1.5 ANALYSIS OF PRIMARY VS. SECONDARY FRACTION OF FORMALDEHYDE IN THE HOUSTON AREA DURING TEXAQS-II

B. Rappenglück *, D. Byun, B. Czader, S. Kim, M. Leuchner
Department of Geoscience, University of Houston, Houston, USA

S. Alvarez, L. Kauffman, M. Shauck, G. Zanin
Baylor University, Waco, USA

M. Buhr
Air Quality Design Inc., Golden, USA

P. Dasgupta
Department of Chemistry, The University of Texas at Arlington, Arlington, USA

M. Estes
Texas Commission on Environmental Quality, Austin, USA

W. Luke
NOAA-ARL, Silver Spring, MD 20910, USA

1. INTRODUCTION

Formaldehyde (HCHO) is considered to play a significant role in summertime photochemistry in the Houston area. In particular it is considered an important source of radicals. Secondary formation seems to be the most important fraction of ambient HCHO. Primary sources are primarily due to incomplete combustion processes. Potential sources may include mobile sources such as traffic exhaust. Other possible sources may include point sources e.g. from petrochemical production.

In this study we focus on a continuous in-situ formaldehyde data set based on the Hantzsch reaction which was obtained in the Ship Channel area (HRM3 and Lynchburg Ferry site) and at the Moody Tower for several weeks during the Texas Air Quality Study-II (TexAQS-II). We also include in-situ HCHO measurements obtained with the same technique aboard the Baylor aircraft during TexAQS-II flight missions. HCHO data is related to other trace gases that are supposed to be coemitted including CO, ethylene, and SO_2.

* *Corresponding author address*: Bernhard Rappenglück, Department of Geoscience, University of Houston, 4800 Calhoun Rd, Houston, TX 77204, USA; e-mail: brappenglueck@uh.edu

2. Experimental setup

Fig. 1 shows the location of the in-situ HCHO measurement sites during the TexAQS II campaign in summer 2006. The University of Houston (UH) ran an Aero-Laser AL4021) at the Moody Tower site. The same instrumentation was used aboard the Baylor University (BU) aircraft. The University of Texas (UT) at Arlington used their own Hantzsch based instrumentation at HRM3 and Lynchburg Ferry sites, two sites of the Continuous Ambient Monitoring Site

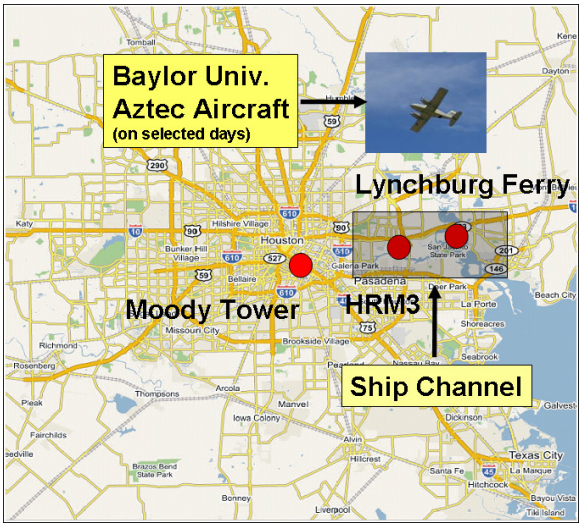

FIG. 1. HCHO measurement sites.

(CAMS) network. In addition to HCHO, data for volatile organic compounds (VOC) was obtained online using GC/FID techniques at the Moody Tower, HRM3, and Lynchburg Ferry site. Canisters were taken aboard the BU aircraft and analysed for VOCs using the UH GC system. At most measurement platforms measurements of CO, NO, NO_2, and SO_2 were performed (however no CO and SO_2 measurements were available for HRM3 and the Lynchburg Ferry site). At the Moody Tower site also speciated measurements for peroxiacetic nitric anhydride (PAN) were carried out.

3. Results and discussion

Figure 2 shows time series of in-situ HCHO measurements at HRM3, Lynchburg Ferry, and Moody Tower. Among the three sites the Lynchburg Ferry site always exhibits the highest mixing ratios. The time periods marked with letters in Fig. 2 indicate times which show particular features:

(A) overall enhanced HCHO background values. This feature does not only hold for HCHO. Measurements of CO and VOCs seem to indicate similar patterns. At this point it is unclear what contributes to this enhancement.

