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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emissions and photochemistry of oxygenated VOCs in urban plumes in the Northeastern United States" *by* R. Sommariva et al.

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We thank Referee 1 for the detailed comments to our paper. A new version of the manuscript will be prepared soon and will address the major concerns of the referees. Here is our reply to the comments.

SPECIFIC COMMENTS

The impact of background concentrations on enhancement ratios is not discussed in this manuscript (p. 12376) in detail, especially it is questioned if dilution affects both VOC and CO in the same way (as stated on p. 12377, l. 3). The effect of dilution on emission ratios has been addressed in recent papers by de Gouw et al. (2005)

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and Warneke et al. (2007) where ratios relative to acetylene were presented. But here ratios to CO are used. Compared to acetylene, CO has a much longer life time and the encountered mixing ratios of less than 200 to 400 ppbv are only little above the background concentrations of 100 ppb. Thus, enhancement ratios as determined during the flights are expected to be influenced by the dilution with background air. As a result, enhancement factors for the primary emitted compounds should be reduced compared to purely photo-chemically altered enhancement factors due to the fact that mixing yields a stronger concentration decline in time for VOCs than for CO. However, for compounds like methanol or acetone with significant background concentrations (de Gouw et al., 2005) this effect might be partly compensated for or even reversed. Anyways, this needs more discussion.

Enhancement ratios, in this manuscript, are defined as the ratios of enhancements in mixing ratios relative to background values. Enhancement ratios were determined from the slopes of linear regression fits to the data, as shown in Fig. 4. The background mixing ratios in long-lived species such as CO and oxygenated VOCs determine the intercept of the linear regressions but not the slope. The reviewer is correct to point out that the ratios between species depend on dilution, but the enhancement ratios determined from the slopes depend less strongly on this. In the revised manuscript we have added a more detailed discussion of the effect that dilution has on enhancement ratios. In addition, we have added references and discussions of three papers that discuss the interplay between mixing and chemistry:

McKeen, S. A., and Liu, S. C.: Hydrocarbon ratios and photochemical history of air masses, Geophys. Res. Lett., 20, 2363-2366, 1993.

McKeen, S. A., Liu, S. C., Hsie, E. Y., Lin, X., Bradshaw, J. D., Smyth, S., Gregory, G. L., and Blake, D. R.: Hydrocarbon ratios during PEM-WEST A: A model perspective, J. Geophys. Res., 101, 2087-2109, 1996.

Parrish, D. D., Stohl, A., Forster, C., Atlas, E. L., Blake, D. R., Goldan, P. D., Kuster,

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W. C., and de Gouw, J. A.: Effects of mixing on evolution of hydrocarbon ratios in the troposphere, J. Geophys. Res.-Atmos., 112, D10S34, doi:10.1029/2006JD007583, 2007.

In Fig. 5, three different approaches are compared: (1) the enhancement ratios calculated form measurements which are influenced by both, photo-chemistry and dilution (see above) (2) the empirical parameterization by de Gouw et al. (2005) which represents a fit to real atmospheric conditions and thus should include implicitly dilution effects (3) the MCM simulation which considers neither background concentrations nor dilution. This situation is further complicated by the fact that different time scales might be used: the parameterization uses a photo-chemically determined time from the ratios of toluene to benzene which may differ from the 'real' time if background concentrations of benzene and mixing are considered. Thus, differences between the three approaches are expected and it is hard for the reader to understand why so different conditions were compared. This part should be accordingly changed to either resolve or better explain the effects of the different conditions encountered. Finally, it may be expected that the emission ratios of OVOCs derived in Warneke et al. (2007) for the conditions encountered in 2004 (ICARTT) are used for the parameterization. Using those of NEAQS 2002 which were substantially different from those in 2004 (see Warneke et al., 2007) and comparing them to observations from 2004 is hard to understand and should be thoroughly justified.

While we arrived at the enhancement ratios versus time shown in Fig. 5 in completely different ways, the intent is to compare the same quantity from measurements and models and to study how well the MCM model captures the VOC evolution in an urban plume as observed in 2002 and 2004. In the revised manuscript, we explain in more detail why the three parameters were assumed to be the same. In all three approaches (model, parameterization and measurements), background concentrations in CO and oxygenated VOCs were accounted for and this is explained more clearly in the revised manuscript. See also our response to the previous comment. As the reviewer correctly points out, the processing time in the parameterization from de Gouw et al. (2005) was determined from hydrocarbon ratios. To convert hydrocarbon ratios to time, an average OH during transport is required, which is quite uncertain. The curve shown in Fig. 5 was calculated using an average OH concentration of 3×10^6 molecule cm^{-3}. In the revised manuscript, we have replaced the curve by a shaded area indicating the significant uncertainty in the average OH concentration. Finally, emission ratios for oxygenated VOCs from 2002 were used in this manuscript, as these were also used in the parameterization from de Gouw et al. (2005). The comparison with data from 2004 in Fig. 5 does not reveal large discrepancies. The differences in OVOC emissions ratios between de Gouw et al. (2005) and Warneke et al. (2007) are not likely due to actual differences in emissions between the two years; for example, Parrish et al. (2009) compared VOC emissions among mega-cities and found very similar VOC compositions among different regions and years (but with steadily declining absolute concentrations). Instead, we believe that the differences between de Gouw et al. (2005) and Warneke et al. (2007) reflect the uncertainties in determining OVOC emission ratios and we have made that clearer in the revised manuscript. We have also added the emission ratios from Warneke et al. (2007) to Fig. 5.

