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Sky-Scattered Solar Radiation Based Plume Transmissivity Measurement to Quantify Soot Emissions from Flares

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For gas flares typical of the upstream energy industry and similar point sources, most current methods for characterizing soot emissions are based on plume opacity rather than a quantitative measure of mass flux. The absence of more quantitative approaches is indicative of the inherent complexity of soot and the difficulties in characterizing emissions in an unbounded plume. A new experimental approach has been developed for the investigation of soot emissions in industrial plumes. Referred to as sky-LOSA, the diagnostic permits evaluation of 2D spatially resolved monochromatic sky-light transmissivity data over the width of a plume, where sky-light intensities behind the plume are obtained via an interpolation algorithm. By using Rayleigh–Debye–Gans Fractal Aggregate theory to relate transmissivity data to soot concentrations, and with knowledge of the velocity of the plume, it is possible to quantify mass flow rates of soot in a plume. Experiments on an unconfined lab-scale soot plume were used to support a detailed uncertainty analysis under a wide range of conditions and to estimate sensitivity limits of the technique. Results suggest field measurements of soot emission from flare plumes should be possible with overall uncertainties of less than 32%. This represents a significant advancement over existing techniques based on opacity measurements.

Introduction

Airborne particulate matter (PM) is a primary atmospheric pollutant that is linked to serious health effects in humans (1, 2) and environmental damage (3). PM is further implicated as an important component in climate forcing (4) with at least one prominent study suggesting this effect may be as great as 55% of the current global warming effect of carbon dioxide (5). Although PM is a regulated emission in most jurisdictions, for unconfined sources such as industrial flares there are critical gaps in our ability to obtain quantitative release data.

In the upstream energy industry, gas flares are commonly used to destroy unwanted flammable gas via combustion in

an open atmosphere flame. Recent satellite imagery data suggest that global gas flaring associated with petroleum production exceeds 135 billion m³ annually (6). Although flares produce PM in the form of carbonaceous soot, direct quantification of these emissions remains elusive. Extractive sampling approaches are prohibitively challenging since flare plumes are inhomogeneous—both the relative amounts of species and overall degree of dilution vary within the plume (7). Moreover, plumes are subject to atmospheric turbulence so that position and flow direction are generally unsteady. Optical measurement methods show the greatest promise for meeting these challenges, but to date little progress has been made in accurately measuring particulate emissions from flares.

In line with these difficulties, most regulatory standards for PM in plumes are based on a human-observed visual opacity standard, as outlined in U.S. Environmental Protection Agency Method 9 (8). For EPA Method 9, plume opacity is defined as the proportion of broadband sky-light that is blocked by a plume, as visually estimated by trained human observers. By nature, this technique is unavoidably subjective. Attempts have been made to improve Method 9 by replacing the human observer with a digital camera in methods referred to as Digital Opacity Compliance System (DOCS) (9, 10) and Digital Opacity Method (DOM) (11). In the DOCS/DOM approaches, opacity is determined from digital images by comparing the pixel intensity from regions containing unobstructed sky, to regions where the sky radiation is transmitted through the plume. Although DOCS/DOM provide automated, more objective, and precise implementations of EPA Method 9, broadband opacity is not directly relatable to PM emission rate.

Line-Of-Sight Attenuation (LOSA) is a well-established nonintrusive optical diagnostic often used for line-averaged measurement of soot concentration in lab-scaled flames (12, 13). Contrary to opacity measurements, LOSA measurements are performed with monochromatic light, enabling the use of light/particle interaction theory to extract quantitative particle concentration data. Recent work (14) has demonstrated the advantages of using a diffuse light source to perform spatially resolved LOSA measurements of soot concentration within flames. This paper explores extension of this approach to integrated soot concentration measurements in flare plumes under field conditions, using sky-scattered solar radiation as an extended source of diffuse light. This new method, referred to here as sky-LOSA, combines transmissivity measurements, optical theory, and plume velocity data to quantify the mass flux of soot in a plume. The technique is developed theoretically and tested in controlled lab-scale experiments. Results coupled with a detailed uncertainty analysis suggest sky-LOSA could be a significant improvement over visual opacity measurements for flares, permitting quantitative estimation of soot emission rates under field conditions.

