Emissions of Radical Precursors and Related Species from Traffic in Houston, Texas - Implications for Air Quality Modeling

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ABSTRACT

The EPA has classified the Houston-Galveston-Brazoria region as in non-attainment for the 1-hour and the 8-hour ozone standards. This study will focus on the precursors of ozone from mobile sources in the Houston region.

Nitrous acid (HONO) and formaldehyde (HCHO) are known to be important precursors for radicals and are believed to favor ozone formation significantly. So far only scarce traffic emissions data that includes both compounds is available. However, this knowledge is needed to further refine and validate air quality modeling as well as to predict/simulate impact of these emissions on air quality. This study reports measurements of HCHO, HONO, CO, $NO/NO_2/NO_x$, peroxycarboxylic nitric anhydrides (PANs), and meteorological parameters which were performed in the immediate vicinity of a highly frequented urban highway junction in Houston. The observational data is compared to emission estimates from currently available mobile emissions models (MOBILE6 vs MOVES) and implications for air quality modeling are mentioned.

INTRODUCTION

Figure 1 describes in principle the fast reaction cycles involved in the formation of secondary species as well as the removal mechanisms from those cycles for nitrogen and carbon containing species. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and controls the atmospheric lifetimes of most trace gases. OH is largely produced in photolysis processes of ozone (O_3), formaldehyde (HCHO) and nitrous acid (HONO). Minor OH sources are associated with photolysis of H_2O_2, $ClNO_2$ and ozonolysis of alkenes, the latter one being an important nighttime source for OH.

OH initiates oxidation reactions with NO_x, CO, anthropogenic and biogenic VOCs. These reactions form peroxy radicals (RO_2) which in turn will cause the conversion of NO to NO_2 and subsequently the formation of O_3. Within the degradation of VOC also carbonyls will be formed which either may be photolyzed (e.g. HCHO) or oxidized by OH and finally contribute to the formation of peroxycarboxylic nitric anhydrides (PANs). Loss mechanisms for OH involve reactions between peroxy radicals leading to hydrogen peroxide (H_2O_2) and organic peroxides, e.g. methylhydroperoxide (MHP) and hydroxylmethylhydroperoxide (HMHP), and reactions with NO_2 leading to nitric acid (HNO_3) and PAN.

Apart from point sources, such as flares, stacks and other industrial sources, mobile sources may emit HCHO[1] and HONO[2]. An analysis using the Community Multiscale Air Quality (CMAQ) 4.71 (Figure 2) shows that while photolysis of ozone is an important source for OH around noon and in the afternoon hours, HCHO may contribute most to OH formation during late morning hours, and HONO is a very efficient source for OH formation during early morning hours[3].

While HCHO may be formed from ozonolysis of terminal olefins, a pathway that does not consume OH, it can also be emitted primarily from incomplete combustion in either mobile or stationary sources[4,5,6,7]. Traffic related emission ratios of HCHO/CO were found around 1.3-1.4 pptv HCHO / 1 ppbv CO in earlier studies[8], while more recent studies report higher values[1,9].

HONO can be emitted primarily from various combustion processes[10,11] and emissions from traffic can significantly contribute to observed HONO levels. For example, Sarwar et al.[12], found that direct emissions contributed ~14% to the HONO budget in their model, based on emission ratios on literature values[10,11]. So far only scarce traffic emissions data is available for HONO. Most of them have been performed more than a decade ago. The results indicated exhaust emission ratios of HONO to NO_x in the range of 0.3-0.8%[10,11,13]. Different emission ratios may reflect a different composition of the car fleet. The first two measurements were obtained in tunnel studies. However, tunnel measurements may be biased due to the restrictions for specific vehicles (e.g. heavy duty vehicles) and due to significant surface to volume ratio that may have been impacted by heterogeneous NO_2 to HONO on the tunnel walls.

So far only scarce traffic emissions data is available which includes both compounds. In particular for HONO, traffic related data was obtained more than a decade ago. A better knowledge of today's HCHO and HONO emissions related to traffic is needed to further refine and validate air quality modeling such as CMAQ v4.7. Here we will report results from longterm roadside measurements performed in Houston, TX and compared the observational data to emission estimates from currently available mobile emissions models (MOBILE6 vs MOVES). While there have been some comparisons between MOBILE6 and MOVES with regard to differences model performance[14,15], to our knowledge no comparison and validation with roadside measurements has been carried out so far.

METHODS

Experimental Data

During the time period July 15- October 15, 2009 continuous ambient air measurements were taken in the immediate vicinity of the Highway Junction I-59 South/610 located in the Galleria, Houston, area (Figure 3). Figure 4 shows pictures of the measurement location. This Highway Junction has one of the highest traffic loads in Houston, including high amounts of heavy duty diesel vehicles. A mobile measurement facility was set up close to a pumping station maintained by the Texas Department of Transportation (TxDOT). Table 1 lists selected measurements performed at this site. This location was completely surrounded by highway lanes, ramps, and other roads and impacted by traffic emissions regardless of the wind direction. Since the measurements of speciated peroxycarboxylic nitric anhydrides (PANs) had the longest measurement interval (10 min) all the data was merged to a 10 min interval data base.

In order to determine traffic related emissions of HONO and HCHO only a subset of 10-min averaged data was used which met the following prerequisites:

1) weekdays
2) rush hour time 4:00-8:00 am CST
3) global radiation < 10 Wm^{-2}
4) PAN < 50 pptv
5) no precipitation
6) RH > 80%

(1)-(2) considered changing sunrise times throughout the campaign while making sure that only rush hour times with negligible radiation was included. (4) was applied to discriminate freshly emitted air masses from photochemically processed air masses. While (1)-(4) already yielded high correlation

coefficients for various relationships, e.g. CO vs NO_x or HCHO vs CO, the inclusion of (5)-(6) led to significant increase of r^2 for relationships including HONO.

Above prerequisites are very strict conditions. For instance condition (3) limited further significantly the available data sets for rush-hour times as sunrise often occurred before 8:00 am CST. Also, (4) is a very strict condition keeping in mind the wide range of PAN values as shown in Table 2. As a test for the validity of this approach a correlation analysis of CO vs. NO_x was performed first. The results are shown in Figure 5 The data set displays strong relationship of CO vs NO_x (r^2=0.91) with a slope of 6.01 ppbv CO / 1 ppbv NO_x. This is in very good agreement with Parrish et al.[25] for rush hour times in selected cities. We thus consider our data screening to be representative for traffic emissions. CO/NO_x ratios have decreased in the US over the last years due to a slow decrease of CO emissions slightly compensated by an increase in NO_x emissions[25].

Emission Modeling

The traffic emissions models MOBILE6 and MOVES [Motor Vehicle Emission Simulator] were used for the area of the measurement site for 9/28/2009 as an exemplary day. This day was chosen, since the experimental data showed maximum data availability for one given day based on the data screening approach described further below. An hourly link based calculation was performed, including all the emissions coming from all the links around 1000 feet radii around the intersection. Following is the explanation of the different inputs that went into each model.

MOBILE6:

The emissions were calculated using the latest available MOBILE6 emission factor model, MOBILE6.2[16] and the TTI [Texas Transportation Institute] Suite of programs[17] to estimate link based emissions using MOBILE6. The VMT (Vehicle Miles Travelled) was calculated using EMME2 as the travel demand model. The following parameters were chosen to calculate the hourly Harris county emission factors for on-road:

1) Observed meteorology at the Galleria site for the model day: September 28, 2009
2) 2009 local registration distribution
3) 2009 local diesel fractions
4) 2009 local VMT per hour
5) Local inspection and maintenance program
6) Anti-tampering program
7) Reformulated gasoline

Then the emission factors were adjusted, using the TTI Suite of programs, for the Texas Low Emission Diesel and the Motorcycle Rule[18]. The emissions calculations were done using the adjusted emission factors, the 2009 VMT mix and the hourly link VMT and speeds activity estimates calculated with EMME2. The output is link-level emissions by vehicle type in grams.

The emission calculations were performed for the following pollutants: NO_x, VOC, CO and formaldehyde. It was decided not to perform the calculation for CO_2 since MOBILE6 has a very simple capability to calculate CO_2 emissions and is mainly based on fuel economy, and unlike other pollutants, these CO_2 emissions are independent of temperature, speed, fuel content or effects due to the inspection and maintenance program. As a consequence, these CO_2 emission estimates should only be used to model areas and time periods that are large enough to assume that the variation of these parameters do not have a significant impact.

All these calculations were done considering the diesel/gasoline split on the arterial and freeway facility types as shown in Table 3. The splits were calculated using TxDOT (Texas Department of Transportation) traffic counts for each facility type. Figure 6 shows the diurnal weekday variation of VMT for the Galleria site study area for 2009. It clearly reflects the different periods as defined in Table 3, in particular it shows the two rush hour periods with VMT in the range of 30-35,000 per hour and the mid-day period which has about 60% of the rush hour VMT. During the overnight periods VMT is usually in the 2-5,000 range.

MOVES2010a and 2010b:

The emissions were calculated using MOVES2010a[19] as an emission factor model for the following pollutants: NO_x, CO, VOC, Formaldehyde, CO_2 (atmospheric), NO, NO_2. Then, when MOVES2010b[19] became available, HONO was also calculated.

The emissions were calculated using the TTI Emission Inventory Estimation Utilities Using MOVES: MOVESUTL[20] to estimate link based emissions. The VMT was calculated using EMME2 as the travel demand model. The following tables were used to enter local data into the County Data Manager to calculate the hourly Harris county emission factors for on-road and off-network:

1) Avgspeeddistribution – lists the average speed data specific to vehicle type, road type, and time of day.
2) Dayvmtfraction – lists the daily VMT fractions according to day type, source type, road type and month.
3) Fuelformulation – lists properties of fuels.
4) Fuelengfraction – lists the vehicle types with different types of fuels [represents the old diesel fractions on MOBILE6]
5) Fuelsupply – lists the market share for each fuel.
6) Hourvmtfraction – lists the hourly VMT fractions according to the hour, source type, road type and day type.
7) Hpmsvtypeyear – lists the year VMT for each source use type
8) Imcoverage – lists information regarding inspection and maintenance programs.
9) Monthvmtfraction – lists monthly VMT fractions according to month type and source type
10) Roadtypedistribution – lists the distribution of vehicle miles traveled by road type.
11) Sourcetypeagedistribution – lists the distribution of vehicle counts by age.
12) Sourcetypeyear – lists the number of vehicles in geographic area per source type.
13) Zonemonthhour – lists the temperature and humidity data.

Then the emission factors were adjusted, using the TTI utilities, for the Texas Low Emission Diesel and the Motorcycle Rule. For on-road and off-network sources, the emissions calculations were done using the adjusted emission factors, the 2009 SUT (source use type) mix, the off-network activity (vehicle population, source hours parked, starts and extended idle hours), and the hourly link VMT and speeds activity estimates calculated with EMME2. The output is hourly link-level emissions by SUT/fuel type combination. Please note that for on-road emissions, only the links selected for the study area were used in the calculations; for off-network emission, the total county emissions were adjusted according to the VMT ratio of the study area versus county area.

RESULTS AND DISCUSSION

Table 2 lists some statistical data about the field campaign measurements. It is worth to note that median HONO values were at relatively high levels about 0.5 ppbv, while median values of other predominantly primarily emitted compounds (NO_x, CO) showed some modest values. HONO maximum values of about 5 ppbv occurred in the early days of September 2009, when the Houston CAMS

(Continuous Ambient Monitoring Station) sites reported high ozone values. Highest ozone values on September 3, 2009, reached up to 157 ppb at Bayland Park (CAMS 53). On the same day HCHO and PAN at the Galleria site reached maximum values.

Figures 7 and 8 display the diurnal observational averages of PAN, HONO, CO, NO_x, HCHO, and global radiation. It can be seen that HONO and HCHO increase together with CO and NO_x during the morning rush hour, about 4:00-8:00 am CST (see (I) in Figure 7). After 7:00 am CST, still during the rush hour period, breakdown of the nocturnal boundary layer leads to a decrease of NO_x and CO. Both, HCHO and HONO, follow NO_x and CO in a similar way until about 7:00 am CST. Then, HONO and HCHO show different behaviour: HONO decreases, while HCHO increases. The increase of HCHO is primarily due to photochemical formation of HCHO from VOCs, as global radiation starts to increase. Photochemical production is also indicated by the increase of PAN and the elevated PAN levels during the day (see (II) in Figure 7). Still, some fraction of ambient HCHO is also likely due to ongoing traffic emissions. As seen in (III) in Figure 7 sustained CO levels at around 300 ppbv prevail during daytime and are higher than during nighttime, when lower planetary boundary height would favor accumulation of CO. Also, HONO stays at relatively high levels (about 600 pptv), although photochemical and consequently photolysis processes are high, as indicated by (II) in Figure 7. The high levels of HONO may likely be due to direct traffic emissions. Other potential formation pathway might be conversion of HNO_3 to HONO on primary organic aerosol[21].

