Vehicle Emissions of Radical Precursors and Related Species Observed in the 2009 SHARP Campaign

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The value for Moody Tower HCHO vs. CO (g/kg) during the 2009 SHARP campaign was calculated following the procedure of Parrish et al. (2012), who showed in an analysis of an earlier (2006) Moody Tower data set that a day-by-day analysis using additional screening criteria is necessary to minimize contributions from other HCHO sources and arrive at an estimate of the HCHO/CO ratio from vehicle exhaust. Their criteria included a peak CO value of greater than 480 ppbv, and (to discriminate against industrial emissions) a wind direction other than east, and a peak SO₂ concentration less than 0.6 ppbv. We had to modify these criteria somewhat in order to select 7 days from the 45 days of tabulated data. The CO criterion was loosened, so that peak CO values for included days ranged from 340 to 550 ppbv, and two days of the seven, 18 and 27 May, had single transient SO₂ plumes with 1.5 ppbv and 2.3 ppbv peak values, respectively, but in neither case were these events correlated with an east wind or a corresponding increase in HCHO.

Time series and correlation plots for examples of accepted and rejected days in the HCHO analysis are given below. Two of the seven accepted days are shown in Figures S1 and S2. HCHO/CO values derived from the seven cases range from 0.0017 to 0.0043. Expressed as a molar ratio, the weighted average for HCHO/CO for the selected 7 days is 0.0024 ± 0.00013 , or $0.24\% \pm 0.013\%$, which can be compared to the Parrish et al. 13-day weighted average of $0.30\% \pm 0.02\%$. Figures S3 through S6 give examples of days which did not meet one or more selection criteria, including inadequate CO enhancements, winds from the east, and the

observation of large SO₂ plumes during the rush hour time period. The HCHO/CO ratios derived from these days are all substantially larger than those from all but one of the accepted days.

Parrish et al. also presented a discussion of a best estimate for an on- road vehicle emission ratio based on a single day's observations. It is not clear that an equivalent day is found in the 2009 data set, but it is of interest to examine one day that was excluded from the seven days used in the average, not based on any of the screening criteria but only because the correlation was poor. In some cases, poor correlation can suggest other sources of HCHO, just the artifact the screening criteria are meant to guard against, but in this case the most important reason may be the low values of HCHO observed throughout the rush hour period. This makes this case worth examining in the context of identifying upper limits for direct HCHO emissions from vehicles, so we present it here in detail. Figure S7 gives the time series and correlation plots, and Table S1 decomposes the Parrish et al. discussion of the properties of their best day (September 18, 2000) into a series of points, to which we compare the properties of May 26, 2009. It can be seen that in addition to the much poorer correlation, and a more complex wind direction history, the 2009 day did not reach the low levels of pollutant species before rush hour began that the 2000 day achieved, with the exception of HCHO itself.

Figure S1. Time series and correlation plot for one of seven days accepted to contribute to an average Moody Tower HCHO/CO ratio.

Figure S2. Time series and correlation plot for one of seven days accepted to contribute to an average Moody Tower HCHO/CO ratio.

Figure S3. Time series and correlation plot for one of the days not accepted to contribute to an average Moody Tower HCHO/CO ratio, rejected on the grounds that wind directions in the 4 a.m. to 8 a.m. time period ranged from north to east, and the east wind could have brought air from industrial regions.

Figure S4. Time series and correlation plot for one of the days not accepted to contribute to an average Moody Tower HCHO/CO ratio, rejected on the grounds that the change in CO, only about 70 ppbv, was not adequate to qualify as a strong rush hour CO enhancement suggesting a traffic source.

Figure S5. Time series and correlation plot for one of the days not accepted to contribute to an average Moody Tower HCHO/CO ratio, rejected on the grounds that the change in CO, only about 70 ppbv, was again not adequate to qualify as a strong rush hour CO enhancement suggesting a traffic source.

Figure S6. Time series and correlation plot for one of the days not accepted to contribute to an average Moody Tower HCHO/CO ratio, rejected on the grounds that wind directions in the 4 a.m. to 8 a.m. time period ranged from southwest to southeast, and due to the observation of a large SO₂ plume (peak concentration 19 ppbv at 5:55 am), both suggesting contributions from industrial sources.

Figure S7. Time series and correlation plots for a day in which the rush hour enhancement in CO was substantial, but the correlation with HCHO yields a small value of the HCHO/CO ratio.

Table S1. Comparison of the “nearly ideal” day for evaluating a vehicle emission HCHO/CO ratio, discussed by Parrish et al. with the 2009 day shown in Figure S7.

<u>Parrish et al.</u>	<u>This work</u>
18 September 2000	26 May 2009
entire preceding day the wind remained southerly (171 ± 19) preceding day winds in 280 to 340 range (NW)	
and brisk ($4.5\pm1.3\text{ms}^{-1}$).	and speed 4 m/s
	then at 6 pm changed to 180 (S)
	by 10 pm, alternating W and S
	through morning
These winds brought relatively	but always still in the 4 to 5 m/s
range past 1 a.m.	
clean marine air to the Moody Tower site;	
for example, between midnight and 01:00 a.m.	between 1:45 and 4:15 a.m.
CO = 93 ± 2 ppbv,	CO = 143 ± 3 ppbv (higher),
O ₃ = 9.6 ± 0.2 ppbv,	O ₃ = 19 ± 2 ppbv,
NO _y = 2.4 ± 0.2 ppbv,	NO _y = 3.9 ± 0.5 ppbv,
and HCHO = 0.84 ± 0.04 ppbv.	and HCHO = 0.93 ± 0.05 ppbv.
Between midnight and 06:00 a.m. the wind decreased	
in speed and rotated through westerly to northerly.	
By 06:00 a.m., winds were nearly calm allowing traffic	in the 1:45 to 6am period,
emissions to accumulate in the resulting stagnant air.	wind speeds were under 2 m/s
Since the petrochemical facilities lie generally east of the	
Moody Tower, no industrial emissions are expected to have	
impacted the measurements...This expectation is supported	
by the measured SO ₂ , which remained below 0.6 ppbv	remained below 0.24 ppbv
during the predawn period.	
From the predawn CO minimum to the morning maximum,	
HCHO was well correlated with CO ($r^2 = 0.92$)	$r^2 = 0.23$
with a linear regression slope of 0.0026 ± 0.0003	0.00057 ± 0.00029