Response to reviewer

Anonymous Referee #2:

Authors describe both positive and negative interferences of commercial NO_2 instrument in highly polluted conditions (tunnels and smog chambers). The first section of the manuscript dealing with the problems with chemiluminescence instruments with molybdenum NO_2 converters does not represent a new contribution to scientific progress. Problems with molybdenum converters have been known for over 40 years. Similarly, the detailed discussions of problems with Luminol NO_2 instrument is equally irrelevant as this technique has not be used by atmospheric scientists for many years given the numerous well understood interferences with this NO_2 measurement technique.

The only "new" results presented in the manuscript relate to the performance of the 3 instruments: NO_2-LOPAP, chemiluminescence-blue light converter (CL-BLC), and FTIR in a smog chamber. Specifically, the new finding is an interesting hypothesis on why a single channel NO/NOx CL-BLC would under predict calculated NO_2 in highly to extremely polluted conditions. These conditions require high the photolysis of glyoxal leading to the production of HO_2 and OH, which can directly (or indirectly via OH reactions with alkanes and alkenes) convert NO to NO_2 in the BLC chamber.

While this is an interesting phenomenon, I disagree with the authors that this potential artifact has any significant importance in the "real" world outside of tunnels and smog chambers. Atmospheric measurements with CL-BLC and one of the selective spectroscopic techniques (DOAS, LIF, CRDS, etc) showing real-world importance of this HO_2/RO_2 NO_2 artifact would be a substantial scientific finding. Without having to resort to a new study, a agree with reviewer #1 that box model calculations of this NO_2 artifact using real-world levels (from published rural and urban studies) of NO, NO_2, O_3, glyoxal, alkanes, alkenes, etc would help prove the potential significance of this artifact.

Response:

We also would like to thank reviewer #2 for his interest and the comments to our paper. Reviewer #2 mainly raised the same two issues than reviewer #1, i.e. a) to delete the section on the well known NO_y interferences of molybdenum chemiluminescence instruments and of the Luminol technique and b) to add a model description of the negative interference under conditions of the real atmosphere. In addition, reviewer #2 doubts whether the negative interferences are of importance for the “real” atmosphere.

Thus, we will only shortly summarize our answers, which we gave in detail to reviewer #1:

To point a):

Since the relative overestimation caused by NO_y interferences in metal converter instruments was higher compared to all other studies we are aware of (up to a factor of four overestimation for the average two week campaign data), the data from the Santiago de Chile campaign may be of interest for the reader. In addition, we added this section and also the limited Luminol interference discussion caused by the general topic of this manuscript (see title). We wanted to show, that all “standard” chemiluminescence instruments have certain problems under certain conditions and that none of them can be used under all conditions (remote to tunnel conditions). In our opinion, this needs also the presentation at least of some data from of all instruments discussed.

To the luminol technique:

Although we agree with the reviewers comment, that also positive PAN and O_3 interferences have already been documented, these instruments are still often used in field campaigns. In addition, negative interference caused by quenching at high levels of pollutants (e.g. NO)

which can be of importance in laboratory experiments is commonly not known. Thus, another example showing interferences of this technique under photo smog conditions may be still of interest, at least for those readers who are using this technique. In addition, in the manuscript, only a very small section (20 lines in section 3.3) deals with the results from this technique and even less on the problems of this technique ("detailed discussions of problems with Luminol NO_2 instrument"), which is added here caused by the general topic of the manuscript.

To point b):
In contrast to the comment by the reviewer, negative interferences are not only a problem of single channel CL-BLC, but a general problem of these converters (our used "Ansyco blue light", is a dual channel instrument).
As already also pointed out in detail in the answer to reviewer #1 model calculations will not help to quantify real interferences in photolytic converters for measurements in the open atmosphere, since not only glyoxal will cause problems (as suggest by the referee), but all species which form directly or indirectly radicals in photolytic converters. Since all these species are typically unknown and even if measured also not all explicitly included in the chemical degradation scheme even of the most explicit MCM model, the magnitude of these interferences in atmospheric measurements cannot be quantified in a box model. Besides this, the spectral resolved actinic flux inside the different converters is unknown and experimentally not easy assessable. Thus, intercomparison studies in the real atmosphere are recommended.
To show that the negative interferences identified in our study can also be a problem under less polluted conditions in the "real" world and not only in a smog chamber or in a tunnel, we will extent the small section about the intercomparison at a kerbside station in the revised manuscript.
However in contrast to the comment by the reviewer, we never mentioned in our manuscript that this interference is of general importance under all atmospheric conditions but only referred to highly polluted conditions, see e.g.:
Page 4283, line 22: "…will still suffer from negative interferences for high pollution levels.";
Page 4282, bottom: "…are inaccurate for highly polluted conditions such as can prevail in street canyons, tunnels and smog chambers. However, because of the second order reaction kinetics, these negative interferences are not expected to be of significant importance in the less polluted atmosphere").
The photolytic converters work well under remote – urban background conditions, but not for high pollution levels. By adding the new section we hope that the range of conditions, which is of interest here, will be better characterized.