

Response to reviewer

Anonymous Referee #1:

This paper discusses the interferences observed in measurements of nitrogen dioxide (NO₂) by different instruments. A number of data sets taken over many different years and field projects are used to demonstrate both positive and negative interferences in NO₂ data under mostly polluted conditions, some extremely so. The discussion revisits some well-known problems with NO₂ measurements by the luminol and photolysis-chemiluminescence (P-CL) techniques and presents data on a previously unreported problem with the latter method. The paper is generally well-written with ample supporting literature cited and the figures are clear and to the point. However, I feel that the authors dwell too much on previously described interferences and not enough on what is new. I have the following recommendations: First, delete the entire discussion of the Santiago study, as well as Figure 1 and the description of the Mo-CLD instrument. This has been discussed sufficiently in the literature.

Second, show the smog chamber correlation plots of [NO]+[glyoxal] vs [NO₂] via FTIR, which are important to the proposed P-CL interference mechanism. Finally, verify the proposed mechanism of the negative interference in the P-CL system with box modeling of the chemistry in the photolytic cells (both ECO and Ansyco). While the proposed explanation for this problem is plausible, box model results using data from the smog chamber study would provide a solid and quantitative understanding, and perhaps could provide information concerning the atmospheric levels when this would be a problem for given P-CL instrument conditions (e.g., wavelength(s) of lamp sources; cell residence times).

With the support from the modeling results and the other two changes, I can recommend that this paper be published in AMT.

Response:

We would like to thank reviewer #1 for his interest and the comments to our paper. Reviewer #1 mainly raised two issues, i.e. a) to delete the section on the well known NO_y interferences of molybdenum chemiluminescence instruments and b) to add a model description of the negative interference from the photolytic converter instruments:

To point a):

We completely agree with the reviewer, that the interference of NO_y species for the catalytic conversion of NO₂ on heated metal converters is a generally well-known problem in atmospheric science. Our intention to show the results from this type of instrument from Santiago as another example was twofold:

First of all, we found that the data shown for the average campaign data (not any exceptional outliers) is really impressive, which is to our knowledge the highest relative overestimation published. In the afternoon, the campaign averaged overestimation by the NO_y interferences can account for up to a factor of four (see Figure 1), whereas the maximum overestimation for single days of only a factor of two was observed recently in Mexico City (Dunlea et al., 2007; e.g. see page 2694, bottom of left column). Since Mexico City is already a quite photochemical active and polluted environment, our data may show the upper limit overestimation by the NO_y interference in the atmosphere. Also the correlation with O₃ was higher compared to the study by Dunlea et al., clearly confirming a photochemical origin of most interfering species.

The second reason to show this example was the general topic of the manuscript (see title), which should show that all chemiluminescence instruments typically used in network stations, but also in science, do not work properly under certain conditions. Since metal converters are still most common, we also wanted to add one example for this technique. In addition, as yet only briefly mention for the kerbside intercomparison (see section 3.2), we found it very

interesting, that for certain conditions (close to emission sources) metal converter instruments can be even more accurate compared to photolytic converter instruments, which users of these instruments would not have expected (see section 4 for discussion). They would have interpreted the higher levels of metal converter instruments by their well-known positive interferences, however under these conditions, the negative interferences in the photolytic converters is of higher importance. Thus, we found that adding also metal converter instruments to the results may be of interest for the reader. According also to the comments by reviewer #2 we would like to extend the manuscript by explaining in more detail the intercomparisons at the kerbside station to give more information on the atmospheric conditions under which the two main different interferences are of importance, and to show that the negative interferences can be also a problem in the open atmosphere and not only in smog chamber or tunnel studies. This data would again include a metal converter instrument. And finally, since metal converters are still used in most network stations, we feel that their interferences cannot often enough be mentioned, unless these instruments are not anymore used and recommended, e.g. by the EPA or EU legislation.

To point b):

We generally also agree to this point and we will add a correlation plot of the negative interferences against $[\text{glyoxal}] \times [\text{NO}]$ for both instruments from the smog chamber experiments to support our explanation of the interferences.

However, box model calculations of the photochemistry in the photolytic cells are out of the scope of the present study by several reasons:

- 1) To model the photochemistry in the photolytic converters the spectral resolved actinic flux inside the converters has to be known. However, this is experimentally difficult, especially for the very small blue-light converter glass cell, which is inside a light scattering block and which has only 4 mm inlets. To our knowledge no such small 2π light collecting device is available, that could be connected to a spectroradiometer to measure the actinic flux inside this cell. It is not only glyoxal that will form radicals inside the cell, but especially for the Xenon lamp converter, many other species, for which their photolysis frequencies have to be known to model the primary radical formation, which is of interest here. To calculate photolysis frequencies, the spectral resolved actinic flux has to be known.
- 2) Even if one could describe the negative interferences only caused by glyoxal in the smog chamber experiment by a box model, extrapolation to real interferences in the open atmosphere or in complex photo smog mixtures is impossible, since not only glyoxal will cause problems, but all species which form radicals in photolytic converters. As shown in the smog chamber experiment, not only direct radical sources are of importance (here generally much more species than only glyoxal have to be considered), but also secondary RO_2 sources caused by the OH initiated degradation of any VOCs in the cell (OH formed by the primary sources, see text and see Figure 3: addition of n-butane and alpha-pinene). Thus, even box model studies for only glyoxal would not provide information on the range of pollution levels, under which these interferences are a general problem in the atmosphere. Only intercomparison studies under many different atmospheric conditions will give robust information on the limits of these instruments. According also to referee #2 we will thus extend the manuscript by another intercomparison study under less polluted conditions to show that these negative interferences can already be a problem under urban conditions in the open atmosphere and not only in tunnel and smog chamber studies.
- 3) Our paper is about an experimental study and should simply show that instruments using photolytic converters (especially Xenon lamp converters) show strong negative interferences under polluted conditions. Thus, the main conclusion from this study is simply not to use these instruments under the conditions we mentioned in the manuscript (kerbside/tunnel/smog chamber), but more selective instruments. Any box model

calculations cannot help here, caused by the unknown, variable complexity of the atmosphere and the even more complex photochemistry in the photolytic converters. Should any data point of such instruments be corrected by a full MCM model run, including the measurements of all VOC species? Besides this unreasonable effort, not all VOC species are explicitly included in the chemical degradation scheme even of the most explicit MCM. In addition, typically only half of the VOCs of the atmosphere are measured in field campaigns (see reactivity measurements) and typically especially not those are measured (oxygenated), which are of interest here. And finally, you typically get the VOC data with much lower time resolution compared to a NO_x monitor. Thus, any correction of data from these instruments by model studies is impossible.

- 4) Such a model study would cover a significant fraction of a PhD thesis and since we have no modeller at the moment in our group, this would be completely out of the scope of this experimental study.

In conclusion, although it might be of scientific interest to describe quantitatively the negative interference from glyoxal in the smog chamber by box model calculations, this will not help to improve the quality of the data of photolytic converter instruments under polluted conditions and thus would not justify the effort necessary for such a theoretical study.