Field Measurement of Black Carbon Emissions from Gas flares near Poza Rica, Mexico using Second Generation sky-LOSA Technology

December 1st-2nd, 2011

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November 19, 2012

Report submitted to Petroleum Technology Alliance of Canada, Natural Resources Canada, and the World Bank Global Gas Flaring Reduction (GGFR) Partnership,

1. Executive Summary

Black carbon is a potent short-lived climate forcer whose net warming effect in the atmosphere is likely second only to that of CO_2. Global gas flaring is implicated as a potentially critical source of black carbon emissions, in large part due to the very significant volumes of gas flared annually (which exceed 140 billion m^3 according to satellite estimates). However, efforts to date to accurately assess, manage, and mitigate flare generated black carbon have been severely hampered by a dearth of quantitative emissions data for flares, an absence of reliable emission factor models, and a lack of quantitative, in-situ measurement techniques. As discussed in this report, this has the potential to change with the emergence of the sky-LOSA technique for directly quantifying black carbon emission rates in flares under field conditions. The method is based on Line-Of-Sight Attenuation (LOSA) of sky-light which, in combination with image correlation velocimetry and Rayleigh-Debye-Gans theory for Fractal Aggregates (RDG-FA), enables accurate quantification of black carbon mass emission rates in atmospheric plumes of flares.

The primary objectives of the work described in this report were to conduct field measurements of black carbon emission rates at available field sites in Mexico both as a means to collecting some of the first-ever in-situ measurements of black carbon emission rates from flares and also as an opportunity to refine the sky-LOSA technology and test improved hardware and algorithms for the first time. Measurements were ultimately performed at two flare sites in Mexico on December 1st and 2nd, 2011. On December 1st, 2011, sky-LOSA frames were acquired in Punta de Piedra for one of two adjacent 10 m high flare stacks. 14,441 frames were acquired, equivalent to 184 sec of continuous acquisitions split into 7 frame series recorded over a time span of 30 minutes. Images were difficult to analyse because of the presence of trees in the background and because of unstable flare operation. However, soot emission rates were successfully calculated, and the measured flare was found to emit black carbon at an average rate of 0.029 g/s, with instantaneous emission rates (95%-probability interval) ranging from 0.000 g/s - 0.181 g/s, and with soot emission peaks reaching 0.55 g/s. The most striking observation was the wide variability in emission rates of this flare during normal operation in relatively consistent wind conditions.

On December 2^{nd}, 2011, 36,260 sky-LOSA frames were acquired for a 20 m-high flare at a turbocompressor in Poza Rica. An equivalent to 717 sec of continuous measurements were acquired in 13 frame series collected over a 1 h 30 min time span. Although the flare was producing soot emissions that were only barely visible to the human eye, they were readily quantified with the sky-LOSA system. In contrast to the flare measured on December 1, the emission rates were quite stable with an average value of 0.053 g/s and a 95%-probability interval of 0.014 g/s - 0.105 g/s. A detailed uncertainty analysis was performed, and the mean emission rate of 0.053 g/s was quantified with an overall uncertainty of -15.9% to +20.1% that was mostly attributable to uncertainties in soot optical properties.

Because data were not available on the compositions or flow rates of gas being directed to the flares, it was not possible to calculate fuel-mass- or fuel-energy-specific black carbon emission rates. However, a preliminary analysis was performed to assess the context of the field measurement results and make comparisons with ongoing lab-based work aimed at flare-generated black carbon emissions factor development. Results of this comparison suggest that for an assumed flare gas exit velocity in the range of 4 m/s, the 0.053 g/s soot emission rate measured by sky-LOSA on December 2^{nd} was consistent with lab-scale flare emissions measurements for light fuel mixes representative of methane-rich natural gas. This is a very encouraging result for the prospect of future efforts to combine results of in-situ field measurements using sky-LOSA with controlled lab-scale experiments to significantly improve current emission factor approaches for estimating flare generated black carbon emissions. Moreover, the success in applying sky-LOSA to a very lightly sooting flare, and the high degree of accuracy achieved during measurements, demonstrate the potential of this new technology in supporting future mitigation efforts where quantitative measurements of black carbon emissions reductions are required.

Contents

2. Introduction

Particulate matter (PM) emissions into the atmosphere are a well-recognized health concern and exposure to PM is linked directly to adverse human health effects and mortality (US EPA, 2010). PM in the form of soot generated from combustion of fossil-fuels contains mostly black carbon, which is widely recognized as a critical source of anthropogenic climate forcing (e.g. (US EPA, 2012; IPCC, 2007). The net effects of atmospheric black carbon emissions from fossil-fuel soot and solid-biofuel soot are thought to be the second most important cause of global warming after CO_2 (Jacobson, 2010). However, because black carbon has a very short lifetime in the atmosphere (typically weeks), efforts to reduce black carbon emissions have the potential for significant near-term impacts in reducing climate forcing.

Since the lifetime of black carbon is much shorter than the characteristic mixing time of the atmosphere (1-2 years), the effects of black carbon depend heavily on where and when it is emitted (US EPA, 2012). This unfortunately confounds simple impact measures such as the commonly applied global warming potential (GWP) used to compare relative effects of different greenhouse gases in the atmosphere to those of CO_2. Nevertheless, illustrative GWP values for black carbon range from 330 to 2240 on a 100-year time horizon to up to 4900 on a 20-year horizon (US EPA, 2012).

Global gas flaring has been specifically identified as a critical source of black carbon emissions for which uncertainties are high and measured data are lacking (Arctic Council, 2011; US EPA, 2012). Concern over flare emissions is directly related to the very large volumes of gas flared globally. Primarily using industry reported data aggregated by individual countries, the United States Energy Information Administration estimated that approximately 122 billion m^3 of gas were flared or vented in 2010 (U.S. Energy Information Administration, 2012). Separate estimates derived from visible light satellite imagery suggest that for 2011, global flare volumes alone were on the order of 140 billion m^3 (NOAA, 2012).

Efforts to accurately quantify, regulate, and mitigate particulate matter emissions from flaring have been hampered by a lack of in-situ measurement techniques. Furthermore, very limited emissions data are available for flares under controlled conditions and existing emission factor data used by many regulatory agencies to inventory flare generated particulate matter are of questionable applicability (McEwen and Johnson, 2012). Lab-scale experimental work is ongoing to improve the knowledge of flare soot emissions with the promise of developing a broader experimental basis for development of new emission factor models (e.g. McEwen and Johnson, 2012). However, the various constraints on these experiments necessitate complementary measurements under field conditions, both as a means for model validation and as a tool to quantify soot emission in conditions not possible to generate in a laboratory setting.