Theory. The key premise of an attenuation measurement is that the amount of light attenuated by a constituent of a medium can be quantitatively related to the concentration of that constituent. For monochromatic light, attenuation is predicted by the Beer–Lambert–Bouguer law (eq 1) (15, 16). Equation 1 defines the local, wavelength-specific extinction coefficient of the medium, $K_{\lambda}^{(e)}$, which is exponentially related to transmissivity, τ_{λ} , the ratio of transmitted, and source light intensities, $I_{\lambda}/I_{\lambda 0}$.

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$$\tau_{\lambda} = \frac{I_{\lambda}}{I_{\lambda_0}} = \exp\left[-\int K_{\lambda}^{(e)} dx\right] \quad (1)$$

Depending on the selected wavelength and the composition of the medium, the extinction coefficient may be related to the integral of the local concentration of a species of interest along the optical path.

For plumes of flares, available data suggest that near-field composition will principally consist of gas-phase species (17–21) and comparatively small amounts of soot aggregates (17), all diluted with ambient air. For optical measurements made at visible wavelengths, constituents in the gas phase are transparent (16). Light attenuation is then only a function of concentration of soot and any other aerosol species, if present. Although flares burning large amounts of methane will produce significant water vapor in the combustion products, the existence of condensed phase water in flare plumes is not expected, and to the authors' knowledge has not been observed in available literature (e.g., 17–19). This is consistent with calculations of water vapor saturation pressure as a function of heat release, radiative heat transfer, and convective cooling and mixing with ambient air over a wide range of potential scenarios which show that near-field condensation will not occur (22). Depending on flare gas composition, some flares also emit gas-phase sulfur dioxide and oxides of nitrogen, which could potentially transform in the atmosphere to secondary particulate in the form of sulfate and nitrate aerosols (23). However, the mechanisms and time scales of the conversion pathways are such that these secondary aerosols should not be a concern for measurements made in a plume immediately downstream of a flame (22). Thus, for near-field measurements in flare plumes, visible light optical attenuation measurements should be sensitive to the presence of soot only.

Flame-generated soot consists of nearly spherical, carbonaceous primary particles, joined together in branched, open-structured aggregates. Despite this complex geometry, it is now well-established (24–27) that the interaction of light with soot aggregates is well described by Rayleigh–Debye–Gans Fractal Aggregate theory (RDG-FA). This theory permits prediction of the amount of light scattered by soot aggregates and reveals the key detail that light absorption is proportional to the volume of soot present along the optical path. From RDG-FA theory, soot concentration relates to extinction coefficient via eq 2

$$f_v = \frac{K_{\lambda}^{(e)} \lambda}{6\pi(1 + \rho_{sa})E(m)_{\lambda}} \quad (2)$$

where $E(m)_{\lambda}$ is the soot absorption refractive index function and ρ_{sa} is the ratio of the total scattering coefficient $K_{\lambda}^{(s)}$ to the absorption coefficient $K_{\lambda}^{(a)}$. Both $E(m)_{\lambda}$ and ρ_{sa} are wavelength-dependent optical properties of soot aggregates, which have been studied by a variety of researchers (28–33).

An important consideration for a field measurement is the potential for light from adjacent sky-regions to be scattered by the plume in the direction of the camera. This “in-scattering” would partially balance the “out-scattering” of light from behind the plume and reduce the effective magnitude of ρ_{sa} . By modeling the sky impacting an elevated plume as a hemispherical source, it is possible to calculate an effective scattering to absorption ratio, ρ_{sa}^* , directly, using RDG-FA theory. Considering a very wide range of potential soot morphologies (i.e., primary particle diameters, d_p , from 20 to 50 nm; mean particles per aggregate, N_g , from 10 to 300; aggregate distribution widths, σ_g , of 2 to 3.5; and measurement wavelengths of 400–700 nm), results of a Monte Carlo analysis show that in the field, a significant fraction (80–85%) of the out-scattered skylight is compensated for by in-scattered