Figure 8 shows that the average HONO/NO_x ratio varies between 2% during the morning rush hour and up to 5% during nighttime hours. This is a range which is similar to values found elsewhere[22,23], but seems to be slightly higher than in urban environments with very high NO_x ambient levels[24]. The HONO/NO_x ratio shown in Figure 8 is primarily determined by emissions, removal processes and transport of air masses which may contain different amounts of NO_x and/or HONO.

According to Figure 9 the experimental data reflects an emission ratio of 3.67±0.09 kg CO / kg NO_x. Figure 9 also shows the experimental results for September 28, 2009, which was the day used for MOBILE6 and MOVES modeling. The results are slightly lower, with 3.51 kg CO / kg NO_x. For the rush hour period MOBILE6 significantly overestimates the CO/NO_x emission ratio (7.06 kg CO / kg NO_x), while MOVES is getting closer to the observed values (4.56 kg CO / kg NO_x), but still about 30% higher than the observed values. Figure 10 shows the CO/NO_x ratio for light duty gasoline and heavy duty diesel vehicles calculated using MOVES, which are 9.2 and 0.42 respectively for the early morning hours (4:00 – 8:00 am).

Figures 11-15 display results for correlation analyses for the radical precursors HCHO and HONO vs CO and HONO vs NO_x and relate them to corresponding MOBILE6 and MOVES results. For HCHO/CO (Figure 11) the observational data yields an overall slope about 3.14±0.14 g HCHO / kg CO. On September 28 an emission ratio of 2.69 g HCHO / kg CO was determined. MOBILE6 largely underestimates this ratio, showing a HCHO/CO [g/kg] of 0.7 all throughout the day. MOVES calculates higher HCHO/CO ratios for the same morning rush hour period, an average of 1.87 g of HCHO per kg of CO, but is still lower than the observed ratio. MOVES shows surprisingly high HCHO/CO ratios during the early morning hours due to heavy duty diesel off-road emissions. Potential reasons for these emissions are idling and starting trucks. Figure 12 show the HCHO/CO [g/kg] ratio for light duty gasoline and heavy duty diesel vehicles calculated using MOVES, which are 0.67 and 24.43 respectively for the morning rush hour period..

The differences of the modeled CO/NO_x and HCHO/CO ratios between MOBILE6 and MOVES are due to higher NO_x emissions in MOVES (30% increased from MOBILE6) and higher HCHO emissions in MOVES (57% increased from MOBILE6); CO emissions were about the same in both models, as shown in Figure 13.

Contrary to any previous traffic emissions model MOVES2010b is the first model which allows to model HONO emissions. Figure 14 shows a constant HONO/NO_x emission ratio of 0.008 kg HONO / kg NO_x, which reflects results made in earlier tunnel studies[11]. The correlation analysis based on

observational data during rush hour reflects the relative change ΔHONO vs ΔNOx and can thus be interpreted as an emission ratio, contrary to Figure 8 which displays instantaneous HONO/NO_x ratios. The observed HONO/NO_x emission ratio is around 0.016 kg HONO / kg NO_x, which is twice as high as in MOVES.

A potential reason might be that previous tunnel studies did not include heavy duty diesel vehicles and/or that today's traffic fleet composition does not coincide with those studied about 15 years ago. Also, the same HONO/NOx ratio is used throughout for all vehicle categories in MOVES, which may not necessarily be the case[11] . Figure 15 includes an analysis of HONO vs CO. Using CO as a tracer for traffic emissions plot shows a very good correlation of HONO vs. CO (r^2=0.75) with a slope of about 0.0045±0.0002 kg HONO / kg CO. The close correlation with combustion processes is also reflected in the correlation of HONO vs CO_2 (r^2=0.66; plot not shown). It is worth to note that the relationship of HONO vs CO and CO_2 are even better than HCHO vs CO (r^2=0.68) and CO_2 (r^2=0.39). While it is obvious that due to the lower HONO/NO_x emission ratios, MOVES will also likely calculate lower HONO/CO emission ratios, rush hour measures indicate an average emission ratio of 0.0045 kg HONO / kg CO (and 0.0036 kg HONO / kg CO on September 28), while the modeled ratio is 0.0021 kg HONO / kg CO for the early morning hours and thus significantly lower.

Figure 16 displays results for the NO_2/NO_x emission ratio. In earlier experimental studies[11] a NO_2/NO_x emission ratio of about 5% was determined. Here MOVES results for the rush hour time indicate a ratio of about 9.3% for all vehicles, with an average of 9.2% and 10.6% for heavy duty diesel and light duty gasoline vehicles respectively (not shown) . The experimental data shows even higher values (18% for September 28, 2009; 16% for all data). It may be possible that the model still tends to underestimate NO_2 emissions, most likely from heavy duty diesel. Relatively high NO_2/NO_x measured ratios of about 13% have also been found in recent studies[24], where diesel driven buses might have contributed significantly. Unlike that study, however, our study area in particular included heavy duty diesel trucks which frequented the highways.

The potential impact of diesel driven vehicles is further supported by CO/CO_2 ratios (Figure 17). The experimental data shows overall CO/CO_2 emission ratios about 0.0033±0.0002 kg CO / kg CO_2. Unfortunately, there is no data available for September 28, 2009. However, it is plausible to assume that the VMT split on that day did not differ much from any other weekday included in the overall data set. The comparison with MOVES shows that MOVES calculates three times higher CO/CO_2 than observed. It appears likely that MOVES overestimates the emission ratio of CO/CO_2 from light duty gasoline vehicles since for heavy and light duty diesel vehicles the CO/CO_2 emission rates are close to the overall observed CO/CO_2 ratio which is about a magnitude lower than for gasoline vehicles as shown in Figure 18.

CONCLUSIONS

During the time period July 15- October 15, 2009 continuous ambient air measurements were taken in the immediate vicinity of the Highway Junction I-59 South/610 located in the Galleria area, Houston. This study aimed at primary emissions of radical precursors such as HCHO and HONO from mobile sources and comparing these results to emission estimates from currently available emissions models (MOBILE6 vs. MOVES). Following main results were found:

- a molar CO vs NO_x: ratio of around 6.01 ppbv CO / 1 ppbv NO_x (r^2 = 0.91) was found which is in agreement with other studies[25]. Both, MOBILE6 and MOVES, overestimate the corresponding observed emission ratio. However, MOVES tends to get closer to the observed values, but is still 30% above the observed value.
- For HCHO/CO an overall slope about 3.14±0.14 g HCHO / kg CO. While MOBILE6 largely underestimates this ratio, MOVES calculates higher HCHO/CO ratios, but is still lower than the observed ratio. MOVES shows surprisingly high HCHO/CO ratios during the early

morning hours due to heavy duty diesel off-road emissions. Potential reasons for these emissions are idling and starting trucks.

- The differences of the modeled CO/NO_x and HCHO/CO ratios are largely due to higher NO_x emissions in MOVES (30% increased from MOBILE6) and higher HCHO emissions in MOVES (57% increased from MOBILE6); CO emissions were about the same in both models.
- The observed $HONO/NO_x$ emission ratio is around 0.016 kg HONO / kg NO_x which is twice as high as in MOVES.
- The observed NO_2/NO_x emission ratio is around 0.18, which is a bit more than 50% higher than in MOVES.
- MOVES overestimates the CO/CO_2 emission ratio by a factor of 3 compared with the observations, this overestimation coming from light duty gasoline vehicles.

The above findings indicate that MOVES is performing better than MOBILE6. However, the findings suggest that the CO emissions are overestimated in MOVES, with this overestimation coming from light duty gasoline vehicles. Fixing this overestimation could solve the problem of the underestimation of HCHO/CO and overestimation of CO/NO_x. Also, the findings suggest that emissions ratios of $HONO/NO_x$ and NO_2/NO_x from heavy duty diesel are underestimated by MOVES, which attributes the same emission ratio for all vehicle types. We believe that these ratio underestimations come from underestimating the emissions of HONO and NO_2 from diesel vehicles which are the main sources of these emissions. These species directly foster ozone formation.

REFERENCES

1) Rappenglück, B.: Dasgupta, P.K.: Leuchner, M.: Li, Q.: Luke, W.,"Formaldehyde and its relation to CO, PAN, and SO2 in the Houston-Galveston airshed," 2010, Atmos. Chem. Phys., 10, 2413-2424
2) Czader, B.H.; Rappenglück, B.: Percell, P.: Byun, D.: Ngan, F.: Kim, S., "Modeling nitrous acid and its impact on ozone and hydroxyl radical during the Texas Air Quality Study 2006," Atmos. Chem. Phys., 12, 6939-6951, doi:10.5194/acp-12-6939-2012.
3) Rappenglück, B.: Lefer, B.: Czader, B.: Li, X.: Golovko, J.: Alvarez, S.: Flynn, J.: Haman, C.: Grossberg, N., "University of Houston Moody Tower 2010 Ozone Formation Research Monitoring"; Project Grant No. 582-5-64594-FY10-14, Prepared for the Texas Commission on Environmental Quality, TX 2011
4) Zweidinger, R.B.; Sigsby, J.E.: Tejada, S.B.: Stump, F.D.: Dropkin, D.L.: Ray, W.D.: Duncan, J.W., "Detailed hydrocarbon and aldehyde mobile source emissions from roadway studies," Environ. Sci. Technol., 1988, 22, 956-962
5) Altshuller, A.P.,"Production of aldehydes as primary emissions and from secondary atmospheric reactions of alkenes and alkanes during the night and early morning hours," Atmos. Environ., 1993, 27A, 21-32
6) Chen, J.; So, S.: Lee, H.: Fraser, M.P.: Curl, R.F.: Harman, T.: Tittel, F.K.,"Atmospheric Formaldehyde Monitoring in the Greater Houston Area in 2002," Appl. Spectrosc., 2004, 58, 243-247
7) Dasgupta, P.K.; Li, J.: Zhang, G.: Luke, W.T.: McClenny, W.A.: Stutz, J.: Fried, A.,"Summertime Ambient Formaldehyde in Five U.S. Metropolitan Areas: Nashville, Atlanta, Houston, Philadelphia, and Tampa," Environ. Sci. Technol., 2005, 39, 4767-4783
8) Anderson, L.G.; Lanning, J.A.: Barrell, R.: Miygishima, J.: Jones, R.H.: Wolfe, P.,"Sources and sinks of formaldehyde and acetaldehyde: An analysis of Denver's ambient concentration data," Atmos. Environ., 1996, 30, 2113-2123

9) Rappenglück, B.; Schmitz, R.: Bauerfeind, M.: Cereceda-Balic, F.: v. Baer, D.: Jorquera, H.: Silva, Y.: Oyola, P.,"An urban photochemistry study in Santiago de Chile," Atmos. Environ., 2005, 39, 2913-2931
10) Kirchstetter, T. W.; Harley, R.A.: Littlejohn, D., "Measurement of Nitrous Acid in Motor Vehicle Exhaust," Environ Sci Technol, 1996, 30(9), 2843-2849
11) Kurtenbach, R.; Becker, K.H.: Gomes, J.A.G.: Kleffmann, J.: Lörzer J.C.: Spittler, M.,: Wiesen, P.: Ackermann, R.: Geyer, A.: Platt, U., "Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel," Atmos. Environ., 2001, 35(20), 3385-3394
12) Sarwar, G.; Roselle, S.J.: Mathur, R.: Appel, W.: Dennis, R.L.: Vogel, B., "A comparison of CMAQ HONO predictions with observations from the Northeast Oxidant and Particle Study," Atmos Environ., 2008, 42, 5760-5770
13) Kleffmann, J.; Kurtenbach, R.: Lörzer J.C.: Wiesen, P.: Kalthoff, N.: Vogel, N.: Vogel, B., "Measured and simulated vertical profiles of nitrous acid. Part I: field measurements," Atmos Environ., 2003, 37, 2949-2955
14) Kota, S.H.; Ying, Q.: Schade, G.W. "MOVES vs. MOBILE6.2: Differences in Emission Factors and Regional Air Quality Predictions", Presented at Transportation Research Board 91st Annual Meeting, Washington DC, January 2012; paper #12-4438
15) Vallamsundar S., Lin J. (2011): MOVES Versus MOBILE - Comparison of Greenhouse Gas and Criterion Pollutant Emissions, Transportation Research Record: Journal of the Transportation Research Board, 2233, 27-35, doi: 10.3141/2233-04
16) EPA MOBILE6 Vehicle Emission Modeling Software, http://www.epa.gov/oms/m6.htm
17) Texas Transportation Institute Emission Inventory Utilities User's Guide, Texas Department of Transportation, July 2009
18) H-GAC Conformity Determination- Appendix 5. http://www.h-gac.com/taq/airquality_model/conformity/2012/docs/Appendix5.pdf
19) EPA MOVES (Motor Vehicle Emission Simulator), http://www.epa.gov/otaq/models/moves/index.htm
20) Texas Transportation Institute Inventory Estimation Utilities Using MOVES: MOVESUTL User's Guide, Texas Department of Transportation, August 2011
21) Ziemba, L.D.; Dibb, J.E.: Griffin, R.J.: Anderson, C.H.: Whitlow, S.I.: Lefer, B.L.: Rappenglück, B.: Flynn, J., "Heterogeneous conversion of nitric acid to nitrous acid on the surface of primary organic aerosol in an urban atmosphere," Atmos. Environ., 2010, doi:10.1016/j.atmosenv.2008.12.024
22) Lammel, G.; Cape, J.N., "Nitrous acid in the atmosphere," Chem. Soc. Rev., 1996, 9, 361-369
23) Elshorbany, Y.F.; Kurtenbach, R.: Wiesen, P.: Lissi, E.: Rubio, M.,: Villena, G.: Gramsch, E.: Rickard, A.R.: Pilling, M.J.: Kleffmann, J., "Oxidation capacity of the city air of Santiago, Chile," Atmos. Chem. Phys., 2009, 9, 2257-2273
24) Villena, G.; Kleffman, J.: Kurtenbach, R.: Wiesen, P.: Lissi, E.: Rubio, M.A.: Croxatto, G.: Rappenglück, B.,"Vertical Gradients of HONO, NO_x and O_3 in Santiago de Chile, Atmos. Environ., 2011, 45, 3867-3873, doi:10.1016/j.atmosenv.2011.01.073
25) Parrish, D.D.: Allen, D.T.: Bates, T.S.: Estes, M.: Fehsenfeld, F.C.: Feingold, G.: Ferrare, R.: Hardesty, R.M.: Meagher, J.F.: Nielson-Gammon, J.W.: Pierce, R.B.: Ryerson, T.B.: Seinfeld, J.H.: Williams, E.J., "Overview of the Second Texas Air Quality Study (TexAQS II) and the Gulf of Mexico Atmospheric Composition and Cl Climate Study (GoMACCS)," 2009, J. Geophys, Res., 114, doi: 10.1029/2009JD011842

