

**DOAS-measurement
of NO₂ formation rate**

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DOAS-measurement of NO₂ formation rate from NO_x emissions in the atmosphere

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Abstract

In the present work we deal with emissions originating from combustion processes containing SO₂, NO and NO₂, emitted in the atmosphere by a localized source. We present a method for measuring the NO₂-formation rate (due to conversion of NO to NO₂) from measurements of SO₂- and NO₂-slant column densities across different plume sections, under the (usually justified) assumption that the SO₂-flux is constant. The advantages of the proposed method are that the measurements can be performed from an arbitrary location, without explicit reference to the wind speed and direction in the plume. We present results of ground based DOAS-measurements of SO₂ and NO_x emissions from an oil refinery located in the northern part of Montevideo Bay.

1 Introduction

Sulphur- and nitrogen-containing compounds are typical emission products from combustion processes. Their residence time in the atmosphere is affected by photochemical processes (i.e. by natural solar radiation), by wet and dry deposition, through interaction with aerosols as well as by chemical reactions with other species (e.g. ozone) already present in the airmass. Due to the role of nitrogen oxides in the chemistry of the atmosphere and the interplay with various cycles of other compounds, there is strong interest in having a tool for estimating their presence and time evolution together with other gases.

Remote sensing is an important tool for monitoring trace gases emitted in the atmosphere by stacks and other sources. A variety of active and passive systems (see e.g. Platt and Stutz, 2008; Bobrowski et al., 2006; Weibring et al., 2003; Louban et al., 2009; McGonigle et al., 2004; Frins et al., 2006, and the references therein) are used for this purpose.

A widely used method to study chemical constituents of the atmosphere is the Differential Optical Absorption Spectroscopy (DOAS) (Platt and Stutz, 2008). A passive

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DOAS system with the sun as light source is the most simple and affordable way (Louban et al., 2009; McGonigle et al., 2004; Frins et al., 2006; Bobrowski et al., 2007) for monitoring the gases emitted by a localized source, e.g. a volcano or a stack. In particular SO₂ and NO₂ can be measured with passive DOAS, but not NO. The plume emitted by the source is cross-scanned through a vertical plane and the obtained absorption spectra are then analyzed using DOAS to retrieve the total slant column densities (SCDs). The data obtained at various distances from the emission source contribute to the knowledge of how the emitted gases are dispersed into the atmosphere, how they interact among themselves and with other gases, and also to achieve a better estimate of the formation rate of the gases involved in the measurement (Bobrowski et al., 2006; Hönninger, 2004; Rivera et al., 2010; Frins et al., 2011).

In order to calculate fluxes of the emitted gases, the knowledge of wind velocity in the plume is a necessary prerequisite. However, in general, the wind data (speed and direction) at the precise location of the plume is not accessible from the remote site of the measuring station. All this produces an inherent uncertainty in the determination of the trace gases fluxes and restricts the possibility of gaining information along the path of the plume.

In the present work we will deal with emissions from combustion processes containing SO₂, NO, some NO₂ and other compounds, emitted by a stack or similar source originating from an oil refinery. Oxides of nitrogen are emitted mostly in the form of NO and some NO₂. NO reacts rapidly (time scale of minutes) with ozone to yield NO₂ (Seinfeld and Pandis, 2006), i.e.



During daytime there is a photochemical back-reaction to Reaction (R1):



where $h\nu$ denotes a photon with wavelength below 420 nm. Reaction (R1) is immediately (in the troposphere) followed by:



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where M denotes any air molecule. Initially and at night Reaction (R1) dominates, but in sunlight Reactions (R1)–(R3) eventually establish a photo-stationary-state ratio between NO₂ and NO (the well known “Leighton Ratio”). Similarly, SO₂ is oxidized in the gas phase, since it possesses a relatively high solubility in water, e.g. contained in clouds, fog or aerosols, also liquid-phase oxidation plays a role. However, due to the relatively low rate of these reactions (time scale of days) SO₂ can be considered a stable compound in comparison to NO (Lee et al., 2011).