skylight. Thus while ρ_{sa} has a magnitude of 0.24 (refer to Table 1) in the controlled experiments presented below where the diffuse light source is effectively planar, calculations show ρ_{sa}^* would be <0.07 for all cases in the field. In-scattering is therefore quite beneficial for a field measurement, since it reduces the magnitude of the scatter correction in the analysis and thus reduces the associated uncertainty and dependence on knowledge of optical properties when calculating transmissivity and mass flux.

Soot Emission by Sky-LOSA. In a typical implementation of a LOSA diagnostic, transmissivity is calculated from a sequence of four monochromatic light intensity measurements taken: with the light source on and the attenuating medium present (*transmission*), with the light source on and the attenuating medium removed (*source*), without both the light source and the attenuating medium (*dark*), and with the attenuating medium present but without the light source, e.g., the natural emission of the medium (*emission*). Two-dimensional measurements are achieved by measuring intensities with a CCD camera. The 2D spatially resolved transmissivity is then calculated using data from corresponding pixel locations in the images as

$$\tau_{\lambda} = \frac{\text{transmission} - \text{emission}}{\text{source} - \text{dark}} \quad (3)$$

In a sky-LOSA field application, it is not possible to acquire a *source* image by simply turning off the plume. Instead, a modified *source* image, *source**, is calculated from the *transmission* image by interpolating for sky intensity values within the plume region. Since plume temperatures would always be sufficiently low that direct radiative emission in the visible would be negligible, the *emission* and *dark* images would be equivalent. Thus, the sky-LOSA method only requires the acquisition of two images: the *dark* image, acquired with the lens blocked to account for detector dark-current, and the *transmission* image.

$$\tau_{\lambda} = \frac{\text{transmission} - \text{dark}}{\text{source}^* - \text{dark}} \quad (4)$$

Coordinate axes for a sky-LOSA measurement can be defined where z is the direction of plume propagation, x is the direction of the optical axis (perpendicular to the plane of the acquired images), and y is the remaining orthogonal coordinate that defines the “width” of the plume. Invoking RDG-FA theory, eqs 1, 2, and 4 can be combined to calculate the integral of the local soot concentration along the optical path, according to eq 5. For simplicity of notation it is understood but not written that variables are also functions of z , and measurements could be performed at different locations along the plume axis.

$$\int f_v(x, y) dx = \frac{-\lambda \ln \tau_{\lambda}(y)}{6\pi(1 + \rho_{sa})E(m)_{\lambda}} \quad (5)$$

If the plume velocity can be assumed uniform along the measurement chord, eq 5 can be integrated over the plume width to calculate the mass flux of soot through the plume

$$\dot{m}_{soot} = \rho_{soot} \iint u(y) f_v dx dy = \frac{\rho_{soot} \lambda}{6\pi(1 + \rho_{sa})E(m)_{\lambda}} \times \int u(y) (-\ln[\tau(y)]) dy \quad (6)$$

where ρ_{soot} is the soot density and $u(y)$ is the plume velocity.

In a field setting, plume velocity can be determined in a number of ways including mast mounted anemometers (e.g., 34), SODAR (e.g., 35), and LIDAR (e.g., 36). However, for visible plumes, it is likely simplest and most accurate to directly measure the motion of the plume from fast frame-rate movie