In this context, there is a critical need for quantitative field measurements of soot emissions from flares *in situ*. However, few methods are available for experimental investigation of particulate matter in plumes in real operating contexts. Presently, the principal regulatory requirement in the US for particulate emissions in plumes is the opacity standard known as EPA Method 9 (U.S. E.P.A, 2010), which is based on human observation or digital imaging (DOCS) (McFarland et al., 2007). A critical limitation of simple opacity measurements is that they relate only to the aesthetic nature of the plume and are not sufficient to quantify emission rates. Furthermore, flares are even more complex compared to fixed stacks for which Method 9 was designed, primarily because of their inherent variability both in design and operating conditions.

Recently, a new technique for quantitatively measuring soot emission rates in flare plumes under field conditions has been demonstrated (Johnson et al., 2011; Johnson et al., 2010), which has potential to significantly improve understanding of flare generated black carbon emissions. Known as sky-LOSA (where LOSA is an acronym for Line-Of-Sight Attenuation), this optical technique measures plume velocity and monochromatic transmissivity of sky-light through the plume, which can be quantitatively related to mass emission rate of soot via Rayleigh-Debye-Gans theory for fractal agglomerates. Since the underlying physics of the measurement technique involve relating the light absorption by the plume to soot concentration independent of light scattering, the result is essentially a direct measure of black-carbon emission rate.

The sky-LOSA concept was first demonstrated in a field application in a measurement of a large (1.05 m diameter), visibly sooting flare in Uzbekistan (Johnson et al., 2011). Soot emission rates of 2.0 g/s were measured with a calculated uncertainty of ±33%. This rate was approximately equivalent to that of 500 diesel fueled city buses running continuously. This was the first known direct measurement of soot emission rates from an industrial flare under field conditions.

The soot emission measurements by sky-LOSA in Uzbekistan, while a landmark proof-of-concept success in the development of a new quantitative measurement technique, also revealed several challenges to be addressed in future measurements as well as opportunities to improve the technique in general. These included:

- *Image Quality*: The signal intensities captured by the detector used for the LOSA aspect of the diagnostic were low and the images exhibited poor spatial homogeneity due to low shutter speed, leading to 20% uncertainty on reference sky evaluation alone;
- *Velocity Measurement Synchronization*: Because available technology required measurements using two separate cameras, it was also necessary to compute emission rates using separately determined average velocity and concentration fields rather than integrating synchronized instantaneous data directly;
- *Sample Size*: Sky-LOSA was only applied to a single flare in Uzbekistan over a 5-minute sampling interval and there is a clear need to obtain soot emissions data from various types of flares to better understand the range of black carbon emissions from real-world flares; and
- *Fuel Specific Emission Rate Data*: No data were obtainable for the composition or flow rate of gas directed to the flare in Uzbekistan, so that specific emission rate data (i.e. mass of black carbon per mass or volume of fuel) could not be determined.

Working with the World Bank Global Gas Flaring Reduction (GGFR) partnership, Natural Resources Canada, and the Petroleum Technology Alliance of Canada (PTAC) / Canadian Association of Petroleum Producers (CAPP), and in cooperation with Petróleos Mexicanos (Pemex), these considerations motivated a second sky-LOSA measurement campaign that took place in December 2011 in the region of Poza Rica, Mexico. Many aspects of the experimental set-up, acquisition procedure, and analysis method were improved upon, in particular with the use of second-generation analysis algorithms and new hardware that allowed simultaneous evaluation of LOSA and velocity. Sky-LOSA measurements were successfully performed on flares at two production facilities. This report summarizes the results of these measurements, progress made in improving the sky-LOSA technology, context of the measured emission rates and preliminary comparisons with results of ongoing lab-scale research aimed at developing improved emission factor models, as well as suggested next steps.

3. Principle of Sky-LOSA

Sky-LOSA is based on the analysis of the extinction propensity of soot aggregates populating the tested plume. The transmissivity of the plume τ is evaluated using sky-light as reference light source with acquisitions at a single wavelength (532 nm for the present measurements). τ is evaluated as the ratio of the plume image to a reference clear-sky frame obtained via image processing. Plume images are also used to evaluate the local velocity field in the plume via image correlation velocity. Atmospheric conditions must also be considered (e.g. sun irradiance level, sky-irradiance spatial distribution), since external light sources lead to scattering by the soot aggregates in addition to the extinction of sky radiance coming from behind the plume. Although this is a complex process, the detailed mathematics of the sky-LOSA measurement algorithms make this possible with a high degree of accuracy (Johnson et al., 2012). Using Rayleigh-Debye-Gans theory for Fractal Aggregates (RDG-FA), transmissivity and velocity are combined to provide instantaneous, local soot fluxes within each measured image frame. Total soot emissions rates are then obtained via integration along a control surface through which the plume propagates. Monte-Carlo uncertainty analysis is used to precisely calculate measurement accuracy considering a range of soot morphology and optical property data. Full details of the governing theory for the sky-LOSA method and associated underlying equations are provided in (Johnson et al., 2010; Johnson et al., 2011; Johnson et al., 2012).

4. Details of Field Measurements & Experimental Protocol

Sky-LOSA measurements were performed at two different flare sites near Punta de Piedra and Poza Rica, Mexico on December 1 and 2, 2011. Details of the measurement apparatus used and data acquired are provided below. An overview of the data reduction and processing is given in Section 4.3 as necessary to calculate the results presented in Section 5.

4.1. Sky-LOSA set-up

As summarized in Table 1, significant improvements were made to the sky-LOSA hardware over the initial proof-of-concept system used previously for measurements in Uzbekistan (Johnson et al., 2011). A new, scientific Complementary Metal-Oxide-Semiconductor (sCMOS) camera (pco.edge) enabled acquisitions of high-quality images with 16 bit dynamic range and 1600×1080 pixel resolution at frame rates of 100 frames per second (fps) or with 2560×2160 pixel resolution at frame rates of 50 fps. This made it possible to use the same sets of images for both transmissivity and velocity calculations. Instantaneous velocity fields could then be used instead of the averaged velocity field in mass emission rate calculations, which is a significant improvement over the previous poof-of-concept system (Johnson et al., 2011). The sCMOS camera employed a global shutter, allowing simultaneous readout of all pixels with a common exposure gate of 1 ms for all pixels.

As shown in Figure 1, the camera was controlled by a ruggedized computer workstation with 24 Gb of RAM memory. The large memory capacity was required to handle the high data throughput of the sCMOS camera during high-speed image acquisition. Electricity was provided to the computer and the camera via a power inverter connected to a battery of a nearby vehicle.

The sCMOS camera was coupled with a 50-mm, f/1.2 Nikon lens (AF Nikkor) and a narrow band filter centered at 531 nm. The bandwidth of the filter was 40 nm and the transmissivity was greater than 95% within the bandwidth, allowing for a 10 fold increase in the light throughput relative to the 10 nm bandwidth, 50% transmission filter used in Uzbekistan. The increased filter efficiency and faster camera lens increased the signal level leading to a notable reduction in shot noise uncertainty.

