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Atmospheric
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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.

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We would like to start this statement by clarifying that the manuscript was suggested to be a contribution to a special issue for an air pollution measurement campaign conducted in Gothenburg city in 2005 (Göte-2005). In the discussion within the group of scientists around the measurement campaign it was decided that our contribution, in addition to an analysis of the spatial variation in pollution (based on measurements and modelling) in a part of the city with heavy traffic, should contain basic information covering the meteorological and pollution conditions during the campaign. This has obviously not been considered in the review process (and it is of course up to the Journal

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to decide if such basic information is to be included in a special issue). A substantial part of our study is based on the measurements using passive diffusion samplers. It is then somewhat surprising that ACP appointed two reviewers, who are obviously not familiar with that technique, its constraints and opportunities. Since the manuscript has already been rejected by the editors of ACP, we focus this reply on general responses to the reviewers' comments, rather than on detailed descriptions of all changes that could have been undertaken, provided that the manuscript would have been considered for publication.

Material and methods

The reviewers raised a large number of questions related to the measurement technique, especially requesting a more detailed description and evaluation of the passive diffusion samplers. The reviewers also asked for detection limits and more information on the hourly NO_x and O_3 measurements at the permanent monitoring sites.

Passive diffusion sampling is a well established technique used in Sweden (Svanberg et al., 1998; Ferm and Svanberg, 1998), UK (Stevenson et al., 2001), Canada (Gilbert et al., 2003) and many other parts of the world (Carmichael et al., 2003; Ayers et al., 1998; Ferm and Rodhe, 1997). Several studies have described and evaluated the passive diffusion sampling technique in detail e.g. (Ferm and Svanberg, 1998; Ferm, 2001; Vardoulakis et al., 2009; Yu et al., 2008). In passive diffusion sampling, the pollutant is transported by molecular diffusion to a sorbent. The time-integrated average ambient concentration of the pollutant is calculated using Fick's first law of diffusion after analysing the sorbent (in this case at the IVL accredited laboratory). According to the IVL accredited laboratory the detection limit for sampling times of five days with passive samplers is $<$6.5 ppb for NO, $<$0.29 ppb for NO_2 and $<$3.3 ppb for O_3at 0˚C. For NO_2 comparisons performed under normal monitoring conditions in both urban and background sites showed that the passive samplers were within 15% of active techniques (Ferm and Svanberg, 1998). In our study duplicates were always used of which an average was calculated. Passive samplers have many advantages since they are small, light, cost-efficient, soundless and do not require electricity. The drawback is of course the limited time resolution. The aim of our study was to increase the spatial resolution of measurements through complementing the permanent monitoring stations and evaluate monitoring site locations accordingly. For this purpose passive diffusion samplers are ideal since it would be nearly impossible to use active measurement methods at the sites closest to the traffic route (see also Fig.1), and in the numbers required to cover the local scale variability.

The focus of our study was not to evaluate the passive diffusion sampling technique. However, here follows some additional details on the comparison between the passive diffusion samplers and the hourly measurements at Femman for NO_2, which is the regulated pollutant of most concern in urban areas such as Gothenburg. The 5-day averages received from the passive samplers are compared to the corresponding 5-day averages calculated from the hourly data measured with chemiluminescence at Femman. We also added 3 data points (7-day averages) from measurements at the same site in August 2007. There was very good agreement between the two measurement techniques. The equation of the regression line was *passive samplers* = 1.2 * *instrument* -2.5 and the variation around the 1:1 line was very small with a R^2 value of 0.91.

An evaluation the O_3 passive diffusion samplers showed that the passive samplers had very good accuracy compared to a continuously measuring UV-absorption instrument. The equation of the regression line was *passive samplers* = 1.0* *instrument* -0.6 and the variation around the 1:1 line was very small with a R^2 value of 0.97.

The NO measurements with passive samplers are more problematic than NO_2 and O_3. The detection limit is $<$6.5 ppb for passive samplers for a five day exposure period at 0°C. The comparison with the traditional instrument suggested that the NO samplers show a too high value at low ambient concentrations. As referee #2 points out this does not have to be caused only by a higher detection limit for NO but could also be due to chemical interference of some kind. More research is needed to improve the understanding of this problem.

NO and NO_2 at Femman is measured using chemiluminescence (Tecan CLD 700 AL) with a detection limit of ∼0.1 ppb. More information about the Opsis DOAS system used at the Gårda and Haga monitoring sites are available at http://opsis.se/. At Gårda the measurement distance was 186 m, which gives a detection limit of 5.4 and 2.7 μg m^{-3} for NO and NO_2 respectively. The measurement time was 1 minute every 6 minutes. At Haga the measurement distance was 146 m which gives a detection limit of 6.8 and 3.4 μg m^{-3} for NO and NO_2 respectively. The measurement time was 1 minute every 4 minutes. Hourly data from these three sites were used. Hours with concentration of NO_2 $<$5 ppb (∼10 μg m^{-3}at 0°C) from the DOAS system were excluded to avoid influence from NO_x data below the detection limit. It was our mistake to omit the information concerning detection limits.

TAPM configurations

The reviewers requested further information concerning the TAP Model, including boundary conditions, dry deposition velocities and the chemical mechanism used.

The innermost domain for air pollution (3.1×5.1 km) covered the studied road and the city centre including the urban background site Femman. It should be noted that this study focused on the NO_x-O_3 variation close to a busy road. Emissions from nearby roads were not included in the model. To compensate for these emissions, hourly NO_2 and O_3 at the Femman site were appropriate to use as the air pollution boundary condition in this study.

