APPENDIX

AERODYNE RESEARCH MOBILE LABORATORY PARTICULATE MEASUREMENTS TCEQ 2010 FLARE STUDY

Introduction

The content of this appendix is focused on the particulate black carbon results. The primary focus of the tests was to determine the flare combustion characteristics. As a result the measurement effort and initial analysis centered on the uncombusted process gas hydrocarbons, the products of combustion (for example, carbon dioxide [CO_2], carbon monoxide [CO], water [H_2O], and oxygen [O_2] deficit) as well as the gaseous species formed as intermediate products of combustion (formaldehyde, propylene oxide). At the same time, measurements of the particulate constituents in the flame were also monitored on a sample line designed to transmit particles. The instrumentation on this sample line examined particulate composition, mass, and number.

This appendix provides a brief descriptions of the instrumentation in the Aerodyne Mobile Laboratory used to measure particle phase species during the TCEQ 2010 Flare Study, followed by preliminary results arrived at after analysis of data. The scope of the analysis focused on the chemical composition and size of particles and differences in those parameters with the composition of the vent gas, as well as levels of steam and air assist. The mass spectra of black carbon (BC) measured from these flares was compared to other BC source mass spectra to evaluate any differences in the BC mass spectral signature, which could potentially be used to identify the source of a BC plume.

Particle Phase Inlet Details

The particulate phase instruments on board the Aerodyne Mobile Lab sampled from a dedicated particle line separate from the majority of the gas phase instruments. Approximately 2 standard liters per minute (slpm) of the sample flow was extracted to the particle line and an additional 10.6 slpm of dilution flow (molecular nitrogen) was added to the particle line in order to cool the sample and prevent condensation of vapor species in the exhaust flow. Flow was verified to be laminar with a Reynolds number of 1123 and for 100 nanometer (nm) particles the transmission through the line was 98.3% with a pressure drop of 0.7 torr through the line. A 2.5 micrometer (μm) diameter size cutoff inline cyclone removed large particles from the sample line. The sample line was 125 feet long and 5/8-inch inner diameter (ID) copper tubing was used. A 12.6 slpm flow through the line resulted in a sample flow residence time of 35.9 seconds. The Soot Particle-Aerosol Mass Spectrometer (SP-AMS) instrument, Multi-Angle Absorption Photometer (MAAP) instrument, Scanning Mobility Particle Sizer[8] (SMPS), and a Licor instrument for CO_2 measurements all sampled from the particle line. Licor instruments conducted CO_2 measurements on both particle and gas phase lines to ensure that both lines were sampling the same volume of air.

Particle Phase Instrumentation

SP-AMS

The Aerodyne Soot Particle-Aerosol Mass Spectrometer (SP-AMS) instrument is a standard Aerodyne high resolution time of flight aerosol mass spectrometer (HR-ToFMS) with an intracavity, continuous wave (CW) laser vaporizer[1]. The SP-AMS was operated to provide online chemically speciated mass and sizing measurements of both non-refractory and refractory particles between roughly 50 – 600 nm in aerodynamic diameter. Details pertaining to the SP-AMS are presented in Onasch, et al[1]. In the SP-AMS, particles containing refractory materials (i.e., black carbon and many

metals) are vaporized with a 1064 nm laser. The resulting vapor is ionized with electron impact and detected with the HR-TosFMS. A heated tungsten surface (600 degrees Celsius [°C]) that is typically used in traditional Aerodyne AMS instruments[2,3] was also used to measure the composition of any non-refractory particles. A consequence of this vaporizer set up is that the species measured at any point in time are a combination of species vaporized with the conventional heater and species vaporized with the 1064 nm laser. Particulate matter (PM) measurements were conducted at 1 second time resolution for the majority of the campaign because of the transient nature of the flare plume due to wind conditions. BC and organic species mass concentrations were obtained from the SP-AMS mass spectra following methods outlined by Onasch, et al[1]. Mass spectral intensities (in units of Hz) are converted to mass units (micrograms per cubic meter [μg/m^3]) using factors that account for species-dependent ionization efficiencies and laser-particle beam overlap. The latter is dependent on several factors including laser/particle beam alignment as well as detailed particle properties (size and shape). For this study, relative ionization efficiencies for refractory black carbon of 0.2 measured by Onasch, et al[1] are used together with a collection efficiency, to account for incomplete particle and laser beam overlap of 0.15 determined by comparison of MAAP BC and SP-AMS BC measurements.

MAAP

The MAAP (Thermo-Fisher Model #5012) produced measurements of black carbon particles with 1 second time resolution. The MAAP measures PM light absorption, which has been shown to be proportional to BC mass[4]. The MAAP system has been used in prior black measuring experiments with at least partial emphasis on combustion plumes not directly related to flares[5,6,7]. Flow through the MAAP was regulated to 9.5 slpm.

SMPS

The Scanning Mobility Particle Sizer[8] (SMPS), which integrates the TSI Model 3080 electrostatic classifier with the TSI CPC Model 3776 and TSI DMA column Model 3081, was utilized to determine the size distribution of particles by number and volume concentrations. The SMPS was operated with a 2 minute sampling time and scanned from 10-700 nm. The SMPS has experience in measuring combustion emissions[5,7]. (Onasch, et al., 2009; Slowik, et al., 2007; Chang, et al., 2007). Flow through the SMPS was 300 centimeters^3/minute.