The purpose of this paper is to present a method for measuring the formation rate of NO₂ (due to conversion of NO to NO₂) when SO₂ emissions are also present. Since we retrieve NO₂- and SO₂-SCD simultaneously from the same spectrum, i.e. both species are measured under the same conditions, it is possible to reference NO₂ against SO₂. Thus, by scanning the plume across different plume sections, it is possible to determine the formation rate of NO₂ (assuming that the total SO₂-flux is known and constant). The advantage of this approach relies on the fact that the measurements can be performed without explicit knowledge of the wind data at the different cross-sections of the plume.

In the next section we describe the proposed method, and in Sects. 3 and 4 experimental results are presented and discussed.

2 Remote measurement of the NO₂ formation rate

An approach for monitoring the fluxes of trace gases emitted by a localized source and the formation rate of secondary compounds is schematically shown in Fig. 1. The technique uses a spectrometer attached to a telescope to scan the plume at different elevation angles (α_i) and cross-sections. In Fig. 1, the dashed lines represent the directions along which the telescope is pointing, \hat{n} denotes the unit vector orthogonal to the corresponding cross-section, and \mathbf{v} is the wind velocity.

The fluxes of NO₂ and SO₂ (to be denoted as Φ_{NO_2} and Φ_{SO_2} , respectively) are defined as

$$\Phi_{\text{NO}_2, \text{SO}_2} = \int_{\alpha} \int_r c_{\text{NO}_2, \text{SO}_2}(r, \alpha) \hat{n} \cdot \mathbf{v} r dr d\alpha \quad (1)$$

where $c_{\text{NO}_2, \text{SO}_2}(r, \alpha)$ are the NO₂- and SO₂-concentrations as function of the elevation angle α , and r is the distance to the plume measured from the instrument location.

Assuming that the geometrical cross section of the plume is small in comparison with the distance R between observation site and plume center, and that the difference between two consecutive elevation angles is small ($\alpha_{i+1} - \alpha_i = \Delta\alpha_i \ll 1$), we can approximate expression (1) as

$$\begin{aligned} \Phi_{\text{NO}_2, \text{SO}_2} &= \hat{n} \cdot \mathbf{v} R \int_{\alpha} \int_r c_{\text{NO}_2, \text{SO}_2}(r, \alpha) dr d\alpha \\ &= \hat{n} \cdot \mathbf{v} R \int_{\alpha} S_{\text{NO}_2, \text{SO}_2}(\alpha) d\alpha \\ &\approx \hat{n} \cdot \mathbf{v} R \sum_i S_{i, \text{NO}_2, \text{SO}_2} \Delta\alpha_i \end{aligned} \quad (2)$$

where $S_{i, \text{NO}_2, \text{SO}_2}$ denotes the slant column densities of NO₂ and SO₂ measured at the elevation angle α_i , i.e.

$$S_{i, \text{NO}_2, \text{SO}_2} = \int c_{\text{NO}_2, \text{SO}_2}(r, \alpha_i) dr. \quad (3)$$

As the slant column densities of NO₂ and SO₂ are obtained from the same spectrum, at a given elevation angle α_i we will have the same values of $\hat{n} \cdot \mathbf{v}$ and R for both species. Thus, eliminating the factor $\hat{n} \cdot \mathbf{v} R$ from Eq. (2) one easily obtains

$$\Phi_{\text{NO}_2} = \Phi_{\text{SO}_2} \frac{\sum_i S_{i, \text{NO}_2} \Delta\alpha_i}{\sum_i S_{i, \text{SO}_2} \Delta\alpha_i}. \quad (4)$$

For the sake of simplicity, in the following we will consider that the SO_2 - and the NO_x -flux are constant during the time interval (minutes, see above) necessary for the measurements.