KEY WORDS

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Figure 1: Daytime photochemical Processes.

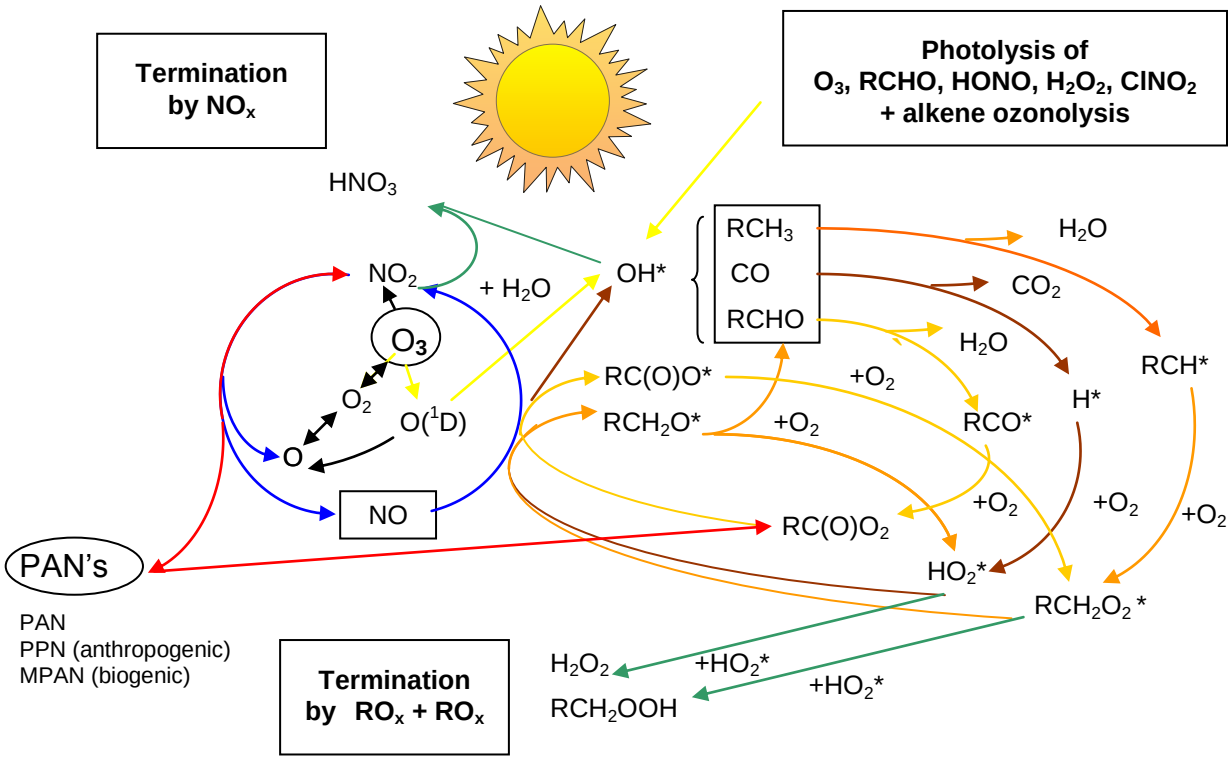


Figure 2: CMAQ modeling[3] of contribution of O_3, HONO, HCHO, and H_2O_2 to hourly HO_x formation for the Moody Tower site in Houston/TX on September 19/20, 2009. Above: data extracted from the first model layer; below: data averaged up to the height of the planetary boundary layer.

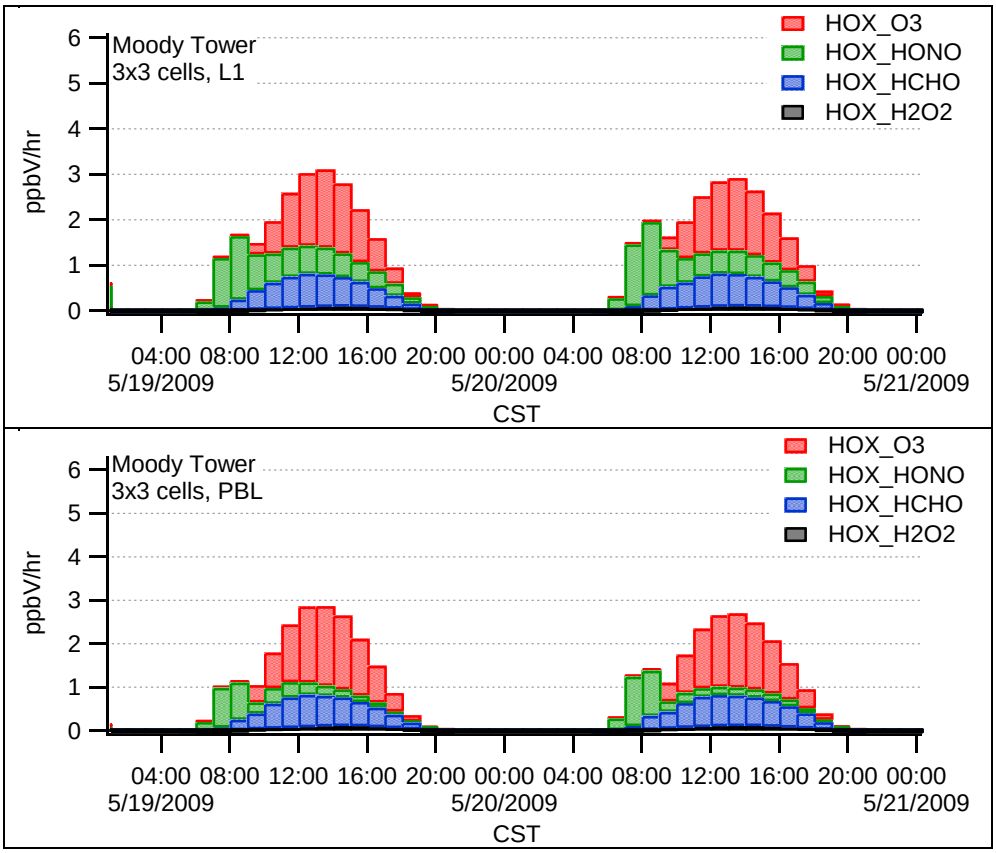


Figure 3. Location of the Galleria measurement site in immediate vicinity of the Highway Junction I-59 South/610 in the Houston area. The red dot indicates the location of the measurement site.

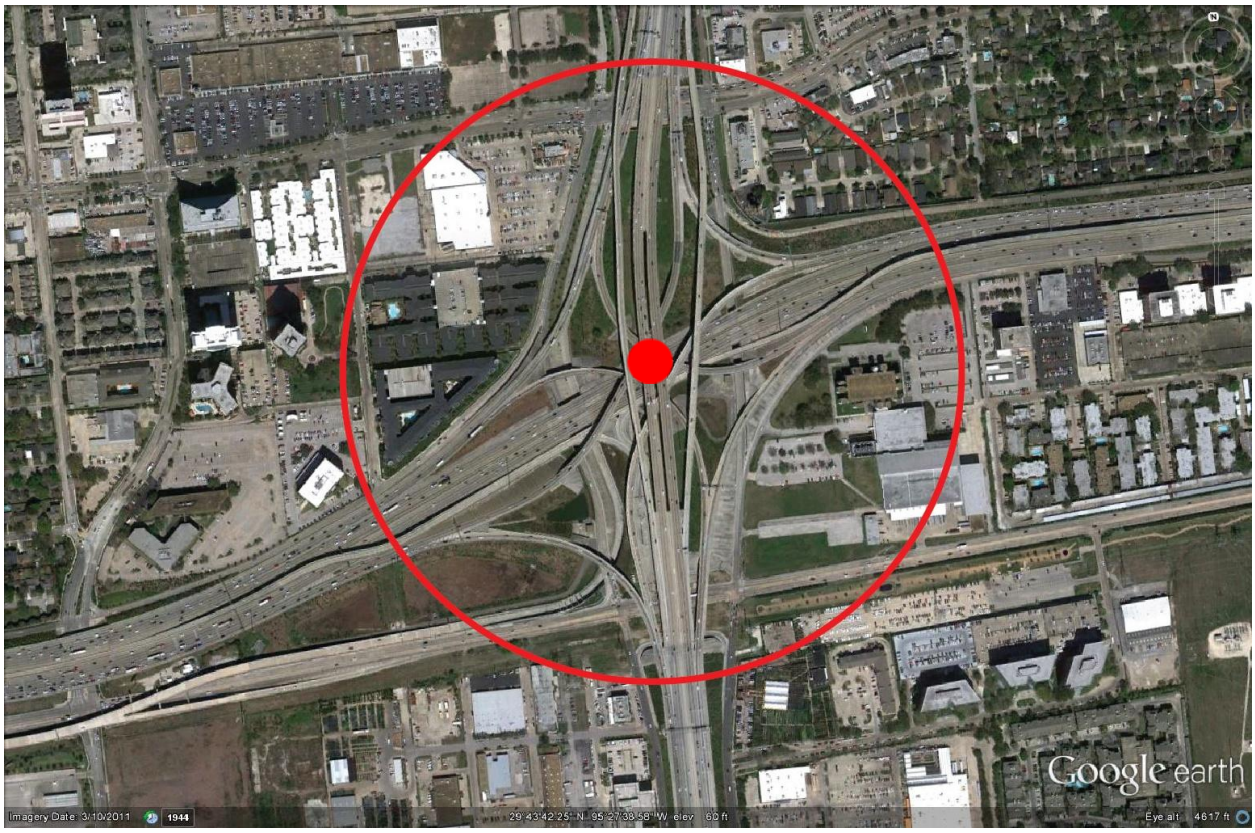


Figure 4. Left: Enlargement of measurements location. Right: Partial view of the Highway junction.

Table 1. List of measured variables and measurement techniques at the Galleria site.

Parameter	Method	Instrument
HONO	Long Path Absorption Photometer	LOPAP 03
NO	Chemiluminescence	TE 42i TL
NO_2	Chemiluminescence/ photolytic conversion	TE 42i TL / BLC
HCHO	Hantzsch/Fluorescence	AL4021
CO	Gas Filter correlation	TE 48i TLE
CO_2	Differential, non-dispersive infrared absorption	LI-7000
Peroxyacyl nitrates (PANs)	GC/ECD	Modified Metcon GC/ECD
Met. Parameters	various	Vaisala WXT510

Table 2. Statistical data for the Galleria site measurements (data base: 10 min).