(B) September 14: maximum HCHO values of slightly more than 30 ppbv at the Moody Tower.

(C) September 19/20: elevated nighttime HCHO levels observed at HRM3 and the Moody Tower

(D) September 27: at the Lynchburg Ferry site and HRM3 highest HCHO values of the entire measurement period were observed.

(E)) September 29: an early morning HCHO event at the Moody Tower (occurs after rush hour).

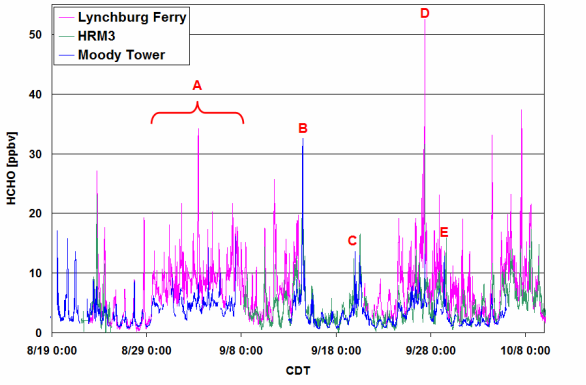

FIG. 2. In-situ HCHO time series. Median and maximum values (in brackets) were: Lynchburg Ferry site: 6.62 ppbv (52.44 ppbv); HRM3: 3.54 ppbv (31.53 ppbv); Moody Tower: 2.88 ppbv (32.54 ppbv).

HCHO can either be formed secondarily or emitted primarily. In order to evaluate the potential impact of traffic, CO can be used as a tracer for traffic-related exhaust emissions. Figure 3 shows results of HCHO-CO relationships obtained at the Moody Tower discriminated between wind sectors predominantly impacted by air masses originating from urban areas and those originating from the Ship Channel. The data set is also split into night and daytime measurements. Nighttime measurements include the rush hour times. Best correlation between HCHO and CO is found for “urban” air masses at night with a slope of about 7 pptv $ppbv^{-1}$. Though for nighttime “Ship Channel” air masses the correlation is weaker indicating additional dependencies, the slope is quite similar.

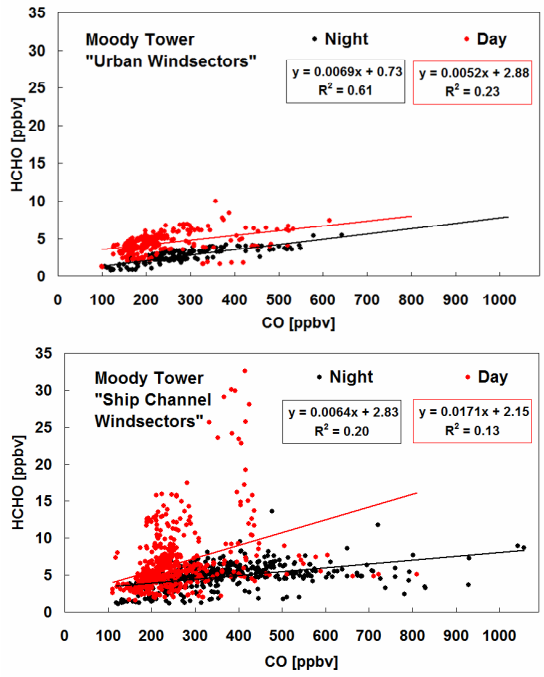

FIG. 3. Relationships of HCHO to CO obtained at the Moody Tower during nighttimes (8 pm -8 am CST), including rush hours, and during daytime (8 am – 8 pm CST). “Urban” (panel A) is defined as wind direction between 270° – 360°, whereas “Ship Channel” (panel B) is defined as wind direction between 22.5° – 112.5°. In both cases only wind speeds > 0.5 m/s were considered.

From these observations we estimate an upper limit for the primary emissions of formaldehyde from mobile sources to be around 0.5-0.7 % of the CO emissions. During the daytime, “urban” and “Ship Channel” air masses have weaker relationships most

probably due to photochemical impacts. For the "urban" air masses it seems that the changes in the daytime vs. nighttime regression line are basically due to a different HCHO background level. These enhanced daytime values can be attributed to enhanced photochemical formation of HCHO. Similar enhanced background values between 2-3 ppbv can be observed for the "Ship Channel" sector for day- and nighttime conditions.

