2014

FEAT Math II and a Discussion of Negative Measurements

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FEAT Equations for CO, HC and NO.   G. A. Bishop Last updated Feb. 2014.

ASSUMPTIONS:

Fuel C:H ratio is 2 and non-oxygenated. Applies to gasoline and diesel in general.

Fuel is approximated with a mix of Octane and Benzene that averages the molecular formula of CH_2.

Fuel out tailpipe is similar (to make the math simpler we have chosen for the exhaust HC to be a multiple of the input HC) to calibration gas which is propane.

Concentrations are calculated on a dry basis and corrected for any excess air not involved in combustion (these equations are correct for gasoline vehicles, but only the ratios are correct for diesel vehicles) and assume an 8cm path length. For a direct tailpipe comparison for diesel vehicles, the measurement comparison either must consider only the ratios, or must be corrected for the considerable excess oxygen not involved in typical diesel combustion).

Equal amount of seen HC's and unseen HC's in the exhaust (Singer & Harley et al, Environ. Sci Technol. 1998, 32, 3241-3248) Singer factor of 2.

$$CH_2 + m(0.21\ O_2 + 0.79\ N_2) \rightarrow$$
$$aCO + bH_2O + c(C_3H_6 + inv\ C_3H_6) + dCO_2 + eNO + \left(0.79m - \frac{e}{2}\right)N_2$$

$$Q = \frac{CO}{CO_2} = \frac{a}{d} \qquad Q' = \frac{HC}{CO_2} \qquad Q" = \frac{NO}{CO_2} = \frac{e}{d}$$

by Carbon balance :   a + 6c + d = 1

by Hydrogen balance: 2b + 12c = 2

by Oxygen balance: a + b + 2d + e= 0.42m

Eliminate a: a = dQ   c = dQ'

a + 6c + d = 1   dQ + 6dQ' + d = 1

$$d = \frac{1}{Q + 6Q' + 1}$$

Eliminate b: 2b + 12dQ' = 2 ;   b = 1 - 6dQ'

dQ + b + 2d + e= 0.42m;   dQ + 1 - 6dQ' +2d + e= 0.42m substituting d from above:

$$0.42\,\frac{m}{d} = Q + \frac{1}{d} - 6Q' + 2 + Q'' = Q+Q+6Q'+1-6Q'+2+Q'' = 2Q + 3 + Q''$$

From the combustion equation the mole fraction of CO_2 is:

$$fCO_2 = \frac{d}{a + 2c + d + e + 0.79m - \frac{e}{2}}$$

divide numerator and denominator by d:

$$fCO_2 = \frac{1}{\frac{a}{d} + 2\frac{c}{d} + 1 + 0.5\frac{e}{d} + 0.79\frac{m}{d}}$$

substituting from above for a/d, c/d and e/d to get:

$$fCO_2 = \frac{1}{Q + 2Q' + 1 + 0.5Q'' + 0.79\frac{m}{d}}$$

multiply numerator and denominator by 0.42:

$$fCO_2 = \frac{0.42}{0.42Q + 0.84Q' + 0.42 + 0.21Q'' + (0.79)(0.42\frac{m}{d})}$$

substituting from above (0.42 m/d = 2Q + 3 + Q”) leads to:

$$fCO_2 = \frac{0.42}{2.79 + 2Q + 0.84Q' + Q''}$$

from which follows:

$$\%CO_2 = \frac{42}{2.79 + 2Q + 0.84Q' + Q''} = \frac{100}{6.64 + 4.76Q + 2Q' + 2.38Q''}$$

$$\%CO = Q * \%CO_2 \qquad \%HC = Q' * \%CO_2 \qquad \%NO = Q'' * \%CO_2$$

Some useful conversions are:

