Vehicle emissions of radical precursors and related species observed in the 2009 SHARP campaign

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The 2009 Study of Houston Atmospheric Radical Precursors (SHARP) field campaign had several components that yielded information on the primary vehicular emissions of formaldehyde (HCHO) and nitrous acid (HONO), in addition to many other species. Analysis of HONO measurements at the Moody Tower site in Houston, TX, yielded emission ratios of HONO to the vehicle exhaust tracer species NOx and CO of 14 pptv/ppbv and 2.3 pptv/ppbv, somewhat smaller than recently published results from the Galleria site, although evidence is presented that the Moody Tower values should be upper limits to the true ratios of directly emitted HONO, and are consistent with ratios used in current standard emissions models. Several other Moody Tower emission ratios are presented, in particular a value for HCHO/CO of 2.4 pptv/ppbv. Considering only estimates of random errors, this would be significantly lower than a previous value, though the small sample size and possible systematic differences should be taken into account. Emission factors for CO, NOx, and HCHO, as well as various volatile organic compounds (VOCs), were derived from mobile laboratory measurements both in the Washburn Tunnel and in on-road exhaust plume observations. These two sets of results and others reported in the literature all agree well, and are substantially larger than the CO, NOx, and HCHO emission factors derived from the emission ratios reported from the Galleria site.

Implications: Emission factors for the species measured in the various components of the 2009 SHARP campaign in Houston, TX, including HCHO, HONO, CO, CO2, nitrogen oxides, and VOCs, are needed to support regional air quality monitoring. Components of the SHARP campaign measured these species in several different ways, each with their own potential for systematic errors and differences in vehicle fleets sampled. Comparisons between data sets suggest that differences in sampling place and time may result in quite different emission factors, while also showing that different vehicle mixes can yield surprisingly similar emission factors.

Introduction

Recently, Rappenglück et al. (2013) reported ambient air measurements at the interchange of Interstate 610 and US 59 in the Galleria area of Houston, TX. Species measured included formaldehyde (HCHO), nitrous acid (HONO), carbon monoxide (CO), carbon dioxide (CO2), and nitrogen oxides (NO/NO2/NOx). This study, Traffic Emissions of Nitrous Acid and Formaldehyde (TRENF), was a subexperiment of the 2009 Study of Houston Atmospheric Radical Precursors (SHARP) field campaign (Olaguer et al., 2014). A second SHARP component, the HONO Inter-comparison (HINT), involved measurement of most of the same species, and more, on the roof of one of the Moody Tower dormitories at the University of Houston. A third subexperiment, Formaldehyde and Olefins from Large Industrial Releases (FLAIR), included several on-road and tunnel measurements of vehicle exhaust emission ratios by the Aerodyne Mobile Laboratory, not only for HCHO but also for a wide range of volatile organic compounds (VOCs). These measurement programs all provided information on the primary vehicular emissions of HCHO and HONO, whose photolysis is responsible for much of the HOx radical (OH and HO2) production that initiates ozone formation processes (Rappenglück et al., 2013; Olaguer et al., 2014). In this paper, the TRENF results are compared to analyses of HINT data taken at Moody Tower and FLAIR measurements of emission factors in the Washburn Tunnel. Comparison of the roadside observations of Rappenglück et al. with those from Moody Tower, which is further away from traffic sources, requires some care, while tunnel measurements have potential for their own artifacts, so examination of all three types of
vehicular emissions measurements for roughly the same time and area can be instructive.

Methods

An overview of the Moody Tower measurements in 2009 is found in Ren et al. (2013). The HONO instrumentation used in the HINT study has been reviewed by Pinto et al. (2014). In all, six HONO instruments were operated for various time periods, with all instruments operational between May 16 and May 30, 2009 (referred to as the common measurement period). Agreement between the instruments was good enough that, for our purposes, almost any data stream would suffice for most time periods. Since we are most familiar with its characteristics, we focused on the Harvard/Aerodyne continuous-wave Tunable Infrared Differential Absorption Spectrometer (cw-TILDAS) (Lee et al., 2011a; Lee et al., 2013) measurement, based on HONO line strengths reported by Lee et al. (2012). Since there were significant times when this instrument did not report data, we also included data from the long path absorption photometer (LOPAP) operated by the University of Houston, which is also the instrument used at the Galleria site by Rappenglück et al. (2013). These two instruments agreed well: correlating all simultaneous data points during the common measurement period yielded a slope (LOPAP with respect to cw-TILDAS) of 0.98 ± 0.02 with an \( r^2 \) of 0.55 (Pinto et al., 2014). The LOPAP instrument is described in Kleffmann et al. (2006) and references therein.