A laser range finder provided an accurate measurement of the distance from the camera to the stack. The distance was used for spatial scaling of the plume images, required as part of the quantitative measurement of soot emission rates. The manufacturer of the range finder specified an uncertainty of ±0.1 m on the measured data. Distances measured in the field were obtained with a repeatability in the range of ±1 m, which equates to a satisfactory uncertainty of better than ±2% for measured distances (48 m and 67 m). This is a significant improvement compared to the ±5% uncertainty of the scaling achieved in the only previous demonstration of sky-LOSA (Johnson et al., 2011).

a) b)

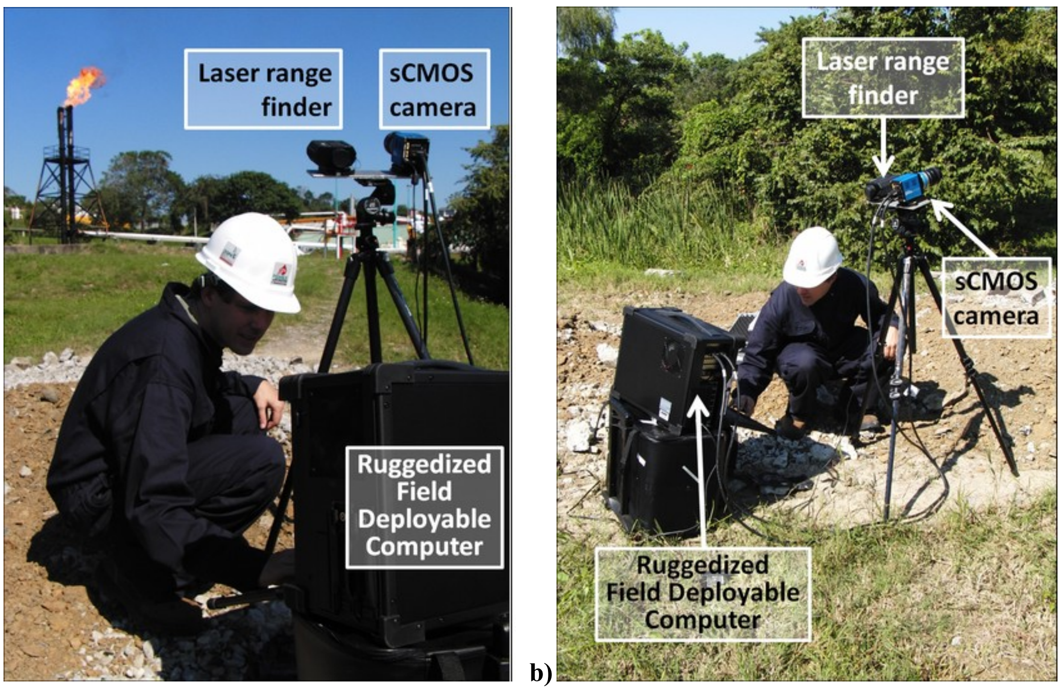


Figure 1. Sky-LOSA experimental set-up (pictures taken on December 2, 2012 at the turbocompressor station Poza Rica II)

Table 1. Characteristics of the sky-LOSA set-ups. Comparison between the set-up used in Uzbekistan in July 2008 and the present set-up used in Mexico in December 2011.

		Uzbekistan, 2008	Mexico, 2011
Transmissivity	Camera	Princeton Instruments PIXIS 1024	pco.edge
	Lens	Nikon 105 mm/2.8	Nikon 50 mm/1.4
	Filter	532 nm ±5 nm	531 nm ±20 nm
	Sky signal	1,500 to 2,500 counts	15,000 to 45,000 counts
Velocity	Camera	Casio	pco.edge
	Exposure	~3 ms	1 ms
	Frame rate	300 fps	up to 100 fps
	Resolution	512 × 384 pixels	1600 × 1080 pixels to 2560 × 2160
Spatial Scaling		From stack image	Laser range finder

4.2. Field Measurement Details

Figure 2 locates the measurement sites on a map of the Vera Cruz region of Mexico. Field data were acquired at two sites on December 1st and 2nd, 2011 by Prof. Matthew Johnson (Carleton University, Ottawa, CAN) and Dr. Robin Devillers (National Research Council, Ottawa, CAN). On December 1st, data were acquired for two flares at a pipeline terminal in Punta de Piedra, approximately 50 km away from Poza Rica. On December 2nd, measurements were performed on a flare at a turbo-compressor station near Poza Rica. Details of the measurement locations are provided in Table 2.

Table 2. Site locations for sky-LOSA measurements performed near Poza Rica on December, 2011.

	Punta de Piedra	Poza Rica II
Location	N 20°48'26.2", W 97°13'58.0"	N 20°29'32.8", W 97°24'19.2"
Altitude	5 m	150 m
Sky	Clear sky	Clear sky
Weather data	Tuxpan and Cazones de Herrera	Poza Rica
Temperature	25°C	23°C
Wind	East, 10 km/h	North West, 11 km/h

a) b)

Figure 2. Map of Mexico displaying the sky-LOSA measurement locations. a) General map of Mexico for the region of Vera Cruz and the Gulf of Mexico. b) Close-up map around the Poza Rica area. The red pins indicate the locations of the 2 measurement sites. Punta de Piedra was visited on Dec. 1st, 2011, and Poza Rica II on Dec. 2nd, 2011. The green pins on map b) indicate the locations on weather stations whose data were used for measurements in Punta de Piedra.

4.2.1. December 1st, 2011 – Punta de Piedra

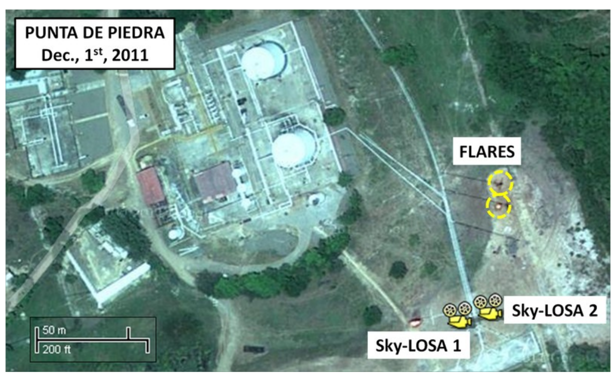


Figure 3 Satellite view of the sky-LOSA measurement site in Punta de Piedra (from Google Maps). The location of the measured flares are shown with yellow circles. The locations of the sky-LOSA set-ups are labeled Sky-LOSA 1 and Sky-LOSA 2, corresponding to the distances to the flares presented in Table 3.