For grams/gallon assume fuel density of 726 g/l, a fuel carbon fraction of 86%, 3.79 l/gallon and for CO 28g/mole; for HC (propane, C_3H_8) 44g/mole for NO 30g/mole; for C 12g/mole:

$$\frac{gmCO}{gal} = \frac{28*Q*0.86*726*3.79}{(1+Q+6Q')*12}$$

$$\frac{gmHC}{gal} = \frac{2*44*Q'*0.86*726*3.79}{(1+Q+6Q')*12}$$

$$\frac{gmNO}{gal} = \frac{30*Q''*0.86*726*3.79}{(1+Q+6Q')*12}$$

We now prefer to use grams of pollutant/kg of fuel because it requires no assumption about the fuel density:

$$\frac{gmCO}{kg} = \frac{28*Q*860}{(1+Q+6Q')*12}$$

$$\frac{gmHC}{kg} = \frac{2*44*Q'*860}{(1+Q+6Q')*12}$$

$$\frac{gmNO}{kg} = \frac{30*Q''*860}{(1+Q+6Q')*12}$$

If you want to express the measured ratios in the units of other molecules, for example gmNO_2/kg since all emitted NO will eventually oxidize in the atmosphere to NO_2, you only have to change the molecular weight of the species in the appropriate equation.

Derivation for methane powered vehicles:

ASSUMPTIONS:

Singer factor of 3.13.

$$CH_4 + m(0.21\ O_2 + 0.79\ N_2) \rightarrow$$
$$aCO + bH_2O + c(CH_4 + 2.13\ CH_4) + dCO_2 + eNO + \left(0.79m - \frac{e}{2}\right) N_2$$

$$Q = \frac{CO}{CO_2} = \frac{a}{d} \qquad Q' = \frac{HC}{CO_2} \qquad Q" = \frac{NO}{CO_2} = \frac{e}{d}$$

by Carbon balance : a + 3.13c + d = 1

by Hydrogen balance: 2b + 12.52c = 4

by Oxygen balance: a + b + 2d + e= 0.42m

Eliminate a: a = dQ c = dQ'

a + 3.13c + d = 1 dQ + 3.13dQ' + d = 1

$$d = \frac{1}{Q + 3.13Q' + 1}$$

Eliminate b: 2b + 12.52dQ' = 4 b = 2 – 6.26dQ'

dQ + b + 2d + e= 0.42m; dQ + 2 – 6.26dQ' +2d + e= 0.42m

substituting d from above:

$$0.42\ \frac{m}{d} = Q + \frac{2}{d} - 6.26Q' + 2 + Q" = Q+2+2Q+6.26Q'-6.26Q'+2+Q" = 3Q + 4 + Q"$$

from the combustion equation the mole fraction of CO_2 is:

$$fCO_2 = \frac{d}{a + 3.13c + d + e + 0.79m - \frac{e}{2}}$$

divide numerator and denominator by d:

$$fCO_2 = \frac{1}{\frac{a}{d} + 3.13\frac{c}{d} + 1 + 0.5\frac{e}{d} + 0.79\frac{m}{d}}$$

Substituting from above for a/d, c/d and e/d to get:

$$fCO_2 = \frac{1}{Q + 3.13Q' + 1 + 0.5Q" + 0.79\frac{m}{d}}$$

Multiply numerator and denominator by 0.42:

$$fCO_2 = \frac{0.42}{0.42Q + 1.32Q' + 0.42 + 0.21Q" + (0.79)(0.42\frac{m}{d})}$$

Substituting from above (0.42m/d = 3Q + 4 + Q")

$$fCO_2 = \frac{0.42}{3.58 + 2.79Q + 1.32Q' + Q"}$$

From which follows:

$$\%CO_2 = \frac{42}{3.58 + 2.79Q + 1.32Q' + Q"} = \frac{100}{8.52 + 6.64Q + 3.14Q' + 2.38Q"}$$

$$\%CO = Q * \%CO_2 \qquad \%HC = Q' * \%CO_2 \qquad \%NO = Q" * \%CO_2$$

For grams/gallon for LNG assume fuel density of 450 g/l, a fuel carbon fraction of 75%, 3.79 l/gallon and for CO 28g/mole; for HC (methane, CH_4) 16g/mole for NO 30g/mole; for C 12g/mole:

$$\frac{gmCO}{gal} = \frac{28 * Q * 0.75 * 450 * 3.79}{(1 + Q + 3.13Q') * 12} \qquad \frac{gmCO}{kg} = \frac{28 * Q * 750}{(1 + Q + 3.13Q') * 12}$$

$$\frac{gmHC}{gal} = \frac{3.13 * 16 * Q' * 0.75 * 450 * 3.79}{(1 + Q + 3.13Q') * 12} \qquad \frac{gmHC}{kg} = \frac{3.13 * 16 * Q' * 750}{(1 + Q + 3.13Q') * 12}$$

$$\frac{gmNO}{gal} = \frac{30 * Q" * 0.75 * 450 * 3.79}{(1 + Q + 3.13Q') * 12} \qquad \frac{gmNO}{kg} = \frac{30 * Q" * 750}{(1 + Q + 3.13Q') * 12}$$

White paper on negative readings in FEAT databases.

