

***Interactive comment on “Validation of urban NO<sub>2</sub> concentrations and their diurnal and seasonal variations observed from space (SCIAMACHY and OMI sensors) using in situ measurements in Israeli cities” by K. F. Boersma et al.***

**K. F. Boersma et al.**

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We thank referee 1 for his/her thorough comments that we address below.

*General Comments: It is not clear what motivated authors to focus just on 8 surface sites from Israel, while there are many stations in North America and Europe. The number of coincident measurements is still very small in contrast to what motivated authors to use surface measurements. I believe that authors would be able to find many measurement sites in developed countries. Why not extend the validation exercise to larger domain if they are looking for a large statistical data set for validation?*

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The focus of our paper is on Israeli cities. Extending to Europe and North America is a logical next step but would be a separate study. We have now included a paragraph in the introduction explaining why we care about air quality in Israel, which motivates this work.

The paragraph reads: Air pollution in Israel is strongly influenced by the country's unique geographical features (the south/east is influenced by large deserts, the north/west by a Mediterranean climate). Most economic activity and half the population are concentrated in the coastal plain, a less than 15 km wide strip of 170 km length (North-South). The small geographical scale, in combination with the high population density and the high emissions lead to substantial air pollution, whose pattern and trends are not easily captured by a few ground monitoring stations. Indeed, since the 1990s, mixed emission trends have been observed for different NO<sub>x</sub> sources. This unique situation calls for development of remote sensing abilities that compensate for the lack of spatial and temporal scales provided by ground monitoring stations. In this study, we are making first steps towards developing such tools for this region.

*Authors rely entirely on the quantification of interference in molybdenum converter analyzer from the field campaign at Mexico City to correct for interference in molybdenum converter measurements at Israeli cities. This raises a number of questions regarding how robust the correction approach is. For example, the field situation at Mexico City can be very different than at Israeli cities. The MCMA field campaign was held in the month of April, and Dunlea et al., 2007 have not explored the interference in other months. The authors first need to investigate if they could apply the correction approach as described by Dunlea et al., 2007 to the measurements at Israeli sites. There are a number of possibilities- (a) Use simultaneous photolytic and molybdenum converter measurements from Europe and North America (and other regions if available) to examine if the correction based on ozone concentration matches with the difference between photolytic and molybdenum converter measurements. (b) The Israeli measurement sites likely provide the measurement of NO, which along with O<sub>3</sub>*

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*could be used to calculate the photostationary steady state NO<sub>2</sub>. That would allow to infer the interference in molybdenum converter measurements. There are other approaches like the one used by Lamsal et al., 2008. Authors must be aware that insufficient/inappropriate correction in the surface measurements would have large impact in the scientific intent of the manuscript.*

We followed the suggestion of the referee and tested the approach published by Dunlea et al. [2007] with the CHIMERE chemistry-transport model over Europe, taking advantage of its high-resolution (0.25 deg lon x 0.125 deg lat). We used simultaneous measurements from photolytic and molybdenum converters in the CHIMERE domain for Taenikon to evaluate the model simulations. The simulations show that in urban areas with NO<sub>2</sub> concentrations similar to those observed in Israeli cities (0-25 ppb), the NO<sub>2</sub>:NO<sub>x</sub> ratio at 14:00 exceeds 0.92 for all seasons. For January, April, July, and October, NO<sub>2</sub>:NO<sub>x</sub> ratios were [0.98, 0.96, 0.92, 0.97], and correction factors derived from CHIMERE with the Dunlea-approach are similar and small anyway ([0.99, 0.98, 0.95, 0.98]). NO<sub>2</sub>:NO<sub>x</sub> ratios for rural areas simulated with CHIMERE are lower (as expected) and for the grid cell of Taenikon consistent with observed correction factors over Taenikon (CHIMERE: [0.89, 0.55, 0.44, 0.75], observations: [0.85, 0.54, 0.50, 0.80]). We now include this discussion in the first paragraph of section 3. Detailed visualizations of the CHIMERE results can be found at [www.knmi.nl/boersma/publications/papers/interference.pdf](http://www.knmi.nl/boersma/publications/papers/interference.pdf).