Results

All time series data have been analyzed to determine the ratio of BC loading relative to CO_2 mixing ratio. The examples described in Figure 1 and described below are available in a separate spreadsheet. The quantification of particulate loading per quantity of CO_2 producing process gas can be computed with unit conversion:

$$\frac{\text{BC } \mu\text{g}}{\text{m}^3 \text{ ppm CO2}} * \frac{22.4\times10^{-3}\text{m}^3}{\text{mole gas}} * \frac{1 \text{ ppmv CO2}\cdot10^6 \text{ mole gas}}{1 \text{ mole CO2}} * \frac{1\text{g}}{10^6 \ \mu\text{g}}.$$

This implies that for *n* μg BC per m^3 per parts per million (ppm) CO_2 observed in the plume, the loading in grams per moles of process gas is *n* * 0.0224. The conversion of the measured emission ratio to a mass fraction relative to the process gas is dependent on process gas composition. The

BC production relative to CO_2 production has been determined for all test points where these measurements were successfully conducted utilizing the MAAP BC measurement and the CO_2 measurement conducted on the particle line. Graphs 1-6 depict the ratio of BC in pounds to the heat content of the vent gas in millions of British thermal units (MMBtu), normalized to CO_2 parts per million by volume (ppmv, to account for variations in plume intensity) versus the destruction and removal efficiency (DRE) of the vent gas which was being combusted. Graphs 1-6 represent the total body of test points during the campaign that have both MAAP and CO_2 measurements and in general it is evident that as DRE is increased black carbon production also increases although there are certainly differences in both the magnitude of BC relative to CO_2 and its rate of increase with respect to increasing DRE as the type of fuel burned and the type of assist is varied.

Three test series have been analyzed in detail with the SP-AMS instrument to gain insight into the chemical speciation of the particles produced by the flare. They are one experiment with mix utilizing steam assist (test series number S5), one propylene mix experiment with air assist (test series number A3), and one propane mix experiment with steam assist (test series number S12). Figure 7 depicts a time series of SP-AMS- (black) and MAAP- (gray) derived black carbon and organic mass concentrations and CO_2 for propylene mix vent gas with steam assist. The CO_2 measurements are the primary indicator of the degree of dilution, which may be occurring in the open test environment. The correlation between PM signals and CO_2 in Figure 7 verifies that the PM measured is due to the flare source. In this case a DRE change of 3% varying from 98% to 95% resulted in roughly a factor of 10 decrease in BC particle mass and particulate matter concentrations dropped off rapidly with decreasing DRE. Negligible BC particle mass was measured at the lowest DRE (65%) in this time series shown on the right side of the graph. A similar decreasing trend in organic PM material is also observed as a function of DRE in Figure 7. It is also evident from the time series plot that the mass of organic PM coating is minimal relative to the BC core where in the largest magnitude plume BC is approximately 200 $\mu g/m^3$, while the organic coating is approximately 12 $\mu g/m^3$.

Table 1 presents the measured enhancement in the ratios of BC to CO_2 within the plume as a function of DRE for propylene mix and propane mix flares for the three tests analyzed in detail with the SP-AMS. The results of tests S5 (propylene mix steam assist), S12 (propane mix steam assist) and A3 (propylene mix air assist) are depicted. In both S5 and A3 rapid reductions in BC/CO2 ratios were observed as DREs were changed between 100 and 90%. The drop-off in BC emissions was observed at a much higher DRE for the steam-assist flare relative to the air-assist flare. The air-assist flare lost BC PM rapidly between DREs of 100-90%, but still maintained a level of black carbon that is enhanced relative to background for all mass spectral carbon peaks down to a DRE of 60% while the steam-assist flare had BC concentrations at background levels with a DRE of 93% or lower, with the exception of fullerenes, which are discussed in detail in a later section of this document. Propane flares were found to emit very little black carbon. For the test series S12 reported in Table 1, every test point was found to have plume BC mass indistinguishable from background as measured by both MAAP and SP-AMS. The data in Table 1 show that the addition of steam and air assist do reduce BC concentrations substantially. When assessing flare DRE, BC concentrations should be considered along with destruction of the vent gases[4,9,11].

Size distribution of particles was determined with the SMPS system. Figure 8 shows the average size mode of higher DRE (95-98%) test points for the propylene mix vent gas with steam and air assist along the top and propane mix with steam and air assist at the bottom, as averaged over the whole campaign. These signals are normalized to CO_2 on a one second time scale to account for variations in plume intensity. Particle number concentrations for propane mix vent gas are lower than for propylene vent gas. The propane mix flare emits particles with a broader size distribution than the propylene mix flare and a smaller mode than the propylene mix flare. Figure 9 depicts the change in propylene mix flare particle number distributions as a function of DRE. At high DREs the steam-assist size mode mobility diameter peaks around 90 nm and the air-assist size mode mobility diameter appears close to 70 nm. As DRE is reduced the particle size mode shifts to smaller sizes with size distribution peaks shifting to 30 and 20 nm for propylene mix with steam and air assist, respectively. Considering that the soot particles measured are fractal in nature and the SMPS determines a mobility diameter rather than a geometric diameter the possibility that changes in mobility diameter may actually be due to changes in the shape of the soot particle rather than a change in the geometric diameter of the particle can not be ruled out. (DeCarlo, et al., 2004; Slowik, et al., 2004; Park, et al., 2003).

The mass spectral signature of the flare exhaust measured by the SP-AMS is useful in the determination of the chemical nature of the PM emitted from the flares. Figure 10 depicts a comparison between propylene mix flare air- and steam-assist SP-AMS spectra with a vehicle exhaust SP-AMS spectrum[17]. The mass spectral peaks corresponding to BC and organic chemical species are depicted in each spectra. A clear difference between the flare and vehicle exhaust spectra is seen between mass-to-charge ratios (m/z) of 400-1000. BC mass spectra of propylene vent gas flares with spacing of 24 atomic mass units corresponding to fullerenes are seen in the high m/z range. These characteristic BC fullerenes are present at all DREs tested, even when low m/z C1-C5 BC components are at background levels. Although the total fullerene signal is only a small fraction of the total BC (0.2-0.3% at a DRE of 98, up to 10% at a DRE of 38), it dominates the signal above m/z 400. When considering the quantification of fullerinic soot it is important to consider that fullerenic soot may have a different sensitivity in the SP-AMS relative to the low m/z C1-C5 BC components that tend to dominate both the mass spectrums of most measured soot sources as well as the calibration source. A Regal Black (Cabot labs) soot standard was used for calibration which contains no fullerene signature, and past laboratory calibrations have shown a higher sensitivity to fullerenes than to the low m/z C1-C5 BC components. A fullerene calibration was not done during this campaign so a calibration based on fullerene cannot be directly applied, but the numbers above should be considered as upper bounds given the prior evidence of increased sensitivity with respect to fullerenes. It is clear in Figure 10 that no characteristic fullerene signatures are present in the truck diesel exhaust mass spectrum from another campaign. Other internal combustion engine sources examined including generators (Multiquip/DCA25USI) and aircraft engines (CFM56-2-C1 High Bypass Turbofan Jet) were also found to have no fullerene signature in a small sample set. More studies are needed to verify this lack of a fullerene signature with internal combustion engines but it appears that the presence of a fullerene signature may be a clear distinguishing factor between open flame sources such as flares and internal combustion

