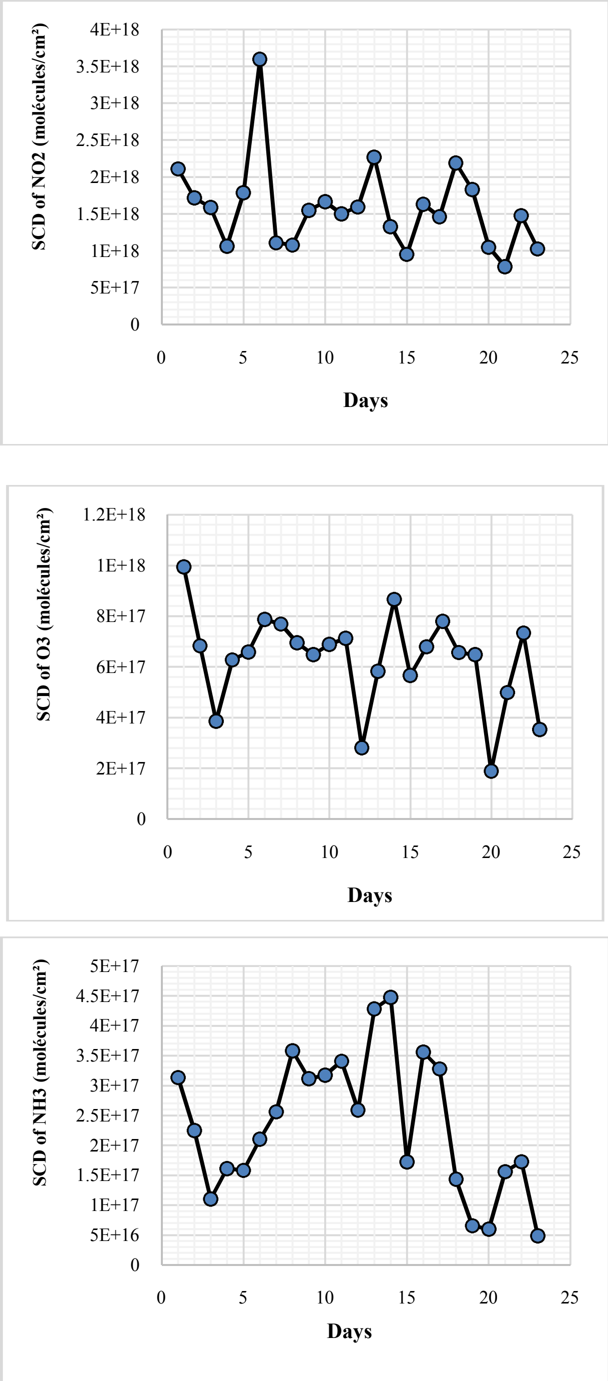


Figure 4 Variations of the slant column density (SCD) of the gas traces considered obtained.

The average values of the SCD of the four considered tropospheric trace gases SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns are mentioned in the following table (table 1).

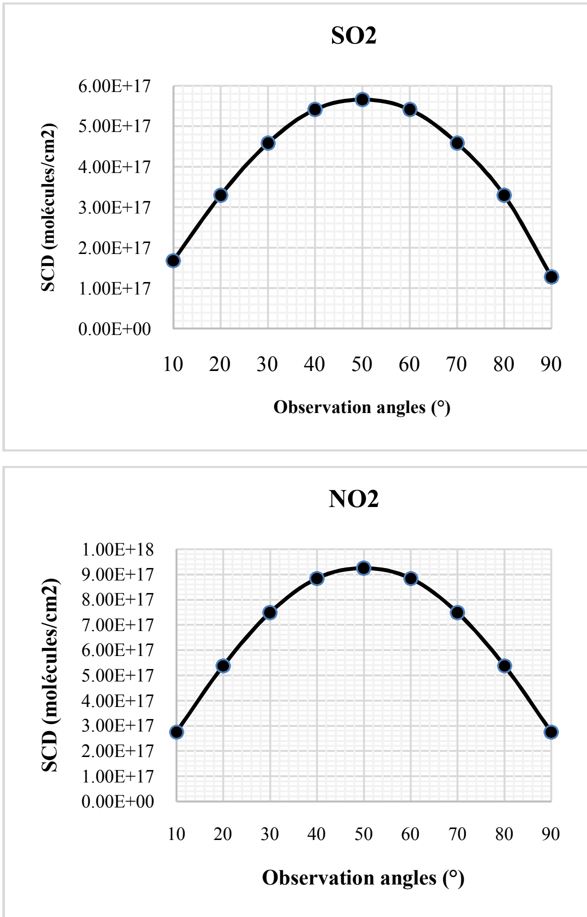
Table 1 Average values of SCD of the four considered tropospheric trace gases, SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns

