Atmos. Chem. Phys. Discuss., 9, S142–S149, 2009
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Spatial variation of modelled and measured NO, NO_2 and O_3 concentrations in the polluted urban landscape – relation to meteorology during the Göte-2005 campaign" *by* J. Klingberg et al.

Anonymous Referee #2

Received and published: 5 February 2009

1. General comments

The manuscipt shows measurements and model results for NO, NO_2 and O_3 in a high-latitude urban environment during winter. The results are interesting, but there are also some major problems. I am reluctant to recommend publication unless the problems can be resolved.

The main problem is that the measurement techniques are not documented. Most of the measurements appear to be based on a technique that has never been described

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in peer-reviewed literature and is not described here. A more thorough description of the technique and results of the measurement intercomparison are needed to establish the viability of this approach.

In addition, there are many places where more detailed information about either methods or results are needed. The manuscript frequently makes claims that are supported by limited results, when there is data available do do a more meaningful evaluation. In some cases this involves repeating the analysis using 'continuous' measurements rather than passive samplers, which only provide 5-day average values. In other cases the results raise questions that can be answered by expanding the current analysis.

The specific comments below include many requests for an expanded analysis. I hope the authors will be able to do this. At a minimum, they need to establish the validity of the measurement technique, or else re-focus the paper to use the more reliable 'continuous' measurements.

2. Specific comments

1. The bulk of the study appears to rely on measurements of NO, NO_2 and O_3 that were performed using passive diffusion samplers of the IVL type (p. 2086). The only reference for this measurement technique is a conference paper. This is unsatisfactory, both because the method has not been published in a peer-reviewed journal and because the information is generally not available to readers.

If this technique has never been described in the scientific literature, then the authors need to provide a complete description and evaluation of the technique. This paper might provide an opportunity to do this, but much more information would be needed.

2. From the description on p. 2086 (line 17) and 2095 (line 25) it appears that the measured NO, NO_2 and O_3 all represent 5-day averages. The results shown in Figures 5 and 7 also appear to represent 5-day average values. This is a problem because NO, NO_2 and O_3 are routinely measured for much shorter time intervals. The species also

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show strong diurnal cycles. I am not sure whether publication based solely on 5-day average measurements can be justified.

At a minimum, the text needs to clarify when the measurements represent 5-day averages and when they represent shorter time intervals (and what the shorter intervals are). Only Figure 4 appears to be based on the shorter intervals. The use of 5-day average data should also be stated more clearly on p. 2086.

The paper would have much greater validity if the important results were also shown based on the 'continuous' measurements (apparently available at three sites) rather than just the 5-day average data. This should include the equivalent to Figures 5 and 7 using continuous measurements. (The continuous measurements actually represent measurements with a short time interval, e.g. 10 s. The time interval should be stated.)

3. The text refers to NO, NO_2 and NO_x measured using various equipment types (p. 2087). No references are given. The O_3 measurement (UV absorbtion) is standard enough that a reference is not needed, but the other measurements are not routine and a reference should be given.

4. The text (p. 2087, line 26 and after) describes a test of the passive diffusion samplers by comparison with the instruments at Femman (presumably those described on p. 2087, line 8). The text goes on to state that the average deviation of the NO, NO_2 and O_3 samplers was 25 %, 5 % and 1 % respecively. This is critical information and should be presented in much greater detail.

Does this refer to a comparison between 5-day average measurements and the 5-day average from measurements at more frequent time intervals (referred to in the text as 'continuous')? If so, what is the range of continuous measured values in comparison to the 5-day averages?

A 25 % average deviation is poor performance for two instruments in the same location. Does the comparison also show a difference in the average value over the period, sug-

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gesting that one instrument may be biased high or low? Does the comparison suggest any systematic errors associated with high or low NO, or with the gradient between high and low NO? It would also be useful to show scatter plots for the intercomparison.

5. The model description (p. 2088-2089) does not give the boundary concentrations for NO, NO_2 and O_3. This is critical information because the model value for O_x (=O_3 + NO_2) is determined largely by the boundary conditions.

The text says that the hourly NO_2 and O_3 at the Femman site were used as urban background values. Does this mean that the measured values at Femman were used as boundary conditions? If this is the case, then the model application is very limited. The model would only be useful for identifying the effect of local emission and dynamics over the 1 km distance that separates Femman from the other sites. If this is correct, it needs to be stated clearly. However the model domain (p. 2088, line 15) is much larger than 1 km and the Femman measurements would not be appropriate as boundary conditions.

The model description also does not give dry deposition velocities. Instead, the text refers to Hurley et al., 2005 for more details. Hurley et al refer to Harley et al., 1993, who refer to a report to the U.S. EPA from 1986. The text should provide some information on this. For example, the text could give the daytime and nighttime deposition velocities for the urban land use type that is most relevant to the study (since deposition velocities are varied by land use type).

Lastly, the text should state how the photolysis rate for NO_2 is derived. Calculation of photolysis rates requires some assumption about cloud cover, or else it should be based on measured surface radiation. In either case a description is needed.

6. The model chemistry (reported by Hurley et al., 2005) is probably adequate for this study, but only because there is relatively little photochemical production and loss within the urban center in winter. The chemistry is probably dominated by photolysis of NO_2 to form NO and O_3 and the reaction of NO with O_3 to form NO_2. Even for this

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limited case it is worrisome that the model does not include formation of HNO_3, which occurs on a time scale of 3-12 hours. This is likely to compete with dispersion as a removal process for NO_x. The text should include a caveat about this.