engine exhaust sources of BC. There is literature detailing the presence of fullerenes and polyaromatic hydrocarbons (PAHs) in flame soot in prior studies not particular to flares (Hebgen, et al.; Loffler, et al.; Reilly, et al.). The ratio of fullerene to total BC is also found to increase as DRE decreases as is shown in Figure 11. It is uncertain at this time what controls this ratio, but it is likely due to changes in combustion conditions driven by assists.

A distinguishing feature of the flare SP-AMS spectra is the relative lack of signal due to inorganic or organic coatings on emitted BC particles. The ratio of organic signal (typically although not necessarily due to a coating on the BC particle) to black carbon is relatively small compared with measurements of other BC sources that might typically be encountered in a refinery environment. Pie charts depicting the ratio of organic to BC (ug/m^3) for high and low DRE test points with the propylene mix utilizing steam and air assist, and diesel generator and diesel truck exhaust[17] are shown in Figure 12. The diesel truck and generator plume have an age of 15 and 20 seconds respectively while the flare age is approximately 35 seconds. In this analysis, the raw signal (in units of Hz) is converted to mass units using species-dependent ionization efficiencies and collection efficiencies particular to each campaign. In all of the flare test points, organic mass is less than 25% of the sum of organic plus black carbon while in both internal combustion engine plumes the organic is close to 50% of the sum of black carbon and organic. In diesel exhaust, condensation of unburned lubricating oil is known to account for a large fraction of the measured organic PM[18] and the lack of lubricating oil in a flare may account for much of the reduced organic component relative to internal combustion engines. One key component of remaining analysis yet to be done is to examine the organic spectra that is present in the 150-500 m/z range for evidence of PAHs and any other detailed speciation that can be done at these higher mass ranges. Organic fragments will also be looked at in greater detail to evaluate ratios of organics with different levels of oxidation.

Summary

Particulate measurements of flares conducted during the TCEQ 2010 Flare Study highlight the effect of adding steam and air assist technology to industrial flares in a large-scale open-air environment. Propylene mix flares tested were found to have a significant BC content, which was very sensitive to steam-assist and somewhat less sensitive to air-assist levels. Optimum flare operating conditions need to destroy vent gases without emitting high concentrations of BC and these measurements indicate that for the steam-assisted flare tested combusting the propylene mix vent gas stream, a DRE as high as 93% does not elevate BC above background conditions, while with the air-assisted flare tested, BC is elevated at all points examined (DRE 63% and higher) relative to background. Propane mix flares did not produce black carbon above background levels for any examined condition indicating that a high DRE for these flares does not lead to high emissions of BC. Flare mass spectra were found to contain fullerenes at higher levels than other combustion sources especially internal combustion engines. The organic to black carbon PM ratio present in flare plumes was also found to be lower than in exhaust plumes from internal combustion engine and gas turbines. These unique properties of flare plumes may assist in the source attribution of ambient atmospheric black carbon PM. The examination of specific organic signals is a continuing process still under development.

References

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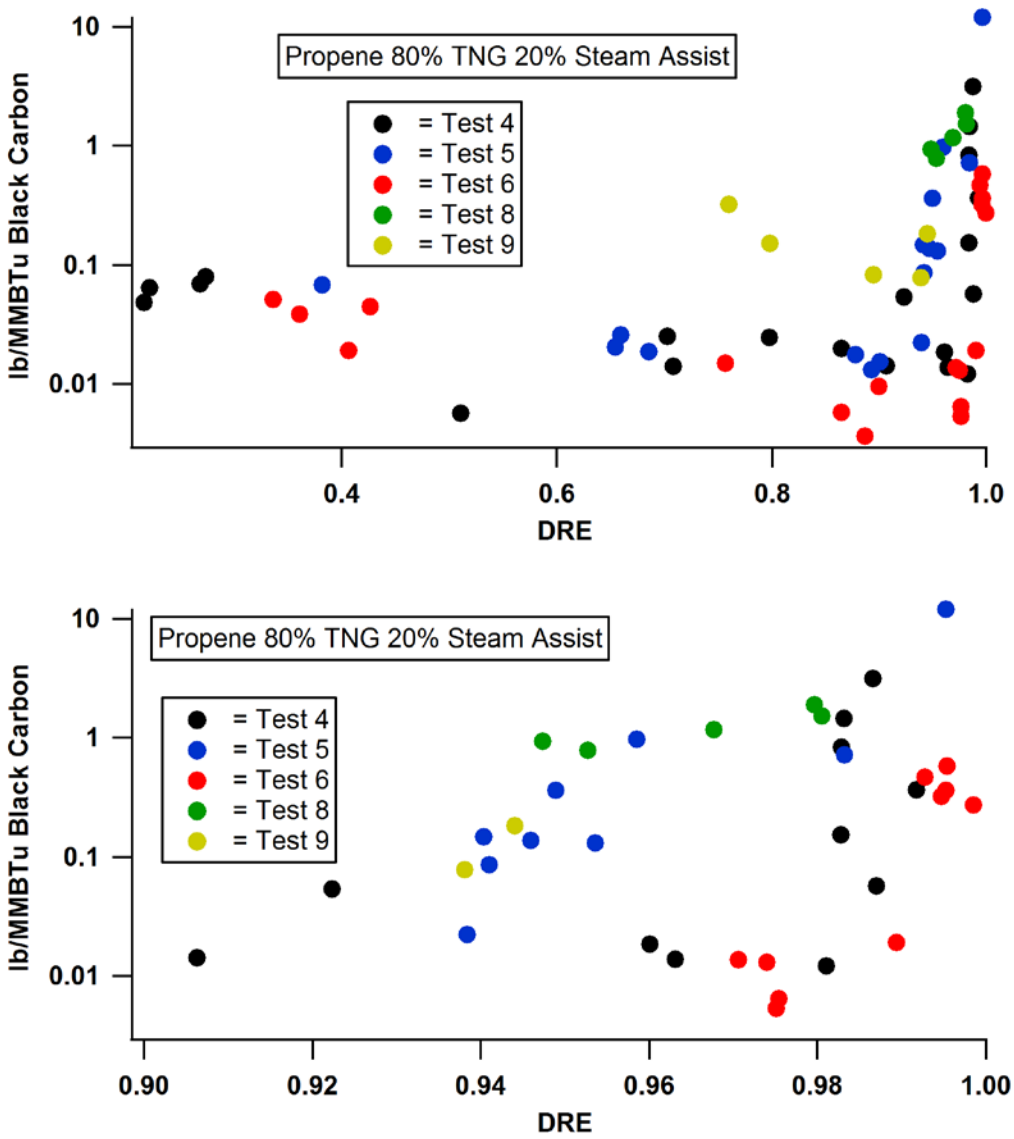