The Moody Tower HCHO measurement used here was one of a number of species measurements made by a proton transfer reaction mass spectrometer (PTR-MS) (Jobson et al., 2005). Since the HCHO proton affinity is near that of water, the PTR-MS required a special cryogenic trap for reducing the humidity of the sampled air. The long-path DOAS, which was one of the six HONO measurements, also measured HCHO (Platt and Stutz, 2008), but in this analysis we used only the PTR-MS since it was an in situ point measurement like the HONO data sets we used, with a collocated inlet. A set of standard or modified trace gas analyzers, operated by the University of Houston but in some cases provided by the NOAA Air Resources Laboratory, provided measurements of CO (Thermo Electron 48c-TLE), NO/NO\(_2\)/NO\(_3\) (Thermo Electron 42c-TL), and SO\(_2\) (Thermo Electron 43).

Figure 1 shows the position of the Galleria and Moody Tower sites with respect to major highways (and hence high traffic emissions), downtown Houston, and the city’s industrial area, which extends to the east along the Houston Ship Channel beginning around the Turning Basin. The Galleria site is inside the highway junction of I-610 and I-69/US 59. The Moody Tower site is in a triangle of more distant freeways, 1.6 km SSW of the closest freeway (I-45/Gulf Freeway). The closest distance (WNW) to S288/South Freeway is about 3.5 km, and the I-610/South Loop E Freeway is 4 km to the south.

The Aerodyne Mobile Laboratory houses a suite of state-of-the-art trace gas and particulate measurement instrumentation, meteorological instrumentation, global positioning system (GPS), and a digital video recorder for making mobile air quality measurements (Kolb et al., 2004). Most of the instrumentation has relatively rapid response times (~1 sec), making the suite suitable for characterizing plumes and other transient encounters in the atmosphere. For SHARP, the mobile laboratory made measurements downwind from industrial facilities in several regions in the Houston area (Wood et al., 2012; Knighton et al., 2012) and was also operated to collect emissions from mobile sources. In particular, two passes through the Washburn Tunnel (which passes under the Houston Ship Channel about 6 km east of the Turning Basin) were made on each of three days: April 23, April 26, and May 22, 2009. Some on-road “chases” were also conducted, and continuous data collection during transit to and from industrial sites led to a substantial database of vehicle plume observations.

Among the mobile laboratory measurements utilized here, the combustion tracers CO and CO\(_2\), NO\(_2\), and the trace gases ethene (C\(_2\)H\(_4\)) and HCHO were measured spectroscopically. CO\(_2\) was determined by nondispersive infrared absorbance using a LiCor 6262 instrument. The other species were measured by TILDAS instruments using pulsed quantum cascade laser systems (McManus et al., 2010; Dallmann et al., 2013). Calibrations of these instruments were checked using certified gas standards. NO was measured with a Thermo Electron 42i chemiluminescent analyzer, and the NO\(_3\) measurement reported here is the sum of this NO and the TILDAS NO\(_2\). A modified proton transfer reaction mass spectrometer operated using either H\(_2\)O\(^+\) (PTR mode) or NO\(^+\) (Knighton et al., 2009) as the chemical ionization reagent ion was used to measure a set of VOC and ozone precursor species. Washburn Tunnel transits were made while the PTR-MS was operating in the proton transfer mode only on May 22, while during the April passes it was operated in the NO\(^+\) mode. Although these two modes of operation detect a somewhat different suite of target species, they also detect some of the same species, and the results showed satisfactorily similar emission ratios in these cases. Species measured included benzene, toluene, C2-
benzenes (sum of \( C_8H_{10} \) isomers), and C3-benzenes (\( C_9H_{12} \) isomers), and (in PTR mode) acetaldehyde, propenes, and butenes, or (in NO\(^+\) mode) 1,3-butadiene and styrene. In this paper, the last four species are not reported, since vehicle exhaust can contain other species that interfere with the mass peaks used for propenes and butenes, and the NO\(^+\) mode was rarely used in on-road measurements.