There are two questions that have to be addressed when discussing negative FEAT measurements. The first is how do negative measurements come about and the second is how are negative readings used in emissions calculations.

1) What are the sources of negative readings

FEAT measures emissions ratios, i.e. CO/CO_2, HC/CO_2, NO/CO_2 etc. These ratios are determined from the slope of a straight line fit to the time series of measurements collected behind each vehicle. The infrared detectors (IR) produce a voltage which is proportional to the amount of heat they see from the source on the opposite side of the road. The ultraviolet (UV) photodiode detector outputs a photon count which it sees from the xenon arc lamp in the source on the opposite side of the road. Each of these outputs varies as the amount of tailpipe gases pass in and out of the beam. The IR detectors are non-dispersive and see an entire wavelength region while the UV detectors are dispersive and only see discrete wavelengths of light. The resultant absorptions are converted into a measured concentration of tailpipe gas using a laboratory generated response curve for each species, i.e. a known concentration of carbon monoxide produces a specific voltage drop or a known concentration of nitric oxide produces a specific drop in the photon count at a particular wavelength.

When a vehicle enters and leaves the light beam FEAT collects information from all of its channels (both IR and UV) from in front of the car and immediately behind the car. Correction are made for changes in light intensity during this process as well as for compensating for the amount of each species in the air in front of the car. At the end of this process we have a time series of 50 data points of concentrations for the each of the tailpipe species we measure. Because there are situations where there is more of a particular gas in front of a car than behind it, i.e. a high emitter for CO is followed by a low emitter of CO, you can end up with absorptions that correlate with negative concentration values. This does not mean that you necessarily end up with a negative CO/CO2 ratio measurement, as we will discuss below, because we do not force the intercept of the linear fit through zero.

Figure 1 shows an example of the measurement time series for a vehicle with very high emissions. These data are calculated from the raw voltage readings that have been converted into “pseudo-concentrations”. We use this term because the concentrations plotted in the following figures assumes that all of the absorbance observed behind the car occurred in a gas plume this is exactly 8cm across. Absolute concentrations can only be established with a known path length and in the lab the response curves generated for each species were assembled using an 8cm cell. Behind the car we have no idea what the actual path length is but the absorbance changes observed are equal to the 8cm path length concentrations plotted. Whether these concentrations are accurate or not is not relevant because in Figure 2 we correlate the species of interest with CO_2 which has the same gas path length behind the car and the measured ratio, CO/CO_2, is now path length

