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Atmospheric
Chemistry
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Discussions

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

Anonymous Referee #1

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The paper presents an analysis of photochemical processes of mainly oxygenated VOCs in urban plumes from the Boston/New York area. It compiles data and emissions obtained in the New England Air Quality Study (NEAQS 2002 and 2004) and during ICARTT 2004 which have been published elsewhere. A model based on the Master Chemical Mechanism (MCM) is run to simulate the evolution of selected oxygenated VOCs in the plume over a period of 5 days. Model results are compared to enhancement ratios obtained from airborne measurements (ICARTT 2004) and to a semi-empirical parameterization presented in a previous paper. The major primary emitted VOC which contribute to the photochemical formation of acetone, methyl ethyl ketone and acetaldehyde are identified from the model. The paper is closely linked

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to a paper on the formation of organic nitrates using the same data sets and MCM mechanism (Sommariva et al., 2008).

Analyzing relevant photochemical processes leading to the formation and decay of OVOCs is certainly in the scope of ACP. Especially the validation of the model results by the observations is appreciated. The identification of precursors of oxygenated VOCs is the major new result and the strongest part of the paper. The concept is not principally new (see Sommariva et al., 2008) but its use for oxygenated VOCs is new and allows new insights. The paper is well structured, language is clear and references are appropriate. However, there are several questions and comments the authors are kindly asked to address in a revision of the paper. These mainly concern the treatment of background concentrations and mixing, and the compilation of the (initial) conditions for model and parameterization, and the comparison with observational data.

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) 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.

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.

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 concentration (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

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low biogenic emissions in the plume, however, 1740 ppt of isoprene are not really low) and it should be corrected.

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 pptv/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) 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.

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

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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.

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.

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.

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. 10: The ratio acetylene/CO should have units: 3.6 pptv/ppbv.

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.

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

p. 1378, l.7: add: '... and (4) a background concentration'

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)?

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. 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.

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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.

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

Fig. 9: Please recheck the structures of M2BKBO and PROL1MCO3, I think there are too many C-atoms.

References as used in the manuscript.

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

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