Parrish, D. D., Kuster, W. C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P. D., de Gouw, J. A., Koike, M., and Shirai, T.: Comparison of air pollutant emissions among mega-cities, Atmos. Environ., 43, 6435-6441, 2009.

The initial values are of great importance for the model and its comparison to the observations (page 12377, Table 1 and Fig. 5). However, it is hard for the reader to understand how they have been derived and the authors should provide more and clear information on this issue. Especially, an equation relating the used emission ratios from Table 1 of Warneke et al. (2007) to the initial concentrations given in Table 1 of the manuscript should be given in the text (delta(VOC) = ER delta(CO), with delta(CO)=332.5ppb-100ppb). Furthermore, the initial concentrations of oxygenated VOC in Table 1 appear to be calculated from simply multiplying the acetylene concen-

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tration (of Table 1) with the emission ratios by de Gouw et al. (2005) without considering the primary biogenic emissions and the background level. Thus determined concentrations are partly substantially lower than those using the correct formula by de Gouw et al. (2005). The reason for this change is not understandable (the authors argue with low biogenic emissions in the plume, however, 1740 ppt of isoprene are not really low) and it should be corrected.

In the revised manuscript, we have added a clearer description of the initial values used in the model. The reviewer makes a good point about the biogenic sources of oxygenated VOCs. The intent was to describe the evolution of an urban plume and to separate this from the biogenic VOCs to the extent possible. However, biogenic VOCs such as isoprene were present in these plumes and cannot be ignored in the chemical model. Using the level of isoprene in the model used here and Table 1 from de Gouw et al. (2005), we estimate the potential biogenic sources of the oxygenated VOCs studied here. In the revised manuscript, we have added a description of these estimates and how they affect the comparison of the modeled oxygenated VOCs with the data.

It is stated in the text that the mixing ratios given in Table 1 are used to initialize the MCM model. However, with the data provided in Table 1, the starting points of the MCM simulation could not be realized, i.e. for toluene/CO a ratio of 1.83 ptv/ppbv is calculated, if a CO background of 100 ppb (p. 12377, l. 11) is considered the ratio is 2.62 pptv/ppbv. Both numbers are well below the simulation curve in Fig. 5 which starts at more than 3.5 pptv/ppbv. Evidently, the start points of the simulation curves in Fig. 5 are mostly the same as those of the semi-empirical parameterization curves. The latter have been adapted from the paper by de Gouw et al. (2005) except for benzene and toluene for which slightly modified emission ratios might have been assumed. The empirical parameterization by de Gouw et al. (2005) was based on ratios to acetylene. These apparently have been transformed into ratios with CO by applying a factor of 4.94 ppbv/pptv which also had been given by de Gouw et al. (2005). This factor, however, is different from the factor of 3.6 pptv/ppbv identified by Warneke et al. (2007)

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for the conditions encountered in the Boston/New York area and which was also used in this manuscript (p. 12377, l. 10) to convert the emission ratios of NMHC. The authors did not explain why a different factor is used. Furthermore, it is not clear why the model is not initialized with the values given in Table 1. This part should be changed and consistent procedures should be used. Of course, this has implications on the comparison to the experimental data.

In view of these comments, we have re-examined the initial values in Table 1 and have explained our assumptions more clearly. We also modified Table 1 to include the initial conditions of all the species in the model (in the present version the table only includes the initial conditions of some important species). The acetylene/CO ratio used here is uncertain, as reflected by the differences between de Gouw et al. (2005) and Warneke et al. (2007). We do believe that this difference reflects more likely the uncertainty in deriving the emission ratios from the different data sets, rather than an actual difference in emissions between different regions of the atmosphere. In the revised manuscript, we acknowledge this uncertainty in the acetylene/CO ratio and describe how this uncertainty affects the results. Notably, we have replaced the dotted curves in Fig. 5 by a shaded area to indicate the uncertainty in acetylene/CO ratios (as well as in the conversion from hydrocarbon ratios to time as mentioned above).

Since no direct emission ratios from measurements in the city area have been determined, enhancement ratios of the night-time flight on Aug 7 are taken as a proxy for this. These results tend to differ from the general picture provided by the curves and the other data points (p. 12380 and Fig. 5). Especially, this is due for toluene where no other major sources apart from primary anthropogenic emissions are expected, but the ratio is lower than those obtained after chemical processing on the first day. The CO enhancement during this flight with mostly less than 170 ppb is only small compared to background conditions of 100 ppb. The uncertainties should be discussed more thoroughly, including the potential effect of different primary emission ratios in the evening, possibly due to lower temperatures.