Pollutant Readings vs Time

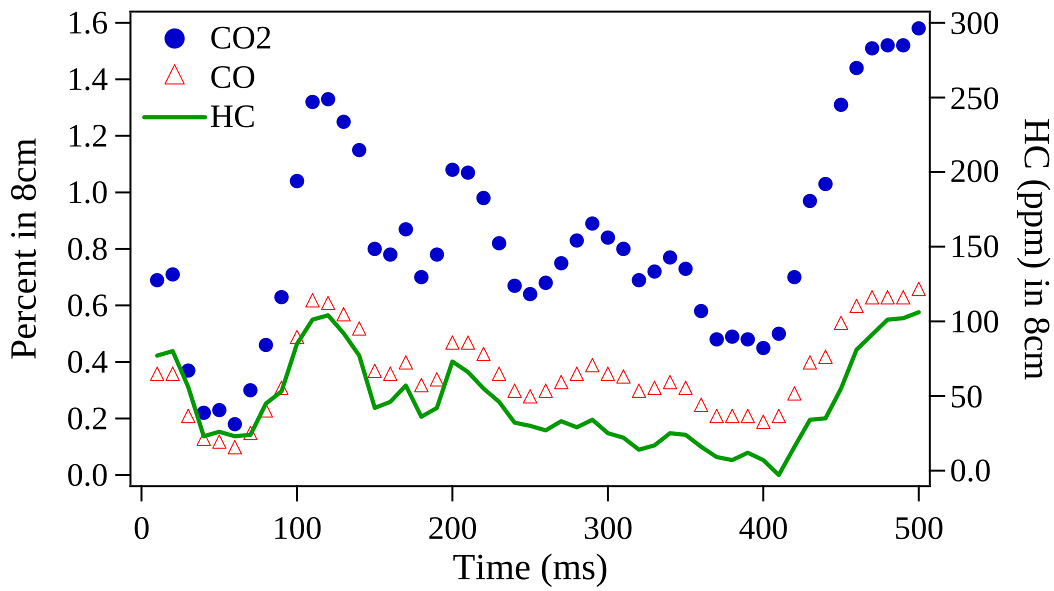

Figure 1. CO, CO_2 (left y-axis) and HC (right y-axis) emissions versus time behind a high emitting vehicle. These data are pseudo-concentrations calculated from the FEAT voltage readings assuming that all of the absorption from the gas plume is contained in an 8cm cell.

Pollutant Ratio Plots

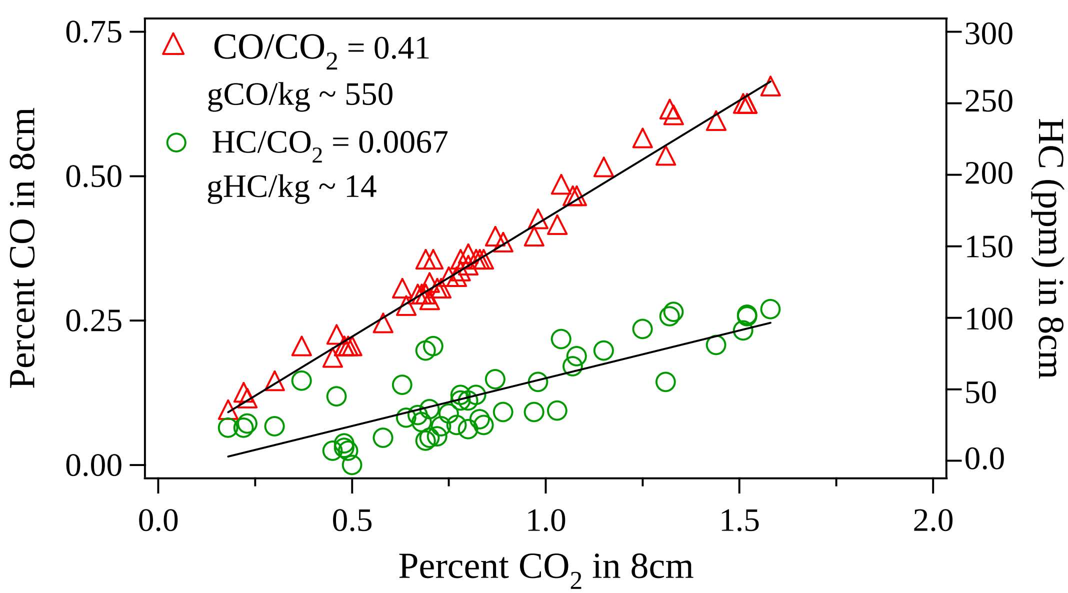

Figure 2. Pollutant ratio plots for the data shown in Figure 1 with CO (left y-axis) and HC (right y-axis) plotted against CO_2. Solid lines are linear least square fit to each data set with the slopes given in the legend and the approximate g/kg of fuel emissions for each.

Independent. The fits for the ratios do not require the intercept to go through zero even though for this vehicle the intercepts are close to zero. This ratio is the basic measurement that FEAT makes for each species on each vehicle.

Figure 3 shows the half second time plot for a vehicle which is really only emitting CO_2. CO and CO_2 are plotted in percent space on the left axis and HC is plotted in ppm's on the right axis. You will notice that the HC data shows considerable noise. The HC channel in FEAT has the poorest signal to noise ratio of all the channels due to the combination of a small absorbance cross section and the tiny amounts of unburned hydrocarbons emitted by vehicles today leading to small absorbances. You should also notice that there are a significant number of HC readings in the plot which are negative. This arises because of a couple of factors, the first is that the normalization voltages collected in front of the car, that determine whether there is more HC in front of the car than behind the car, basically sets the zero line for where the data will scatter about. The second has to do with the interplay of a multiple detector sampling system and the fact that the FEAT reference and hydrocarbon detector intensity changes over the course of the measurements are not always perfectly correlated. Figure 4 show the ratio plots and the lack of increased concentrations for the measured exhaust species while we record a large increase in CO_2. Both fits result in slopes that are essentially zero though it needs to be pointed out that just because pseudo-concentrations for a given species include negative values that does not dictate a negative value for the measured ratio as shown. This is because we do not force the intercept of the fit through zero.