Figure 1. The top graph depicts the results of all test points sampled by MAAP and Licor for black carbon and CO_2 measurements respectfully where the sample gas was an 80% propylene-20% Tulsa natural gas mixture and steam assist was used. The bottom graph focuses on test points between 0.9 and 1 DRE.

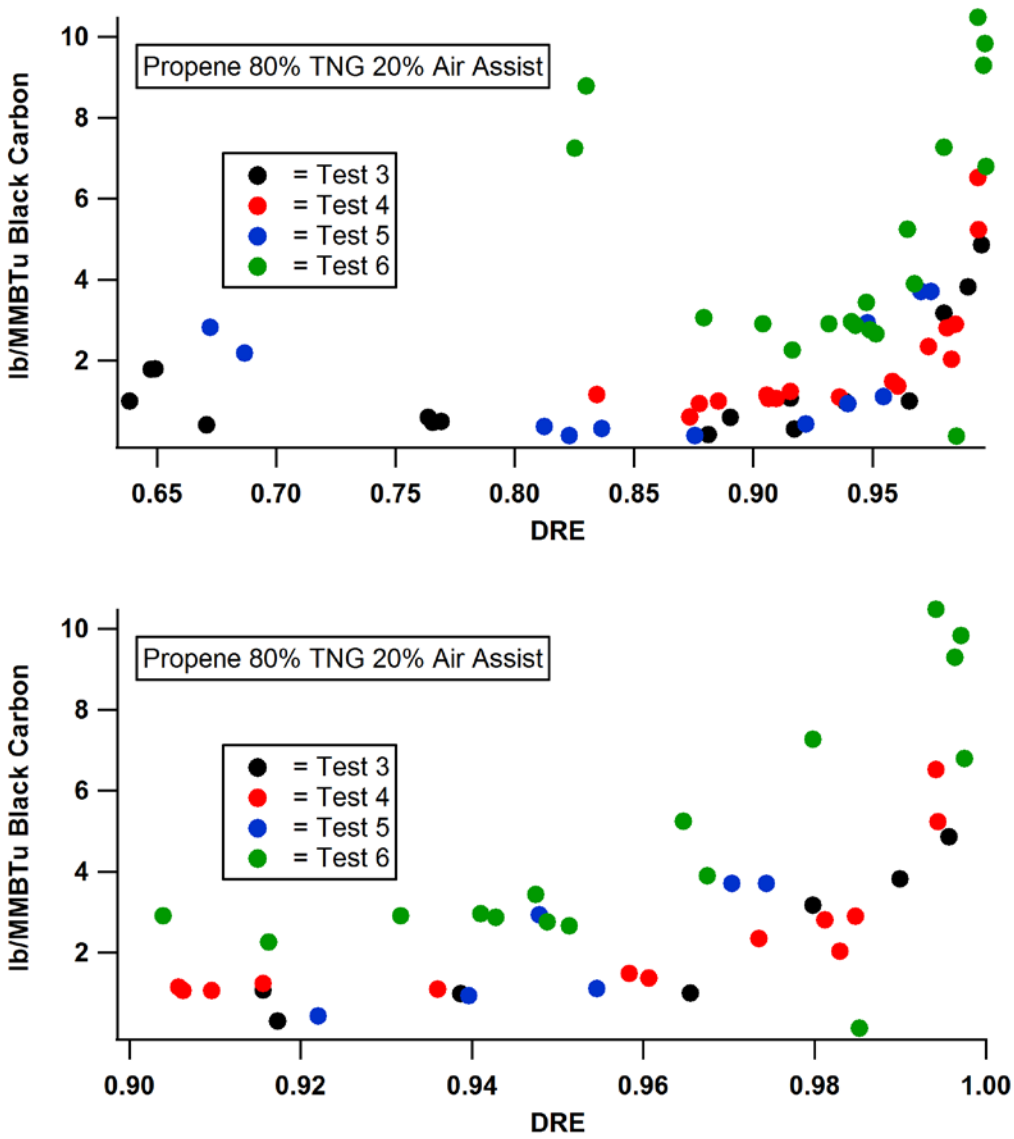

Figure 2. The top graph depicts the results of all test points sampled by MAAP and Licor for black carbon and CO_2 measurements respectfully where the sample gas was the 80% propylene-20% Tulsa natural gas mixture and air assist was used. The bottom graph focuses on test points between 0.9 and 1 DRE.

