Atmos. Chem. Phys. Discuss., 9, C10986–C10992, 2010
www.atmos-chem-phys-discuss.net/9/C10986/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formaldehyde and its relation to CO, PAN, and SO_2 in the Houston-Galveston airshed" *by* B. Rappenglück et al.

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Received and published: 21 February 2010

Reply to Referee #1

We appreciate the important comments made by the reviewer and we hope that our manuscript has improved.

1) Especially the chemistry behind the source appointment regarding the industrial emissions could be improved. The paper would benefit from a more detailed description of how the sulphur dioxide emissions are linked to formaldehyde. Is this just an accidental local co-allocation of the emitters? The data presented in Wert et al for the same region indicate that high levels of sulphur dioxide are not really stringent coinci-

dent with high formaldehyde.

Answer: Based on the Moody Tower data presented in this paper we cannot unambiguously determine whether SO2 is co-emitted with HCHO or whether the emitters are collocated. As shown in figure 1, for sector II the Moody Tower samples air masses coming from the HSC which most likely present multiple overlapping emission sources. These sources may include both, co-emissions of HCHO and SO2, and co-allocated sources of HCHO and SO2. The bottom line here is that when you see from the Moody Tower, the resolution is such that HCHO and SO2 sources appear collocated, it is possible that at a higher resolution they may not be.

The data presented in Wert et al. is based on flights which started between 1000 and 1100 CST and lasted for about 6 hours. The objective of these flights were to capture midday photochemistry and the daily ozone maximum. Thus, the flights were performed mainly during a time period with (1) maximum mixing within the boundary layer and (2) largest amount of secondarily formed HCHO. The flights did not sample during the morning transition times when the nocturnal boundary layer breaks up and when secondary HCHO formation is still limited. It is more likely to observe a relationship between SO2 and HCHO emissions during morning hours. Actually, Olaguer et al report an early morning flight performed by the Baylor Aztec aircraft on August 31, 2006. When the aircraft traversed an industrial plume in the HSC between 8:20-8:25 am they found that elevated levels of HCHO and SO2 co occur.

2) Section 3.2. “Possible contributions to ambient HCHO levels” needs to be reshaped and checked for correct references within the text.

Answer: We think that all references in section 3.2 are correct. However, we elaborated the first paragraph of section 3.2. as follows:

“In the natural atmosphere secondary formation from oxidation of methane and isoprene largely controls the background CO concentration. Hudman et al. (2008) found that CO from biogenic sources exceeds the contributions originating from an-

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thropogenic sources during summer times over the eastern United States. Primary sources for CO are combustion processes. Apart from biomass burning, major combustion processes are associated with anthropogenic activities concentrated in urbanized areas. As shown in aircraft studies by Herndon et al. (2007) the HCHO/CO ratio may vary by a magnitude depending on daytime and sampling locations. According to Herndon et al. this may either be due to direct emission sources which have a different fraction of concomitant CO (or do not have CO at all) or secondary production of HCHO during the daytime. The latter has been verified by satellite studies over a wide range for the south-eastern part of the United States (Millet et al., 2008). Since CO is directly being emitted from combustion, CO has previously been used in urban studies to evaluate the traffic exhaust related HCHO emissions (Anderson et al., 1996; Possanzini et al., 1996; Friedfeld et al., 2002; Rappenglück et al., 2005; Garcia et al., 2006). Dynanometer studies showed that the emission ratio of HCHO/CO is typically 0.001- 0.002 ppbv/ppbv for gasoline engine passenger cars, but can be 10x higher for diesel cars depending on driving conditions (Schmitz et al., 1999)."

3) Line 12, which ratio??, in all cases this?....

Answer: We referred to the HCHO/CO emission ratio. "In all cases this" has been removed Please see the modified paragraph in section 3.2.

4) Line 16. Consequently HCHO/CO ratio.

Answer: We inserted "the". Please see the modified paragraph in section 3.2.

5) Page 2420, line 6: "Previous studies have used CO. . ...(citation is missing).

Answer: The following references have been added: Possanzini et al., 1996; Anderson et al., 1996; Friedfeld et al., 2002; Rappenglück et al., 2005; Garcia et al., 2006.

6) Page 2420, Paragraph in line 6-15 describes PNA HCHO relations, but SO2 is simply given as an indicator for industrial activities.

Answer: The following information was added: According to the USEPA (2005) the

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SO2 emissions by source sector for Harris County, which includes Houston and the HSC, were as follows for the year 2005: industrial processes: 45.5%, fossil fuel combustion: 39.3%, non road equipment: 9.3%, on road vehicles: 2.9%, waste disposal: 2.2%, solvent use: 0.6%, electricity generation: 0.2%, and residential wood combustion: <0.1%.

7) The section about the diurnal patterns, 3.3. "illustrative examples for regression model fit" is not convincing. Very similar patterns of HCHO have been observed in the MILAGRO experiment (de Gouw et al., 2009) and could be explained solely by vertical mixing and photochemical decomposition. Vertical mixing would reduce CO levels as described but downward mixing of very high concentrations of SO2 and HCHO would need extremely high mixing ratios. Additionally the high SO2 and HCHO mixing ratios have been observed already a few hours prior to the decline of the CO mixing ratios, on Sept 29 for two hours, on September 14, for three hours. SO2 in industrial emissions is typically a product of fossil fuel consumption which is also accompanied by an emission of nitrogen oxides. An analysis of the concurrent NO/NO2/NOy measurements could be helpful for a further discussion.

