Ground based measurements of SO$_2$ and NO$_2$ emissions from the oil refinery “la Teja” in Montevideo city

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Abstract. We present preliminary results of ground based measurements of SO$_2$ and NO$_2$ emissions from “La Teja” oil refinery located in the northern part of Montevideo Bay. Our study is part of a long term effort to localize and monitor relevant emission sources in the city area of Montevideo. These measurements were performed with a Miniature Multi AXis Differential Optical Absorption Spectrometry (MiniMAX-DOAS) instrument, which is basically a temperature controlled medium-resolution spectrometer (~0.5 nm) equipped with a small telescope and a stepper motor allowing automatic scans in one dimension.

We present a discussion about the evolution and transformation of both above species in the atmosphere. Our observation site was approximately 1.9 km away from the oil refinery and we were able to perform vertical and horizontal scans of the plume emitted (during our measurements) almost horizontally from its stacks. The maximum value of the SO$_2$ slant column density (SCD) was found to be ~ $4 \times 10^{17}$ molec cm$^{-2}$ directly over the oil refinery decreasing as the plume disperses. In contrast, the NO$_2$ SCD peaks at ~ $1 \times 10^{16}$ molec cm$^{-2}$ directly over the source and increases continuously as the plume disperses. The SO$_2$ flux measured immediately downwind of the refinery was found to be about 1200 kg h$^{-1}$ (±40% uncertainty).

1. Introduction
People living in the surroundings of Montevideo Bay are strongly affected by a petroleum refinery, an electricity power plant, the port and some industries located in this area. VOCs, NO$_x$, and SO$_2$ are products of combustion processes with high impact on the air quality. As part of a long term effort to localize and monitor relevant emission sources in Montevideo city, we present preliminary results of ground based measurements of SO$_2$ and NO$_2$ emissions from the “La Teja” oil refinery located in the northern part of Montevideo Bay. The monitoring of the oil refinery is particularly important because sulphur-containing petroleum causes strong emissions of sulphur dioxide if no precautions are taken.
An important tool to gain knowledge about the emissions of trace gases that affect extensive areas is the ability to monitor remotely the contaminants sources. In this work we present the use of a versatile and handy instrument like a MiniDOAS to solve present challenges.

In section 2 we describe the instrument and method utilized for the measurements, and in section 3 we discuss the experimental results.

2. Method and Instrument

Remote sensing often represents the only feasible technique for monitoring emission sources and their dispersion. Differential Optical Absorption Spectroscopy (DOAS) is a widely used method to study chemical constituents of the atmosphere as well as the emissions of mobile and stationary sources [1].

Remote monitoring systems based on DOAS may use artificial light sources, which simplify the evaluation of the collected spectra to retrieve the mixing ratios or concentrations of the trace gases. However, volcanic emissions or emissions from industrial facilities are usually monitored remotely by analyzing scattered sunlight which has traversed the plume using Multi-AXis-DOAS (MAX-DOAS) [2-7]. The advantage of this method is that during daylight hours, the instrument (usually a MiniDOAS) can be aimed at any position in the sky (except for the sun itself), allowing optimal measurement geometry to the emission source. To retrieve the flux from a stack, the plume is cross-scanned ideally perpendicular to the wind direction.

In particular for this study, we used a MiniDOAS with spectral resolution 0.44 - 0.75 nm in the spectral range between 310 nm and 460 nm. The light is coupled into the spectrometer through a quartz lens (40 mm focal length and 20 mm diameter) and a quartz fiber bundle. The field of view is approximately 0.4° and during the measurements the temperature of the instrument was set to 5.0°C.
**Figure 2.** Evaluation of a spectrum recorded on December 1, 2009, at local noon (12:17), for (a) NO$_2$ and (b) SO$_2$. Plotted are optical densities versus wavelength. The observation elevation angle was 0.5°.