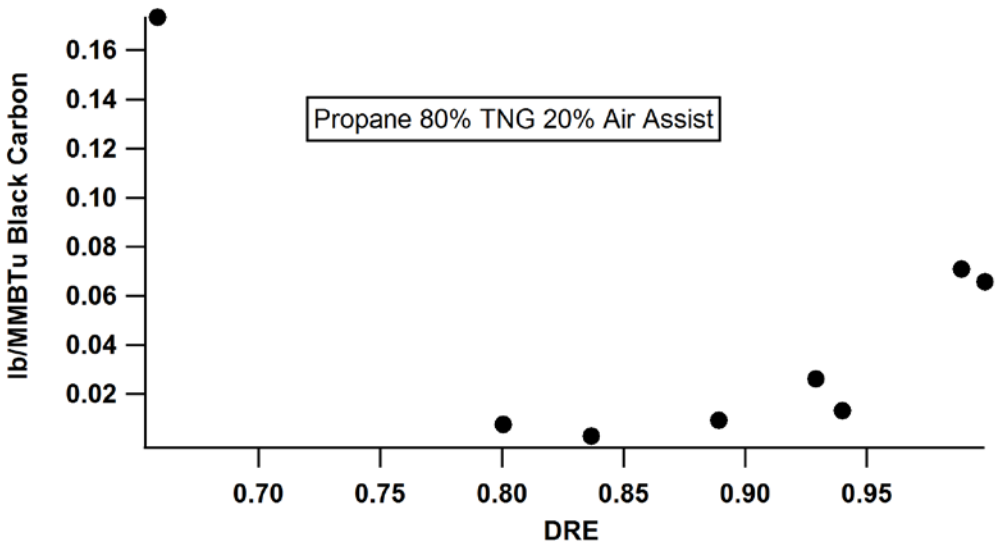

Figure 3. The results of all test points sampled by MAAP and Licor for black carbon and CO_2 measurements respectfully where the sample gas was the 80% propane-20% Tulsa natural gas mixture and air assist was used.

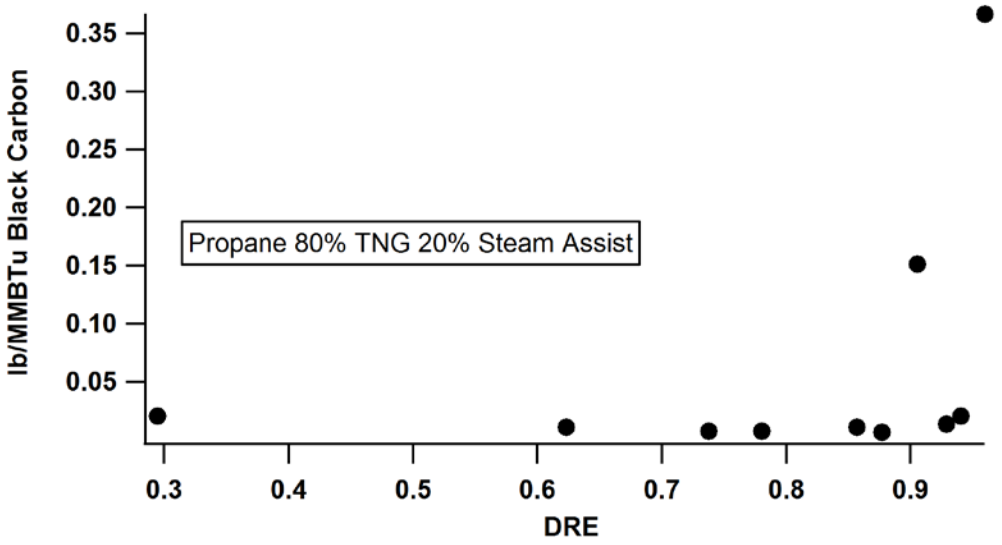

Figure 4. The results of all test points sampled by MAAP and Licor for black carbon and CO_2 measurements respectfully where the sample gas was the 80% propane-20% Tulsa natural gas mixture and steam assist was used.

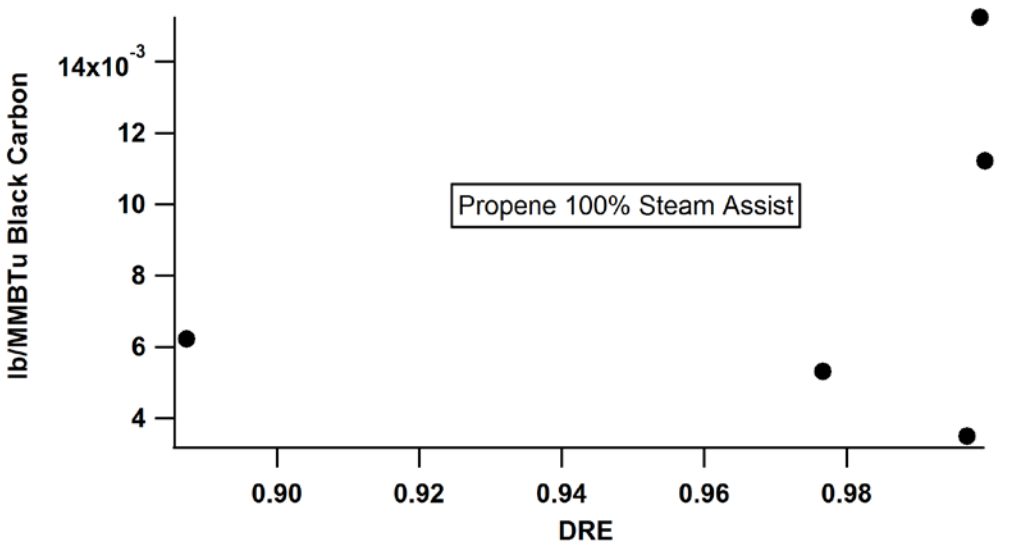

Figure 5. The results of all test points sampled by MAAP and Licor for black carbon and CO_2 measurements respectfully where the sample gas was 100% propylene and steam assist was used.