The chemistry mode in TAPM includes ten reactions for thirteen species. The NO_x-O_3 reactions most related to this study are:

$$NO_2 + hv \rightarrow NO + O_3 \text{ (R1)}$$

$$NO + O_3 \rightarrow NO_2 \text{ (R2)}$$

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$$\mathrm{RP} + \mathrm{NO_2} \quad \rightarrow \mathrm{SGN}\ (\mathrm{R3})$$

The reaction rate for NO_2 photolysis (R1) is estimated by calculated solar radiation and a coefficient which is associated with zenith angle.

$$k = \frac{0.0001 * \delta * TSR}{60}$$

in which TSR is the total solar radiation in W m^{-2}, and

$$\delta = \begin{cases} 4.23 + 1.09/\cos Z; if 0 \leq Z \leq 47 \\ 5.82; if 47 \leq Z \leq 64 \\ -0.997 + 12(1 - \cos Z); if 64 \leq Z \leq 90 \end{cases}$$

where Z is the zenith angle in degrees.

(R3) represents the formation of HNO_3, the important removal process for NO_x, in which RP is the radical pool and SGN is stable gaseous nitrogen products.

Dry deposition is another important process for NO_x and O_3. The dry deposition velocities for gaseous pollutants in the model follow that of Physick (1994).

$$V_d = (r_{aero} + r_{surface})^{-1}$$

in which the aerodynamic resistance is $r_{aero} = r_{aH} + r_{bH} Sc^{2/3}$; r_{aH} and r_{bH} are the resistance function for heat transfer which are in terms of roughness length and stability function.

The surface resistance is:

$$r_{surface} = \frac{r_{si}}{LAI} F_1 F_2^{-1} F_3^{-1} F_4^{-1}$$

where LAI is Leaf Area Index and r_{si} is minimum stomatal resistance. For the urban landscape in the model, r_{si} = 100 (m^{-1}) and LAI =2.0. $F_1$to F_4 is the function associated

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with soil temperature, soil moisture content, specific humidity, vegetation vapour pressure and cloud cover. Sc is the Schmidt Number (the ratio of the molecular diffusivities for water vapour and pollutant concentration).

Results

Referee #2 gave many excellent suggestions for further analysis, which would have been very interesting to follow. Since the manuscript is already rejected we will not present new analysis at this stage with the exception of one important point in Fig. A, but save it for the future. Here follows some clarifications that were also asked for by the reviewers.

As described above passive samplers have many advantages. Without this measurement technique it would not have been possible to measure pollutants at the spatial resolution as was done in this study. We are aware of the drawback with limited time-resolution of passive samplers and therefore the publication is not solely based on 5-day averages. Data from continuously measuring permanent monitoring station is also included as well as modelled data (TAPM).

Part of the aim of this study was to describe the meteorological and air pollutant conditions during the Göte2005 campaign for the special issue. During this time (2 February to 2 March 2005) the weather was rather windy and cloudy and the strong temperature inversions often characterising this time of the year in Gothenburg did not appear. In Fig. 4 it can be seen that high NO_2 was most common on early mornings during weekdays. At this time the morning rush hour causes large NO_x emission while the more stable night time boundary layer has not completely broken up suppressing dispersion. We agree with referee #2 that it would be interesting to further investigate instances with high NO_2. We do think that such a study would give a more interesting result if it was done for another time period than Göte-2005, since the variation in meteorological conditions was relatively small and not fully representative of winter conditions in Göteborg during the Göte-2005 campaign.

Based on earlier measurements it was assumed that the highest concentrations of NO_x would be found at Olskroksmotet. Therefore the measurements and modelling were focused around this area. Unfortunately, the emission database for NO_x in Gothenburg was not complete at the time, so the only NO_x emission source included in TAPM was the line source corresponding to the traffic route as can be seen in Fig. 1. Therefore it is not possible to compare TAPM with hourly measurement data. It would be possible to extend the line emission source to pass the Gårda monitoring site but that would require a rerun of the model. To compare TAPM with the other two continuously measuring sites (Femman and Haga) would be meaningless without the inclusion of other NO_x emission sources in the model. The length of the line source representing the traffic route at Olskroksmotet in TAPM was 1.5 km. Related to the high traffic intensity local emissions are likely to be dominating there.

We agree that the results based on Fig. 7 are relatively weak due to the small amount of data points (five data points to each regression line). Instead we have followed the excellent suggestion of referee #2 and replaced it (or combined it) with a figure similar to Fig.8 but based on continuous measurements. As can be seen in Fig. A (available at: `http://www.dpes.gu.se/english/Personnel/PhD_students/jenny_S/goteperiod_vind`) the hourly measurements show a very similar pattern as the modelled data in Fig 8 with Gårda representing the most polluted permanent monitoring site. The highest [NO_2] ratio occurred at wind speeds of 3-4 m s^{-1} based on measurements while at 2-3 m s^{-1} for the modelled data.

Figure captions

The reviewers request clarifications of when 5-day averages (passive samplers), hourly data from the permanent monitoring stations and/or modelled data are used. Below follows additional information for the figure captions clarifying this.

Fig. 4 is based on hourly data from the permanent monitoring stations.

Fig. 5 compares modelled (TAPM) and observed (passive sampling, 5-day averages)

O_3, NO_2 and NO at the seven sites. Fig. 5d shows NO, not O_3 as it erroneously states on the axis.

Fig. 6 is based on hourly data from the TAPM.

Fig. 7 is based on 5-day averages from passive sampling.

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