*In situ molybdenum converter measurements have been used to validate tropospheric NO<sub>2</sub> columns from GOME (Ordonnez et al., 2006 and Schaub et al., 2006) that has similar overpass time to SCIAMACHY. They report interference in the range of 20-50% with smallest interference in winter and largest in summer. This is in contrast with the present study saying the lack of interference for morning interference (during SCIAMACHY overpass time) following Dunlea et al., 2007. This further suggests that the authors should consider reviewing their correction approach.*

The 20-50% interference correction mentioned by the reviewer has been observed for

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Taenikon, in a rural area with low NO<sub>2</sub>:NO<sub>x</sub> ratios. These observed corrections are not representative for stations in urban areas, where most NO<sub>y</sub> is NO<sub>2</sub>. This is confirmed by Dunlea et al. [2007] who observe very little interference during morning hours in Mexico City in spring, and further supported by CHIMERE simulations that indicate that the bulk (>97%) of NO<sub>y</sub> is NO<sub>2</sub> at 10:00 hrs within urban areas in all seasons. Because both observations and simulations indicate that interference is negligible in urban areas during mid-morning, we refrain from applying a correction for interference for urban station measurements at 10:00. We have included a statement in section 2.3 that CHIMERE simulations further support the assumption that interference is negligible in urban areas in mid-morning.

*Authors assume vertical uniformity in the boundary layer and negligible concentrations above the boundary layer. It appears to me that the latter motivated the authors to compare tropospheric NO<sub>2</sub> columns with BL columns. As a reader I would be interested to know what fraction of tropospheric column is in the boundary layer (and in the free troposphere). Can columns above boundary layer be really neglected? If that is the case it would then be logical to compare tropospheric and boundary layer columns. Moreover, assumed constant profile shape within the boundary layer could yield different conclusions. The manuscript would benefit from some sensitivity studies using the GEOS-Chem model, which they have used to understand diurnal and seasonal variation of NO<sub>2</sub> columns, to examine the effect of these assumptions.*

We followed the suggestions by the reviewer and performed sensitivity studies using GEOS-Chem. The above- boundary layer columns in GEOS-Chem over Israel range from  $0.1 \times 10^{15}$  molecules cm<sup>-2</sup> in winter months to  $0.4 \times 10^{15}$  molecules cm<sup>-2</sup> in summer, presumably from the stronger lightning NO<sub>x</sub> source in that season. For the urban regions studied here, this implies on average a <8% free tropospheric fraction in Summer and >2% free tropospheric fraction in Winter, small enough to be neglected. If we account for GEOS-Chem free tropospheric columns in our validation study, the correlation and slope remain unchanged, and the intercept decreases slightly: from  $-0.4 \times 10^{15}$

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molecules  $\text{cm}^{-2}$  to  $-0.7 \times 10^{15}$  molecules  $\text{cm}^{-2}$ . We also evaluated our assumption of vertical uniformity in the boundary layer by comparing BL columns assuming constant mixing ratios throughout the boundary layer, to the BL columns we obtained thusfar (these assumed vertical uniformity following the well-mixed GEOS-Chem boundary layer that also accounts for the decrease of  $\text{NO}_2/\text{NO}$  ratio with temperature). We find identical agreement ( $r=0.64$ ) between the BL columns and OMI observations, but assuming constant mixing ratios gives a slightly lower intercept and slope ( $y=-0.39 \times 10^{15}$  molecules  $\text{cm}^{-2} + 0.81x$ ). We have updated the third and fourth paragraphs of section 3 accordingly.

*Specific Comments: Title: Suggest removing "(SCIAMACHY and OMI sensors)" from the title and put the information in abstract. Alternatively, remove "space" and make "from the SCIAMACHY and OMI satellite instruments". Make "in situ surface measurements" instead of "in situ measurements".*

Done.

*Page 4304, line 28: Please include Winer et al., 1974 and Grosjean and Harrison, 1985 in the citation.*

Done.

*Page 4307, line 15: What is the detection limit of the instrument (molybdenum converter)? Would the instrument be able to detect in the ppt level? Some measurement sites cap the lower limit to 1 ppb whereas  $\text{NO}_2$  mixing ratio in summer could be lower than 1 ppb.*

The lower detectable limit of the  $\text{NO}_x$  analyzers is 0.4 ppb (60 second averaging time). This has been added to Section 2.