TABLE 1. Uncertainty of the Various Parameters for the Evaluation of the Soot Emission Rate with Sky-LOSA

	variable	value (uncertainty)			contribution to uncertainty of $\dot{m}_{soot}$		
soot properties	ρ_{soot} (29, 42–44)	1.89 g/mL (0.07 g/mL)			3.7%		
	ρ_{sa} (28)	0.24 (0.055)			4.4%		
	$E(m)$ (28–33)	0.334 (0.043)			12.9%		
measurement wavelength	λ	577 nm (1.0 nm)			0.2%		
interpolation width (spatial calibration)	w	21.5 mm (0.166 mm) ^a			0.8%		
plume velocity	u case #1	4.0 m/s (0.19 m/s)			4.8%		
	u case #2	5.6 m/s (0.19 m/s)			3.4%		
	u case #3	7.3 m/s (0.19 m/s)			2.6%		
	u case #4	11.9 m/s (0.19 m/s)			1.6%		
	u case #5	13.6 m/s (0.19 m/s)			1.4%		
	u case #6	16.7 m/s (0.19 m/s)			1.1%		
$\kappa \times 10^3$ as measured by Sky-LOSA		clear	overcast	cloudy	clear	overcast	cloudy
	κ case #1	9.0 (0.62)	10.9 (0.65)	10.4 (2.3)	6.9%	6.0%	22.2%
	κ case #2	6.2 (0.62)	7.6 (0.64)	6.3 (0.89)	10.0%	8.4%	14.2%
	κ case #3	4.5 (0.61)	5.7 (0.70)	4.9 (1.40)	13.4%	12.4%	28.5%
	κ case #4	2.9 (0.61)	3.6 (0.63)	3.2 (0.80)	21.0%	17.2%	25.2%
	κ case #5	2.5 (0.63)	3.2 (0.65)	2.6 (0.87)	25.6%	20.6%	33.6%
	κ case #6	2.5 (0.61)	2.4 (0.80)	2.4 (0.89)	17.5%	33.3%	37.1%
$\dot{m}_{soot}$ as measured by Sky-LOSA	$\dot{m}_{soot}$ case #1	0.110 mg/s	0.133 mg/s	0.127 mg/s	16.4%	16.1%	26.8%
	$\dot{m}_{soot}$ case #2	0.108 mg/s	0.133 mg/s	0.110 mg/s	17.6%	16.8%	20.3%
	$\dot{m}_{soot}$ case #3	0.103 mg/s	0.129 mg/s	0.111 mg/s	19.7%	19.0%	31.9%
	$\dot{m}_{soot}$ case #4	0.108 mg/s	0.135 mg/s	0.118 mg/s	25.4%	22.3%	28.9%
	$\dot{m}_{soot}$ case #5	0.103 mg/s	0.134 mg/s	0.109 mg/s	29.2%	25.0%	36.5%
	$\dot{m}_{soot}$ case #6	0.181 mg/s	0.125 mg/s	0.125 mg/s	22.5%	36.2%	39.8%

^a Uncertainty in spatial calibration of the camera and lens (evaluated considering a one pixel uncertainty on each side of the exhaust nozzle with a 0.0833 mm/pixel image scale). Uncertainties associated with the interpolation are included in the uncertainty in κ .

data using image correlation velocimetry (37, 38). As a first approach and for the present experiments where velocity is directly calculable as detailed below, the velocity u can be assumed uniform over the plume cross section. Thus, the soot emission rate can be determined as shown in eq 7, where the limits of integration correspond to the width of the plume in the LOSA image.

$$\dot{m}_{soot} = -\frac{u\rho_{soot}\lambda}{6\pi(1 + \rho_{sa})E(m)_\lambda} \int \ln[\tau(y)] dy \quad (7)$$

It is convenient to define an average optical thickness over the width of the plume, κ , as presented in eq 8, where w is the characteristic width of the plume (i.e., the interpolation width) in the y -direction. This nondimensional parameter can be used to compare results of experiments with different plume sizes and shapes. Results from lab-scale plumes can then be transposed to industrial-scale plumes in the field.

$$\kappa = -\frac{1}{w} \int \ln[\tau(y)] dy \quad (8)$$

Equation 7 is then rewritten in terms of κ as follows:

$$\dot{m}_{soot} = -\frac{u\rho_{soot}\lambda w}{6\pi(1 + \rho_{sa})E(m)_\lambda} \kappa \quad (9)$$

Values of the various soot parameters required by eq 9 are available in the literature and their uncertainties are considered in the overall uncertainty analysis presented with the results.