Results

Traces for HONO concentrations and several other quantities at the Moody Tower site for an example day are shown in Figure 2. Although on any given day the agreement between cw-TILDAS and UH LOPAP measurements of HONO is no better than seen in the figure, both the good correlation noted earlier and an examination of the entire common measurement period do not support a conclusion of significant systematic bias between the two instruments. The wind speed and direction measured at Moody Tower and the concentrations of CO and NO\(_x\), two species commonly used as traffic tracers (indicators that ambient air contains significant vehicle exhaust emissions), are also plotted in Figure 2.

For the example in Figure 2, both HONO instruments yielded data throughout the morning traffic peak, seen clearly in all four species traces. However, the cw-TILDAS instrument often experienced a problem with condensation in the zero-air line in the early morning, causing data dropouts covering some of the morning rush hour. This made it difficult to derive HONO emission ratios using the method of Rappenglück et al. (2013), a correlation of data streams over the entire morning rush hour time period (in the following, however, this technique is applied to the UH LOPAP HONO data). Instead, since data from both Moody Tower HONO instruments were available in the very early morning and at the rush-hour peak, we calculated differences in HONO concentrations for these two times, and computed ratios to differences in CO and NO\(_x\) for the same times. The two vertical lines in Figure 2 denote the times chosen for that day, 03:35:30 and 05:52. The average times for the 20 days analyzed for cw-TILDAS were 04:22 and 06:09, with standard deviations of 32 and 25 minutes. At these early hours, the HONO destruction lifetime due to both photolysis and reaction with OH is greater than 1 hr (only dropping below 20 min by 8 a.m.), while the transit time from the nearest freeway source is almost always less than 0.5 hr.

Figures 3 and 4 present the results obtained by this process of taking ratios of rush-hour differences, using data from both HONO instruments, and the two traffic tracers CO and NO\(_x\). Rather than plotting against the measurement date, they are plotted against wind speed. Each figure also contains two additional plotting symbols, denoting the average ratios obtained at the Galleria site by Rappenglück et al. (2013) by the correlation technique, and the average ratios obtained by the same technique using the UH LOPAP HONO measurement at Moody Tower. Since these averages are not associated with a particular wind speed, they could be represented by a point at any arbitrary wind speed, or perhaps better by a line extending over all wind speeds, but in the figures we have chosen arrows as plotting symbols, to suggest the key point involved with
plotting Moody Tower observations versus wind speed. This is that the wind speed can be considered to be the inverse of the time from the vehicle exhaust source. Therefore, the Rappenglück et al. (2013) value, obtained in the middle of the traffic source, applies to a transit time much smaller than any associated with a wind speed plotted in Figures 3 and 4, and thus should be compared with an extrapolation extending well to the right of the edge of each figure. The average of the UH LOPAP data set, on the other hand, simply includes all the points in the figure, so its plotting symbol is a double-headed arrow.

Not surprisingly, the correlation between wind speed and the emission ratios in Figures 3 and 4 is by no means perfect. There are many other variables involved that influence the ratios from day to day, including wind direction and distance to the nearest downwind highway. However, all four fits in Figures 3 and 4 have the same qualitative behavior, and the two HONO measurements yield quantitatively similar slopes in both figures. Thus, all four fits in the two figures confirm our expectation that ratios of Moody Tower HONO measurements to more stable vehicle exhaust species are upper limits, and Moody Tower HONO is actually a sum of HONO directly emitted in vehicle exhaust and HONO formed in other ways, quite possibly from precursor vehicle exhaust species, during transit from the source to Moody Tower. At the early hours covered by the figures, there is net HONO formation as high levels of NO in exhaust react with ambient OH, as demonstrated by the model calculations of Lee et al. (2013). Clearly, the correlations in Figures 3 and 4 do not allow a trustworthy extrapolation to a value for directly emitted HONO, but the figures do raise the question of whether the values of Rappenglück et al. (2013) are the best estimates of these HONO emission ratios for Houston in 2009.