The original question was what is the source of negative values in the FEAT data sets? The answer is that for vehicles that emit negligible amounts of pollutants we are measuring a zero ratio for those species. Because of instrument noise and changing environmental conditions repeated measurements of zero will end up producing a normal distribution of results that should be centered at zero. That distribution will have a positive tail and a negative tail. While we are not use to viewing negative results, because many instrument manufacturers truncate their measurements at zero, in FEAT a negative result in general qualifies the significance of the positive results. Figure 5 shows a second vehicle that has negligible levels of CO and HC emissions in its exhaust, however, this time the measurements result is a negative CO/CO_2 and HC/CO_2 ratio. It's important to remember that a negative emissions ratio does not mean the vehicle is cleaning the air but is just a measurement of zero where the instrument noise and or circumstances of the measurement ended up as part of the negative tail of the zero slope distribution.

2) How are negative results used in emissions calculations

As explained above FEAT calculates emission ratios for each species that is measured. Historically those ratios have been converted into percent concentration values and recorded in the databases. To convert from a ratio into percent concentration requires a number of assumption the largest of which is that the vehicle is using gasoline and the exhaust coming out of the tailpipe is sampled by a garage type emissions analyzer that

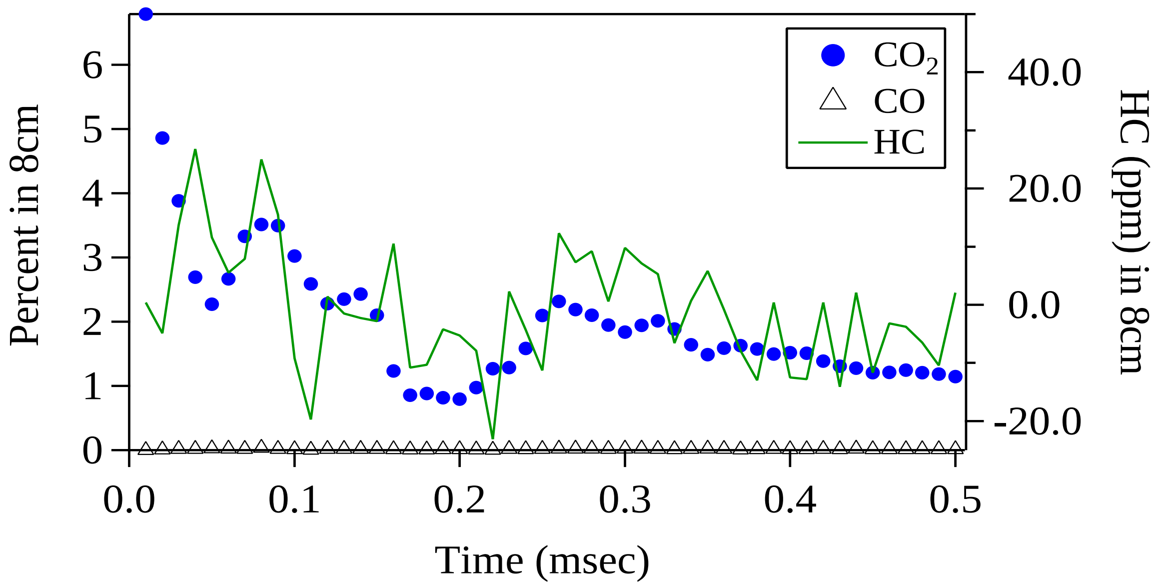

Figure 3. CO, CO_2 (left y-axis) and HC (right y-axis) emissions versus time behind a high emitting vehicle. These data are pseudo-concentrations calculated from the FEAT voltage readings assuming that all of the absorption from the gas plume is contained in an 8cm cell.