Parameter	HONO [pptv]	NO [ppbv]	NO_2 [ppbv]	NO_x [ppbv]	HCHO [ppbv]	CO [ppbv]	CO_2 [ppmv]	PAN[1)] [pptv]	PPN[2)] [pptv]
Maximum	5185	137.9	64.3	161.7	16.9	1309	527.3	4148	859
Average	615	9.3	13.4	22.9	2.8	262	407.8	306	28
Median	500	5.6	11.5	18.5	2.3	238	403.8	175	15

1) Peroxyacetyl nitrate
2) Peroxyproprionyl nitrate

Figure 5. Correlation of CO vs. NO_x as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level.

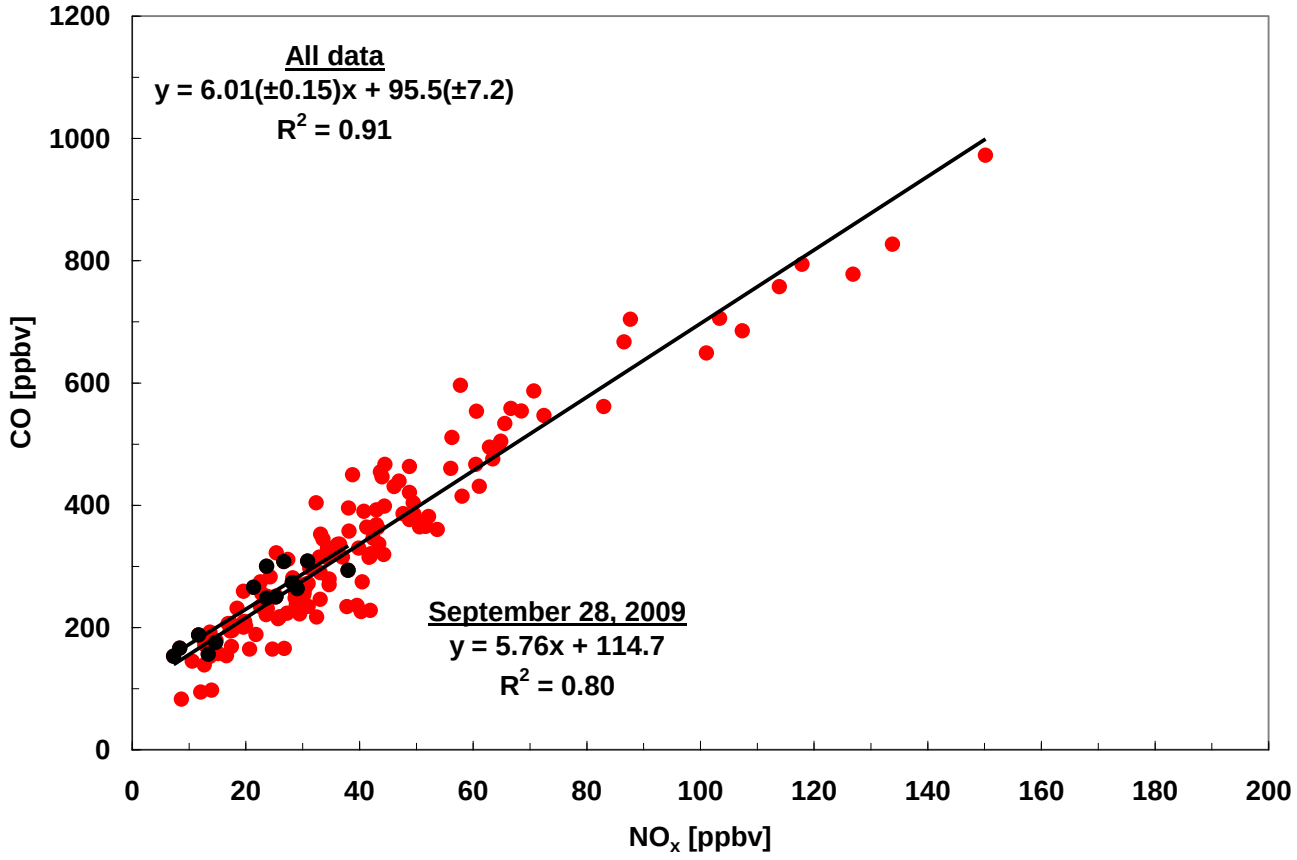


Table 3. Diesel/gasoline split on the arterial and freeway facility types used as input for MOBILE6 and MOVES calculations (AM: morning peak from 6:00 - 9:00 am CST; MD: mid-day period from 9:01 am - 3:00 pm CST; PM: afternoon peak from 3:01 - 7:00 pm CST; OV: overnight period from 7:01 pm - 6:00 am CST).

Time of day-Facility Type	Diesel percentage	Gasoline Percentage
AM_Arterial	7%	93%
AM_Freeway	5%	95%
MD_Arterial	11%	89%
MD_Freeway	9%	91%
PM_Arterial	6%	94%
PM_Freeway	5%	95%
OV_Arterial	7%	93%
OV_Freeway	7%	93%

Figure 6. Diurnal variation of VMT for the Galleria site study area September 28, 2009.

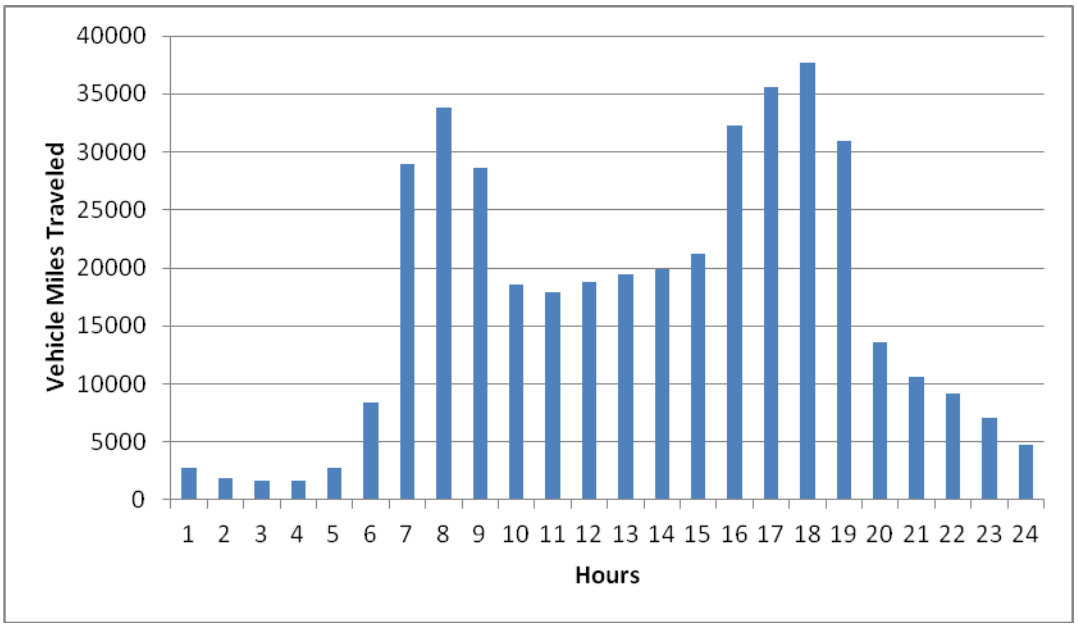


Figure 7. Average diurnal variation of PAN, HONO, CO, NO_x, HCHO and global radiation at the Galleria site during July 15 – October 15, 2009: The number indicate following sections: (I) Morning rush hour, (II) photochemical processes, and (III) elevated levels throughout the day due to ongoing traffic.

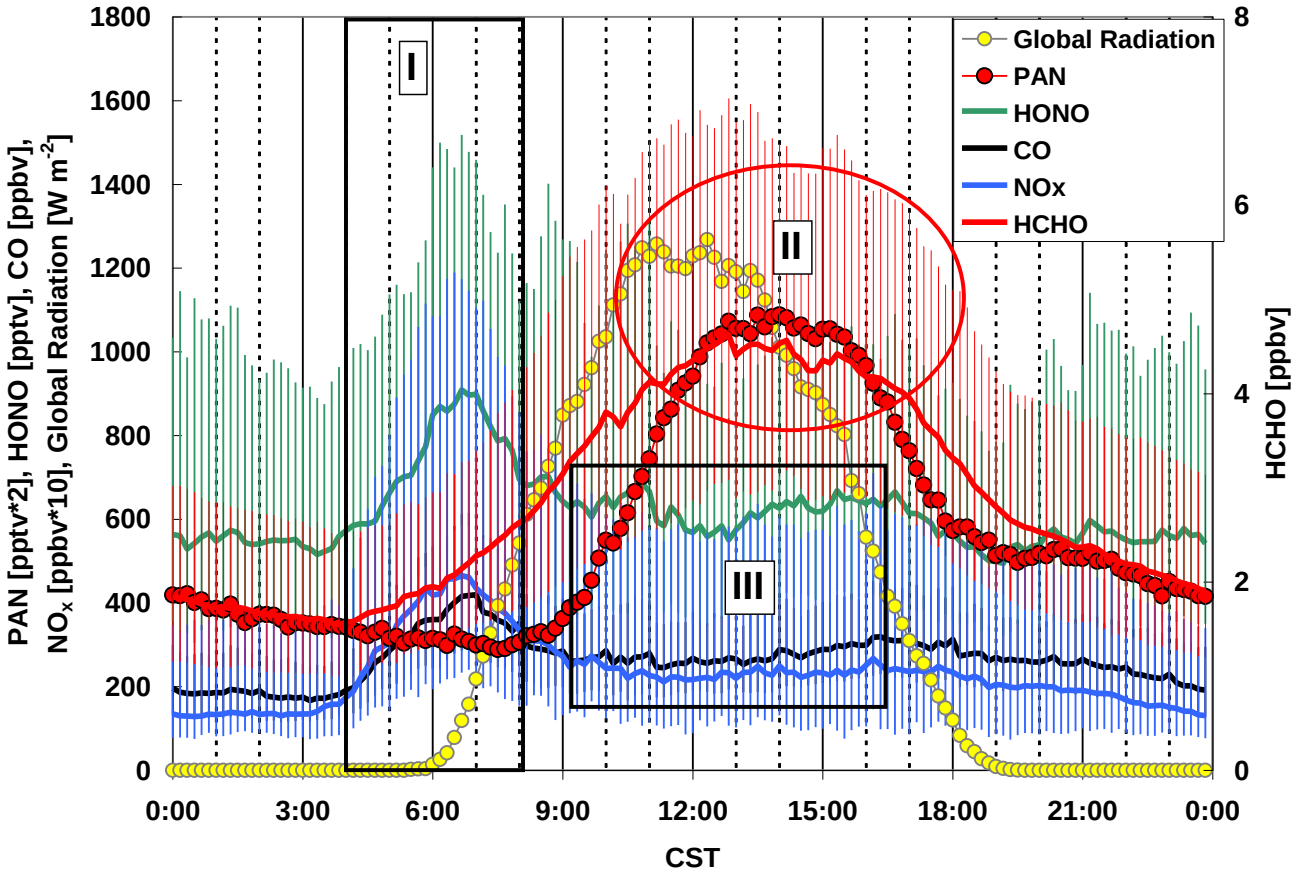


Figure 8. Average diurnal variation of HONO, HONO/NO_x, and global radiation at the Galleria site during July 15 – October 15, 2009.