As shown in Figure 3 and Figure 4, two flares were running in Punta de Piedra. The stacks were approximately 10 m high with an outer diameter of 0.21 m (evaluated by spatial scaling of the images). As detailed in Table 3, the sky-LOSA set-up was installed at two locations (67 m away from the stack, as measured with the laser range finder). Plume images were acquired at 100 and 66.7 fps for each location with the sCMOS camera. Images were acquired over a period of

1h10min (from 3:03pm to 4:13pm). In addition, fifty digital pictures of the flares and the experimental set-up were taken as well as various 60 fps .AVI movie clips of the operating flares.

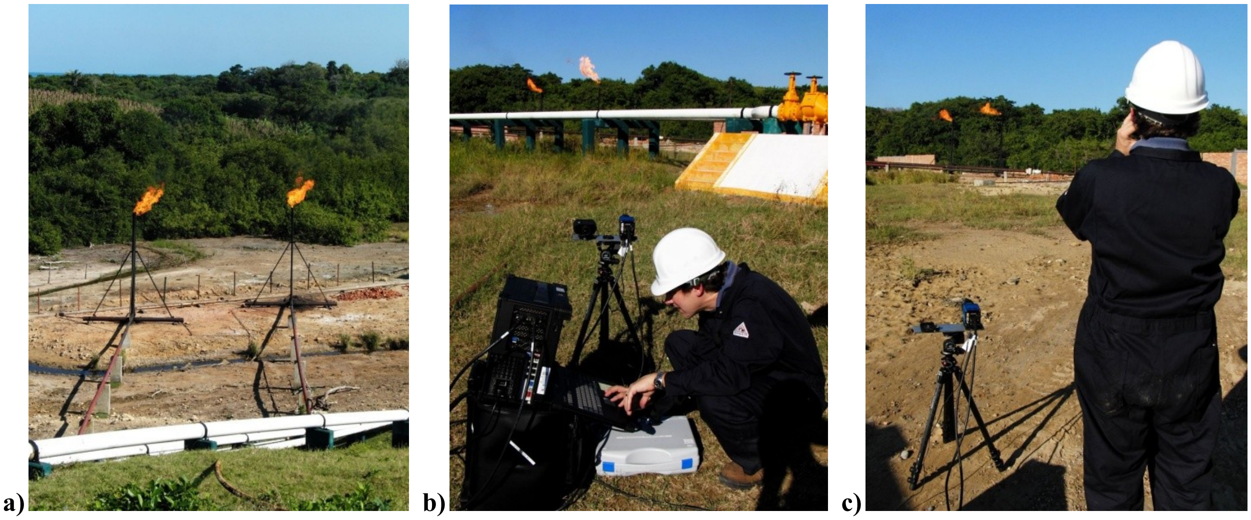


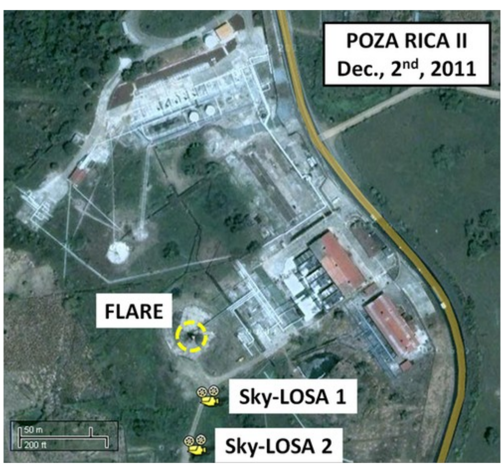
Figure 4. a) Pictures of the operating flares in Punta de Piedra. b) and c) Pictures of the sky-LOSA set-up for measurement positions 1 and 2 presented in Table 3.

Table 3. List of Sky-LOSA acquisitions made in Punta de Piedra on December 1st, 2012. The camera inclination to horizontal is labeled "camera INCL" and the camera azimuth angle is labeled "camera AZ".

Test location	Time	Distance to stack [m]	camera INCL	camera AZ	fps	Frame size [pix × pix]	Frame number	Duration [sec]
1	3:16pm				100.0	1600 × 1080		
	3:30pm				67.7	1600 × 1600		
2	3:45pm	67	7.4°	26°	67.7	1600 × 1600	2063	30.47
	3:47pm	67	7.4°	26°	67.7	1600 × 1600	2063	30.47
	3:50pm	67	7.4°	26°	67.7	1600 × 1600	2063	30.47
	3:56pm	67	7.4°	26°	67.7	1600 × 1600	2063	30.47
	4:04pm	67	7.4°	26°	100.0	1920 × 1080	2063	20.6
	4:07pm	67	7.4°	26°	100.0	1920 × 1080	2063	20.6
	4:13pm	67	7.4°	26°	100.0	1920 × 1080	2063	20.6
TOTAL							*14441*	*184*

4.2.2. *December 2nd, 2011 –Poza Rica*

At the Poza Rica II turbo-compressor facility, two flares with attached stacks were operating in immediate proximity as shown in Figure 5 and Figure 6. The stacks were approximately 20 m high and the flares were reportedly running at purge conditions. However, one of the flares was visibly operating at a much lower flow rate than the other and it was possible to position the camera to focus on the larger flare with minimal interference of the smaller flare. As detailed in Table 4, the sky-LOSA set-up was installed at two different locations (46 m and 68 m away from the stack, as measured with laser range finder). Flare images were acquired at 100 and 50 fps for each location with the sCMOS camera over a period of 1h40min (from 10:47am to 12:26pm). Clear-sky pictures (e.g. without plume in the frame) were also acquired in order to quantify the error on the interpolation process. In addition, fifty-four digital photographs of the stack and the experimental set-up were taken as well as various 60 fps .AVI movies of the operating flare.

a) 

b) 

Figure 5. Poza Rica site where sky-LOSA data were acquired on December 2, 2011. a) Satellite view of the turbocompressor station in Poza Rica (Google Maps). The flares are shown with yellow circles. The location of the two sky-LOSA measurement positions are labeled Sky-LOSA 1 and Sky-LOSA 2. b) Picture of the operating flares.

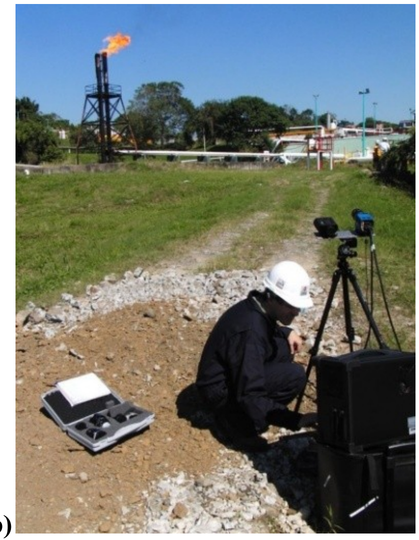

a)

b)

Figure 6. Pictures of the sky-LOSA set-ups for the two measurement locations used in Poza Rica II on December 2, 2011. a) 46 m away from the stack. b) 68 m away from the stack.