In Table 1 we present average values of these and other emission ratios for the Galleria and Moody Tower data sets. These are based on a different analysis than used to make the points fit in Figures 3 and 4. In Table 1, points for all selected days were used in a single correlation plot, and the slope of the fit line through the combined set of points is taken as the average emission ratio. The selected days are also different: May 17 through 23, 25, and 29 through 31 (originally selected as a set of clear days, before it was found that there were not

| Galleria vs. | Slopes of correlation plots (kg/kg unless otherwise noted) for Galleria site (July 15–October 15, 2009—all days) (Rappenglück et al., 2013) and Moody Tower (UH LOPAP measurements) (May 17–31, 2009—11 clear days) for morning rush hour (4 a.m. to 8 a.m.) |
|-------------|-------------------------------------------------------------------------------------------------|
| CO vs. NOx  | 3.67 (± 0.09) ($r^2 = 0.91$)                                                                     | 3.13 (± 0.18) ($r^2 = 0.87$) |
| HCHO vs. CO (g/kg) | 3.14 (± 0.14) ($r^2 = 0.68$)                                                                 | 2.57 (± 0.28)*               |
| HONO vs. NOx | 0.017 (± 0.0009) ($r^2 = 0.75$)                                                                | 0.014 (± 0.0012) ($r^2 = 0.67$) |
| HONO vs. CO  | 0.0046 (± 0.0002) ($r^2 = 0.75$)                                                                | 0.0038 (± 0.0004) ($r^2 = 0.55$) |
| NO2 vs. NOx  | 0.16 (± 0.01) ($r^2 = 0.48$)                                                                    | 0.63 (± 0.02) ($r^2 = 0.93$) |
| NO vs. NOx   | 0.84 (± 0.01) ($r^2 = 0.96$)                                                                    | 0.37 (± 0.02) ($r^2 = 0.81$) |
| CO vs. CO2   | 0.0033 (± 0.0002) ($r^2 = 0.73$)                                                                 | |

*See discussion. Based on individual analyses of 7 days, with $r^2$ values ranging from 0.59 to 0.88.
cloudy days of sufficient quality to form a comparison set). Fortuitously, the average of the UH LOPAP points in Figures 3 and 4 yields the same emission ratios (14 pptv/ppbv or 0.014 g/kg for HONO/NOx and 2.3 pptv/ppbv or 0.0038 g/kg for HONO/CO) as the values in Table 1 (which are also plotted as the double-headed arrows in Figures 3 and 4). It can be seen that the Galleria and Moody Tower values for HONO emission ratios with respect to both NOx and CO lie within two standard deviations of each other. However, if we take the Moody Tower value as an upper limit, this implies a somewhat larger disagreement, and suggests that the Galleria value of 0.017 kg/kg for HONO versus NOx need not be adopted in preference to smaller values currently used in air quality models. The current HONO/NOx value of 0.008 kg/kg (based on the results reported by Kurtenbach et al., 2001) used in the standard U.S. Environmental Protection Agency (EPA) MOVES traffic emissions model is certainly consistent both with the Moody Tower upper limit of 0.014 ± 0.0006 kg/kg in Table 1 and with reasonable extrapolations of the trends in Figure 3. (We also note a recent measurement of diesel-powered generator exhaust by Lee et al. [2011b]) using the same cw-TILDAS instrument, yielding a HONO/NOx value of 0.0082 ± 0.0005 kg/kg.)

Table 1 is modeled after Table 5 of Rappenglück et al. (2013). It is possible to generate Moody Tower comparison points for every entry in that table with the exception of the ratio of CO to CO2 (there was no CO2 measurement on Moody Tower during HINT). The Galleria–Moody Tower difference in NO2 versus NOx and NO versus NOx ratios is what one would expect under the assumption that Moody Tower is farther from the vehicle exhaust sources of NOx, allowing more time for NO to NOx conversion. The lower value of CO/NOx at Moody Tower is surprising, however. The larger distances from Moody Tower to major freeways might be expected to result in a lower fraction of diesel trucks contributing to the CO and NOx emissions, and the longer transport distance could lead to larger losses of NOx than the less reactive CO, but both these effects would have opposite results to the observed difference. On the other hand, Moody Tower is almost adjacent to the University of Houston Hilton hotel, and we can speculate that delivery trucks, observed to be present in the early morning, could be partly responsible for a lower CO/NOx ratio. If this were so, it would be an example of how microscale variations in vehicle mix could affect measurements for a single time and place intended to be representative of an entire region.