*Page 4308, line 8: What is the coincidence criteria that you generally apply? Your statement in Page 4309, line 2 implies that the coincidence criteria is different than 0.1 deg. How would your result change if you consider only the observations with surface*

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*sites located within OMI/SCIAMACHY pixels? Do you include all OMI/SCIAMACHY pixels? Did you examine how your results would change if exclude the OMI pixels at larger viewing angles? What are your criteria for cloud?*

As stated in the caption of Table 1 and Figure 2, OMI pixels with a pixel center within 0.1 deg latitude/longitude of the station have been selected. For the larger SCIAMACHY pixels, we used coincidence criteria of  $\pm 0.25$  deg (mentioned in the caption of Table 2 and Figure 2). Our statement on Page 4309, line 2, describes how results change for SCIAMACHY if we choose a tighter coincidence criterion. We included all SCIAMACHY and OMI pixels provided they had cloud radiance fractions  $< 50\%$  (consistent with cloud fractions of approximately  $< 20\%$ ), and were not measured during a Solar eclipse (as on 20 March 2006). We chose to exclude pixels with viewing zenith angles  $> 35$  deg, because (1) these have much larger footprints, complicating the representativeness of the comparison between surface data and satellite spatial mean, and (2) these have a higher probability of being measured during the previous ( 12:05 local time) or next ( 15:05 local time) orbit.

*Page 4308, line 18: Would the correction of in situ measurements lead to increased correlation?*

The correlation between surface NO<sub>2</sub> and OMI tropospheric NO<sub>2</sub> is similar whether or not correcting for interference, with the uncorrected case doing slightly better.

*Page 4308, line 20: Annual average of 8% seems too small based on earlier studies. Relative contribution of other reactive nitrogen species is expected to be higher in summer leading to higher interference in summer. How do the corrected surface concentrations change with season versus uncorrected concentrations?*

*Page 4308, line 22: The number reported here (0.7 ppb) may be weighted by winter concentrations. It will be useful to provide the range of values classified by month or season.*

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That our interference is smaller than previously published is because our study focuses on stations in urban environments, where fresh NO<sub>x</sub> constitutes the largest contribution to NO<sub>y</sub>. The earlier studies the reviewer refers to focused on the rural sites of Taenikon and Rigi, where NO<sub>y</sub> is for a large part photochemically aged NO<sub>x</sub> from sources up-stream. Here we are right in the NO<sub>x</sub> source area. Corrected seasonally averaged NO<sub>2</sub> concentrations in Israeli cities (on days that OMI sampled a cloud-free scene) are [8.4, 7.2, 5.7, 8.0] ppb for DJF, MAM, JJA, SON. The uncorrected values are [9.2, 6.6, 6.1, 7.2] ppb. This corresponds to correction factors of [0.91, 0.91, 0.95, 0.90], comparable to what we infer with CHIMERE using NO<sub>2</sub>/NO<sub>z</sub> ratios for urban areas ([0.98, 0.96, 0.92, 0.97]).

*Page 4309, line 13-14: BL NO<sub>2</sub> column is surface concentration multiplied by boundary layer height. Would you expect to have different correlation between BL columns and tropospheric NO<sub>2</sub> columns versus surface concentrations and tropospheric NO<sub>2</sub> columns?*

Yes. When taking into account the seasonal variability in BL depth, we obtain a slightly improved correlation between the constructed BL columns and OMI ( $r=0.64$ ), than if we would take into account the surface concentrations and a constant BL depth ( $r=0.60$ ).

*Page 4309, line 26: Apparently there is no grey dashed line in Figure 3.*

Corrected. It should have been the dashed-dotted line.

*Page 4310, line 6: Would not this seasonal variation caused by the change in NO<sub>x</sub> emissions?*

This seems unlikely as most NO<sub>x</sub> sources are known to be rather constant throughout the year. For instance, NO<sub>x</sub> emissions from mobile sources contribute more than 60

*Page 4316, line 5-13: Make 2008a and 2008b for the references of Boersma et al*

Done.

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*There are few references in the list which are not cited in the text.*

Corrected.

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**ACPD**

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