

We like to thank the reviewers for their effort to evaluate our manuscript and for their valuable comments, which helped to improve the quality of our manuscript. In response to the reviewers' comments we rewrote several paragraphs of the manuscript. Our answer and the major changes performed in the manuscript are the following:

### Comments/answers to Referee 1:

#### Specific Comments

It seems that the present study has completely ignored the multiple scattering in the atmosphere (including inside the targeted plume). When the multiple scattering occurs in the plume, the integration of trace gas concentration over  $r$  (the distance to the plume measured from the instrument location) does not match the slant column density (SCD) retrieved by DOAS, making the equation (3) invalid. Moreover, the difference can be dependent on the distance between the plume and the source, due to different aerosol (smoke) and solar illumination (i.e., solar azimuth angle) conditions. Thus, I strongly recommend interpreting the retrieved SCDs with a consideration of the effects of multiple scattering or recommend adding some statements justifying the omission of multiple scattering.

According to the equation (2), the flux (denoted as  $\phi$ ) should be a quantity covering the whole range of elevation angles in which SCDs are significantly high. In the equation (8), however, whereas  $\phi(\text{SO}_2)$  is based on the above definition,  $S$  values are not, but based on a limited range of elevation angles at which DOAS measurements were made. In particular, test measurements at Montevideo only cover part of the plume at elevation angles less than 10 degrees. Does this inconsistency impact the results of this study (e.g., the result that the  $\text{NO}_2$ -formation rate per unit distance has been estimated to be  $25 \text{ kg (h km)}^{-1}$ )? Perhaps in relation to this, on p.5726, line 1-8, the authors have shown results obtained from a limited set of SCDs within 3-degree elevation angles of the center of the plume. Similar to this sensitivity analysis, I recommend testing some more different ranges of elevation angles (e.g., 0-8 degrees, 0-5 degrees) and discussing the results in the paper.

We found no evidence of multiple scattering in our measurements; the measurements were performed at a sunny day with good meteorological conditions (a quite clear ambient atmosphere, free from clouds and with good visibility). The plume was transparent and we did not observe any scattering inside the plume, thus we conclude that there was negligible aerosol scattering.

We estimated the visibility range at about 30 km, corresponding to an aerosol scattering coefficient of about  $0.13 \text{ km}^{-1}$ . At an estimated plume width (along the line of DOAS observation) of 0.2 km this would correspond to a scattering probability of about 0.03 within the plume, clearly multiple scattering will be negligible under these conditions. The virtual absence of multiple scattering was also confirmed by the evaluation of  $\text{O}_4$ . As recommended by the referee, in the revised manuscript version we include a statement justifying the omission of multiple scattering considerations (added in the new manuscript version Sec. 3.2, p. 7, lines 18-26).

As mentioned in the manuscript (p. 5724, line 12-14), it was found that the trace gases concentrations for viewing directions looking at the plume were significantly higher than outside the plume (background). Thus, our experimental results demonstrate that the relevant elevation angle interval was 0-10 degrees. Measurements at elevation angles of 45, 70 and 90 degrees, well outside the plume, were also made, but are not shown in Fig. 3. The choice of a limited elevation angle interval responds to the purpose of performing multiple rapid scans across different plume cross-sections (added in the revised manuscript version Sec. 3.1, p. 6, lines 19-23).

We showed that the results obtained from a limited set of SCDs within few degrees of elevation angles in which SCDs are significantly high (Fig. 5(b)), do not substantially differ from that obtained in a wider range of 0-10 degree (Fig. 5(a)). These results are discussed in p. 5726, line 1-19 (revised version of the manuscript, p. 8, line 27 to p.9, line 4).

### Technical corrections

Abstract and p.5723, line 19: Please mention the latitude and longitude of the measurement location.

In the revised manuscript version the latitude and longitude of the measurement location is given.

p.5721, line 8: I guess that the unit of alpha is degree. To make it clear, please give a unit just after "1". At this sentence, the authors approximate the equation (1), since the difference between two consecutive elevation angles is much smaller than 1 degree. Is this approximation really valid? Please mention a difference between consecutive elevation angles for test measurements at Montevideo in section 3.1.

In Eq. (1) the unit of "alpha" is radian, as usual in equations involving angular variables (we state this explicitly in the revised version). In Fig. 3 the elevation angles were indicated in degrees, which is more intuitive for illustrative purposes. In Sect. 3.1 we now mention that the difference between consecutive elevation angles is of the order of 0.5-1 degree (added in revised manuscript version Sec. 3.1, p. 6, line 19-23), which is quite consistent with the assumption  $\Delta\alpha \ll 1$  (rad).

p.5723, line 12: It is unclear to me what the "significant values" mean. According to Figure 3, the NO<sub>2</sub> SCD is still high even at an elevation angle of 10 degrees. Does omitting the range of elevation angles beyond 10 degrees influence the estimate of NO<sub>2</sub> formation rate?

The test measurements at Montevideo cover the whole range of elevation angles in which SCDs are significant higher than the background (see above Specific Comments).

p.5724, line 5: Please give the original words for MAX-DOAS.

In the revised manuscript (now p. 6, line 16) we added the meaning of the acronym "MAX-DOAS".

p.5724, line 12-14: The authors state that trace gas concentrations outside the plume were negligibly small. I think that it would be better to state this quantitatively, for example, in comparison to the detection limit and/or uncertainty of the measurements.

Outside the plume the SO<sub>2</sub>-SCDs were of the order of  $2 \times 10^{17}$  molec/cm<sup>2</sup>, which is close to our detection limit ( $\sim 0.5 \times 10^{17}$  molec/cm<sup>2</sup>). In the revised manuscript we add this information (now p. 6, line 30-31).

p.5724, line 24-26: Would it be reasonable to add HCHO in the SO<sub>2</sub> evaluation?

HCHO was also included in the test evaluations, but its inclusion did not significantly affect the SO<sub>2</sub> results.

p.5724, line 27: "molecule" should be "molecules".

p.5724, line 28: What do "These figures" indicate?

We changed "molecules" to "molecule". The expression "These figures" was substituted by "Concentrations".

Section 3.2: While the test measurements were made for a long time period from December 2009 to March 2011 (as mentioned in section 3.1), why does the section 3.2 focus on only two days of 29 March 2011 and 1 December 2009?

We concentrated our effort to validate the method proposed in the present manuscript in the period February-March 2011, and we consider of interest to use some data acquired in a previous period (December 2009). In the revised manuscript we correct the ambiguous statement of Sect. 3.1.

p.5725, line 8: It may be better to delete a comma just after "SCD".

We delete the comma just after SCD.

p.5725, line 19: Why does S(SO<sub>2</sub>) decrease?

A reason for the decrease of S(SO<sub>2</sub>) is the widening of the plume cross-section. But this does not imply a Flux decrease since the flux also depends on the wind speed.

p.5726, line 15 and 16: "Figure" should be "Figures". "shows" should be "show".

We delete the "s" in "Figures" and "shows".

p.5726, line 15-19: How much is the estimate of NO<sub>2</sub> formation rate for the case of 1 December 2009? What about its comparison with the estimate for 29 March 2011? Can the difference be explained by different conditions (e.g., season) between the two cases?

The data acquired on December 2009 shows the same behaviour, i.e. an increasing NO<sub>2</sub>/SO<sub>2</sub> ratio along a horizontal cross scans, as expected. But we do not have any internal information on the working regimes of the refinery, so we can not quantitatively compare the estimate of March 2011 with that of December 2009.