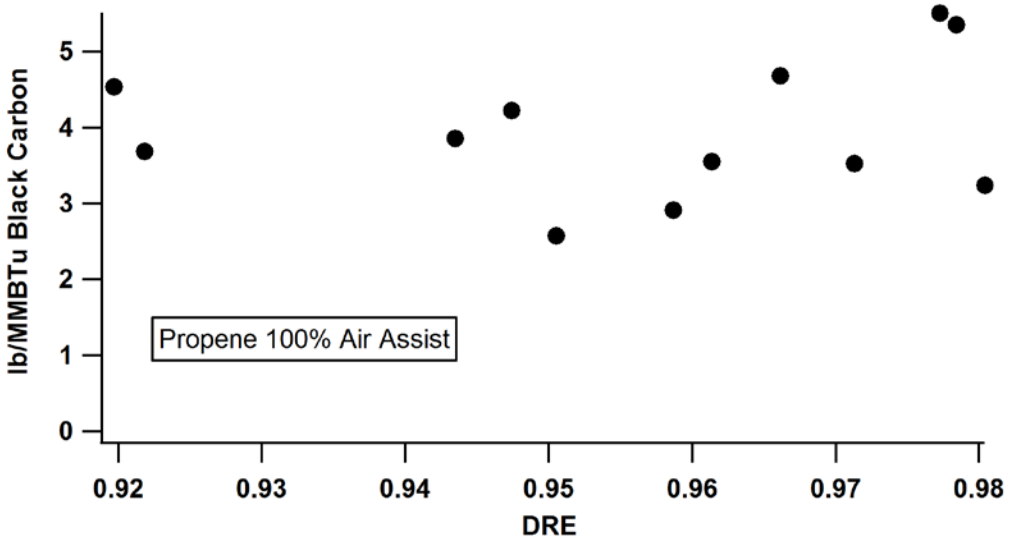

Figure 6. The results of all test points sampled by MAAP and Licor for black carbon and CO_2 measurements respectfully where the sample gas was 100% propylene and air assist was used.

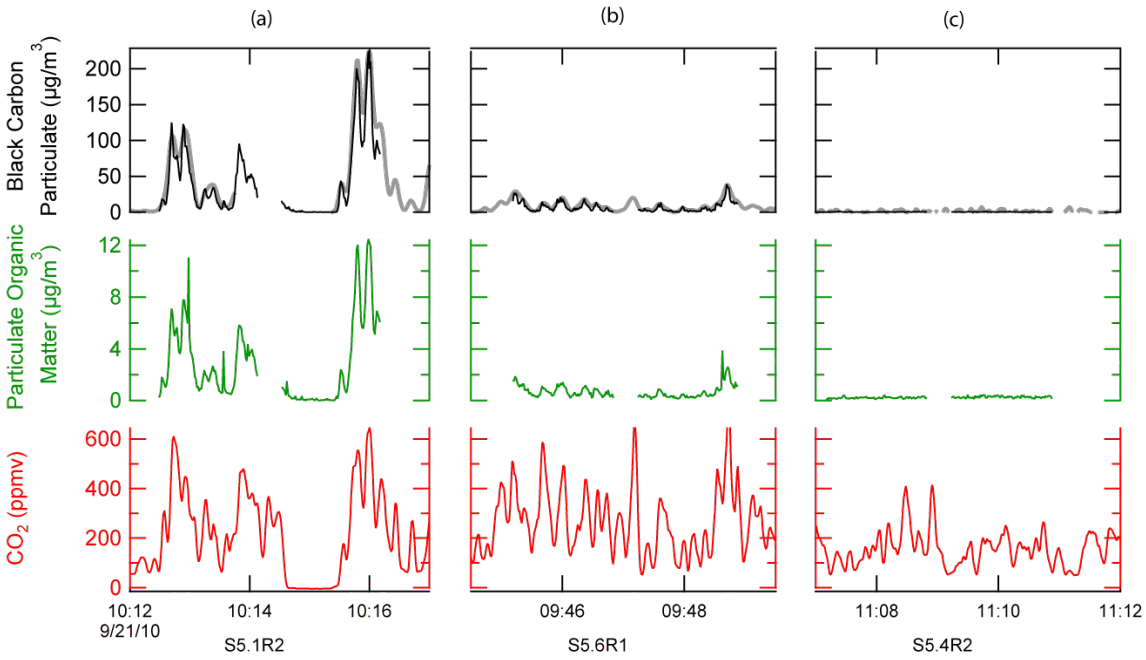

Figure 7. Particulate data time series during the S5 flare test series. The measured black carbon loading from MAAP (gray) and SP-AMS (black), particulate organic loading, and CO_2 mixing ratio are plotted against selected times within three of the S5 test sequences. The computed DRE values based on in-situ sampling analysis are 98±1, 95±1 and 65±3 for the tests noted by (a), (b), and (c), respectively. The incipient smoke point was actually being determined during period S5.1, R2 so this time period is very close to the maximum allowed BC concentration. Sample flow is diluted by a factor of 5.3 with N_2 and diluted concentrations are depicted.

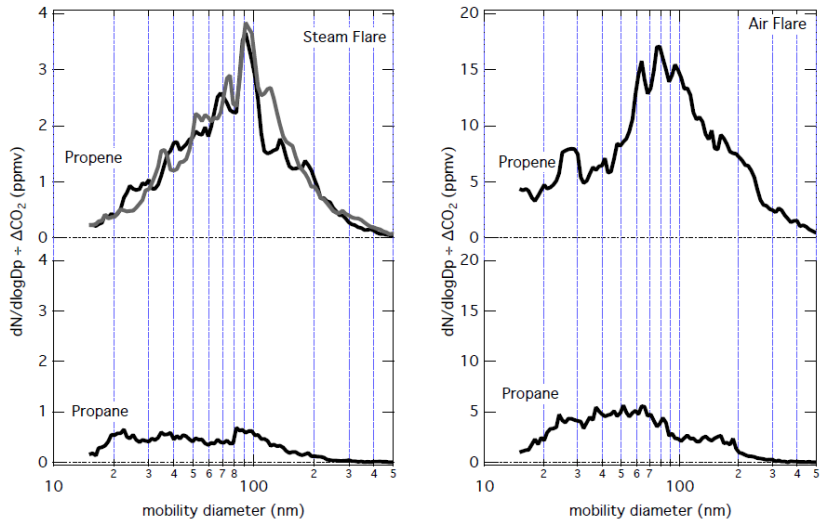

Figure 8. The average size mode as determined by SMPS of high DRE (95-98 %) test points for propylene mix vent gas with steam and air assist and propane mix with steam and air assist is depicted. These average size modes are normalized to excess CO_2