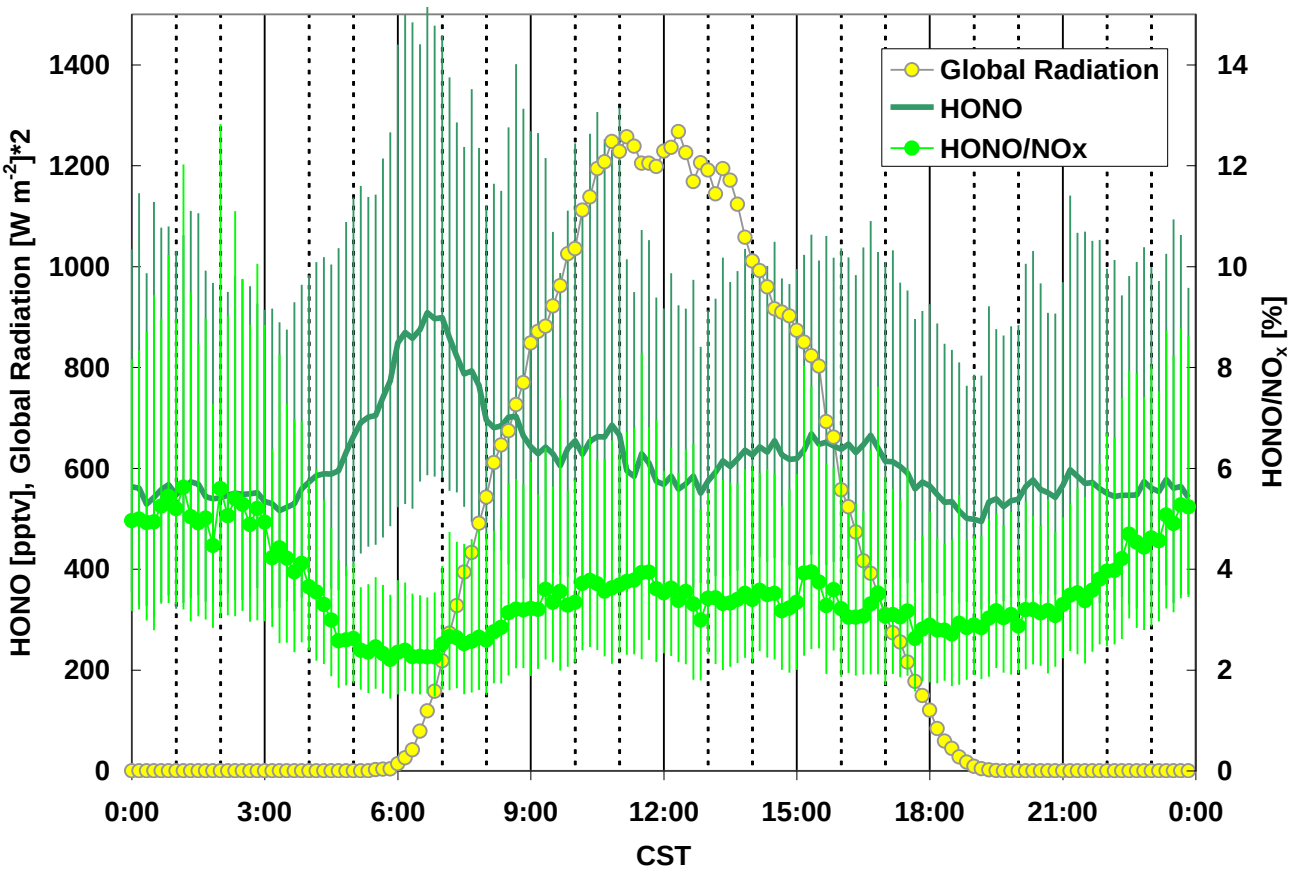
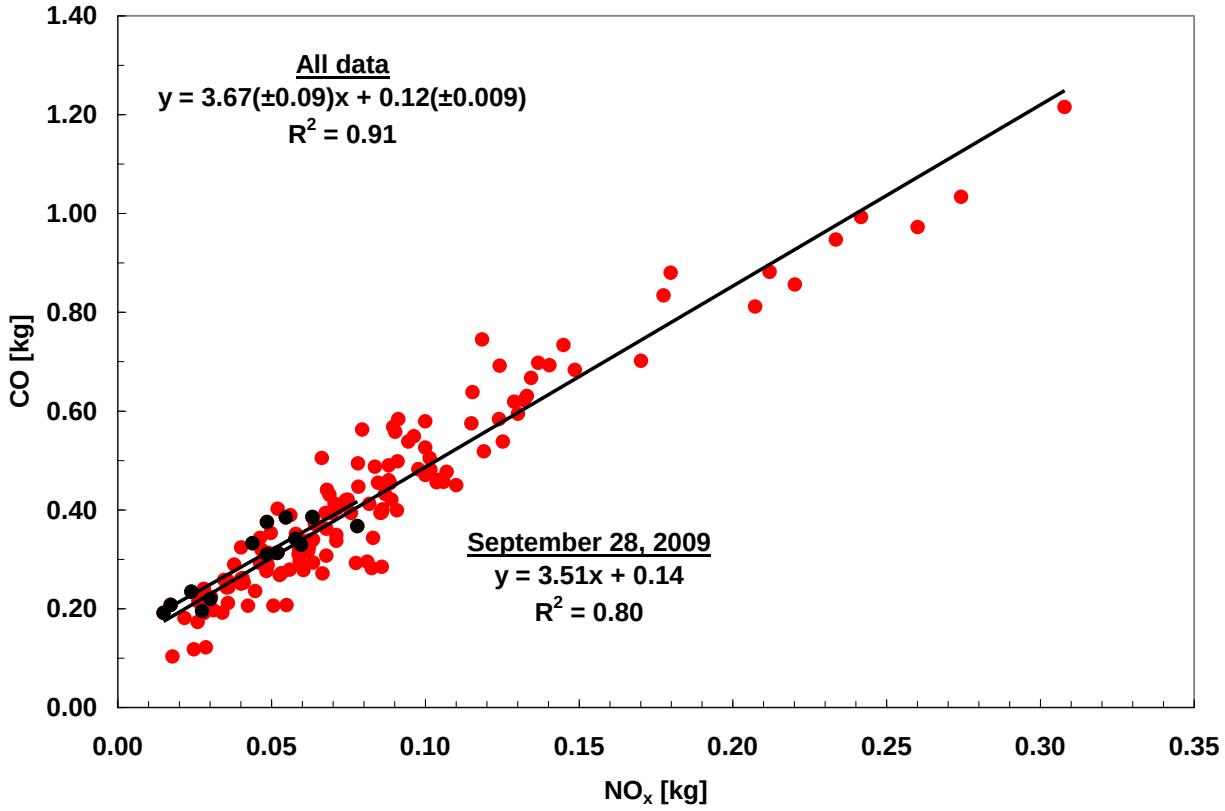


Figure 9. Above: Correlation of CO vs. NO_x in [kg/kg] as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level. Below: Diurnal variation of the CO/NO_x ratio for the Galleria study site for September 28, 2009, as calculated by MOBILE6 and MOVES. The average of the early morning hours is 4.56 kg of CO per kg of NO_x using MOVES, and 7.06 kg of CO per kg of NO_x using MOBILE6. The green box indicates the hours used to take the average.



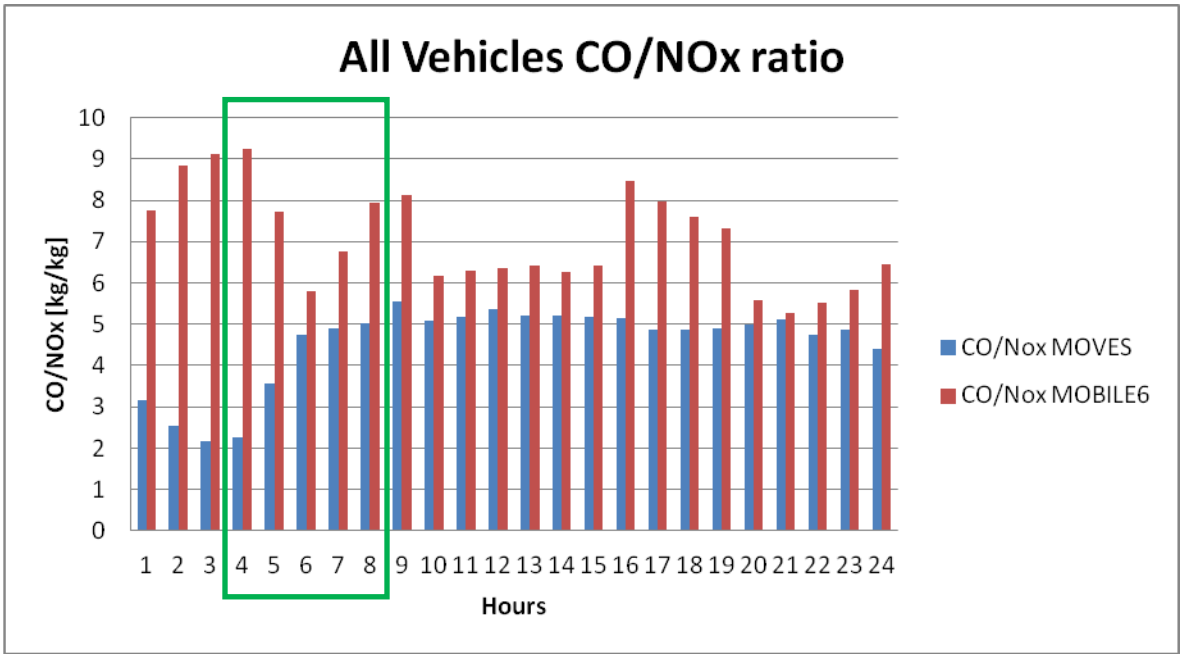
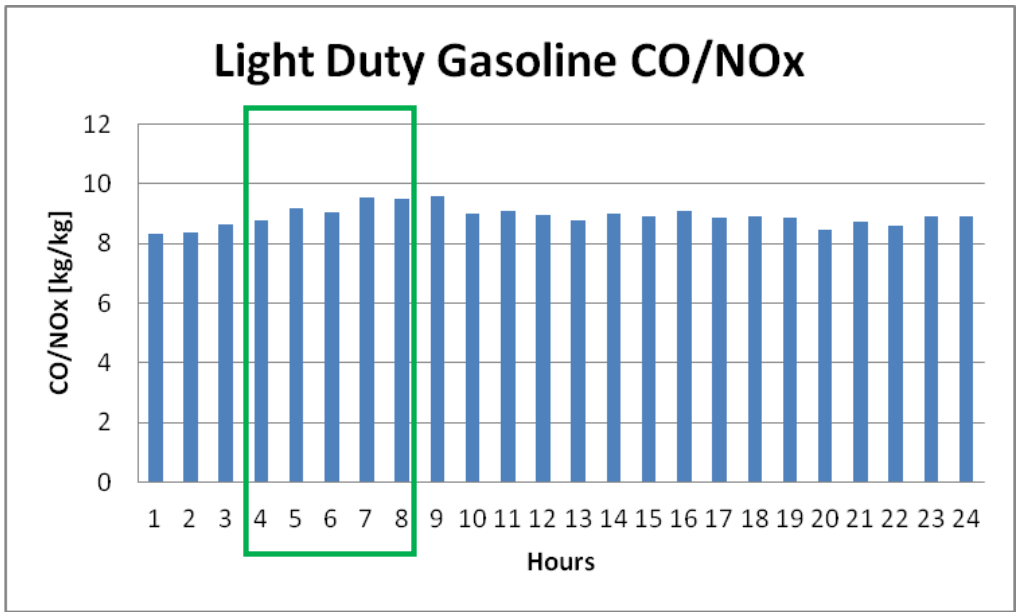


Figure 10: Diurnal variation of CO/NO_x ratio for light duty gasoline and heavy duty diesel vehicles calculated using MOVES. The average of the early morning hours is 9.20 kg of CO per kg of NO_x and 0.42 kg of CO per kg of NO_x, respectively. The green box indicates the hours used to take the average.