Then, comparing the measurements at two different cross sections of the plume, denoted as cross section "1" and cross section "2", from Eq. (4) it is possible to estimate the NO_2 -formation rate (molec/s or equivalent) in the volume between the cross sections:

$$\begin{aligned} \frac{dn_{\text{NO}_2}}{dt} &= \Phi_{\text{NO}_2} \Big|_2 - \Phi_{\text{NO}_2} \Big|_1 \\ &= \Phi_{\text{SO}_2} \left[\frac{\sum_i S_{i,\text{NO}_2} \Delta\alpha_i}{\sum_i S_{i,\text{SO}_2} \Delta\alpha_i} \Big|_2 - \frac{\sum_i S_{i,\text{NO}_2} \Delta\alpha_i}{\sum_i S_{i,\text{SO}_2} \Delta\alpha_i} \Big|_1 \right], \end{aligned} \quad (5)$$

where n_{NO_2} is the number of NO_2 -molecules (or equivalent), and the subscripts 1 and 2 denote the cross section "1" and cross section "2", respectively.

Expressions (4) and (5) can be simplified by introducing mean slant column densities defined as

$$\bar{S}_{\text{NO}_2, \text{SO}_2} \equiv \frac{\sum_i S_{i,\text{NO}_2, \text{SO}_2} \Delta\alpha_i}{\sum_i \Delta\alpha_i} \quad (6)$$

where the index i runs through the slant column densities measured across the plume.

Substituting Eq. (6) into Eq. (4), one obtains

$$\Phi_{\text{NO}_2} = \Phi_{\text{SO}_2} \frac{\bar{S}_{\text{NO}_2}}{\bar{S}_{\text{SO}_2}}, \quad (7)$$

and then, from Eq. (5) it finally results

$$\frac{dn_{\text{NO}_2}}{dt} = \Phi_{\text{SO}_2} \left[\left(\frac{\bar{S}_{\text{NO}_2}}{\bar{S}_{\text{SO}_2}} \right)_2 - \left(\frac{\bar{S}_{\text{NO}_2}}{\bar{S}_{\text{SO}_2}} \right)_1 \right] \quad (8)$$

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This expression tells us that, under the assumption that Φ_{SO_2} is known (and constant), one can obtain the NO₂-formation rate (dn_{NO_2}/dt) alone from the measurement of slant column densities without explicit knowledge of the wind velocity and distance to the plume. In fact, the plume may be changing its shape, i.e. the wind may change its speed and direction between consecutive cross-scans. Even more, the distance between the measuring site and the plume (R) may be changing in time, e.g. the observation site may be in movement between consecutive cross-scans. Note, however, that the wind velocity inside the plume could actually be measured by correlation techniques (Galle et al., 2010), but this was not attempted in our study.

Actually, since we are assuming that the geometrical cross section of the plume is small in comparison with the distance to the observation site, we can consider that the range of elevation angles in which the slant column densities have significant values is relatively narrow. Thus, as a first approximation, in Eqs. (7) and (8) the mean values $\bar{S}_{\text{NO}_2, \text{SO}_2}$ could be calculated by considering only the slant column densities restricted to that interval of elevation angles.

3 Test measurements at Montevideo

3.1 Measurement procedure

In order to validate our proposal, we performed some test measurements of emissions from a petrochemical facility, located on the north of the Montevideo Bay. The measurements were made in the period December 2009–March 2011.

The refinery has many stacks and there is no public information about its emissions. For the flux estimation, we simplify the analysis by assuming a single emitter and use the slant column density data downwind after the last stack of the group.

The measurements were performed from the west side of the Bay, approximately 1.9 km away from the stacks of the refinery. From this place, we were able to perform vertical scans of the plume at different distances from the source. Also, from this place

it was easy to find reference points in the city (e.g. telecommunication building, etc) which allow evaluating the length of the traversed distance by the plume. A panoramic picture of the site is shown in Fig. 2 (the dotted rectangle indicates the location of the main stack group).

5 A miniaturized MAX-DOAS instrument with a spectral range of 311–460 nm and spectral resolution of ~ 0.44 – 0.75 nm was used. A detailed description of the instrument is in Bobrowski et al. (2006) (see also Hönninger, 2004; Frins et al., 2011).