2.1. Measurement procedure.

The measurements were performed from a site on the west side of the Bay, marked with A on figure 1, approximately 1.9 km away from the stacks of the refinery. From this place, we were able to perform vertical and horizontal scans of the plume emitted from the refinery and to find reference points in the city (e.g. telecommunication building, electricity power plant, etc). During the period of the measurements the electricity power plant, located also in this bay, was turned off except for some sporadic tests.
The emission plume from the refinery was vertically and horizontally scanned at different distances from the sources. Our measurement routine began first with some sets of quick vertical scans (short exposure time) to localize the longitudinal axis (horizontal axis) of the plume. Then, assuming that plume was stable, we proceeded with its horizontal scan.

In order to quantify the emission flux using single slant column density measurements, the cross section of the plume was scanned and the radial plume integration method was applied [3]. We assumed that the plume moves parallel to the wind direction. We used wind data provided hourly by Carrasco Airport, located 22 km east and Melilla Airport at 10 km north from our measuring site. The trace gases concentration for viewing directions outside the plume (background) was found negligible in comparison with that within the plume.

2.2. Spectra evaluation.

In order to retrieve the slant column density of each measured spectrum, we applied the DOAS analysis. A Zenith spectrum collected at midday of the same day was used as reference.

The NO$_2$ and SO$_2$ slant column densities were computed using the WINDOAS software [8], which implements the spectral analysis via a minimization algorithm. The software was developed for analysis of UV-visible spectra by Differential Absorption Spectroscopy (DOAS). It main features are DOAS intensity fitting, calibration and the handling of cross sections.

In our study, NO$_2$ and SO$_2$ were evaluated in the spectral ranges 430 nm - 460 nm and 315 nm – 325 nm respectively. For the NO$_2$ evaluation, the absorption cross sections of O$_4$ [9] and NO$_2$ [10] at 294 K, O$_3$ [11] at 273K and water vapor at 300K [12] were utilized. Additionally a synthetic Ring spectrum was included in the evaluation [13]. As shown in figure 2a, the NO$_2$ absorption can be clearly identified in the measured spectra indicating a good signal-to-noise ratio.

For the SO$_2$ analysis, absorption cross sections of SO$_2$ at 273 K [12], O$_3$ at 293 K [11] as well as a synthetic Ring spectrum (describing the effect of atmospheric Raman scattering) were included. Figure 2b shows the SO$_2$ evaluation of one the spectra measured on December 1, 2009, at noontime, yielding $1.5 \times 10^{17}$ molecules per cm$^2$. Notice the remarkably high presence of SO$_2$.

2.3. Error estimation and detection limit.

The uncertainty estimation of the slant column density SCD’s, values measured in this work is based on the numerical errors determined by the numerical fitting, depending on the size and structure of the residual. The estimated uncertainties (see [14]) on SCD were of the order of 3% and 10% for SO$_2$ and NO$_2$, respectively.

The flux of gases (kg h$^{-1}$) emitted from the refinery stacks was estimated by well-established geometric approximations (see [15]) using vertical scans across the plume. The trace gas concentration and aerosols transported by the plume was affected by the temporal and spatial variability of the wind direction. Thus, detailed information during measurements about the wind (speed and direction) in the site would improve our flux estimation. However the lack of instruments for this purpose in the site of measurement led us to use the information from the meteorological stations at the airports located around 10 and 20 km away from the refinery. We estimate the uncertainty in the wind speed (e.g., due to changes of the wind speed and direction) of about 30%.

The refinery has many stacks. However from our study we can clearly distinguish two emission spots over the refinery area: one is a single stack and the other is a group of several (probably 4 or 5) stacks. For the flux estimation, we simplified the analysis by assuming a single emitter at the mean distance to the main stack group, which results in a distance uncertainty of the order of 6%.
Figure 3. Horizontal scan of the plume, performed on December 1 and 4, 2009. (a) SO$_2$ slant column density as a function of observation azimuth angle ("Viewing direction"). (b) Same for NO$_2$ slant column density. (c) Picture of the refinery, viewed from west to east. The left dashed vertical line corresponds to an azimuth angle of 30 degrees, the right dashed vertical line corresponds to an azimuth angle of 65 degrees.
3. Results and Conclusions

On December 1st and 4th horizontal scans along the longitudinal axes of the plume were performed. These measurements are shown in figure 3a and 3b, respectively. Each horizontal scan took around 25 minutes, starting before the refinery and changing the viewing direction in steps of 5°, following the plume downstream (according to the direction of the wind).