The entry in Table 1 for Moody Tower HCHO versus CO (g/kg) requires some additional discussion. If the same procedure had been used as for the other table entries (a correlation of the combined data sets for the same 11 days) the resulting ratio would have been much larger. However, Parrish et al. (2012), in an analysis of an earlier (2006) Moody Tower data set, showed 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 using data before and during the morning traffic peak. Their criteria (satisfied by 13 days in their data set covering August 13 to October 2, 2006) included a peak CO value of greater than 480 ppbv, and two ways of discriminating against industrial emissions: a wind direction other than east (from the industrial region of the Houston Ship Channel), and a peak SO2 concentration less than 0.6 ppbv. To arrive at the seven days used for the HCHO/CO entry in Table 1, we had to modify these criteria somewhat. The CO criterion was lowered, so that peak CO values for included days ranged from 340 to 550 ppbv (the change in CO over the time period used in the correlation, perhaps more indicative of a substantial traffic contribution, ranged from 180 to 300 ppbv). As to the SO2 criterion, the data on May 12, 24 and 29 pass, based on data from both chemiluminescent analyzer and DOAS instruments, while April 21 and 22 had only DOAS data but also pass the 0.6-ppbv test within the uncertainty of that measurement. The May 18 and 27 data had single transient SO2 plumes with 1.5-ppbv and 2.3-ppbv peaks, 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 in the Supplemental Information. Expressed as a molar ratio, the weighted average for HCHO/CO for the selected seven days is 0.0024 ± 0.00013 (or 0.24 ± 0.013% or 2.4 pptv/ppbv), which converts to the value of 2.57 g/kg cited in Table 1. This ratio can be compared to the Parrish et al. (2012) 13-day weighted average in 2006 of 0.30 ± 0.02% (a discussion of comparison to their best estimate for an on-road vehicle emission ratio based on a single day’s observations is given in the Supplemental Information).

It is also of interest to compare the Galleria site ratios in Table 1 with FLAIR measurements of emission factors in the Washburn Tunnel. We can do this by using the CO/CO2 ratio to convert the other ratios in Table 1 to emission factors in units of g pollutant/kg fuel. As a preface, we discuss the CO emission factor implied by the Table 1 value of 0.0033 kg(CO)/kg(CO2), or equivalently the concentration ratio of 5.2 ppbv/ppmv reported by Rappenglück et al. (2013), each of which converts to an emission factor of 10 g(CO)/kg(fuel). Rappenglück et al. cite Newman et al. (2013) and Rubio et al. (2010) as reporting values of similar magnitude. The latter measured CO/CO2 ratios in different locations of Santiago de Chile city in 2005 to 2007 and reported a range of emission factors, with higher values applying to traffic that was mainly cars with catalytic converters and lower values at sites dominated by diesel-powered public transportation. Rappenglück et al. summarize Rubio et al. as finding emission factors of 10 ± 3 for diesels and 28 ± 16 g(CO)/kg(fuel) for cars.

In their analysis of emissions near Los Angeles, CA, in 2010, Newman et al. assume a CO/CO2 ratio determined in Pasadena, CA, in 2007 and 2008 by correlating excess CO and CO2 measured with a ground-based Fourier-transform spectrometer (Wunch et al., 2010). This ratio includes contributions from other combustion sources in addition to vehicles (although care was taken to remove influence of wildfires), and if it were converted to an emission factor it would yield 22 g(CO)/kg(fuel). Newman et al. cite other studies supporting this assumption, including Vogel et al. (2010) (whose 14C determination of excess CO2 yielded a CO/CO2 ratio equivalent to an average emission factor of 31 ± 11 g(CO)/kg(fuel) with a median of 29 g(CO)/kg(fuel)), and the lower limit of
values reported by Bishop and Stedman (2008) (an emission factor of 18 g(CO)/kg(fuel)). Newman et al. also report values of excess CO and CO₂ from their own measurements, with the ratio at the peak of a rush-hour maximum in CO yielding an emission factor of 23 g(CO)/kg(fuel).