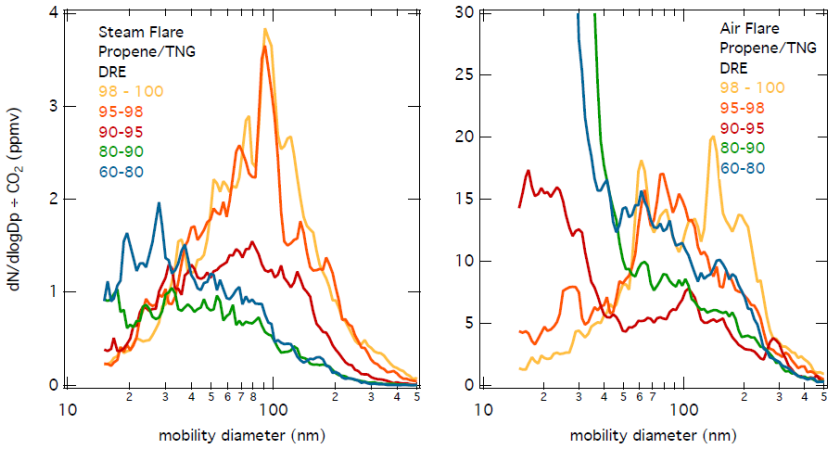

Figure 9. The size modes of PM as determined by SMPS are depicted as a function of DRE for steam- and air-assisted flares. SMPS scanned from 15-500 nm mobility diameter in all cases

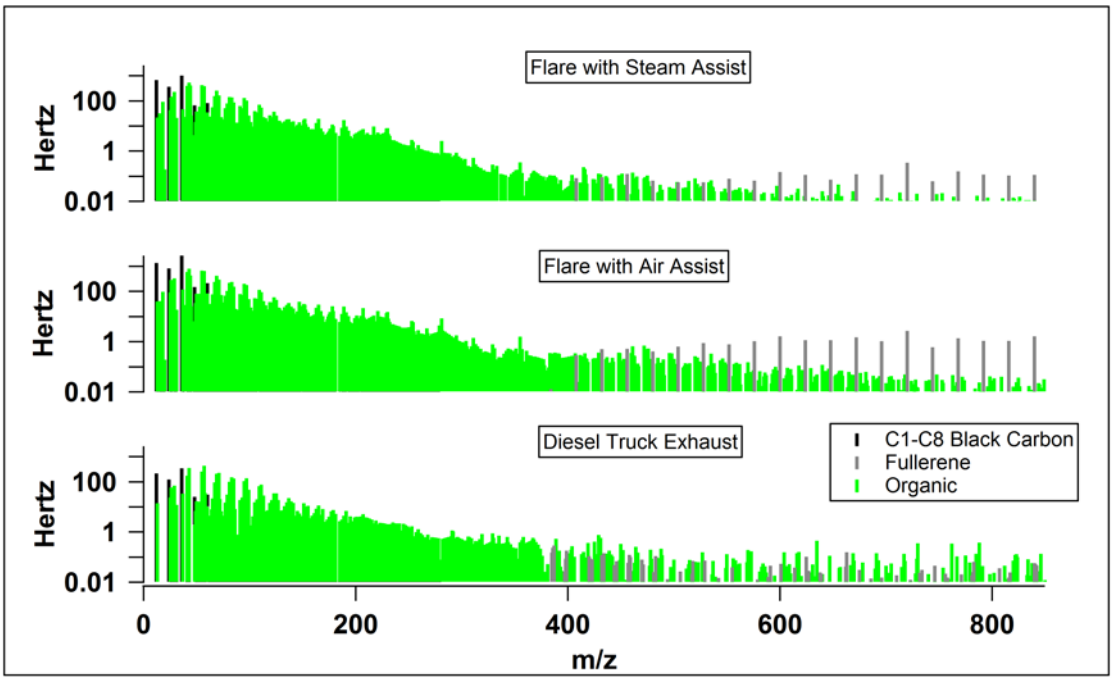

Figure 10. The mass spectra of C1-C8 black carbon, fullerenes, and organics is depicted for air and steam assisted propylene/TNG mix flares at high DRE along with a mass spectrum of diesel truck exhaust[17] examining the same chemical species.

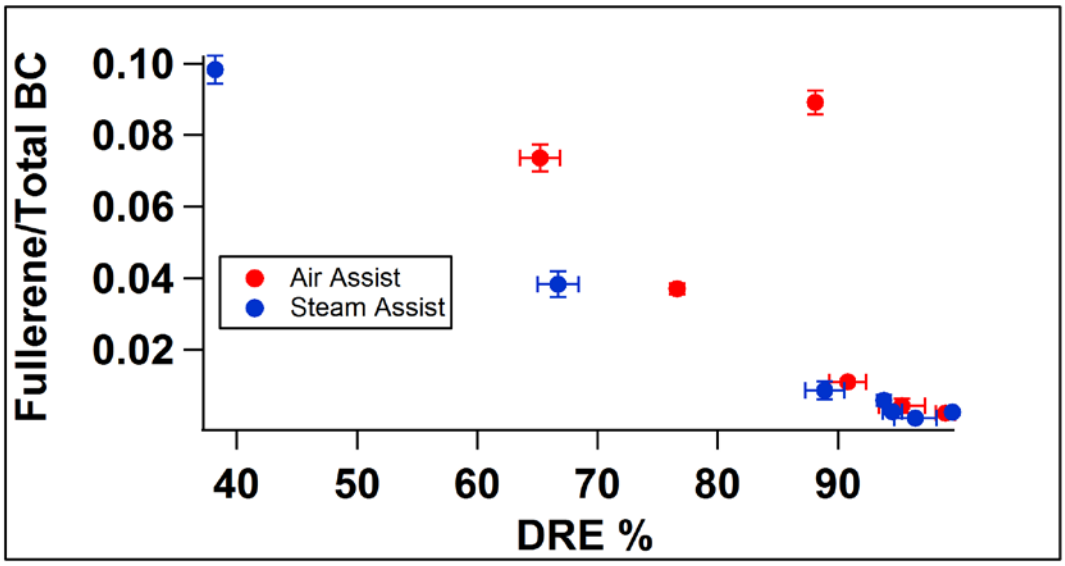

Figure 11. The ratio of fullerene to total black carbon signal as a function of DRE is depicted. Certain assist settings had multiple test points resulting in slightly different DREs and fullerene/total BC ratios are depicted with the error bars at 2*standard deviation of slope.