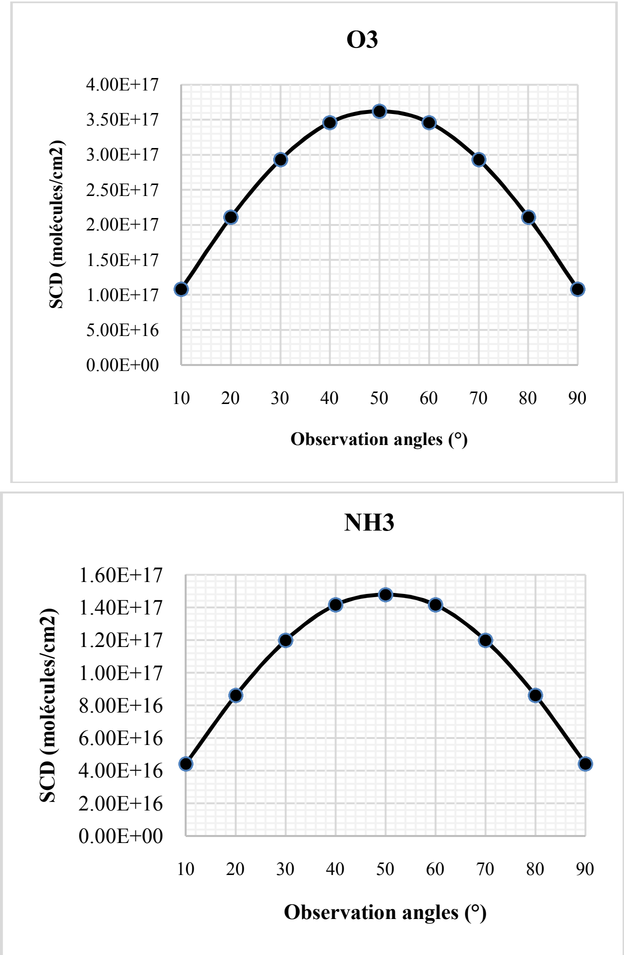
campaigns	SCD traces of gas			
	SO_2	NO_2	O_3	NH_3
1st campaign	9.41E+17	1.69E+18	6.61E+17	2.52E+17
2nd campaign	9.32E+17	1.45E+18	5.96E+17	2.16E+17
Whole	9.37E+17	15.7E+17	6.29E+17	2.34E+17

Daily Variations of the Slant Column Density (SCD) by Observation Angles of the Four Gases

The daily variations of the slant column density (SCD) of those four tropospheric gases, SO_2, NO_2, O_3, and NH_3 by observation angles during the two MAX-DOAS measurement campaigns are represented in the following figure (figure 5.). The observation angles are considered from 10º to 90º with an interval of 10º. We have considered the daily averages of SCD during the two MAX-DOAS measurement campaigns; and we have calculated according to equation (4) at different observation of angles (10°, 20°, 30°, 40°, 50°, 60°, 70°, 80° and 90°).

For the gas SO_2 the daily variations of SCD by observation angles are approximately between the value 1.20 E +17 and the value 5.80 E+17. The daily variations of SCD by observation angles of NO_2 gas are approximately from the value 2.20 E +17 to the value 9.90 E +18. The daily variations of SCD for O_3 gas by observation angles are approximately from 5.90 E+16 to 3.70 E+17. For NH_3 gas the daily variations of SCD are between 4.00 E+16 and 1.50 E+17. The results of daily variations of SCD by observation angles indicate that NO_2 gas presents higher values of SCD, and SO_2, O_3, and NH_3 are respectively consistent values of SCD daily variations by observation angles during the two MAX-DOAS measurement campaigns. And also the corresponding curves are similar and the high values of SCD correspond to 40º, 50º, and 60º, with the higher value corresponds to the angle 50º.