As can be seen from figure 3a, the SO$_2$ measurement displays an almost constant optical thickness upwind of the refinery, followed by a step when scanning the refinery’s first stack, followed by a decrease on the left side. In contrast, the NO$_2$ optical thickness (see figure 3b) increases continuously and there is no obvious step at the location of the refinery stacks as observed in the simultaneously measured SO$_2$. Despite the wind direction being north the 1st of December and south the 4th of December, we observed the same behavior both days.

Also remarkable are the different offsets in the optical thickness of SO$_2$ and NO$_2$ observed on December 4th (southerly wind) compared with the one observed on December 1st (northerly wind). As mentioned in Section 2, we referenced our spectra with respect to a zenith measurement, and thus we can assume that our reference was affected in the same way on both days. We can guess that a possible reason for different offsets is that, as the wind blows from the south the measured optical thickness is affected by the polluted air masses coming from the city, while when it is blowing from the north the air masses are less polluted.

The calculated SO$_2$ and NO$_2$ fluxes emitted by the refinery are presented in Table 1 showing SO$_2$ and NO$_2$ fluxes derived in the way described above from measurements performed on December 2009, March and April 2010. The lowest SO$_2$ and NO$_2$ fluxes measured mostly coincide with high variability.

| Date (d/m/y) | Observation Direction$^b$ | Local Time | Wind Direction$^b$ | Wind Speed (m s$^{-1}$) | SO$_2$ Flux (kg h$^{-1}$) | NO$_2$ Flux (kg h$^{-1}$) |
|--------------|---------------------------|------------|---------------------|------------------------|--------------------------|--------------------------|
| 1/12/2009    | 65°                       | 11:50 NNE  | NNE                 | 5.1                    | 764                      | 77                       |
|              |                           | 12:15 NNE  |                     | 5.1                    | 1020                     | 93                       |
|              |                           | 12:49 N    |                     | 7.7                    | 678                      | 119                      |
| 4/12/2009    | 65°                       | 12:44 SSE  |                     | 2.6                    | 737                      | 96                       |
|              |                           | 12:50 S    |                     | 3.6                    | 697                      | 127                      |
|              |                           | 12:57 S    |                     | 3.6                    | 891                      | 118                      |
|              |                           | 13:07 S    |                     | 3.6                    | 785                      | 105                      |
|              |                           | 13:27 S    |                     | 3.6                    | 889                      | 117                      |
| 9/12/2009    | 95°                       | 12:50 NNE  |                     | 6.2                    | 1297                     | 95                       |
|              |                           | 13:32 NNE  |                     | 5.1                    | 1110                     | 89                       |
|              |                           | 14:13 NNE  |                     | 5.1                    | 1130                     | 106                      |
| 24/3/2010    | 60°                       | 11:09 ESE  |                     | 4.1                    | 731                      | 63                       |
|              | 65°                       | 14:38 ESE  |                     | 7.7                    | 1206                     | 170                      |
| 7/4/2010     | 67.5°                     | 12:55 SE   |                     | 5.1                    | 647                      | 192                      |
|              | 62.5°                     | 13:31 SE   |                     | 5.1                    | 871                      | 134                      |

$^a$ With respect to North.
$^b$ The direction the wind is coming from.
of the wind direction and velocity. The average SO₂ flux measured was 1179 kg h⁻¹ and the NO₂ flux measured at the border of the industrial facility was 113 kg h⁻¹.

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