Experimental Approach

Experimental Setup. *Inverted Burner.* Measurements were performed on soot plumes generated from an inverted coannular nonpremixed burner developed by ref 28 following the design of ref 39. Methane and air were introduced at the

FIGURE 1. Optical setup for the sky-LOSA experiments.

top of the burner while secondary dilution air was introduced below the tip of the downwardly propagating flame to dilute, cool, and mix the combustion products. This arrangement permitted large variations in the soot concentrations and associated transmissivities in test plumes emitted from a converging nozzle placed at the exhaust outlet. Six flow configurations were selected to produce plume centerline concentrations ranging from 142.3 down to 31.4 ppb (transmissivities from 0.974 to 0.995), which corresponded to a variation in κ from 0.0106 down to 0.0025. This range permitted controlled investigation of the sensitivity and uncertainty limits of the diagnostic.

The performance of the sky-LOSA technique was critically assessed through comparison with independent measurements of the same soot plumes obtained using both a proven lab-based diffuse-LOSA system (14) and a commercial laser induced incandescence (LII) system (LII200, Artium, Inc.). These data were then used to support a detailed uncertainty analysis. To ensure computation of reliable test statistics, at least 30 independent measurements were performed at each test condition.

Sky-LOSA Setup. Figure 1 shows the setup used to test the sky-LOSA diagnostic. Skylight was reflected by a 1 m $\times$ 0.76 m mirror and transmitted through the plume. A mirror would not be necessary in a field implementation of the sky-LOSA, but allowed straightforward comparison of the three diagnostics along the same horizontal optical axis. The plume was imaged onto a thermoelectrically cooled 16-bit CCD camera (Princeton Instruments, PID 330 $\times$ 1100v2) via a

105-mm camera lens. A 577-nm narrow band-pass filter enabled a monochromatic LOSA measurement. The magnification was set so that the plume width was approximately 20% of the image width. For the purpose of conducting fully controlled experiments, a screen was positioned to prevent direct sunlight illumination of the plume. The relevance of this is considered further in the discussion below. Measurements were performed in clear, cloudy, and overcast sky conditions and exposure times varied between 0.2 and 1.1 s depending on the sky intensity.

Processing Approach. Sky Interpolation. As discussed above, the *source** image in a sky-LOSA experiment must be obtained via interpolation. In the present work, a synthetic background of sky-intensity within the plume region was interpolated using a Loess algorithm (40). The Loess algorithm fits a second-order polynomial to the data surrounding an interpolated measurement point. It includes a “span” argument within the function to control the domain of neighboring data used in the polynomial fit. The optimal span depends somewhat on the spatial gradients within the data and the width of the plume in the image. The Loess algorithm was applied horizontally in the collected images (i.e., perpendicular to the direction of plume propagation) and the interpolations were performed at all heights above the nozzle of the burner exhaust. In this way, an entire *source** image was calculated from a *transmission* image.

Before interpolation, pixels in the images were binned horizontally and vertically by 10 and 7 pixels, respectively, to improve signal-to-noise. The performance and uncertainty limits of this algorithm were quantified under a wide range of conditions as discussed with the results presented below.

Plume Data Processing. For each of the six burner test conditions, 30 plume *transmission* images were acquired, for each of three sky conditions. During data processing, *source** images were computed as described above, *transmissivity* images were determined via eq 4, and κ values were computed via eq 8 from horizontal strips in the images. The plume width typically spanned 22 superpixels in the binned images. An average κ was obtained for each image and an average and standard deviation of κ was determined over the 30 images.

Results

Sky Interpolation. To evaluate the sky interpolation algorithm, a series of tests were performed with reference sky images in which no plume was present. In these tests, a portion of the images was removed and subsequently predicted using the Loess algorithm. The quality of fit was quantified based on the difference between the predicted (*source**) and actual (*source*) image intensity within the region of interpolation. Using eq 4 (where *transmission* is replaced by *source*) and eq 8, an apparent optical thickness (κ_{interp}) was determined to account for the residual interpolation error (a value of zero indicates a perfect background prediction). A sample result is presented in Figure 2, which shows the actual sky-intensity data and predicted sky-intensity data using the interpolation algorithm, for the region outlined by the dashed box.