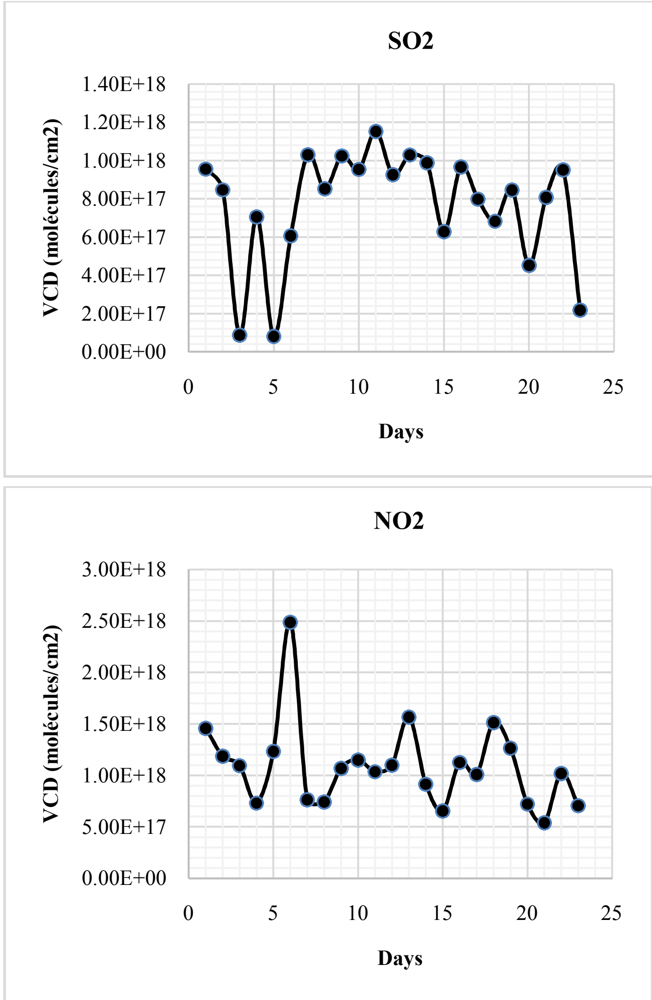


Figure 5 The daily average variations of Slant column density (SCD) of the four considered troposheric trace gases, SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns at different observation of angles (10°, 20°, 30°, 40°, 50°, 60°, 70°, 80° and 90°).

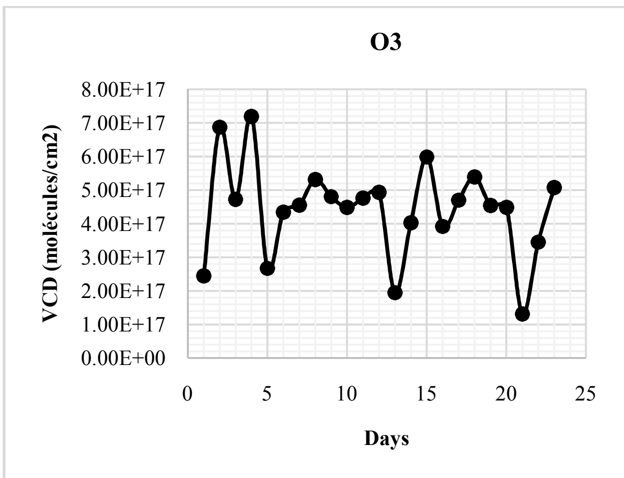
The average values of SCD during the two MAX-DOAS measurement campaigns are mentioned in the following table (table 2).

Table 2 Average values of the slant column density (SCD) of the four considered tropospheric trace gases, SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns

Gas	SCD traces of gas according to angles of observation								
	10°	20°	30°	40°	50°	60°	70°	80°	90°
SO_2	1.69E+17	3.29E+17	4.58E+17	5.41E+17	5.66E+17	5.41E+17	4.58E+17	3.29E+17	1.28E+17
NO_2	2.75E+17	5.38E+17	7.48E+17	8.84E+17	9.25E+17	8.84E+17	7.48E+18	5.38E+17	2.75E+17
O_3	1.08E+17	2.11E+17	2.93E+17	3.46E+17	3.62E+17	3.46E+17	2.93E+17	2.11E+17	1.08E+17
NH_3	4.41E+16	8.60E+16	1.20E+17	1.41E+17	1.48E+17	1.41E+17	1.20E+17	8.60E+16	4.41E+16

Daily Variations of the Vertical Column Density (VCD) of the Four Gases

The daily variations of vertical column density (VCD) of the four considered gases, SO_2, NO_2, O_3, and NH_3 are represented in the below figure (figure 6).For the gas SO_2 the daily variations of VCD are approximately between values 1.00 E+17 and 1.20 E+18. The daily variations of VCD for NO_2 are approximately from the value 5.20 E+17 to the value 2.50 E+18. The daily variations of VCD for the gas O_3 are approximately between values 1.50 E+17 and 7.60 E+17. For NH_3 gas, the daily variations of VCD are approximately from the value 5.00 E+16 to the value 3.50 E+17. The results of daily variations of VCD indicate that the gas NO_2 presents the higher values of VCD; and SO_2, O_3, and NH_3 gases are respectively have high values of VCD in the column of the atmosphere over Bamako city.