Table 4 Record of sky-LOSA frame series acquired in Poza Rica II on December 2nd, 2012. The camera inclination to horizontal is labeled "camera INCL" and the camera azimuth angle is labeled "camera AZ".

Test series	time	Distance to stack [m]	camera INCL	camera AZ	f#	fps	Frame size [pix × pix]	Frame number	Duration [sec]
1	10:47	46	24°	357.8°	4	50.3	2560 × 2160	1720	33.4
	10:55	46	22.9°	354.9°	4	50.3	2560 × 2160	1720	33.4
	10:59	46	23.7°	355.8°	2.8	50.3	2560 × 2160	1720	33.4
	11:05	46	23.7°	355.8°	2.8	50.3	2560 × 2160	1720	33.4
	11:17	46			2.8	50.3	2560 × 2160	1720	33.4
2	11:40	68	16.1°	13.2°	2.8	100.0	1920 × 1080	4500	90.0
	11:48	68	16.1°	13.3°	2.8	50.0	1920 × 1080	4500	90.0
	11:52	68			2.8	50.0	1920 × 1080	4500	90.0
	12:00	68	15.6°	8.3°	2.8	50.0	1920 × 1080	4500	90.0
	12:06	68	15.6°	8.3°	2.8	50.0	1920 × 1080	4500	90.0
	12:14	68	19.4°	7.4°	2.8	50.0	2560 × 2160	1720	33.4
	12:21	68	19.4°	7.4°	2.8	50.0	2560 × 2160	1720	33.4
	12:26	68	19.4°	7.4°	2.8	50.0	2560 × 2160	1720	33.4
TOTAL								*36260*	*717.2*
	12:31	SKY	20.3°	16.5°	2.8	50.0	2560 × 2160	1720	33.4

4.3. Data processing

Data processing was completed according to the following steps. Full details of the mathematical algorithms used to calculate mass emission rates are provided in (Johnson et al., 2012).

1. ***Evaluation of a reference sky frame:***

   Knowledge of the sky irradiance over the full measured image frame is required as a reference to calculate extinction through the plume. For each frame series, intensity histograms were assembled for each pixel in the image to discriminate between clear-sky intensity and plume-attenuated intensity. The frame portions where clear-sky was not visible on a sufficient number of frames were removed from the reference frame and interpolated via a quadratic LOESS algorithm using the neighboring clear-sky portions as inputs.

2. ***Calculation of transmissivity frame***

   Spatially resolved transmissivity data were evaluated by calculating the ratio of the measured frame to the reference sky frame.

3. ***Image Correlation Velocity on the transmissivity frames***

   Plume imagery was used for Image Correlation Velocity to obtain instantaneous velocity field information for each acquired frame. Calculations were performed using LaVision software.

4. ***Soot emission evaluation***

   Transmissivity frames and velocity frames were combined to calculate local soot flux. The reported soot emission values were obtained by integrating the local instantaneous soot flux along a control surface defined 6 m away from the stack tip, as indicated by the red curve on Figure 7.

5. ***Detailed Uncertainty Analysis***

   A detailed Monte-Carlo analysis was performed to quantify measurement uncertainties arising from all aspects of the measurement procedure, including explicit consideration of a range of soot morphological and optical property data required for the emission rate calculations.

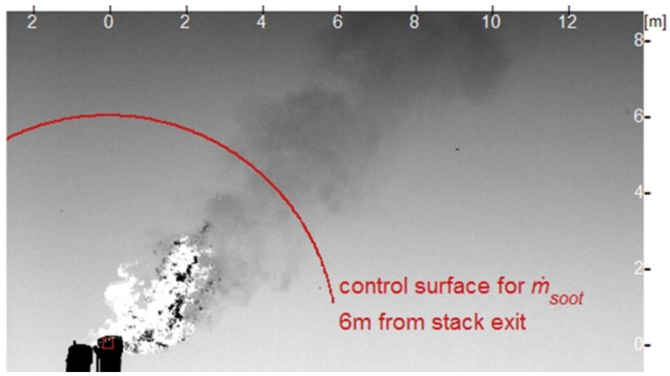


Figure 7. Sample plume image frame used for sky-LOSA showing the control surface (red arc corresponding to a 6 m distance away from the stack tip) used for total soot emission rate calculation. The net soot flux crossing the control surface was obtained via integration to provide time-resolved soot emission rate data.

5. Results

Quantitative measurements were acquired at both measurement sites and are reported below. However measurements acquired in Punta de Piedra on December 1st were complicated by the twin challenges of unstable flare operation and the location of the flare stack in a narrow valley surrounded by trees. The latter issue was partially overcome using a wider-angle lens and selective image processing, but the unstable nature of the flare complicates broader interpretation of the measured results. On the other hand, conditions were optimal for the measurements on December 2nd, and the acquired data were more than sufficient to enable a detailed uncertainty analysis as presented below. The results of these measurements at the Poza Rica site on December 2nd are discussed first.

5.1. Poza Rica II, December 2nd

Site access was ideal for measurements of the flare at the Poza Rica II turbo-compressor station and nine frame series were acquired and used for sky-LOSA processing. Sample plume frames are shown in Figure 8. Soot emissions from the flare were only just visible to the unaided human eye, but the enhanced contrast of the images in Figure 7 makes the plume readily apparent. Although the flare was operating quite stably and the wind conditions were calm, there was still noticeable variation in the instantaneous flame shape, position, and apparent emission rate.

a) Frame #200 (4.0 sec.) **b) Frame #1065 (21.3 sec.)** **c) Frame #1635 (32.7 sec.)**

Figure 8. Sample frames of sky-LOSA image series recorded at 50 fps in Poza Rica II at 10:59 on December 2nd, 2011. Greyscale: 11,000 – 19,000. The times specified in the caption indicate the elapsed time since the start image acquisition.

Instantaneous soot emission rate data for all of the image series are plotted in Figure 9a, which shows that total soot emission rate remained below 0.12 g/s over the 1h30 between the first and the last acquisitions. Variation in the instantaneous emission rate of the turbulent flame is apparent in the spread of the red dots on the figure. A corresponding histogram of these data is plotted in Figure 9b, which shows that these variations were approximately normally distributed, with mean black carbon emission rate 0.053 g/s within a 95% probability interval of 0.014 g/s - 0.105 g/s. The total measurement uncertainty on the mean emission rate of 0.053 g/s was determined to be -0.0085 to +0.0107 g/s (i.e. a 95% confidence interval in the mean emission rate of 0.045 to 0.064 g/s), as further discussed in Section 5.3.