We used wind data provided by a portable weather station located at our site and by Melilla Airport at 10 km north from our measuring site. Actually, we need the wind
10 data only for the purpose of determining the SO_2 -flux, but this flux could eventually be known through other methods.

After some short scans and a quick evaluation in place, it was found that the trace gases concentration for viewing directions outside the plume (background) was negligible in comparison with that within the plume.

15 In our study, NO_2 - and SO_2 -slant column densities were evaluated in the spectral ranges 430–460 nm and 315–325 nm respectively. A zenith spectrum collected at mid-day of the same day was used as reference, and the slant column densities were computed using the WINDOAS software (Fayt and Van Roozendaal, 2001), which implements the spectral analysis via a minimization algorithm.

20 For the NO_2 evaluation, the absorption cross sections of O_4 (Greenblatt et al., 1990) and NO_2 (Vandaele, 1998) at 294 K, O_3 (Burrows, 1999) at 294 K and water vapor at 290 K (Rothman et al., 2005) were utilized. Additionally a synthetic Ring spectrum was included in the evaluation (Wagner et al., 2009).

25 For the SO_2 analysis, absorption cross sections of SO_2 at 294 K (Vandaele et al., 1994), O_3 at 294 K (Burrows, 1999) and a synthetic Ring spectrum were included (Wagner et al., 2009). Since the literature cross sections are given in $\text{cm}^2 \text{ molecule}^{-1}$ we obtain column densities in molecules cm^{-2} and concentrations in molecule cm^{-3} . These figures were converted to kg m^{-3} using the known molar mass of the species measured and the air density at the temperature recorded during our measurements.

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3.2 Experimental results

On 29 March 2011 we performed measurements across six vertical cross sections (numbered from 1 to 6) of the plume emitted by the oil refinery (see Fig. 2). We used a cross scan near the stacks to quantify the flux Φ_{SO_2} . During the measurements
5 across section 1, the mean wind velocity was $\sim 6.4 \text{ km h}^{-1}$ blowing from NNE. Using the measured SO_2 -SCDs as function of the elevation angle in expression (2), we obtained a SO_2 -flux of the order of 300 kg h^{-1} .

The uncertainty estimation of the SCD, values measured in this work is based on the errors determined by the numerical fitting, depending on the size and structure of the
10 residual. The estimated uncertainties (see Stutz and Platt, 1997) of the SCDs were of the order of 30 % and 10 % for SO_2 and NO_2 , respectively. The uncertainty of the wind speed was about 30 % (due to changes of the wind speed and direction). Thus, it results an uncertainty in the fluxes of the order of 40 %.

During the measurements across sections 1–6 the wind was changing in speed (6.4 – 12.9 km h^{-1} corresponding to 1.8 – 3.6 m s^{-1}) and direction (NNE to NNW), but we will assume that the SO_2 - and NO_x -flux emitted by the refinery remains constant in the
15 short time interval (20 min) required for the measurements.

Figure 3 shows the obtained SO_2 - and NO_2 -slant column densities at the different cross sections. The mean SCD-values are plotted in Fig. 4a–b: clearly \bar{S}_{SO_2} decreases
20 and \bar{S}_{NO_2} increases with increasing distance to the source. Only part of the plume was included in the scan, but the column density maximum is clearly visible.

The NO_2 -fluxes (Φ_{NO_2}) at the different cross sections can be easily obtained using the expression proposed in Eq. (7). The normalized NO_2 -fluxes $\bar{S}_{\text{NO}_2}/\bar{S}_{\text{SO}_2}$ (i.e. the NO_2 -fluxes normalized with Φ_{SO_2}) are shown in Fig. 5a. The linear fit shown in this
25 figure tells us that the NO_2 -formation rate per unit distance is approximately a constant of the order of $25 \text{ kg (h km)}^{-1}$ (assuming a SO_2 -flux of 300 kg h^{-1}). The NO_2 -formation rate per unit distance was calculated as the product of Φ_{SO_2} and the slope of the linear fit (slope $\approx 0.083 \text{ km}^{-1}$; correlation coefficient ≈ 0.96).