Although the already-cited emission factors cover a range of not much more than a factor of 3, it is well known that measurements in other places and times have yielded much larger values, and a few smaller values. A recent review (McDonald et al., 2013) tabulates 53 measurements of CO on-road emission factors for gasoline vehicles, with the lowest value, $14.3 \pm 0.7$ g(CO)/kg(fuel), measured in 2010 in the Caldecott Tunnel in Oakland, CA (Dallmann et al., 2013). The corresponding value for diesel vehicles is $8.0 \pm 1.2$ g(CO)/kg(fuel) (Dallmann et al., 2012; Gentner et al., 2013). It has long been known that CO/CO₂ ratios can have a broad distribution, with a few “superemitters” strongly influencing average values (see, e.g., Jiang et al., 2005), so it is of interest to consider whether the Rappenglück et al. (2013) average value of $10 \pm 1$ g(CO)/kg(fuel) is as low as it is due in part to an absence of very-high-ratio vehicles in their observations. Indeed, Rappenglück et al. (2013) tabulate the maximum values of excess CO and CO₂ measured at the Galleria site, and converting those values yields an emission factor for the highest signals observed of 18 g(CO)/kg(fuel). Of course, this was not necessarily the highest ratio observed, and not necessarily CO and CO₂ signals from the same vehicle or even on the same day, but it still stands as a check on the relatively small standard deviation reported for the slope derived from the Galleria data set.

Thus, the context just discussed places the CO/CO₂ ratio reported by Rappenglück et al. (2013) among the lowest literature values observed, and therefore using it to derive emission factors for other species, as is done in Table 2, will result in those emission factors also being relatively low. Comparing them with the emission factors measured by the Aerodyne Mobile Laboratory in the Washburn Tunnel shows this to be so. Of course, it is well known that differences in the vehicle mix, not just from city to city but from neighborhood to neighborhood, can strongly influence emission factor measurements, sometimes even more strongly with the well-documented decrease in emission factors with time. For example, the NOₓ emission factor of 6.6 g/kg(fuel) for gasoline vehicles in the Caldecott Tunnel in 1999 (Kean et al., 2000) is smaller than the 9.5 g/kg(fuel) measured in the Washburn Tunnel in 2000 (McGaughy et al., 2004). As another example, Ban-Weiss et al. (2008) report emission factors for HCHO from several measurements in the Caldecott Tunnel. Their 2006 value of $0.016 \pm 0.0014$ g/kg(fuel), their 2001 value of $0.042 \pm 0.003$, and even the 1999 value (Kean et al., 2001) of $0.043 \pm 0.005$ are all smaller than the 2009 Houston, TX, value of $0.088 \pm 0.010$ in Table 2.

We expect the Washburn Tunnel vehicle population in 2009 to have been strongly biased toward gasoline-powered vehicles, since large diesel trucks were banned from the tunnel. In the preceding, we raised the possibility that the low CO/CO₂ ratio observed by Rappenglück et al. (2013) at the Galleria site could be due to a different traffic mix, either much cleaner cars or a higher proportion of diesel trucks (or both). The Aerodyne Mobile Laboratory, while traveling to and from sites in the Houston Ship Channel area, also observed many on-road vehicle exhaust plumes, expected to be mostly from large diesel trucks. It is of interest to make a comparison between the Washburn Tunnel emission factors and values based on a selection of these on-road plumes, which are tabulated in the third column of Table 2. After an initial screening to eliminate high CO emissions (often indicating self-sampling of the mobile laboratory exhausts) and the rejection of the largest and smallest five values, data from up to 100 plumes were used.

The 95% confidence limits reported in the on-road column of Table 2 only address random errors. Systematic errors were estimated by using several methods to calculate emission ratios. Seventy plumes were analyzed using the integration method used for the Washburn Tunnel data, in which some judgment was used in selecting zero values before and after the plume, while over 50 plumes were analyzed using automated procedures yielding both ratios of integrals and fits through correlation plots of emitted species versus CO₂. Comparisons between sets of plumes receiving more than one of these three procedures suggest that systematic errors present in all three related to choosing zero values are often less than 20% but could for small emission factors reach factors of 2, although much more work would be required to achieve a full understanding of these potential errors. It is remarkable, then, that the on-road and Washburn Tunnel columns in Table 2 agree as well as they do, with differences being equal to the combined error limits including a moderate estimate of systematic errors. However, we can also note that the VOC species that are lower in on-road measurements are all present in fuel, while those that are higher are combustion products (where benzene, though a minor fuel component, is more importantly a combustion product). This suggests that while on-road

