New proposal to measure NO$_2$ formation rate from NO emissions in the atmosphere

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Abstract: As result from combustion processes, SO$_2$, NO, NO$_2$ and other substances are emitted in the atmosphere. We present a new method to measure the formation rate of a trace gas (e.g., NO$_2$), whose precursor (NO) was emitted in the atmosphere by a source like a stack. In the case under study, the presence of ozone determines the formation of NO$_2$. We will demonstrate that measuring the slant column densities across the emitted plume and knowing the flux of another trace gas (e.g. SO$_2$), also emitted by the source but that could be considered stable under the conditions of the observation, it is possible to monitor remotely (from an arbitrary location) the formation rate of NO$_2$ due to conversion of NO to NO$_2$.

1. Introduction

Monitoring the flux of trace gases emitted in the atmosphere by volcanoes, stacks and other sources is an important task for studying the atmosphere and air quality control. At present, a variety of instruments are used to accomplish these goals, e.g. modern industries have installed at the exit of the stacks different sensors to monitor their emissions. Active systems like LIDAR (Light Detection and Ranging) and LP-DOAS (Long-path Differential Optical Absorption Spectroscopy) allow remote measurements of the emitted plume composition. LIDAR is based on the use of pulsed lasers [1][2] and LP-DOAS makes use of high power lamps and more recently LEDs (Light Emitting Diodes) [3].

The use of a spectrometer attached to a telescope to cross-scan the emitted plume and record spectra of the sunlight passing through it is technologically simple and affordable. These spectra are then analyzed using DOAS [4] to retrieve the slant column densities of the trace gases.

In order to calculate the flux of the emitted gases, the knowledge of wind speed and direction in the plume are ineluctable prerequisites. Often the wind data provided from local meteorological stations are used, which causes a high uncertainty on the flux determination.
We present a new method to find the formation rate of trace gases, whose precursor was emitted in the atmosphere by a source like a stack or similar. We will demonstrate that measuring the slant column densities across the emitted plume as a function of the flux of another trace gas, also emitted by the same source but that could be considered chemically stable under certain conditions, it is possible to monitor remotely (from an arbitrary location) the formation rate of the trace gas, without an explicit knowledge of the wind speed and direction in the plume.

To visualize our idea, we will consider emissions originated by combustion processes containing SO$_2$, NO, some NO$_2$ and other compounds. Sulphur dioxide oxidizes in the atmosphere and possesses a relatively high solubility in water, such as clouds, fog or aerosols. However, due to the relative low rate of these reactions it could be considered a stable compound with respect to nitrogen monoxide. Oxides of nitrogen are primarily emitted mostly in the form of NO and some NO$_2$. Nitrogen monoxide reacts rapidly with ozone to yield NO$_2$.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \tag{1}
\]

Since we retrieve NO$_2$ and SO$_2$ simultaneously from the same absorption spectrum, i.e. both species are measured under the same conditions, it is possible to reference NO$_2$ against SO$_2$ as we will discuss next.

2. Remote Flux Measurement

As a first stage to measure the flux of SO$_2$ and NO$_2$ in the plume of a stack of an industrial plant, we proceed to cross scan it with a MiniDOAS instrument. In this way we measure the slant column densities at different elevation angles, as schematically shown in figure 1. The slant column densities are defined as

\[
S = \int_{r} c(r, \alpha) \, dr, \tag{2}
\]

where \(c(r, \alpha)\) is the concentration of the trace gas (NO$_2$ or SO$_2$) as function of the elevation angle \(\alpha\), and \(r\) is the distance to the plume measured from the instrument location.

The flux will be given as

\[
\Phi = \int_{r} c(r, \alpha) \hat{n} \cdot \vec{v} \, r \, dr \, d\alpha \tag{3}
\]

where \(\vec{v}\) is the wind velocity, and \(\hat{n}\) is a unit vector orthogonal to the geometrical cross section.

As NO$_2$ and SO$_2$ slant column densities are retrieved from the same spectrum, we will have the same conditions of wind speed and direction for both species. Assuming that the geometrical cross
section of the plume is small in comparison with the distance $R$ between observation site and center of the plume, from (2) and (3) we can approximate the fluxes of both species as

$$\Phi_{\text{NO}_2, \text{SO}_2} = \vec{n} \cdot \vec{v} R \sum_i \Delta \alpha_i \left( \frac{1}{2} \left( S_i + S_{i+1} \right) \right)_{\text{NO}_2, \text{SO}_2},$$  \hspace{1cm} (4)

where $\Phi_{\text{NO}_2}$ and $\Phi_{\text{SO}_2}$ are the fluxes of $\text{SO}_2$ and $\text{NO}_2$, respectively, $\Delta \alpha_i$ are the differences of two consecutive elevation angles, and $S_i$ is the slant column density at the elevation angle $\alpha_i$ for $\text{NO}_2$ and $\text{SO}_2$, respectively.