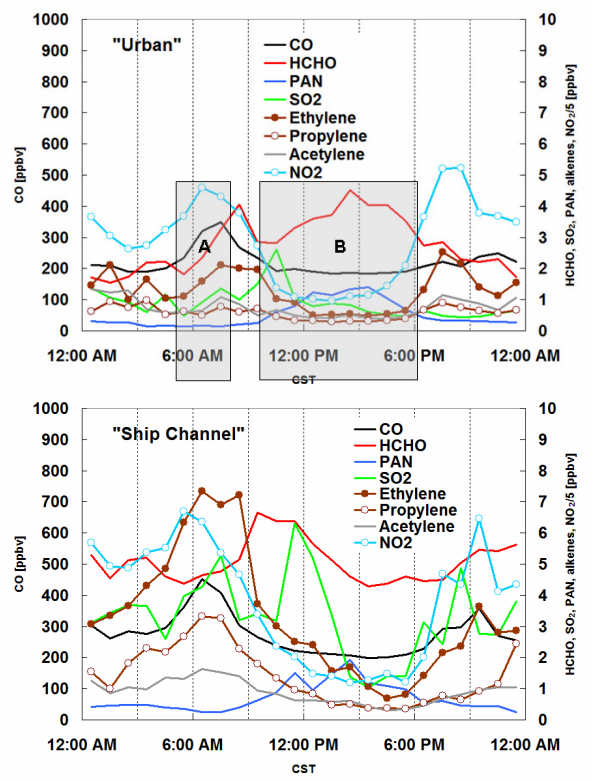

FIG. 4. Composite diurnal variations of CO, HCHO, SO2, and PAN at the Moody Tower for the "Urban" sector (left) and the "Ship Channel" sector (right). Designations "Urban" and "Ship Channel" are defined the same way as for Fig. 3.

Figure 4 reflects the same discrimination approach as in Fig. 3, but displays composite diurnal variations for these conditions. CO is used as a tracer for traffic related emissions, SO_2 as a tracer which also has industrial sources. Fig. 4 shows a quite similar diurnal variation for CO in both air masses with peak times during the morning and evening rush hours. PAN, a compound exclusively produced as a secondary compound and which has negligible background values, usually displays enhanced values between 11 am and 6 pm. HCHO time series for urban air masses reflect nicely this photochemical active time period (highlighted area [B] in Fig. 4). However, an enhanced HCHO peak value also occurs in the morning hours in the absence of elevated PAN values (highlighted area [A] in Fig. 4). This HCHO peak is of the same magnitude as the afternoon HCHO levels. Also, CO values are relatively low after the rush hour peak and after the break up of the morning inversion layer. However, the HCHO peak clearly coincides with a peak in SO_2. For "Ship Channel" air masses it seems that on the average HCHO peak values are exclusively observed in a time window between 9 am and 12 pm. This time window is not related to the traffic rush hour as CO values have already decreased. However, this time window also partly shows enhanced SO_2 and enhanced PAN values indicating a mixture of contributions arising from emission and photochemical processes. Overall nighttime values of HCHO and SO_2 are significantly higher for "Ship Channel" air masses than for "urban" air masses.

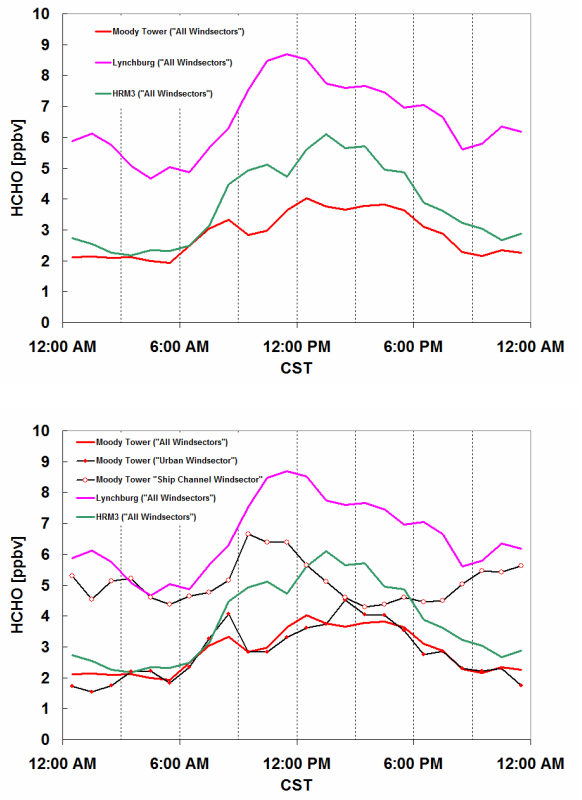

FIG. 5. Composite diurnal variations of HCHO obtained at the Moody Tower, HRM3, and Lynchburg Ferry (top). The bottom plot also shows Moody Tower HCHO data which is split into "urban" and "Ship Channel" wind sectors (see Fig. 4).