Unfortunately no data were available on the composition or flow rate of gases being directed to the flare, nor was there the possibility of measuring these parameters in the field. Thus, fuel specific mass emission rates of black carbon (i.e. mass of black carbon per mass or per cubic meter of flare gas) could not be calculated. This remains a critical goal for future field measurements. Nevertheless, recognizing the novelty of the data obtained as only the second known measurement of in-situ soot emissions from a flare and the first with the current evolution of the sky-LOSA hardware and analysis routines, an effort was made to glean as much information as possible from these results through the comparison with ongoing lab-scale experiments, as discussed in Section 5.4. To provide some additional context, the mean emission rate of this lightly sooting flare was estimated to be equivalent to the soot emissions of approximately 13 diesel buses driving continuously (based on emission factors published by Keogh et al., 2010). These results stand in stark contrast to the emission rate of 2.0 g/s previously obtained for a large (1.05 m diameter) visibly sooting flare in Uzbekistan (Johnson et al., 2011), which was estimated to be equivalent to the emissions of approximately 500 diesel buses.

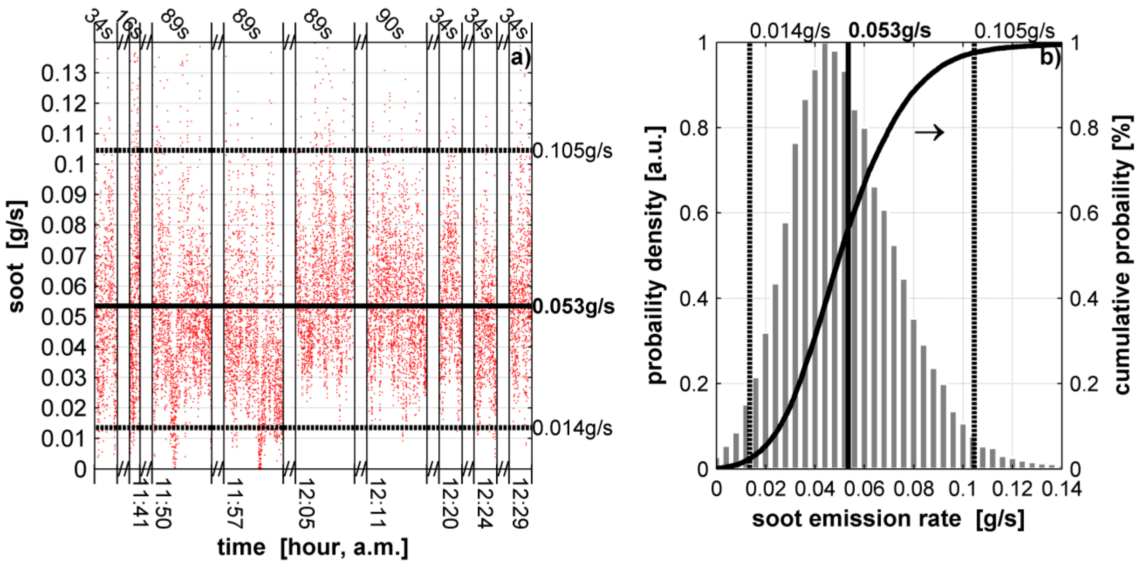


Figure 9. Soot emission rates measured in Poza Rica on December 2nd, 2011. a) Soot emission rates vs. time where each dot represents the instantaneous measured value for one single image frame. b) Soot emission histogram showing data from all acquired frames. The average soot emission rate is indicated by a thick, vertical black line (0.053 g/s). The extremes of the 95%-probability interval are shown with dotted lines (0.014 g/s - 0.105 g/s).

5.2. Punta de Piedra, December 1st

Sky-LOSA images taken on December 1st were more difficult to process and analyze. The two flares were smaller and located in a narrow valley surrounded by trees, which often blocked camera access to sky-light when the plume trajectory was horizontal. In addition, the operation of the flare appeared to be highly unstable which, although still measureable using sky-LOSA, complicates generalization of the results. Sample sky-LOSA image frames are shown in Figure 10. The flare at the center of the frame emitted a plume that was generally obscured by trees in the background and was not measured. While it would have been possible to make measurements on this flare from a different position and camera lens combination, site access and time restrictions meant that measurement effort was instead focussed on the flare seen in the right side of the image frame.

The flare to the right of the image frames shown in Figure 10 generated plumes with unstable trajectories, attributable both to turbulence and buffeting of the wind in the narrow valley, as well as apparent variability in the flow rate and/or composition of the gas/vapour being directed to the flare. When the trajectory of the plume fell below the tree line, it was not possible to make sky-LOSA measurements without access to a different measurement location. However, the plume trajectory was generally upward enabling sky-LOSA analysis on a large fraction of the acquired frames. While soot emission rate data were calculated for these cases, it is critical to note that the reported data are necessarily biased to conditions where the plume was sufficiently elevated, and the true average emission rate for this flare could be higher or lower. Perhaps the most useful observation to be made from the measured data for this flare is that the instantaneous variability in emission rate can be quite substantial as discussed below.

a) Frame #730 (10.8 sec.) **b) Frame #761 (11.2 sec.)** **c) Frame #808 (11.9 sec.)**

Figure 10. Sample plume image frames recorded at 67.7 fps in Punta de Piedra at 3:56pm on December 1st, 2011. Two separate plumes are shown from a flare at the center of the image and from a flare just to the right of the image. Greyscale: 30,000 – 45,000 counts. Values in brackets indicate elapsed time since the start of image acquisition.

Soot emission rates for the flare located to the right of the images shown in Figure 10 are plotted as a function of time in Figure 11a. The emission rate variations are much larger than those of the flare measured on December 2nd, with instantaneous emission rates often larger than 0.20 g/s and peaking as high as 0.55 g/s for several seconds (beyond the range displayed on the graph). This is indicative of the variability in wind conditions and the apparent variability in the flow rate and/or composition of gas/vapour being directed to the flare. Unfortunately no data were available on the composition or flow rates of the flare gas. An average black carbon emission rate of 0.029 g/s was calculated from the available data, however the representativeness of this value is uncertain given the high variability and the inability to make measurements for all plume positions. More interesting is the result plotted in the histogram shown in Figure 11b. The significant spread in instantaneous emission rates illustrates the wide variability that can be seen on a single flare. The 95%-probability interval in the instantaneous emission rate spans 0.000 g/s - 0.181 g/s, and the non-Gaussian distribution shape reveals a large tail toward high emission rate values.