Tests were performed for a range of interpolation widths in the image and span arguments in the Loess interpolation algorithm. κ_{interp} was calculated for the three sky conditions, for different sized regions of interest (15–35% of the width of the image), and for different span parameters within the Loess interpolation algorithm (6–14 binned pixels), to evaluate potential uncertainties over a broad range of conditions/configurations that might be encountered during a field measurement.

For each sky condition and each combination of width and span values, interpolations were performed in 30 different images at 23 separate heights within each image. The average

FIGURE 2. Example sky image before (a) and after interpolation (b) for overcast conditions. The dashed rectangle shows the interpolation area. The lower plot shows absolute and relative comparisons of the actual and interpolated intensities along the two example dashed white lines indicated in the images.

and standard deviation of the apparent κ values were calculated over the 690 individual determinations of κ (i.e., 23×30) at each sky condition. The standard deviations of interpolation errors at different heights in the same image were much larger than the standard deviations of interpolations at the same height repeated over the 30 images. Thus, the interpolation uncertainty within an individual image is the dominant uncertainty, presumably because the sky condition did not change significantly over the thirty image sequence (and would likely not change significantly during a field measurement of a plume). As such, the uncertainty of interpolation was more conservatively calculated based on the 23 determinations within an image (i.e., $\sigma_{\bar{\kappa}} = \sigma_{\kappa} / \sqrt{23}$) rather than 690).

The interpolation of sky images using the Loess algorithm was not especially sensitive to the span parameter, with a span of 8–10 pixels providing the most consistent results over the full range of test conditions. Thus, the span parameter was fixed at 9 pixels for the remainder of the parametric analysis. Figure 3 shows κ_{interp} as a function of interpolation width for the three sky conditions. Perhaps surprisingly, the accuracy of the algorithm is not especially sensitive to sky condition. The error bars indicate two standard deviations of the mean apparent κ from interpolation. If only a single interpolation were made, the uncertainty in the interpolation error would be about 5 times higher (i.e., $\sqrt{23}$). Thus, depending on the attenuation attainable in a given plume, interpolation at multiple cross sections along the length of the plume might be critical for achieving an acceptable uncertainty in the background interpolation.

Figure 3 also reveals that both the mean and standard deviation of the apparent κ from interpolation are minimized for a plume width of 20–25% of the overall image width. Trends, magnitude, and uncertainty of κ_{interp} are similar for all sky conditions, demonstrating the robustness of the interpolation algorithm. At an interpolation width of 20%, the mean κ_{interp} ranged from -0.00057 for clear sky conditions to $+0.00016$ for overcast. The uncertainty of this interpolation error was less than 0.0006 for all conditions. However, different lens and CCD detector combinations could modify the uncertainty of this interpolation error as well as optimal

FIGURE 3. Background κ_{bias} errors calculated for various sky conditions and interpolation width.

span and relative plume width. Therefore, an analysis similar to that presented here should be performed for any different optical arrangement. In practice, it would be feasible and recommended to include this analysis as part of a regular data collection procedure for a plume measurement, by acquiring additional test image data using regions of sky close to the location of the plume to be measured.

Plume Measurements. Data from sky-LOSA measurements under the full range of test conditions were compared to separately obtained measurements using both diffuse-LOSA and LII, as shown in Figure 4. Factoring in velocity data for the plume (calculated in the present case from the metered flow rates and the diameter of the exit nozzle of the burner), the mass flow rate of soot could also be determined in each case as summarized in Table 1. Figure 4a compares measured κ values, where a 1:1 correspondence would imply perfect correlation between the new sky-LOSA approach and the established lab-based diffuse-LOSA technique. For clarity of visual interpretation, the κ values for the cloudy and overcast sky-conditions were offset by 0.0001 in the horizontal direction to avoid error bar overlap. The error bars account for both the uncertainty on the sky interpolation and the shot-to-shot variation of the plume measurements. To be conservative, only the latter is considered a random error that can be reduced by image averaging. These results