The difference between the nighttime flights and the daytime flights closest to urban centers in Fig. 5 can also be due to an actual difference in the emissions probed during these flights. In the revised manuscript, we acknowledge this possibility.

TECHNICAL COMMENTS

p. 12372, l. 18: The paper does not really present the importance of long-chain alkanes, at least it does not demonstrate a high contribution to the formation of those carbonyls under investigation.
p. 12373, l.2: It should be made clear, that '...2 to 5 times more abundant oxygenated VOC than all hydrocarbons combined' is an example and refers to specific studies, furthermore, the word 'nonmethane hydrocarbons' should be used instead of 'hydrocarbons'.
p. 12373, l. 11-14: It is suggested to add that oxygenated VOC in the aerosol phase generally refers to compounds with multiple functional groups and low vapour pressure.
p. 12373, l. 17-18: add: '... and the large variety of different oxygenated VOC encountered...'
p. 12373, l. 19: It is suggested to start with 'In addition to direct emissions, oxygenated VOCs ...', otherwise the misleading impression might be that photochemical production is by far the dominant source.
p. 12374, l. 17-18: The authors state that the life time of OVOCs ranges up to a few days, and in the next sentence an example for a compound with life time of more than a month is given.

We have revised and corrected these sentences, according to the reviewer's suggestions.

p. 12375, l. 8: In Singh et al. (2004), the primary biogenic emissions of acetaldehyde are 3 times higher than photochemical production, this is not really comparable.

Although they reported a rather large range of values, the average sources of acetaldehyde by Singh et al (2004) were of 35 Tg/y from primary biogenic emissions and of 30

Tg/y from hydrocarbon oxidation, (Table 4).

p. 12375, l. 23 (see also specific comment above): It is suggested to make clear in the introduction that data from NEAQS 2004 (ship) are used to initialize NMHC and data from 2002 (ship) to initialize OVOCs for the MCM modelling. Please, also discuss why not the OVOC data from 2004 have been used as they are substantially different. For the validation of the model results, however, the results of airborne measurements from 2004 are used. Thus, the model is compared to conditions which are decoupled from the surface. Furthermore, the results are compared to a parameterization obtained by de Gouw et al. (2005) derived from the NEAQS 2002 data obtained close to the surface on a ship. The reader may be confused by the different data sets and the selection criteria. Thus, they should be clearly explained.

p. 12377, l. 11: In contrast to the original paper by Warneke et al. (2007) with an identified background concentration of 75 ppb for CO, here a number of 100 ppb is used without giving further explanations. Please, add these accordingly.

As mentioned above, we have clarified our assumptions and reasoning in more detail in the revised manuscript.

p. 12377, l.20: The model appears to generate some NO2 night peaks, where are they from?

Those peaks do not occur during the night but at sunset. They are due to lower NO2 loss (as the photolysis rate decreases) while there is still production from slowly decaying peroxy radicals. We have added a sentence explaining these peaks to the revised manuscript.

p. 12379, l. 17: the maximum encountered CO mixing ratios are even higher than the assumed mixing ratios at the time of emission (Table 1)?

The referee is correct that sometimes measured CO mixing ratios were higher than the values with which the model was initialized. However the values in the model were in

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the range of the measurements and, since the analysis concentrated on ratios of the measured species, small changes in the absolute values of the concentrations do not significantly change the results and the conclusions.

p. 12381, l. 1-2: Please, make clearer if only the procedure (eq. 5) provided by de Gouw et al. (2005) has been used, or also the parameters determined in the fit of the 2002 NEAQS data.

The parameters determined in the fit of NEAQS 2002 data were also used. The text has been clarified.

Figs. 6-8: What does the red colour stand for? It is suggested to add the percentage numbers to the more important path ways.

The red color is meant to indicate the key intermediates that link the formation of the alkyl nitrates and of the ketones. The detailed formation of these species has been discussed in our previous paper (Sommariva et al., 2008). It has been clarified in the revised figure captions. The percentages were not shown in the reaction diagrams on purpose, as they change with time and it would make the figures confusing. They are shown in the accompanying plots (Figs. 6 and 8).

p. 12377, l. 10: The ratio acetylene/CO should have units: 3.6 pptv/ppbv.
p. 12377, l.20: The increase of HOx appears to be only in part due to slowly increasing ozone, additionally, i.e. the decline of NOx essentially removes a major HOx-radical loss and other reaction partners of OH like VOC are also reduced.
p. 1378, l.7: add: '... and (4) a background concentration'
p. 12379, l. 25 and Fig. 3: The text and figure caption indicate 3 trajectories. However, in the figure more trajectories appear to be shown.
p. 12384, l. 6: duplicate word 'be'
p. 12385, l. 1: duplicate word 'reaction'
p. 12386, l. 17: Instead of 3-methylpentane (Fig. 8) 2-methylpentane is used.
Fig. 9: Please recheck the structures of M2BKBO and PROL1MCO3, I think there are

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too many C-atoms.

We thank the referee for finding these typos and minor mistakes. The text has been amended in the revised version.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12371, 2008.

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