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**Table 2.** Emission factors, in grams of pollutant per kilogram of fuel burned, from Galleria Interchange and from Aerodyne Mobile Laboratory Washburn Tunnel and on-road measurements.

| Species       | Rappenglück et al. | Washburn Tunnel | On-Road Houston plumes |
|---------------|---------------------|-----------------|------------------------|
| CO            | 10 ± 0.7            | 25 ± 3          | 32 ± 5                 |
| NOₓ           | 2.8 ± 0.07          | 9.0 ± 0.9       | 14 ± 2                 |
| Formaldehyde  | 0.033 ± 0.0015      | 0.088 ± 0.010   | 0.17 ± 0.04            |
| Ethene        | 0.37 ± 0.11         | 1.1 ± 0.35      |                        |
| Benzene       | 0.10 ± 0.021        | 0.2 ± 0.05      |                        |
| Toluene       | 0.18 ± 0.033        | 0.15 ± 0.07     |                        |
| C2 Benzenes   | 0.17 ± 0.032        | 0.15 ± 0.04     |                        |
| C3 Benzenes   | 0.15 ± 0.028        | 0.085 ± 0.03    |                        |
| Acetaldehyde  | 0.071 ± 0.013       | 0.12 ± 0.03     |                        |

*Note. Error limits are 95% expectation values based on standard deviations. A discussion of systematic errors is found in the text.*
measurements are biased toward high emitters, since large exhaust plumes are most easily identified, tunnel measurements give a more accurate picture of both exhaust and evaporative emissions, thus enhancing emissions of those components that are present in both the fuel and the exhaust relative to what is observed on-road.

In contrast to CO and the VOC species, NOx is seen to be significantly higher in the on-road data set. This, of course, is consistent with the expectation that the on-road plumes are primarily from large diesel trucks, which are expected to have higher NOx emissions. In this regard, then, it is interesting to note that although the Galleria value of CO emission factor is only a factor of 3 lower than that in the Aerodyne Mobile Laboratory on-road column, the Galleria NOx emission factor is more than a factor of 7 lower.

The plausibility of the 2009 Houston, TX, measurements made by the Aerodyne Mobile Laboratory (AML) of VOC and ozone-precursor species shown in Table 2 can be reinforced by comparing to AML measurements in Mexico City, Mexico, in 2006 (Zavala et al., 2009) and in the Caldecott Tunnel in 2010 (Gentner et al., 2013). Mexico City in 2006 should have had a higher-emission vehicle fleet than Houston in 2009 (only 80% of the 2006 Mexico City gasoline fleet had catalytic converters [Zavala et al., 2009], compared to essentially all non-diesel vehicles in the Houston fleet), and Oakland, CA, would have had a lower emission fleet (see the earlier discussion of emission factors for NOx and HCHO in Table 2 compared to earlier years in the Caldecott Tunnel), and this turns out to be reflected in the three data sets. Furthermore, the relative amounts of all the species in the table are fairly well preserved: The ratios of Washburn Tunnel 2009 emission ratios to the Caldecott 2010 values range from 2.4 to 6.5, while the ratios of Washburn Tunnel 2009 to Mexico City 2006 values are from 4 to 6 times lower, with the exception of acetaldehyde, which is only 1.3 times lower.

Conclusions

Putting the Galleria interchange roadside measurements of Rappenglück et al. (2013) in the context of other measurements carried out during the SHARP campaign has shown many points of agreement. Even those values that differ the most are often separated by only a few standard deviations, differences that could have one or more explanations, including differences in the observed vehicle mix. The most important of this latter class are the HONO fraction of vehicle exhaust, where values in current models may not yet require the substantial upward revision suggested by Rappenglück et al., and the CO emission factor, whose value as reported by Rappenglück et al. lies at the lower limit of the range of measurements for on-road U.S. vehicles carried out through 2010, while the values obtained by the Aerodyne Mobile Laboratory in the Washburn Tunnel are in better agreement with other comparable measurements and with the values in current traffic emission models.

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Supplemental Material

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