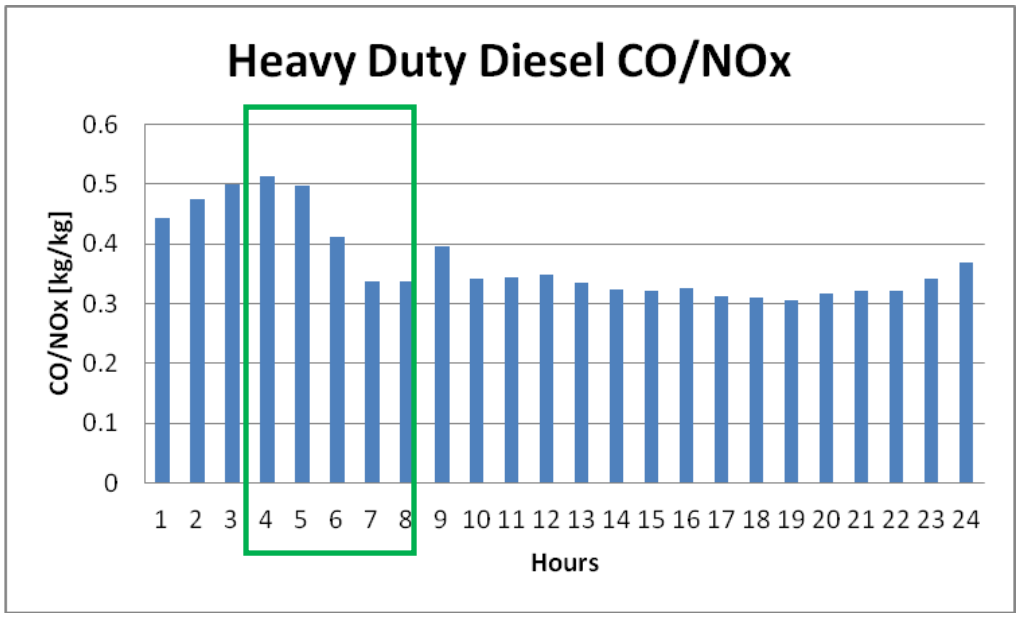
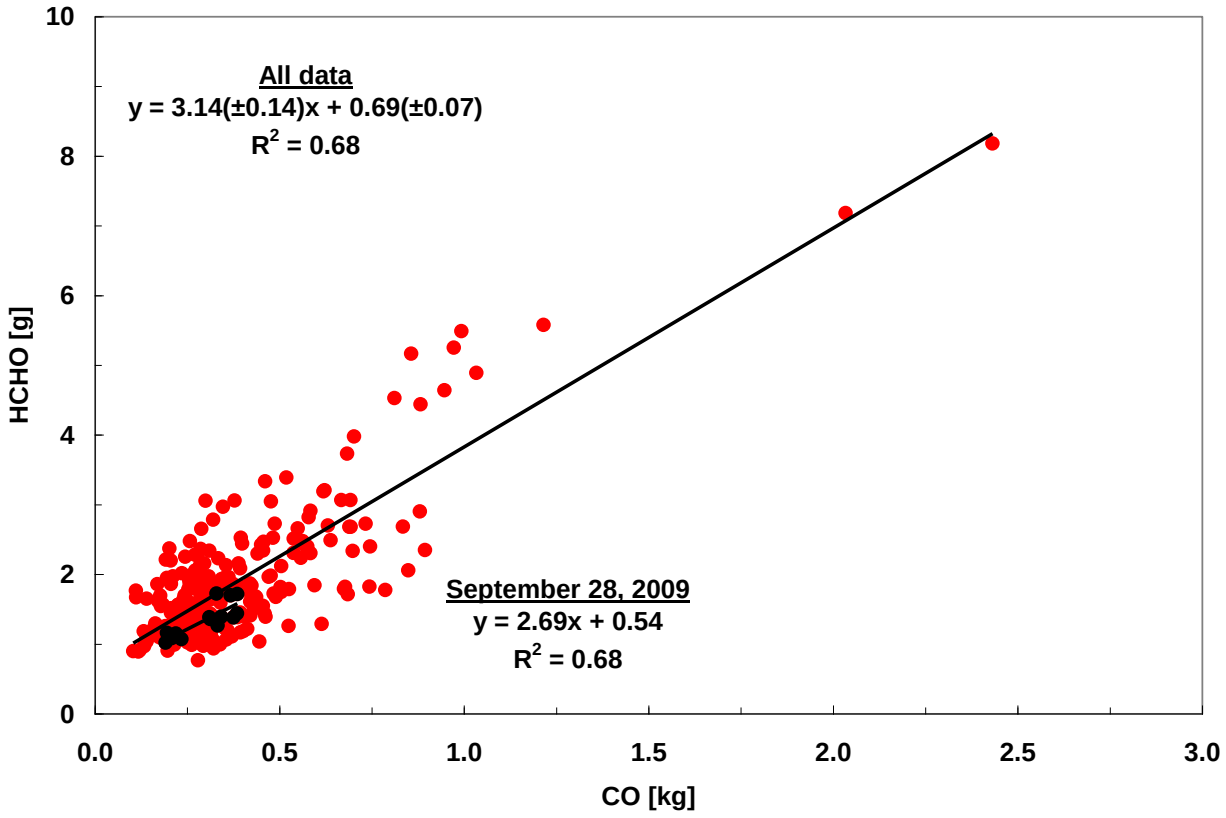


Figure 11. Above: Correlation of HCHO vs CO in [g/kg] as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level. Below: Diurnal variation of the Form/CO ratio for the Galleria study site for September 28, 2009, as calculated by MOBILE6 and MOVES.. The average of the early morning hours is 1.87 g of HCHO per kg of CO using MOVES, and 0.7 g of HCHO per kg of CO using MOBILE6. The green box indicates the hours used to take the average



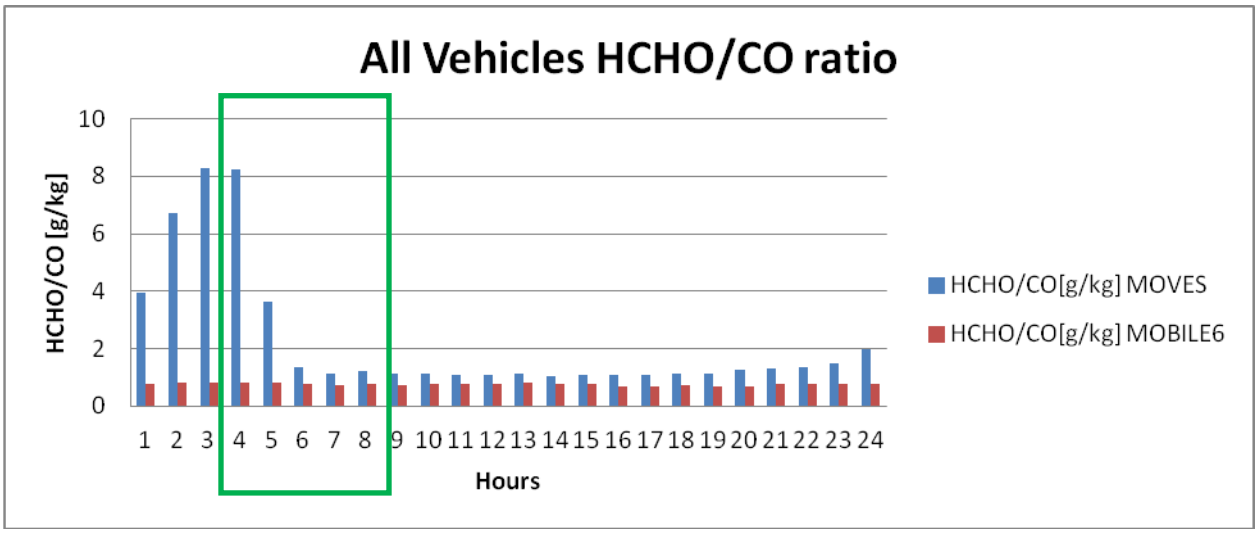
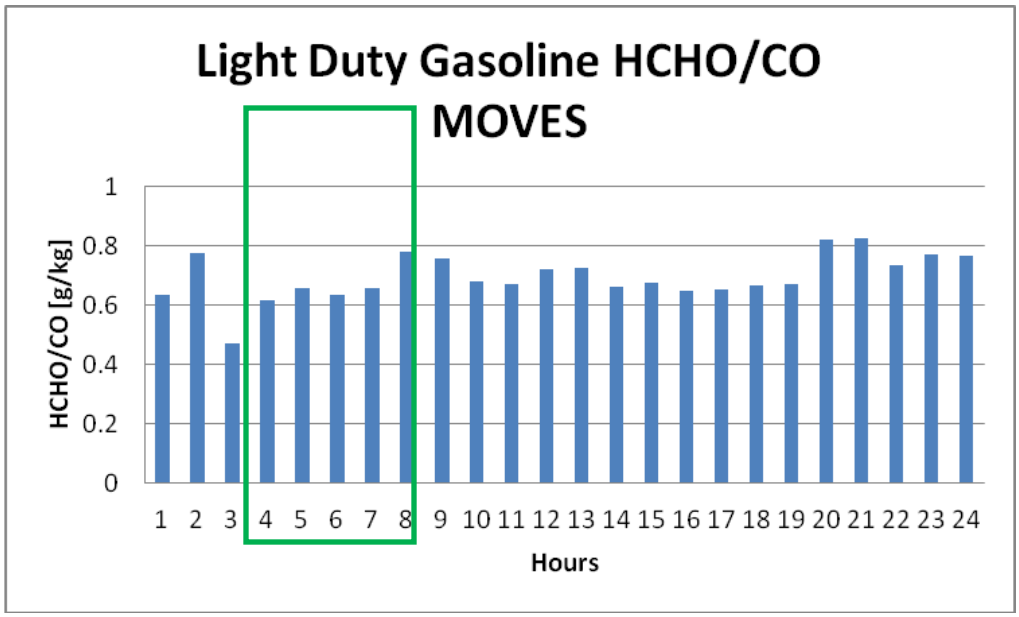


Figure 12: Diurnal variation of HCHO/CO ratio for light duty gasoline and heavy duty diesel vehicles calculated using MOVES. The average of the early morning hours is 0.67 g of HCHO per kg of CO and 24.43 g of HCHO per kg of CO, respectively. The green box indicates the hours used to take the average.



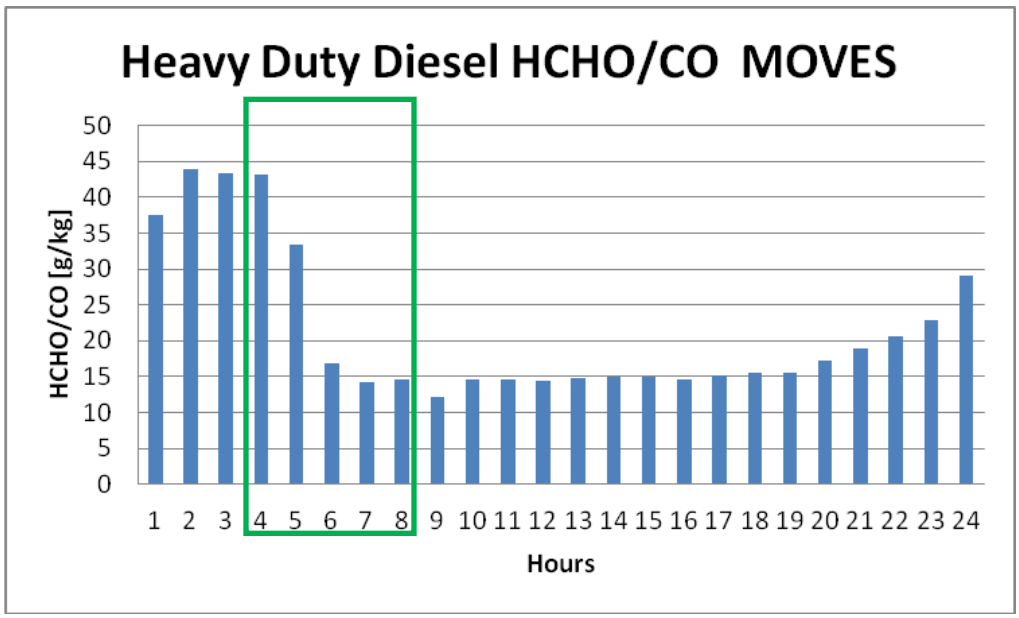


Figure 13: Diurnal variation of NO_x, HCHO and CO emissions for all vehicles calculated with MOBILE6 and MOVES. The NO_x average emissions in the early morning hours is 17.22 kg using MOVES and 12.36 kg using MOBILE6. The HCHO average emission in the early morning hours is 0.12 kg using MOVES and 0.07 kg using MOBILE6. The CO average emission in the early morning hours is 81.65 kg using MOVES and 89.83 kg using MOBILE6. The green box indicates the hours used to take the average