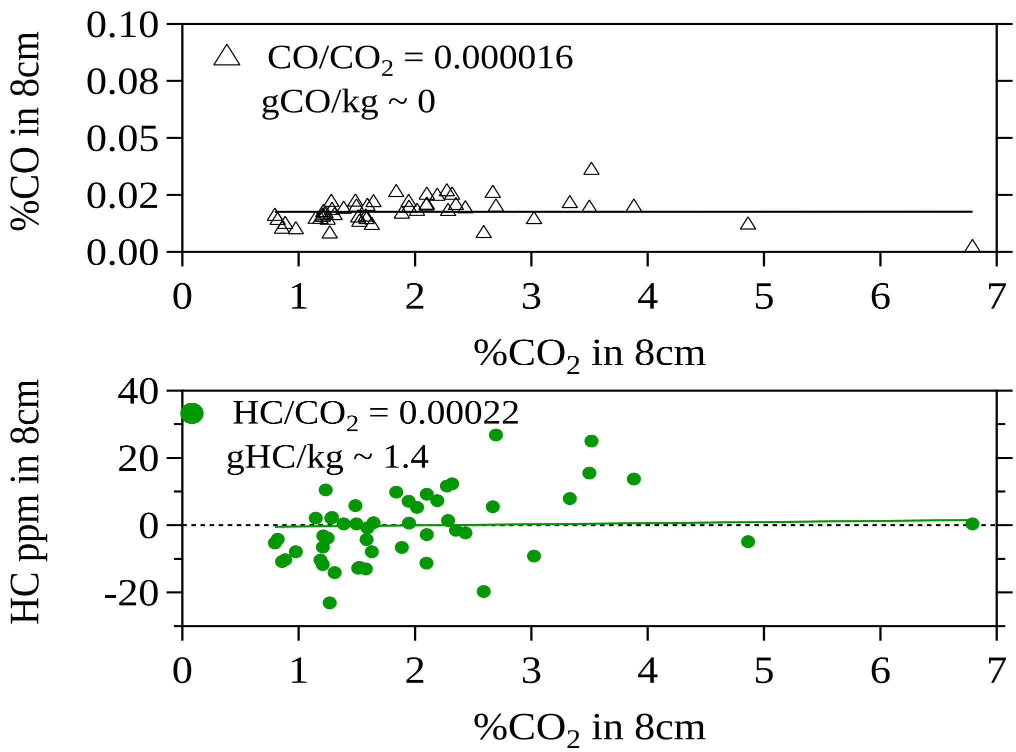

Figure 4. Pollutant ratio plots for the data shown in Figure 3 with CO (left y-axis) and HC (right y-axis) plotted against CO2. Solid lines are linear least square fit to each data set with the slopes given in the legend and the approximate g/kg of fuel emissions for each.