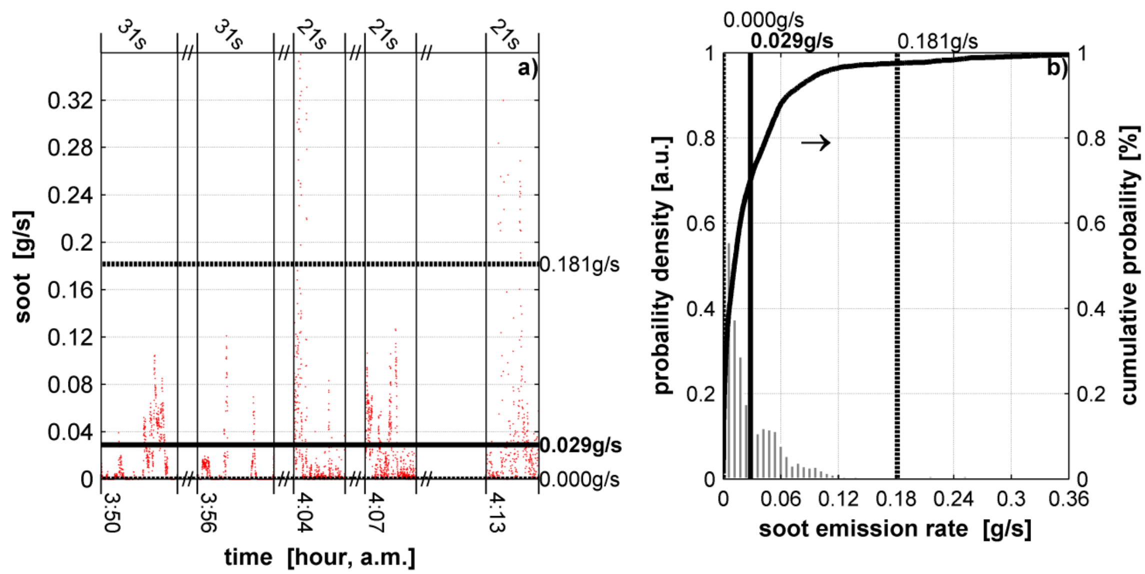


Figure 11. Soot emission rates measured in Punta de Piedra on December 1st, 2011 for flare to the right-hand side of Figure 10. a) Soot emission rates vs. time where each dot represents the instantaneous emission rate calculated for one single image frame. Soot emission rates were evaluated using a control surface 7 m away from the stack tip. b) Soot emission histogram showing the measured emission rate data from all frames. The averaged soot emission is shown by a thick black line (0.029 g/s). The extremes of the 95%-probability interval are shown with dotted line (0.000 g/s - 0.181 g/s).

5.3. Sky-LOSA uncertainty

Using the measurement data collected on December 1, 2011 for the flare at the turbo-compressor station in Poza Rica, a detailed uncertainty analysis was conducted. Calculations were enabled by Monte Carlo simulations taking into account all aspects of the measurement process, especially variability in soot morphological and optical properties as further detailed in (Johnson et al., 2012). The objectives of the uncertainty analysis were firstly to accurately quantify the

95% confidence intervals on the measured emission rate for the flare at the turbo-compressor station in Poza Rica, and secondly to quantify advancements made to the sky-LOSA system through a combination of hardware improvements and enhanced analysis routines. Table 5 summarizes the results of this analysis.

The overall uncertainty in the measured mean black carbon emission rate is very good at -15.9% to +20.1%. In absolute terms, considering the lower amounts of soot being measured, this represents a factor of 60 improvement over the uncertainties achieved in the first demonstration of sky-LOSA (Johnson et al., 2011) obtained using the previous hardware and algorithms (absolute uncertainty of ±0.011 g/s in present measurements vs. ±0.66 g/s previously). The dominant contributor to the overall uncertainty is uncertainty in morphological and optical properties of soot, which is common to any optically based technique for quantifying soot emissions. With the current improvements to the sky-LOSA technique, achievable accuracies are now similar or better than other advanced diagnostic techniques used in lab-based soot measurement, such as laser induced incandescence (Crosland et al., 2012; Crosland et al., 2011).

Table 5. Uncertainty in the sky-LOSA measurement of soot emission rate. Contributions of the various error sources.

Error type	Error sources	Contribution to uncertainty on $\dot{m}_{soot}$	Average soot emission value	Absolute Uncertainty
Soot properties	• Soot density • Optical properties	**-15.9 to +19.2%**		
Experimental uncertainty	• Velocity • Reference sky • Atmospheric conditions	**-7.4 to +8.4%**		
Image scaling		**±2.0%**		±2.0%
TOTAL UNCERTAINTY on soot emission rate		**-15.9 to +20.1%**	**0.053 g/s**	**-0.0085 to +0.0107 g/s**

5.4. Consistency with lab-scale soot emission factors

As noted previously, flare gas flow rate and composition data were not available for either measurement site, nor was there a prospect to measure these data in the field. These data are necessary to calculate fuel mass specific emission factors, and obtaining flare gas flow rate and composition data simultaneously with sky-LOSA measurements of black carbon emissions remains a central goal for any future field experiments. Nevertheless, given the lack of other field measurements in the literature and the lack of black carbon emission rate data for flares in general, an attempt was made to gain further insight through qualitative comparison with results of ongoing lab-scale research. In recent laboratory experiments at Carleton University (McEwen and Johnson, 2012), we have published a very preliminary model for soot emission from lab-scale flares burning various fuel gas mixtures representative of associated gas in the upstream petroleum industry. This model is reproduced in Figure 12, which correlates estimated mass emissions rate of soot per unit volume of fuel with fuel heating value.

Even though the flare gas exit velocities were not known in the present field measurements, it is possible to estimate them to within a reasonable range based on the general appearance of the flame and the quantified velocities in the plume. As shown in Figure 13a, it is then possible to plot an implied black carbon emission factor as a function of an assumed flare gas exit velocity, where the estimated range of emission factor values has been calculated based on the measured average soot emission rate of 0.053 g/s obtained for the lightly sooting flare at the Poza Rica turbo-compressor station measured on December 2, 2011. For an assumed flare gas exit velocity of 0.5 to 4.0 m/s, the implied soot emission factor ranges from ~0.1 to 1.0 kg soot / 1000m^3 fuel. Encouragingly, this estimated range corresponds to the approximate range of emission factors obtained from lab-scale experiments plotted in Figure 12. Although the flare gas composition (and hence the heating value) was also not available, it is possible to extend the comparison further by calculating a hypothetical "consistency curve" as plotted in Figure 13b. This consistency curve shows the specific range of heating value and flare gas exit velocity combinations for the Poza Rica flare that would be necessary for the field measurement results to exactly match the lab-based model. For a heating value of ~40-45 MJ/m^3 consistent with raw natural gas, a flare gas exit velocity of ~1 m/s is implied. Although this is only a qualitative comparison, the conditions required to match the field and lab-scale data seem plausible. This is an important result for the potential of future research efforts to link field measurement results obtained via sky-LOSA with controlled lab-scale experiments, where this combination will be essential to the development of robust black carbon emission factor models for flares.