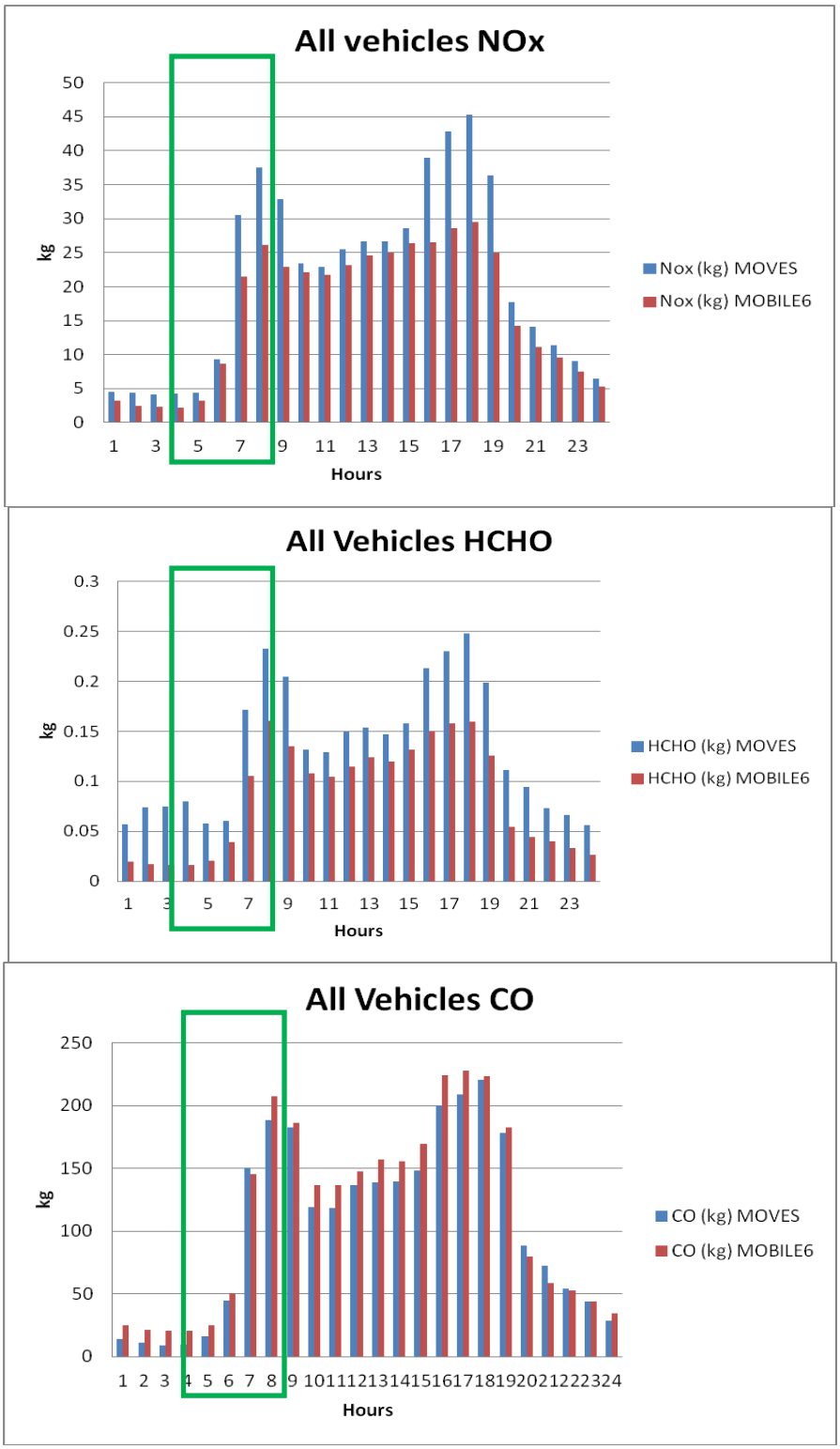
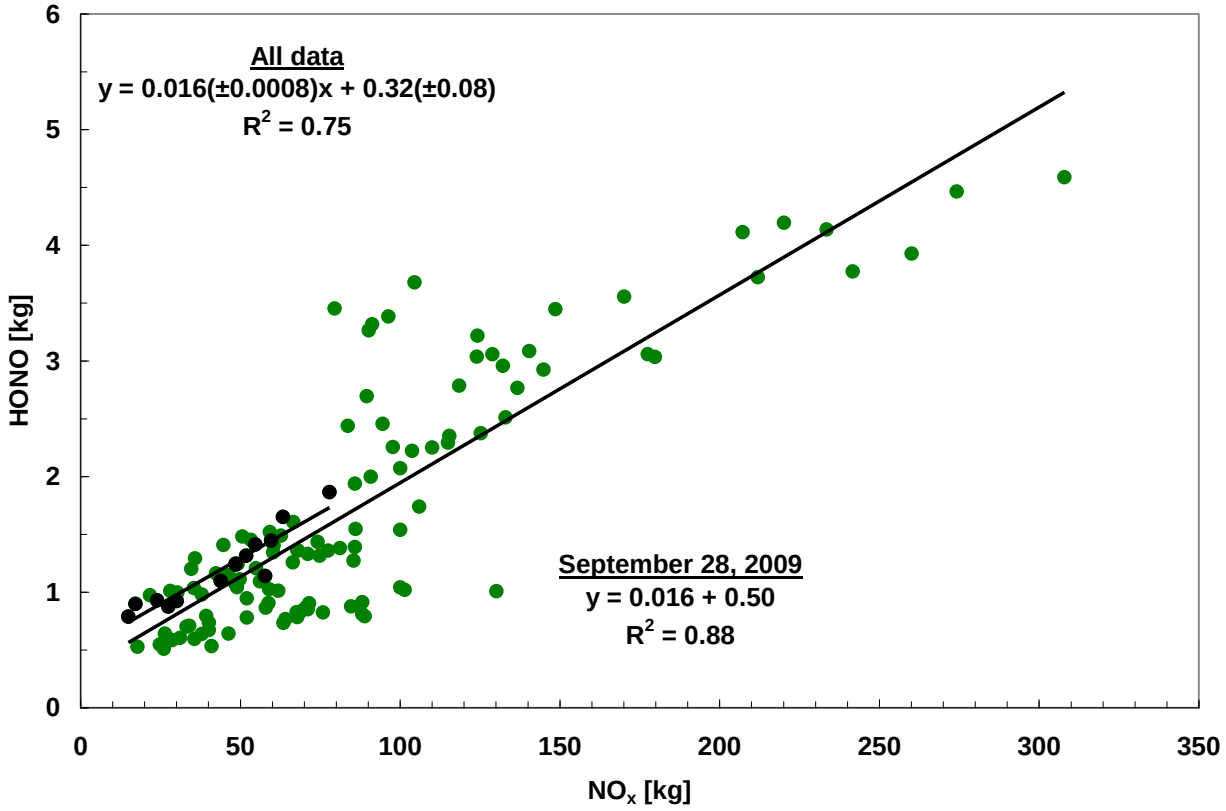


Figure 14. Above: Correlation of HONO vs NO_x in [kg/kg] as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level. Below: Diurnal variation of the HONO/NO_x ratio for the Galleria study site for September 28, 2009, as calculated by MOBILE6 and MOVES. The average of the early morning hours is 0.008 kg of HONO per kg of NO_x. The green box indicates the hours used to take the average.



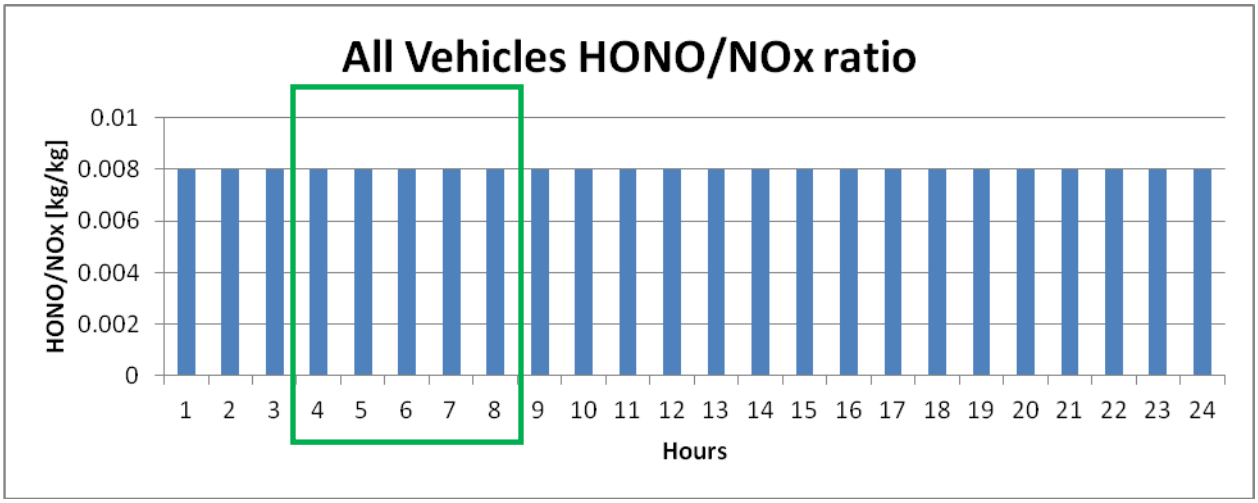
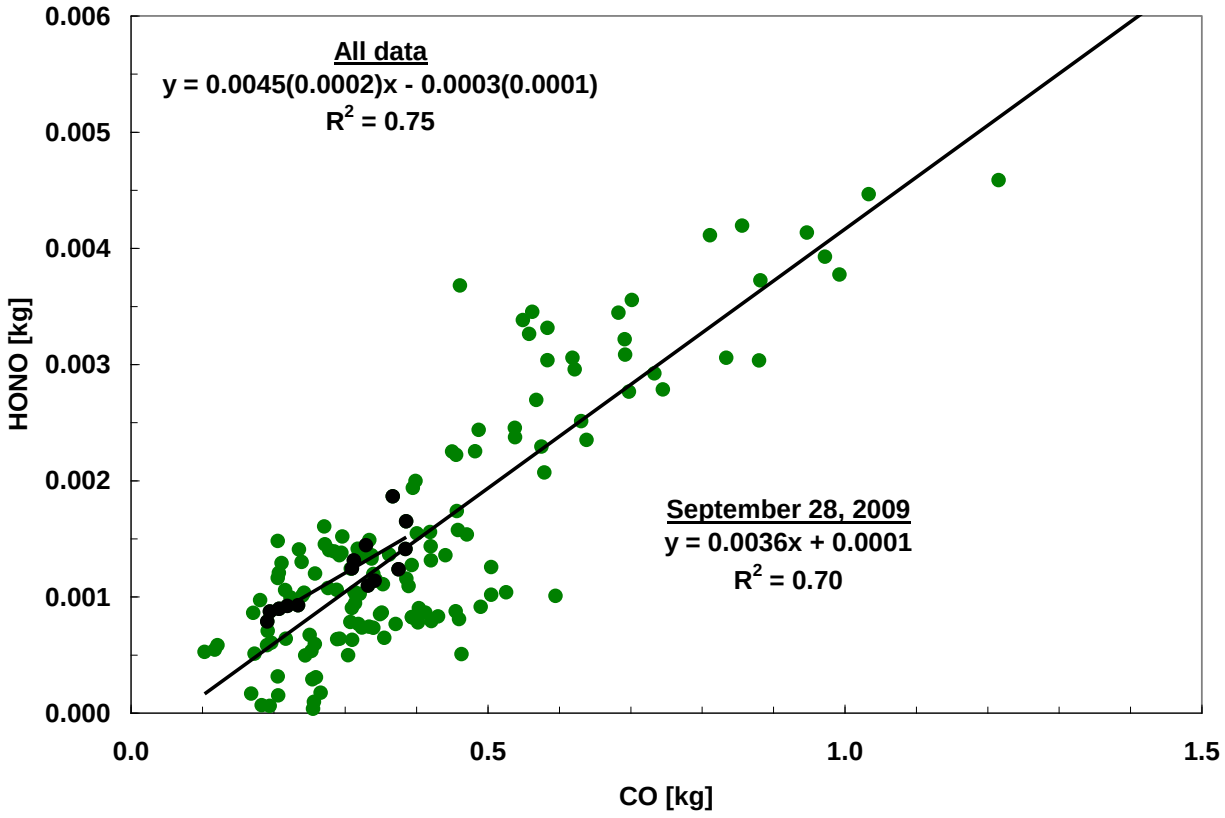


Figure 15. Above: Correlation of HONO vs CO in [kg/kg] as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level. Below: Diurnal variation of the HONO/CO ratio for the Galleria study site for September 28, 2009, as calculated by MOVES. The average of the early morning hours is 0.021 kg of HONO per kg of CO. The green box indicates the hours used to take the average.