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Figure 5b shows the results obtained (from the same measured data as before) when the mean values $\bar{S}_{\text{NO}_2, \text{SO}_2}$ are calculated by considering only the slant column densities restricted to a small interval of elevation angles ($\sim 3^\circ$) around the slant column density maximum. Although in this case there is an increased dispersion of the $\bar{S}_{\text{NO}_2}/\bar{S}_{\text{SO}_2}$ values, the linear fit shows a NO₂-formation rate per unit distance very similar to that shown previously in Fig. 5a. This means that a series of cross scans restricted to a small interval of elevation angles can provide a reasonable first order estimation of the NO₂-formation rate per unit distance

In the particular case when stable wind condition exists and the plume remains approximately horizontal, a quick horizontal scan through the plume (at slant column density maximum) could provide a rough estimation of the NO₂-formation rate per unit distance. This could be well justified in the case when the NO₂/SO₂-mixing ratio is approximately constant through a given cross section, i.e. if $c_{\text{NO}_2}/c_{\text{SO}_2}$ is approximately independent of α_i and r inside a given cross section, then one has $\frac{c_{\text{NO}_2}}{c_{\text{SO}_2}} \approx \frac{S_{\text{NO}_2}}{S_{\text{SO}_2}} \approx \frac{\bar{S}_{\text{NO}_2}}{\bar{S}_{\text{SO}_2}}$.

Figure 6a–c shows results of a horizontal scan through a plume performed on 1 December 2009 at the oil refinery. Figure 6a and b shows the measured values of S_{SO_2} and S_{NO_2} as function of the azimuth angle (azimuth angle zero corresponds to the position of the source). Figure 6c shows the $S_{\text{NO}_2}/S_{\text{SO}_2}$ values increasing with the azimuth angle, which is characteristic of a positive NO₂-formation rate per unit distance.

4 Conclusions

In the present paper we deal with gaseous emissions originating from combustion processes containing SO₂ and NO_x, emitted in the atmosphere by a localized source. We presented a method for measuring the NO₂-formation rate (due to conversion of NO to NO₂) from measurements of mean SO₂- and NO₂-slant column densities across different plume sections. The proposed method is based on the assumption that the SO₂- and NO_x- flux emitted by the source remains constant during the measuring time.

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The advantage of the proposed method is that explicit knowledge of the wind speed and direction across the different plume sections is not required. Actually, the wind may change its speed and direction between consecutive plume cross-section scans, and/or the distance to the plume (R) may be changing in time, e.g. the observation site may be in motion, as long as the line of sight traverses the entire plume section

We present results of ground based measurements of SO₂ and NO₂ from the emissions of an oil refinery located in the northern part of Montevideo Bay. We have shown that an estimation of the NO₂-flux and formation rate could be derived by restricting the averages to a small interval of elevation angles in which the slant column densities have significant values.

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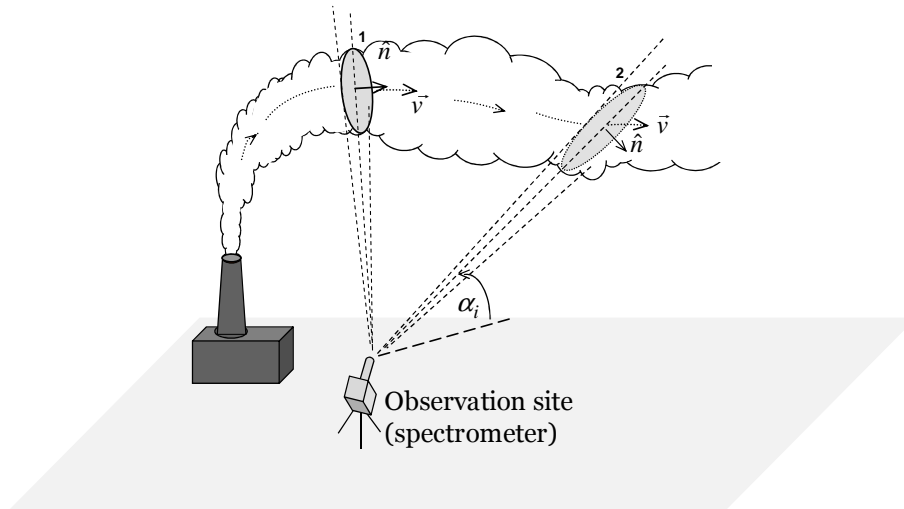


Fig. 1. Flux measurement across two cross-sections of a plume.