Figure 5 shows average HCHO diurnal variations obtained from the three in-situ instruments (Moody Tower, HRM3 and Lynchburg Ferry site). It can be seen that HRM3 and the Lynchburg Ferry site show higher values than the Moody Tower site, especially during photochemical active daytime periods. However, the Lynchburg Ferry site shows overall higher background values (about 2-3 ppbv higher). Also, the diurnal maximum occurs before noon. This peak also seems to be slightly present in the HRM3 and Moody Tower data, though in both cases it is not the diurnal maximum. The bottom plot in Figure 5 shows the Moody Tower HCHO data separated into "urban" and "Ship Channel" wind sector data. Now the "Ship Channel" wind sector data approaches the Lynchburg Ferry diurnal variation. Even, the maximum before noon resembles the HCHO maximum observed at Lynchburg Ferry site.

From these observations we conclude that apart from traffic-related primary HCHO emissions, which are low, industrial releases of HCHO may be non-negligible. The results for the Moody Tower often indicate a relationship between SO_2 and HCHO between 9-12 am. Presumably downmixing of air masses after the break-up of the morning inversion may contribute to this enhancement.

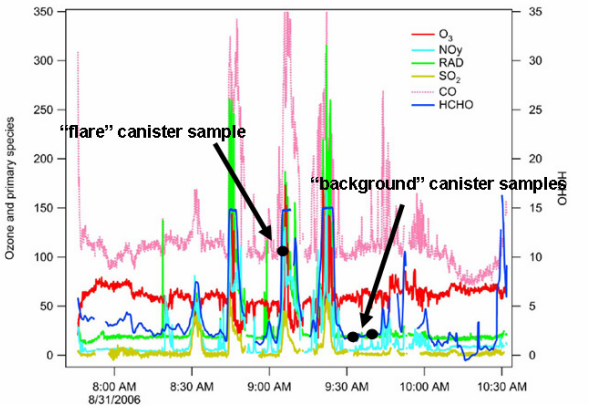

FIG. 6. Results of trace gas time series obtained from multiple traverses through a flare plume performed by the BU aircraft on August 31, 2006 [according to Alvarez et al., 2007].

Figure 6 shows results from multiple traverses through a flare plume performed by the BU aircraft on August 31, 2006. The dots indicate times of canister samplings: two samples were taken outside the plume (considered "background") and one was taken at a time when HCHO showed a strong increase.

Table 1 suggests that HCHO/CO ratios are about 5-7 times than background and about 3 times higher than the traffic induced HCHO/CO ratios reported previously. Table 1 also indicates that while the HCH/Ethylene ratios are enhanced by about the same factor compared to ambient air, the HCHO/Propylene ratio is 12-14 times higher than the background. HCHO values during the time of canister sampling was about 8.8 ppbv. Surprisingly, ethylene and propylene mixing ratios in the plume were relatively modest (ethylene: 6.9 ppbv; propylene: 2.1 ppbv). These findings are based on a very limited data set and would certainly require additional focused flare plume studies, but it seems that either primary emission or at least rapid formation of HCHO occurs in the flare plume.

	"plume"	"back-ground I"	"back-ground I"
HCHO/CO	0.0230	0.0031	0.0041
$HCHO/NO_2$	0.29	6.48	13.72
$HCHO/SO_2$	0.42	0.29	0.85
HCHO/Ethylene	0.00128	0.00038	0.0019
HCHO/Propylene	0.00430	0.00030	0.00036

TABLE 1. Results of trace gases ratios during canister samplings. Ratios are given in ppbv/ppbv. Only for HCHO/Ethylene and HCHO/Propylene the ratios are given as ppbv/pptv.