Answer: Vertical mixing and photochemical decomposition are certainly important factors which control the diurnal variation of trace gases in the boundary layer. However, at the Moody Tower also overlapping horizontal transport plays an important role. As shown in Figure 4 high HCHO values are closely associated with E-NE winds, i.e. when the Moody Tower is downwind of HSC. Figures 7 and 8 show such specific case studies. We are not sure, if this condition can be compared to T1 in MILAGRO. Also, contrary to Mexico City, the Houston area is influenced by a complex land sea - breeze system (see also Rappenglück et al., 2008), which may lead to transport of air masses from the HSC area to the Moody Tower receptor site during the morning under low wind conditions. These specific events lead to the enhanced mean values and large standard deviations of the mean values of the HCHO mixing ratios in the time frame shown in Figure 2.

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CO sources are usually found at the surface. Industrial emissions however may also be released through stacks at higher altitude levels. In addition, the high temperatures of these plumes would lead to an additional rise. In the Houston area low nocturnal boundary layer heights (between 100-200 m agl) may occur during the summer time (see Day et al., 2009). It is thus likely that these industrial plumes may be injected into the residual layer. Indication for stratified SO2 layers aloft have been in reported in Rappenglück et al. (2008). Recently, Olaguer et al. (2009) have reported long path DOAS measurements of SO2 obtained at the Moody Tower for the September 14 case which show elevated SO2 levels along the upper light path (130-300 m agl.) and low values along the lower path (20-70 m agl) before break up of the nocturnal boundary layer. After the break up of the nocturnal boundary layer the picture is reverse: Along the upper light path the SO2 values decreased rapidly and the SO2 values along the lower path increased drastically which coincides with the in-situ SO2 measurements at the Moody Tower. This is most likely due to vertical mixing. We assume that other species which correlate with SO2 during this event, e.g. HCHO, have most likely been in the same air mass and thus involved in the same transport processes. The Olaguer et al reference has been added to section 3.3.

As shown in Figures 7 and 8 the high SO2 levels do not occur prior to the start of the decline of CO. The break up of the boundary layer occurred gradually. We included the following description of the boundary layer development for September 14, 2006 (unfortunately, for September 29, 2006, we only had one radiosonde launch at 700h CDT and another one at 1900h CDT; we did not have tethersonde data on September 29):

"Tethersonde data (Day et al., 2009) suggest low nocturnal boundary layers (100-200 m agl) in the HGA prior to sunrise on September 14, 2006 which is also confirmed by early morning radiosonde data. The break up of the boundary layer occurred gradually until 1000h when radiosonde data indicated a boundary layer height of about 400 m agl. The next radiosonde launch at 1300h finally indicated an increase of the boundary

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layer height to about 1450 m agl and continued to increase until 1600h, when it reached about 1700 m agl. It is important to note that easterly wind directions prevailed up to about 500 m agl in the morning hours. This layer slightly increased until the 1000h radiosonde launch. Above this layer wind shear was observed and winds veered to southerly and then to westerly directions. It is likely that thus a shallow layer existed between the boundary height and the height where the wind shear occurred, which predominantly contained air masses which have passed the HSC area before arriving the Moody Tower area."

As far as NO/NO2/NOy measurements are concerned we inserted additional information for the September 14 and September 29 cases.

September 14: "The initial rise of HCHO is also accompanied by increasing NO, NO2, and NOy values (not shown), while at the same time there is a slight decrease in CO. While PAN would suggest the presence of secondary HCHO it is intriguing that the HCHO/PAN ratio is significantly higher in this morning plume than during the subsequent afternoon (5.4 vs 2.4). The NOx/NOy ratio is about 0.95 at the beginning of the HCHO event; at the time of the HCHO maximum it is still around 0.75. These values are similar or even exceed the NOx/NOy values reported in Wert et al. (2003) for locations close HSC plumes indicating freshly emitted NOx. In the afternoon the NOx/NOy values finally drop to values around 0.4, suggesting higher degree of photochemical processing."

September 29: Similar to the September 14 case, the NOx/NOy ratio stayed at elevated levels at the time of the HCHO peak (about 0.85-0.90). The minimum NOx/NOy ratios (0.53-0.64) occurred during the afternoon when PAN levels showed enhanced values.

8) The wind roses in figures 11 and 12 are very difficult to read especially Figure 12 with too many different data within one figure.

Answer: Figure 11 was enlarged. Lines were made bold. Figure 12 was separated in Figure 12a and 12b. In addition these figures were modified similar to figure 11. See

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supplement.

de Gouw, J.A., Welsh-Bon, D. Warneke, C., Kuster W.C., Alexander, L., Baker, A.K., Beyersdorf, A.J., Blake, D.R., Canagaratna, M., Celada, A.T., Huey, L.G., Junkermann, W., Onasch, T.B., Salcido, A.,Sjostedt, S.J., Sullivan, A.P., Tanner, D.J., Vargas, O., Weber, R.J., Worsnop., D.R., Yu, X.Y., and Zaveri, R.: Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study, Atmos. Chem. Phys., 9, 3425-3442, 2009.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/9/C10986/2010/acpd-9-C10986-2010-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24193, 2009.