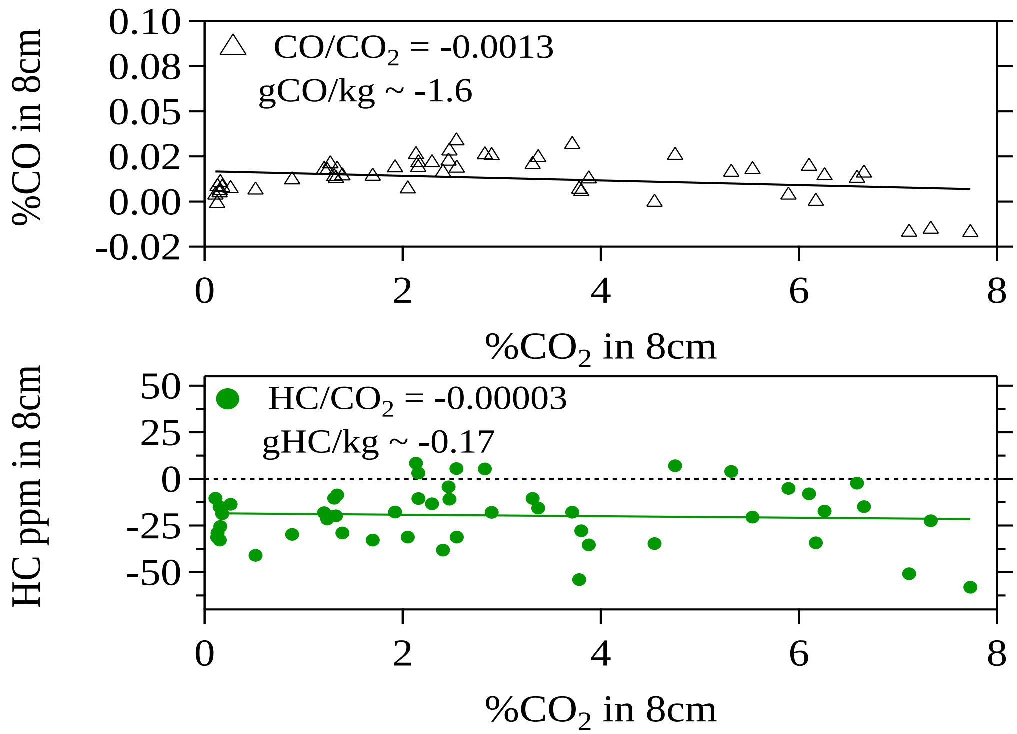

Figure 5. Pollutant ratio plots for a different zero emissions vehicle with CO (left y-axis) and HC (right y-axis) plotted against CO2. Solid lines are linear least square fit to each data set with the slopes given in the legend and the approximate g/kg of fuel emissions for each.

utilizes an 8cm sample cell. However, it is important to remember that despite the fact that percent concentrations are listed in the database the measurement that was collected was a ratio, i.e. $\%CO/\%CO_2$, $\%HC/\%CO_2$ etc. and the original slope can be resurrected by just dividing each measured species percent value with the $\%CO_2$ value listed for the particular record (see the FEAT Math II appendix for details).

At some point we decided that converting the ratios into fuel specific values (grams of pollutant/gallon of fuel or grams of pollutant/kilogram of fuel) made more sense since it is independent of fuel type and eliminated many of the assumption required to convert the ratios to percentages (see the FEAT Math II appendix). All of our more recent published databases now include the original percentages and grams of pollutant/kilogram of fuel values. Within reason all negative ratio results are preserved in the database. At some point large negative results are incorrect and each FEAT channel has a series of quality assurance checks, of which a lower limit for negative values is one invalidity filter, are used to invalidate some of the readings. FEAT databases include these validity flags for each channel other than CO and CO_2 which are always valid for every published record as this is the minimum requirement for a valid record (see attached validity criteria). It is imperative when calculating results from a FEAT database that these validity flags are used to qualify the readings as invalid readings are not zeroed out in the database.

When calculating results from the FEAT databases all of the valid values are used in all of the calculations including all of the negative results. The negative results are not converted into zero and they are not excluded. Doing so will bias the calculation high. If we go back to a pure zero emissions example. If one collects 100 readings with FEAT on a true zero signal source there will be a distribution collected that will result in some number of zero ratios and then an equal number of negative and positive ratios. The 100 readings should average to zero. This will not happen if the negative readings are excluded or zeroed out which will result in an average which is greater than zero and is incorrect.

An additional avenue to show that including the negative readings in the calculation is the correct path is to compare FEAT measured ratios with ratios measured by others. Because the LA basin has been an often location for air quality studies there are a number of studies that have collected measured ratios that we can compare against. Figure 6 shows FEAT and NOAA collected CO/CO_2 and NO_x/CO_2 ratios in various years from the South Coast Air Basin. The majority of the NOAA measurements were collected with various aircraft, though there is one flask measurement collected on the top of Mt. Wilson in 2010, and in general they represent a basin wide average. FEAT ratios were collected at the E-23 La Brea Ave. site and on Sherman Way in Van Nuys. The CO/CO_2 comparison is quite good as we would expect that CO emissions are dominated by vehicle traffic. FEAT's NO_x/CO_2 ratios are in general higher than the basin wide averages after the 2003 measurements as there are an increasing number of sources of CO_2 emissions with low NO_x emissions.

Both FEAT's CO and NO measurements include significant numbers of negative readings. If the negative readings are not included in the calculations the FEAT values would have poorer agreement with the NOAA measurements. In addition to CO in 2010 NOAA compared the basin wide average for the NH_3/CO ratio again using aircraft measurements. Nowak et al. showed that the 2008 FEAT measured NH_3/CO ratio measured at the La Brea Ave site accurately predicted the automobile NH_3 inventory calculated from the 2010 aircraft measured NH_3/CO ratio (62 ± 24 metric tons NH_3/day for the aircraft and 58 metric tons NH_3/day for the FEAT measurements, Nowak et al., Geo. Res. Let., 39, L07804, 2012.