At various occasions during TRAMP enhanced levels of HCHO during nighttime were observed at the Moody Tower. Similar observations were made at HRM3 and in particular at the Lynchburg Ferry site. A first attempt was made to elucidate possible contribution pathways extracting corresponding information from CMAQ (Community Multi-scale Air Quality) modeling. Our first approach was based on the values averaged from 9 grid cells (overall size: 12 km × 12 km) with the Moody Tower site being in the central grid cell of the first and second model layer. Fig. 7 displays first results for the time period September 19-20, 2007, which includes the nighttime period of September 19-20, when enhanced HCHO values occurred, and the daytime period on September 20.

As shown in Figure 7 CMAQ analysis indicates non-negligible contributions from chemical reactions during nighttime that most likely result from olefin-

ozone reactions. Figure 8 shows the contribution of emissions to changes in formaldehyde mixing ratios in the area east of downtown that includes the Moody Tower (indicated by a star) and the Ship Channel. Significant source of formaldehyde emissions, contributing up to 48 ppbv/hr to changes in HCHO mixing ratio, was identified east of the Moody Tower. Additional analysis, including other time periods and also addressing the in-situ ground based HCHO sites at HRM3 and the Lynchburg Ferry site will be necessary. In addition, all these three sites have ancillary online VOC data which will be an indispensable asset for this kind of study.

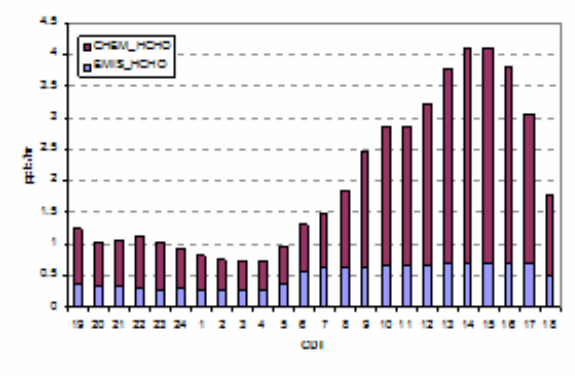

FIG. 7. Contributions of chemical processes (CHEM_HCHO) and HCHO emissions (EMIS_HCHO) to changes in ambient HCHO mixing ratios at the Moody Tower as extracted from CMAQ modeling results for the time period of September 19-20, 2007.

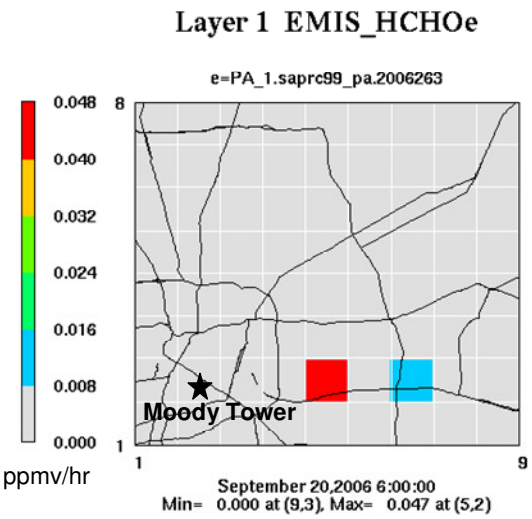

FIG.8. Spatial analysis of contributions of HCHO emissions to changes in ambient HCHO mixing ratios as extracted from CMAQ modeling results for 00:00 CST on September 20, 2007.

4. Conclusion

During TexAQS-II median in-situ HCHO values at the ground sites in the Houston area ranged between 2.9 (Moody Tower) - 6.6 ppbv (Lynchburg site). Maximum values were between 31.5 - 52.4 ppbv. The best correlation of HCHO was found with CO. Primary (traffic related) emissions of HCHO are estimated to be up to 0.7% of the CO emissions. Composite diurnal HCHO variations indicate enhanced HCHO levels at the "Ship Channel" sites. Moody Tower HCHO are also enhanced under wind directions pointing to the Ship Channel. This feature is not only restricted to daytimes, but also occurs during nighttime. It appears that under these conditions there is a tendency towards higher HCHO levels during the morning hours. Airborne HCHO measurements indicate that flare emissions may be up to 3% of flare CO emissions.

CMAQ simulates well HCHO mixing ratios at the Moody Tower; HCHO simulation at Ship Channel sites appears to be more challenging. The reason for this is that most likely Moody Tower observations reflect spatially more homogeneous emission conditions, while Ship Channel sites are exposed to point sources. CMAQ results indicate the possibility for HCHO nighttime formation, most likely through olefin-O_3 reactions.

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4. REFERENCES

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