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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tula industrial complex (Mexico) emissions of SO_2 and NO_2 during the MCMA 2006 field campaign using a Mini-DOAS system" *by* C. Rivera et al.

M. Melamed

megan.melamed@gmail.com

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Measurements of NO2 and SO2 emissions from the Tula industrial complex are critical in order to understand urban air pollution in MCMA. In this paper, the authors present a very important step towards determining emissions from the Tula industrial complex.

However, the paper fails to address a very critical step when using DOAS measurements to calculate emission fluxes, converting the measured differential slant column densities to vertical column densities using an air mass factor. This missing step may be one of the sources for the large variability of the emission fluxes and should be investigated.

First, in the Methods section on page 5157 between lines 18-26, the authors present the retrieval method used in "obtaining the total column of the gases of interest." By definition, the retrieval process described in this paper does not result in the total column of the gas of interest. Instead, the retrieval process results in the differential slant column density between the "clean-air" reference spectrum and the measured spectrum. Therefore, the authors should be clearer about their measurements and state they are measuring a differential slant column density instead of a total column density. If the authors are indeed measuring the total column density, then the method section needs to describe how this is achieved. The authors should also include other absorbers and atmospheric effects in the wavelength regions of their analysis such as O4 and the Ring effect.

Second, emission fluxes should be calculated using the vertical column density and not the differential slant column density. The vertical column density is calculated by applying an air mass factor to the retrieved differential slant column densities. The air mass factor changes due to increases (or decreases) in the optical path length of the photons due to changes in the solar zenith angle and/or multiple scattering within a cloud or by aerosols. The authors stated that for much of the measurement time period clouds where present, which will have a large affect on the retrieved SO2 and NO2 differential slant column densities. There is also likely to be large changes in the solar zenith angle from transect to transect. Nowhere in the article do the authors discuss the air mass factor nor the error associated with not accounting for an air mass factor on the emission fluxes. The influence of changes in the solar zenith angle to the air mass factor can be minimized depending on the reference spectrum used in the retrievals. Therefore, the authors should define when the "clean-air" reference spectrum was taken, why this particular reference spectrum was chosen and if the same reference spectrum was used for all the days.

The DOAS method is an extremely useful tool for studying air pollution and calculating emission fluxes. However, DOAS measurements must be properly interpreted and the

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limits of the measurement technique discussed. I encourage the authors to include a section on determining an air mass factor for their measurements and to apply the air mass factor to their emission calculations.

Some papers that have addressed this issue:

Platt, U. et al. Corrections for zenith scattered light DOAS, GRL 1997, 24, 14

Wagner, T. et al. Cloudy sky optical paths as derived from differential optical absorption spectroscopy observations. JGR 1998, 103, D19

Marquard, L.C. et al. Improved air mass factor concepts for scattered radiation differential optical absorption spectroscopy of atmospheric species. JGR 2000, 105, D1

Wang. P. et al. Measurements of tropospheric NO2 with an airborne multi-axis DOAS instrument. ACP. 2005, 5

Heckel, A. et al. MAX-DOAS measurements of formaldehyde in the Po-Valley. ACP 2005, 5

Wang, P. et al. Airborne multi-axis DOAS measurements of tropospheric SO2 plumes in the Po-Valley, Italy. ACP 2006, 6

Melamed, M.L. et al. Sulfur dioxide emission flux measurements from point sources using airborne near ultraviolet spectroscopy from aircraft. JRG 2008, 113

Fraser A. et al. Intercomparison of UV-visible measurements of ozone and NO2 during the Canadian Arctic ACE validation campaigns: 2004-2006. ACP 2008, 8

Additional Comments.

Page 5155, lines 23-24: If high SO2 concentrations are detected in the northern part of MCMA during night time, then perhaps emissions are higher during the night time from the Tula complex. Since zenith sky DOAS measurements cannot be taken at night, could the DOAS yearly emissions presented in this article be biased low?

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Page 5156, lines 15-16: The term “vertical columns” is used here but the rest of the text uses total column. Please be specific about what column density you are actually reporting and be consistent.

Page 5158, lines 7-8: The total column is defined as the average concentration of the species times the length of the path. DOAS measurements are NOT concentration measurements. They are density measurements.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5153, 2009.