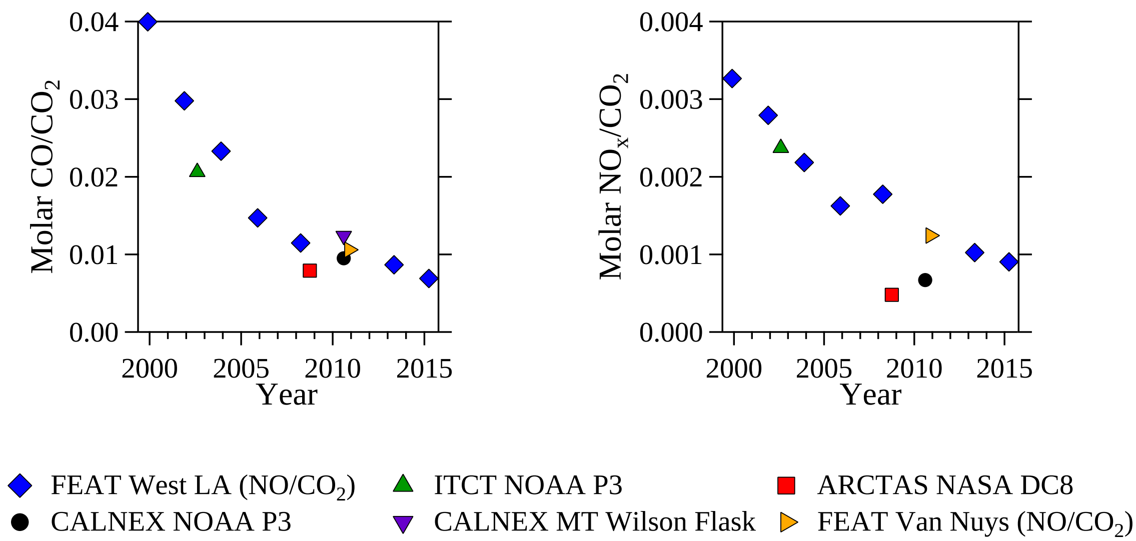

Figure 6. Comparisons of FEAT measured CO/CO_2 and NO_X/CO_2 ratios and data collected in various NOAA measurement campaigns in the South Coast Air Basin by measurement year. FEAT data was collected at the La Brea Ave. site and in Van Nuys.

FEAT criteria to render a reading "invalid" or not measured.

Not measured:

1) Beam block and unblock and then block again with less than 0.5 seconds clear to the rear. Often caused by elevated pickups and trailers causing a "restart" and renewed attempt to measure the exhaust. The restart number appears in the database.

2) Vehicle which drives completely through during the 0.1 seconds "thinking" time (relatively rare).

Invalid:

1) Insufficient plume to rear of vehicle relative to cleanest air observed in front or in the rear; at least five, 10ms averages >0.25% CO_2 in 8 cm path length. Often HD diesel trucks, bicycles.

2) Excess error on CO/CO_2 slope, equivalent to $\pm$20% for %CO. >1.0, 0.2%CO for %CO<1.0.

3) Reported %CO <-1% or >21%. All gases invalid in these cases.

4) Excess error on HC/CO_2 slope, equivalent to $\pm$20% for HC >2500ppm propane, 500ppm propane for HC <2500ppm.

5) Reported HC <-1000ppm propane or >40,000ppm. HC "invalid".

6) Excess error on NO/CO_2 slope, equivalent to $\pm$20% for NO>1500ppm, 300ppm for NO<1500ppm.

7) Reported NO <-700ppm or >7000ppm. NO "invalid".

8) Excessive error on NH3/CO2 slope, equivalent to +50ppm.

9) Reported NH3 < -80ppm or > 7000ppm. NH3 "invalid".

10) Excess error on NO2/CO2 slope, equivalent to +20% for NO2 > 200ppm,

40ppm for NO2 < 200ppm

11) Reported NO2 < -500ppm or > 7000ppm. NO2 "invalid".

Speed/Acceleration valid only if at least two blocks and two unblocks in the time buffer and all blocks occur before all unblocks on each sensor and the number of blocks and unblocks is equal on each sensor and 100mph>speed>5mph and 14mph/s>accel>-13mph/s and there are no restarts, or there is one restart and exactly two blocks and unblocks in the time buffer.