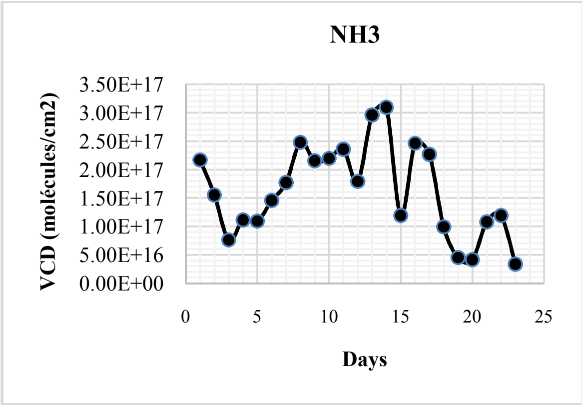


Figure 6 Variations of the vertical column density (VCD) of the four considered troposheric trace gases, SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns.The average values of VCD daily variations during the two MAX-DOAS measurement campaigns are mentioned in the below table (table 3).

Table 3 Average values of VCD of the four considered tropospheric trace gases, SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns

campaigns	VCD traces of gas			
	SO_2	NO_2	O_3	NH_3
1st campaign	7.70E+17	1.18E+18	4.76E+17	1.74E+17
2nd campaign	7.62E+17	9.92E+17	4.07E+17	1.49E+17
Whole	7.66E+17	10.86E+17	4.42E+17	1.62E+17

Daily Variations of the Vertical Column Density (VCD) by Observation Angles of the Four Gases

The Variations of the Vertical Column Density (VCD) by observation angles are mentioned in the below figure (Figure 7). The observation angles are considered from 10º to 90º with an interval of 10º. We have considered the daily averages of SCD during the two MAX-DOAS measurement campaigns and we have calculated according to equation (5) at different observation of angles (10°, 20°, 30°, 40°, 50°, 60°, 70°, 80° and 90°).For the gas SO_2, the values of VCD daily variations are approximately between 1.20 E+17 and 9.70 E+17. The daily variations of VCD for NO_2 gas are approximately between the values 2.70 E+17 and 1.50 E+18.

The gas O_3 presents the values of VCD by observation between are approximately by observation angles approximately between 1.00 E+17 and 6.00 E+17. For the gas NH_3 the variations of VCD by observation angles are approximately from 4.40 E+16 to 2.50 E+17. The results of the daily variations of VCD for those four tropospheric gases, SO_2, NO_2, O_3, and NH_3 present high values for respectively the gases NO_2 and SO_2; and the both gases O_3 and NH_3 present the least high values of the daily variations of VCD during the two MAX-DOAS measurement campaigns in Bamako. The results indicate also that the higher values of VCD daily variations by observation angles correspond to the lower values of observation angles ranging from 10º to 90º with an interval of 10º.