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Fig. 2. Panoramic view of the oil refinery and the Montevideo Bay from the measuring site. The dashed rectangle indicates the emitting stack group. The cross scanned sections are numbered from 1 to 6.

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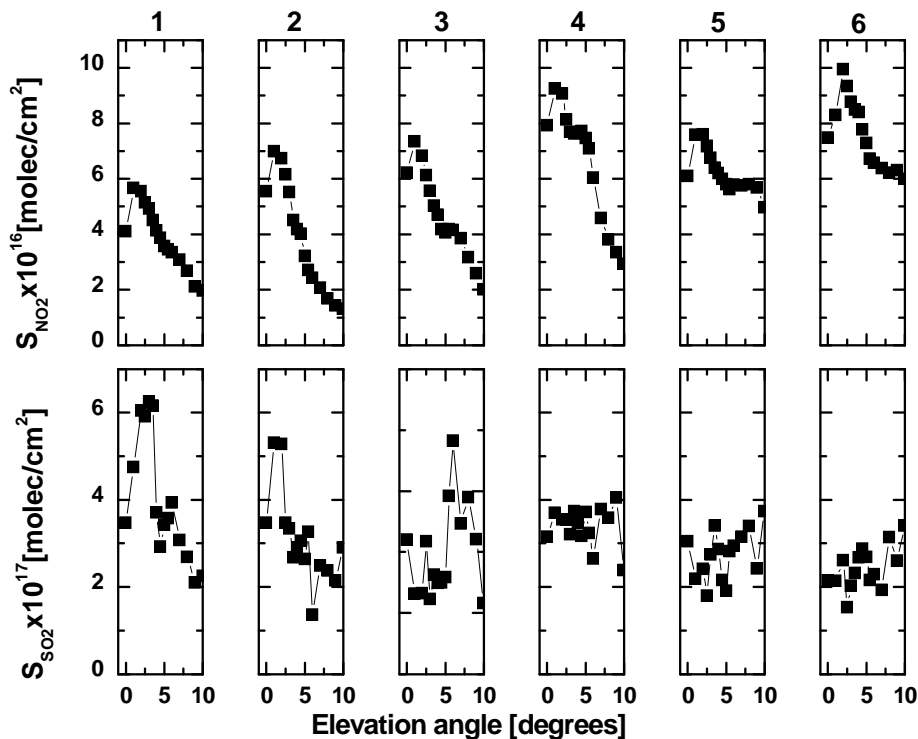


Fig. 3. SO_2 - and NO_2 -slant column densities at the different cross sections at elevation angles between 0° and 10° .

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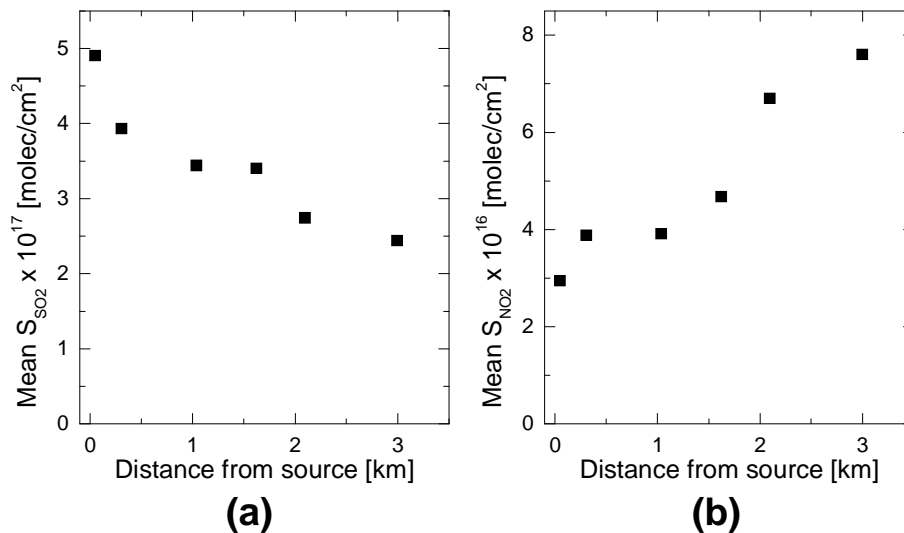