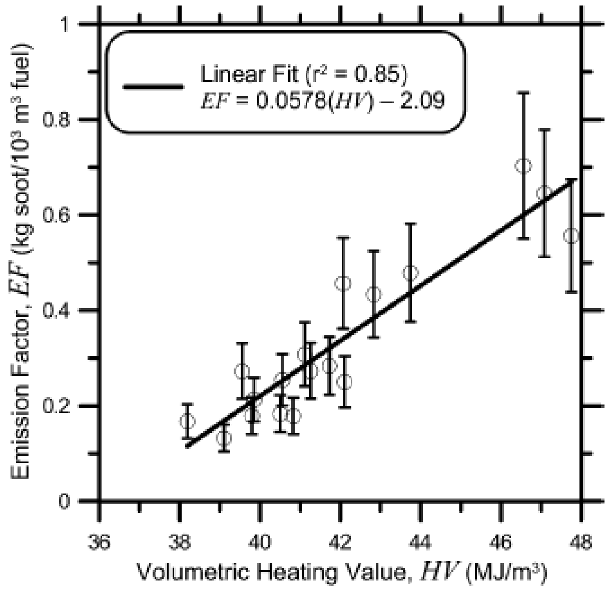


Figure 12. Published soot emission factor *EF* in [kg soot / 1000 m^3 fuel] as a function of the volumetric heating value *HV* obtained for a lab-scale flare (reproduced from McEwen and Johnson, 2012). Measurement results are plotted as circles with calculated uncertainties as indicated by the error bars. The linear fit model to the experimental data is detailed in the legend.

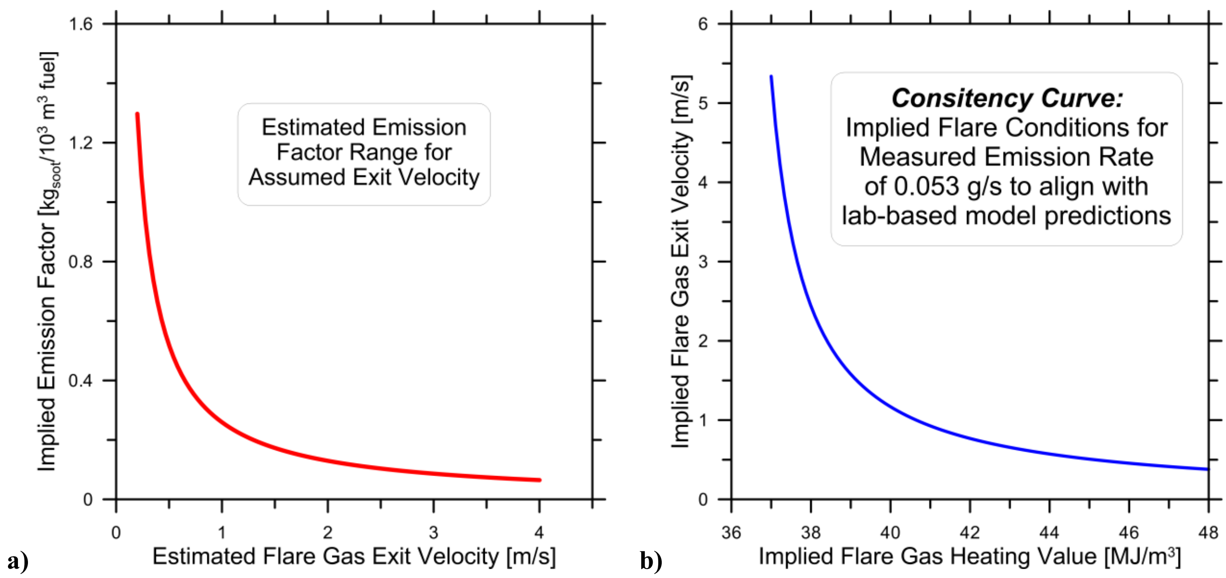


Figure 13. Emission factor analysis based on the average soot emission value of 0.053 g/s measured in Poza Rica on December 2, 2011. a) Implied soot emission factor values as a function of an assumed flare gas exit velocity given on the horizontal axis. b) Consistency curve showing the relation between flare gas exit velocity and heating value for the flare that would be required to match the field measurement result (0.053 g/s) to the lab-scale emission factor model presented in Figure 12.

6. Conclusion

Sky-LOSA was successfully used to make in-situ measurements of black carbon emission rates for two operating flares at Pemex facilities in the vicinity of Poza Rica, Mexico. To the authors' knowledge, this was only the second time that quantitative black carbon emission rates have been measured for an operating flare under field conditions and these were the first measurements to use 2nd generation sky-LOSA hardware and analysis algorithms. Quantitative uncertainty analysis revealed that the improved sky-LOSA system was able to measure emission rates with a total measurement uncertainty of -15.9% to +20.1%, a significant improvement from the ±33% uncertainty achieved previously.

Soot emission rates were quantified for a lightly sooting flare at a turbo-compressor station near Poza Rica, where the plume was only just visible to the human eye. An average black carbon emission rate of 0.053 g/s was determined, with a total measurement uncertainty of -0.0085 to +0.0107 g/s (95% confidence interval). Since flare gas flow rate and composition data were not available, it was not possible to calculate a black carbon emission rate per mass or per volume of flare gas. However, comparisons with lab-scale experimental data suggested that field measurement results were consistent with lab-scale results, which is very encouraging for the prospects of future research aimed at combining these approaches for the purpose of developing robust emission factor models. While the data collected at the second site did not enable exhaustive analysis because of non optimal sky-LOSA set-up conditions and unstable flare operating conditions, the measurements illustrated the large variability in instantaneous emission rates that can be seen for a single flare. Moreover, the wide spread of detected emission rates demonstrated the capacity of sky-LOSA to quantify instantaneous soot emission rate variations over two or more orders of magnitude.

The success of the present sky-LOSA measurement campaign represents a significant step in the development of the diagnostic and its emergence as a practical and accurate technique for in-situ quantification of black carbon emission rates from flares. This is a very promising development for the prospect of future flare emission investigations, and in particular for future improvement of soot emission factors via field measurements performed for known flare gas flow rates and compositions. Moreover, the success in applying sky-LOSA to a very lightly sooting flare, and the high degree of accuracy achieved during measurements, demonstrate the potential of this new technology for supporting future mitigation efforts where quantitative measurements of black carbon emissions reductions are required.

7. Acknowledgements

The collaborative contributions of Dr. Kevin Thomson, National Research Council, have been and continue to be essential to the ongoing development of the sky-LOSA technology. This project was supported by Natural Resources Canada (Project Manager, Michael Layer), the World Bank Global Gas Flaring Reduction (GGFR) Partnership (Project Manager, Francisco Sucre), and Petreoluem Technology Alliance of Canada (PTAC) / Canadian Association of Petroleum Producers (CAPP). We are especially grateful for the assistance of Petróleos Mexicanos (Pemex) staff during the field measurements, and for the collaborative support of Clearstone Engineering Ltd. (Mr. David Picard, principal).

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