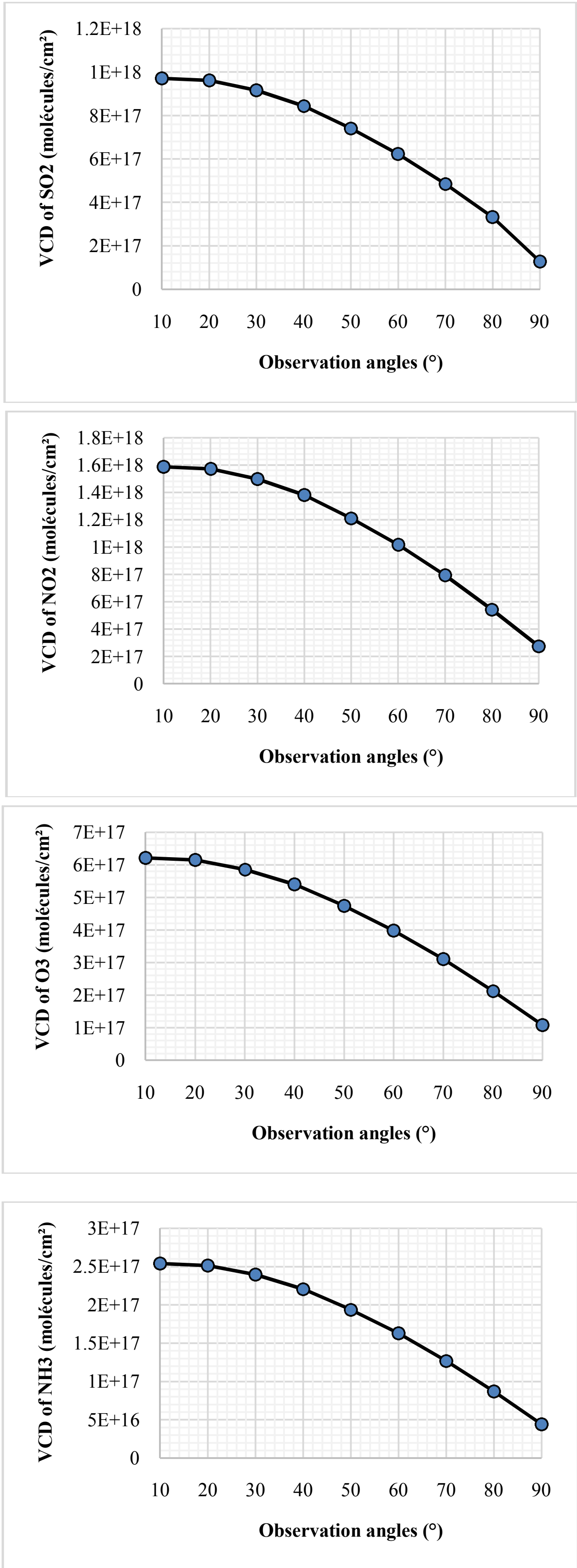


Figure 7 Variations of vertical column density (VCD) of the four gases, SO_2, NO_2, O_3, and NH_3 during the two MAX-DOAS measurement campaigns

Table 4 Values of the VCD averages during the two MAX-DOAS measurement campaigns

	VCD traces of gas according to angles of observation								
Gas	**10°**	**20°**	**30°**	**40°**	**50°**	**60°**	**70°**	**80°**	**90°**
SO_2	1,28E+18	3,32E+17	4,85E+17	6,22E+17	7,41E+17	8,44E+17	9,16E+17	9,61E+17	9,71E+17
NO_2	2,75E+17	5,43E+17	7,93E+17	1,02E+18	1,21E+18	1,38E+18	1,50E+18	1,57E+18	1,59E+18
O_3	1,08E+17	2,13E+17	3,10E+17	3,98E+17	4,74E+17	5,40E+17	5,86E+17	6,15E+17	6,21E+17
NH_3	4,41E+16	8,69E+16	1,27E+17	1,63E+17	1,94E+17	2,21E+17	2,40E+17	2,51E+17	2,54E+17

The average values of VCD daily variations by observation angles from 10º to 90º an interval of 10º during the two MAX-DOAS measurement campaigns are mentioned in the below table (table 4).

CONCLUSION

This study is based on the estimation of column densities of four tropospheric trace gases, SO_2, NO_2, O_3, and NH_3 by MAX-DOAS measurement techniques in Bamako city in Mali during two measurement campaigns. The estimated column densities are the slant column density (SCD), and the vertical column density (VCD). The results during the two MAX-DOAS measurement campaigns indicate that the gas NO_2 presents the higher values of SCD and VCD; and respectively the gases NO_2, O_3, and NH_3, the values of and VCD values for NO_2. The higher values of daily variations of SCD are 15.70 E+17 for the gas NO_2; 9.37 E+17 for SO_2; 6.29 E+17 for the gas O_3; and 2.34 E+17 for NH_3. The higher values of daily of SCD by observation angles are obtained at the angle 50º and they are 9.25 E+17 for the gas NO_2; 5.66 E+17 for SO_2; 3.26 E+17 for O_3; and 1.48 E+17 for the gas NH_3. The higher values of daily variations of VCD are 10.86 E+17 for NO_2; 7.66 E+17 for the gas SO_2; 4.42 E+17 for O_3; and 1.62 E+17 for the gas NH_3. The higher values of VCD by observation angles are also obtained at the angle 50º and they are 1.21 E+18 for the gas NO_2; 7.41 E+17 for SO_2; 4.74 E+17 for O_3; and 1.94 E+17 for the gas NH_3.

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