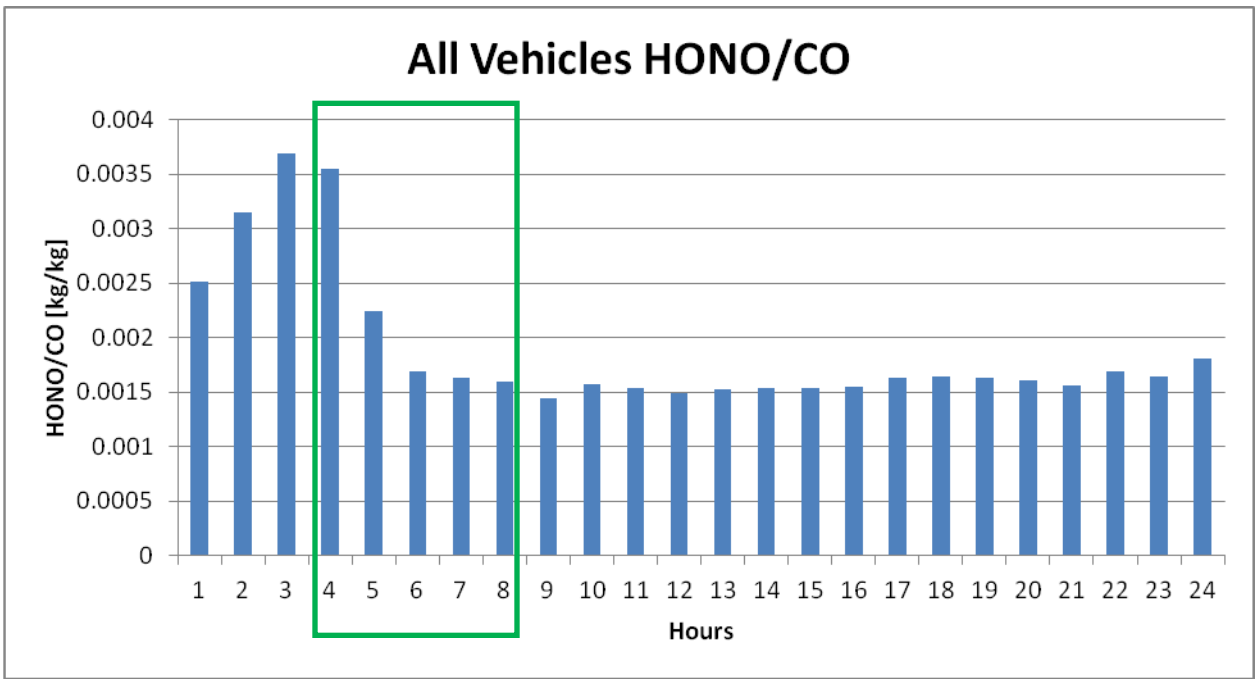
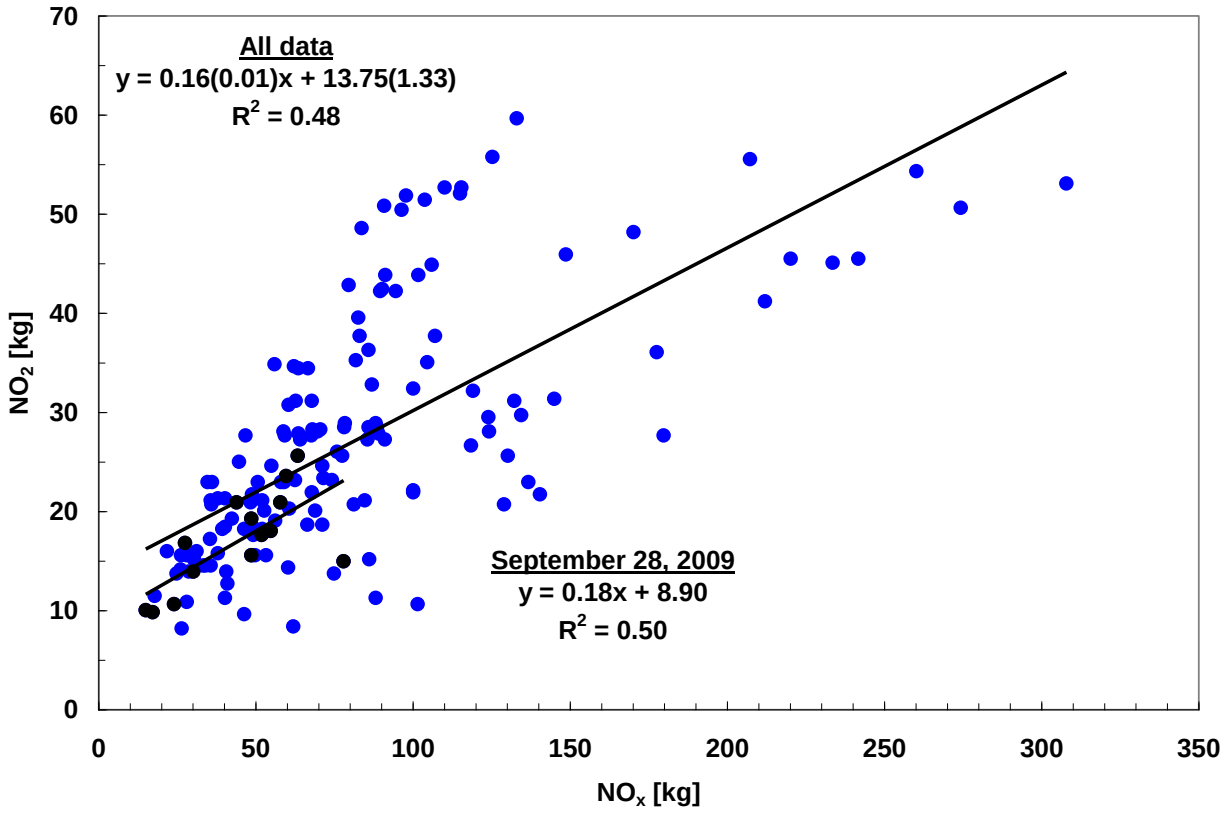


Figure 16. Above: Correlation of NO_2 vs NO_x in [kg/kg] as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level. Below: Diurnal variation of the NO_2/NO_x ratio for the Galleria study site for September 28, 2009, as calculated by MOVES. . The average of the early morning hours is 0.093 kg of NO_2 per kg of NO_x. The green box indicates the hours used to take the average.



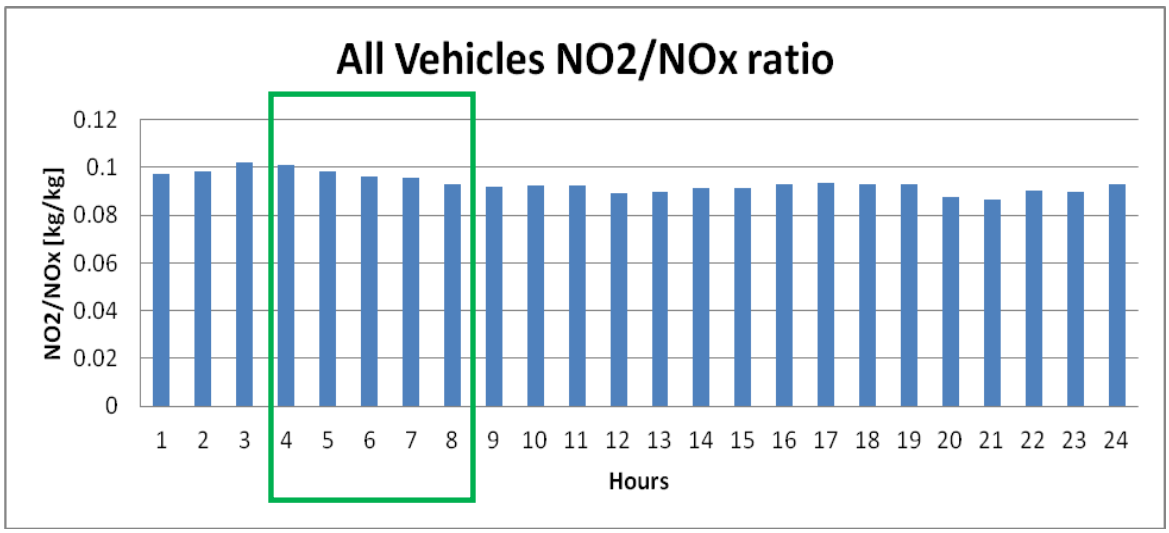
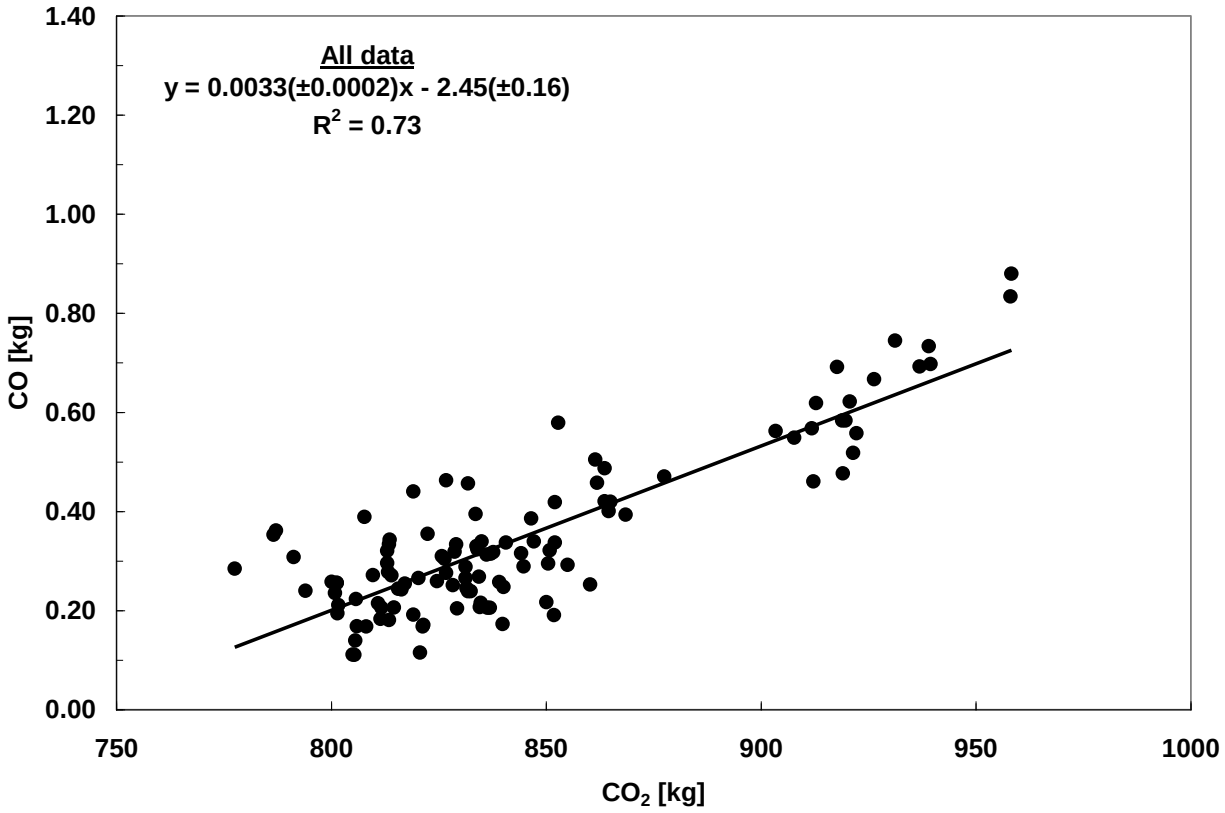


Figure 17. Above: Correlation of CO vs CO_2 in [kg/kg] as obtained at the Galleria site during July 15 – October 15, 2009 for morning rush hour times. Black dots indicate the data for September 28, 2009. Data screened as described in the text. Values based in brackets are based on 95% confidence level. Below: Diurnal variation of the CO/CO_2 ratio for the Galleria study site for September 28, 2009, as calculated by MOBILE6 and MOVES. . The average of the early morning hours is 0.012 kg of CO per kg of CO_2. The green box indicates the hours used to take the average.



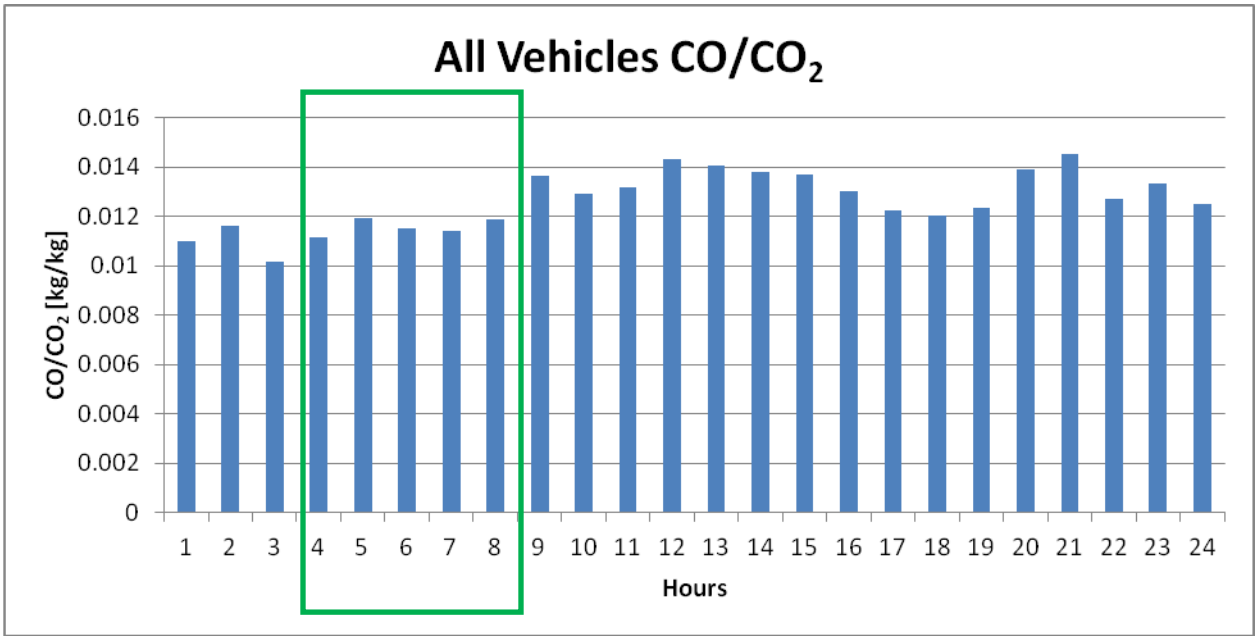


Figure 18: Diurnal variation of CO/CO_2 ratio for light duty gasoline and heavy duty diesel vehicles calculated using MOVES. The average of the early morning hours is 0.013 kg of CO per kg of CO_2 and 0.0032 kg of CO per kg of CO_2, respectively. The green box indicates the hours used to take the average