Fig. 4. Mean values of SO_2 - and NO_2 -slant column densities at the different cross sections.

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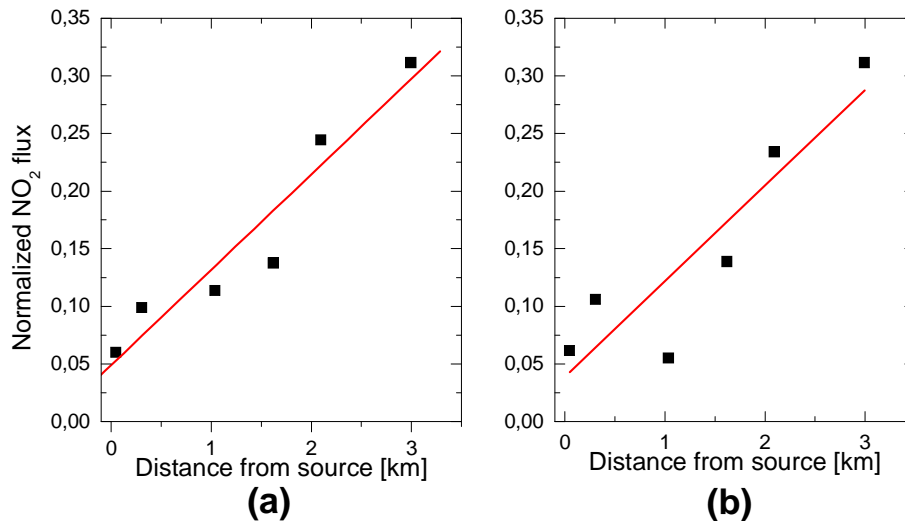


Fig. 5. Normalized NO₂-fluxes $\bar{S}_{\text{NO}_2}/\bar{S}_{\text{SO}_2}$ (after Eq. 7); **(a)** using mean values $\bar{S}_{\text{NO}_2, \text{SO}_2}$ shown in Fig. 4a–b; **(b)** using mean values $\bar{S}_{\text{NO}_2, \text{SO}_2}$ restricted to a small interval of elevation angles around the plume center.

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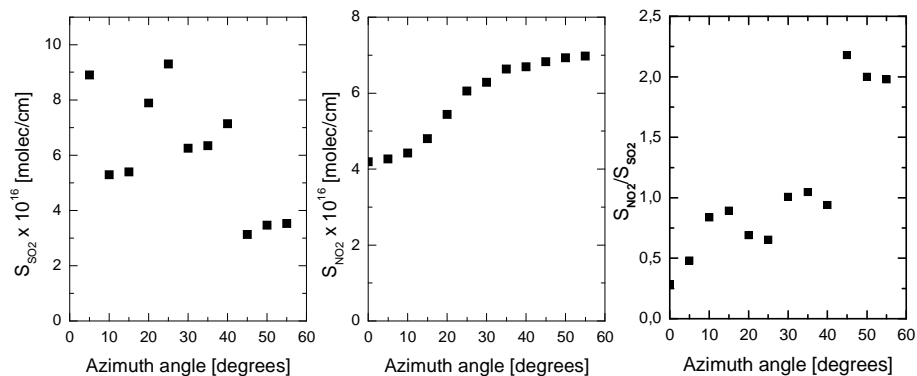


Fig. 6. Horizontal scan through the center of a plume performed on 1 December 2009.

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