For any photochemically active situation there would be major worries: ambient VOC (represented by R_{smog}) is held constant throughout the domain (despite the wide variation in NO_x); decomposition of PAN is omitted, etc.

7. The most important finding (discussed in the context of Table 3, p. 2090-2091 and also on p. 2094) is that NO (and to a lesser extent NO_2) show large variations from site to site over short distances within the urban area. This is only shown based on 5-day and 3-week averages. This could be demonstrated more effectively by showing a time-matched correlation between sites (e.g. NO-Femman versus NO-Garda) using the continuous measurements.

8. Figure 5 is the basis for model evaluation. This seems to be based on 5-day average values for NO, NO_2 and O_3, based on the number of data points. However, there are also continuous measurements at three sites, since data on short time scales appears in Figure 4. If the authors want to make model evaluation a major part of the paper, they should show model-measurement comparisons for these continuous measurements (including scatter plots equivalent to Figure 5 but for shorter time intervals, such as 1-hour averages).

9. There are various problems associated with Figure 7. First, the plot shows individual data points in addition to the lines. These data points are not explained, but it appears as though they may represent 5-day averages.

If the data points do represent 5-day averages, then what do the wind speeds represent? Wind speeds vary greatly over 5 days, and correlations between 5-day averages may not have much meaning. The lines in the figure appear to represent fits to just three data points each. This also involves significant uncertainty.

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If the data in Figure 7 represent 5-day average measurements, then the paper should also show equivalent results for continuous measurements. These should be based on binned data for wind speed intervals (as was done for the model in Figure 8) and include average and standard deviations for each interval. (The result could be compared to the results from both the 5-day instruments and to the model.)

10. Also with regard to Figure 7: some additional results would help to identify the cause of the observed trend in the NO_2 ratio versus wind speed.

The text (p. 2093, line 3, 2096, line 15, p. 2097, line 15) attributes the pattern to enhanced dispersion of NO_x at the less polluted sites and enhanced downmixing of O_3 at the more polluted sites. This hypothesis can be tested easily by showing equivalent results for measured NO_x and O_x versus wind speed.

If the authors are correct, then the NO_x ratio will decrease versus wind speed at all sites andthe O_x ratio will increase versus wind speed at all sites. This would explain the behavior of NO_2, which is constrained by available NO_x when $NO_x < O_x$ and is constrained by O_x when $O_x<NO_x$.

11. The text (p. 2092, line 14) states that the passive sampler detection limit for NO is higher compared to NO_2 and O_3, which could be an explanation for the large intercept of the r egression line between observed and model NO.

This explanation seems unlikely. Figure 5d shows that the large intercept is associated with a large number of measurements of NO between 10 and 20 nmol $mol^{-}1$, corresponding to model NO that is lower by a factor of 2 or more. The detection limit for NO can only be a source of error if it is 10 nmol $mol^{-}1$ or higher.

Regardless, the description of measurements should give the detection limits.

12. The model-measurement comparisons for NO_2 and O_3 in Figure 5 show correlations with slopes of 0.68 and 0.73 respectively. This suggests a tendency to overestimate NO_2 for conditions with high NO_2 and to overestimate O_3 for conditions with high

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O_3.

The situation could be made clearer if results were also shown for O_x. Because O_3 and NO_2 anticorrelate, it is possible that the slope for O_x will be close to 1. O_x in the model is controlled primarily by the dry deposition rate and concentrations at the model boundary. By contrast, the NO_2/O_3 ratio is controlled by total NO_x and the NO_2 photolysis rate. If results for O_x were shown, it might be easier to identify reasons for the difference between model and measured values.

13. The text (p. 2093, line 11) states that a similar pattern was found for model values (Figure 8) and for measurements (Figure 7) of NO_2 concentration ratios versus wind speed. However, it appears that Figure 7 and 8 show contradictory patterns. The measurements only show results for wind speeds between 3.5 and 6 m/s. For this range the model shows the NO_2 ratio decreasing with increasing wind speed at the most polluted site (#4) wheras the measurements show an increase with wind speed. The measurements show a decrease with wind speed at the least polluted site (#7) whereas the model shows no change with wind speed. The text should point out these differences.

14. The text (p. 2092) states that the model results (Figure 6) satisfactorily reproduce the observed diurnal cycle for NO, NO_2 and O_3. The model diurnal cycle for NO and NO_2 is in fact comparable in both magnitude and pattern to the measured diurnal cycle for Garda, shown in Figure 4. However the model results are shown for site #6 rather than for Garda. Since a direct comparison with measurements is available at Garda, model results for this site should be shown.

15. The following are optional suggestions for information that would be useful to provide.

How does O_x vary at urban sites? The text states that O_x is lower at the rural site than at the most polluted site (p. 2091, line 22). If results were given for the urban sites it would help to identify the reason for the variation. (For example: O_x might be higher at

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the urban sites due to increased vertical mixing, or O_x might increase with NO_x due to the effect of emitted NO_2.)

What is the diurnal variation of O_x? I expect that O_x decreases gradually through the night due to surface deposition. This is important as a basis for explaining the cause of high NO_2 (see next paragraph).

The text mentions instances of high NO_2. Are these associated with meteorological conditions and/or time of day? I expect that these occur in early evening, coinciding with both high NO_x and high O_x (since NO_2 is constrained by both NO_x and O_x).

3. Technical corrections

p. 2092, line 20: TAMP = TAPM.

Figure 1 caption should state that the sites numbers are identified in Table 1.

The labels in Figure 5d read " Observed O_3" and "Model O_3". It probably should be "NO".

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 2081, 2009.