Then, from the two expressions summarized in (4) one easily obtains

$$\Phi_{\text{NO}_2} = \Phi_{\text{SO}_2} = \sum_i \Delta \alpha_i \left( S_i + S_{i+1} \right)_{\text{NO}_2, \text{SO}_2}.$$  \hspace{1cm} (5)

Since it was assumed that the $\text{SO}_2$ is chemically stable (on the time scale of our observations) and that the stack emission is constant in time, it is physically reasonable to consider that the $\text{SO}_2$-flux ($\Phi_{\text{SO}_2}$) will remain constant, although the plume may change its shape (e.g., the wind velocity may change). Thus, the expression (5) tells us that one can measure the $\text{NO}_2$-flux ($\Phi_{\text{NO}_2}$) without an explicit knowledge of the wind velocity and the distance to the plume.

Then, comparing the measurements at two different cross sections of the plume, denoted as “cross section 1” and “cross section 2”, from (5) it is possible to estimate the $\text{NO}_2$ formation rate as follows:

$$\frac{d\text{NO}_2}{dt} = \Phi_{\text{NO}_2} \bigg|_2 - \Phi_{\text{NO}_2} \bigg|_1 = \Phi_{\text{SO}_2} \left[ \sum_i \Delta \alpha_i \left( S_i + S_{i+1} \right)_{\text{NO}_2} \right] \frac{\sum_i \Delta \alpha_i \left( S_i + S_{i+1} \right)_{\text{SO}_2}}{\sum_i \Delta \alpha_i \left( S_i + S_{i+1} \right)_{\text{SO}_2}} \left( \frac{1}{2} \right),$$  \hspace{1cm} (6)

where the subscripts 1 and 2 denote the “cross section 1” and “cross section 2”, respectively.

3. Test Measurements at Montevideo

We performed some test measurements to verify our proposal at the petrochemical facility ANCAP, located on the north of the Montevideo Bay. The observation site was on the west side of the bay, approximately 1.9 km from the main group of stacks of the facility. We used a miniaturized MAX-DOAS instrument with an entrance optics (quartz lens, $f = 40$ mm, 20 mm diameter, and field of view $\sim 0.6^\circ$) coupled to a quartz fiber bundle, which transmits light into a commercial miniature fiber-optic spectrometer. It allows measurements in the wavelength range of 310-460 nm with a spectral resolution of $\sim 0.5$ nm.

Figures 2a and 2b show slant column density measurements across the plume performed on March 24, 2010. The cross scans were performed aiming at approximately 200 m (measured at 14:30 local time) and 400 m (measured at 16:30 local time) from the source (stack); (a) corresponds to $\text{SO}_2$ and (b) corresponds to $\text{NO}_2$. (The maxima of the slant column densities correspond to scans across the plume center.)

Taking into account a mean wind velocity of 1.9 km h$^{-1}$ and that the plume is at a distance of the order of 1.9 km from the instrument location, we obtained an average $\text{SO}_2$-flux of 1200 kg h$^{-1}$ (with 40% uncertainty) with equation (4). Using equation (6) we estimated a $\text{NO}_2$ formation rate of the order of 1950 kg h$^{-1}$ (with 40% uncertainty) in the region between the two cross sections.
4. Discussion and conclusions

We have presented a method to measure the formation rate of a trace gas (e.g., NO$_2$), whose precursor (NO) was emitted by a point-like source like a stack. We assumed to have knowledge of the flux of another (more stable) trace gas (e.g. SO$_2$) also emitted by the source. In practice, this knowledge could be provided by the industry if they have installed the corresponding sensors at the stack, or it can be measured directly by DOAS using expression (4).
We have demonstrated that measuring the slant column densities across the plume, it is possible to monitor remotely the formation rate of NO$_2$ without any explicit reference to the wind speed and direction in the plume, assuming the SO$_2$ flux is known. We have presented preliminary measurements performed at a petrochemical facility located on the Montevideo Bay.

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