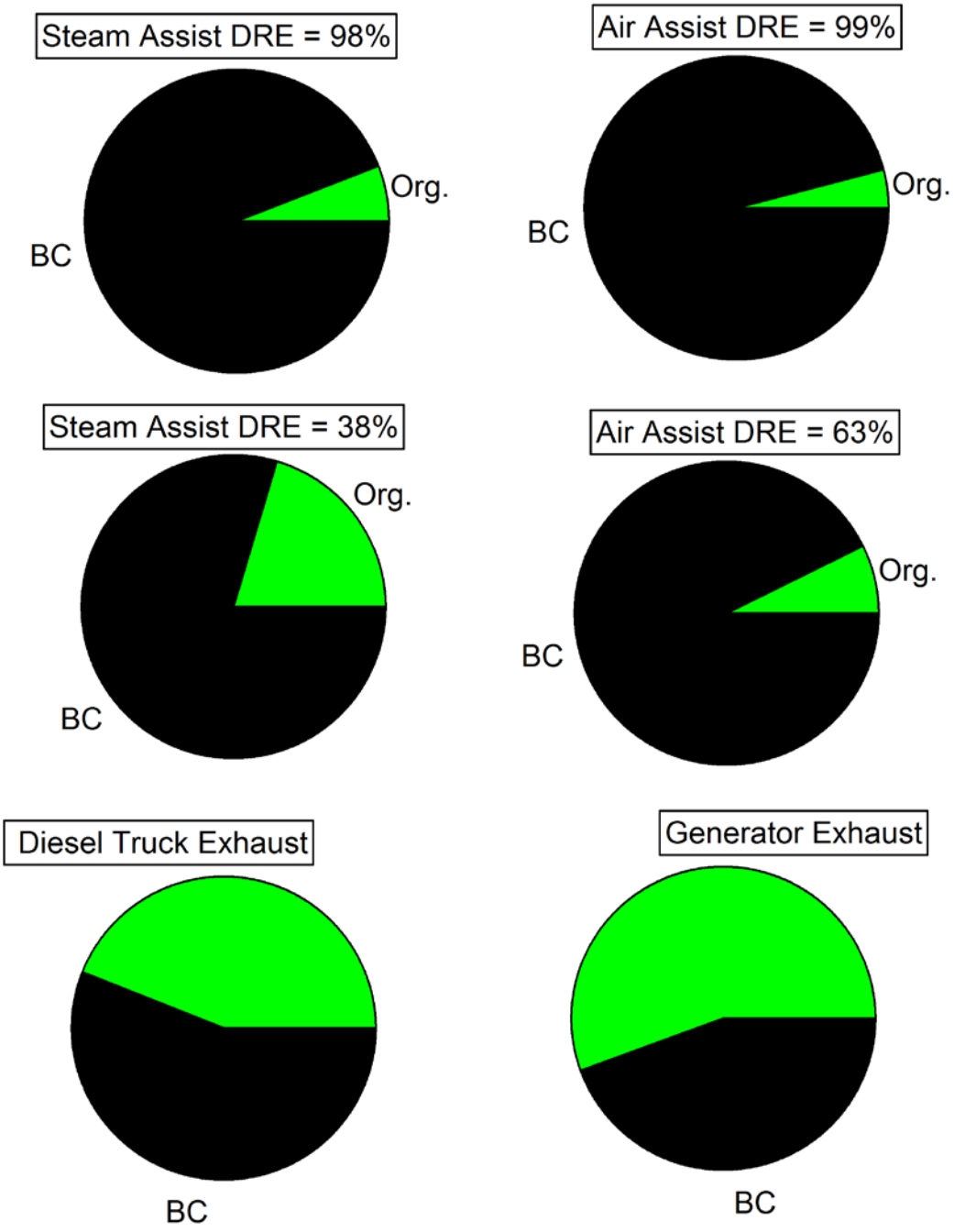

Figure 12. The ratio of organic to black carbon mass concentration (μg/m^3) for high and low DRE test points with the propylene/TNG vent gas mix utilizing steam and air assist, and diesel generator and diesel truck exhaust are shown.

DRE	Propene Steam Assist MAAP Test S5	Propene Steam Assist SPAMS Test S5	Propene Air Assist MAAP Test A3	Propene Air Assist SPAMS Test A3
99	11±.72	10±.72	3.0±.21	2.12±.23
98	.19±.1	.36±.086	4.0±.5	2.52±.24
97	NT[#]	NT	.65±.076	.5±.058
96	.3±.076	.26±.061	NT	NT
95	BDL[*]	.031±.017	NT	NT
94	.05±.0068	BDL	.58±.1	.43±.072
93	NT	NT	NT	NT
92	NT	NT	.47±.054	.36±.032
91	NT	NT	NT	NT

Table 1. The ratio of black carbon mass to CO_2 concentration ([lb/MMBtu]/ppmv) versus DRE is depicted for propylene mix air- and steam-assist flares as tested and the propane mix steam-assist flare as tested. The detection limit for SP-AMS measured BC was found to be 0.129 μg/m^3 with a signal-to-noise level of 2. Error bars are 2*standard deviation. All test points examined did have an observable CO_2 increase indicating that the plume was being sampled. [*] BDL (Below Detection Limit). [#] NT (Not Tested)