demonstrate that the sky-LOSA technique is effective at measuring plume transmissivities (i.e., κ) even at very low attenuation levels. The lowest tested transmissivity value of 0.995 would correlate to an opacity value of 0.5%, which is an order of magnitude better than the target resolution of 5% suggested in EPA Method 9 (8). Although κ was slightly underestimated in the present sky-LOSA experiments when compared to diffuse-LOSA data, the diffuse-LOSA data also have some associated uncertainty that is not plotted, and the differences are mostly within the range of the error bars as shown.

Figure 4b compares plume concentration from sky-LOSA measurements to independent concentration measurements using LII on samples extracted from the plume. Again there is very good agreement between the two data sets within experimental error, and in this case the sky-LOSA data very slightly overestimate the LII measured concentrations. Overall these results confirm that the sky-LOSA technique can achieve quantitative measurements even at very low attenuation levels and suggest that the uncertainties are well-described using the present analysis approach. As shown in Table 1, these experiments also reveal the ability of sky-LOSA to resolve quite small mass flow rates of soot.

Discussion and Uncertainty Analysis. The overall uncertainty in a sky-LOSA measurement of the soot emission rate can be evaluated via a propagation analysis of component uncertainties as in eq 10. The magnitudes of the various potential sources of uncertainty and their contributions to the overall uncertainty in the measured soot emission rate are listed in Table 1 for each of the test conditions.

$$\frac{\sigma_{\dot{m}_{soot}}}{\dot{m}_{soot}} = \left[\frac{1}{\kappa} \left(\frac{\sigma_{sky}}{sky - dark} \right)^2 + \frac{1}{\kappa} \left(\frac{\sigma_{plume}}{plume - dark} \right)^2 + \left(\frac{\sigma_u}{u} \right)^2 + \left(\frac{\sigma_w}{w} \right)^2 + \left(\frac{\sigma_{\lambda}}{\lambda} \right)^2 + \left(\frac{\sigma_{\rho_{soot}}}{\rho_{soot}} \right)^2 + \left(\frac{\sigma_{\rho_{sa}}}{1 + \rho_{sa}} \right)^2 + \left(\frac{\sigma_{E(m)_\lambda}}{E(m)_\lambda} \right)^2 \right]^{1/2} \quad (10)$$

Uncertainties of the soot properties were calculated as 95% confidence intervals of the means of all values reported in the references cited in Table 1. The uncertainty in the interpolation width results from the spatial accuracy of the camera lens system as explained in the footnote to the table. The uncertainty in the evaluation of κ is separately identified and includes the uncertainty of the sky interpolation (κ_{interp} presented above) and the variations of the average κ among

FIGURE 4. (a) Measured κ values for sky-LOSA vs κ values for diffuse 2D-LOSA, (b) comparison of mean plume concentrations measured with sky-LOSA versus concentrations measured using a commercial laser induced incandescence system. Dashed lines indicate 1:1 correspondence.

individual images (accounting for camera noise, plume variations, and fluctuations in the sky itself, etc.). Uncertainties in plume velocities are derived from the rated 1% of full scale uncertainties in the mass flow controllers that meter flows to the burner. Finally, the uncertainty in the measurement wavelength relates to nominal accuracy in the center wavelength of the optical filter.

For the full range of test conditions considered, uncertainties in the measured mass flow rate of soot ranged from 16.1 to 39.8%. Even for test #6 (plume transmissivity of 0.995), the total uncertainty in the measured soot mass flow was still only 22.5–39.8% depending on the sky conditions. The uncertainties decrease as the attenuation of the plume increases.

As with opacity measurements, field measurements in conditions of bright sun-light can be affected by scattering of direct solar radiation by the soot aggregates within the plume. Thus, the estimated uncertainties for measurements in clear sky-conditions need to be interpreted with some caution. The nature of any interference from direct solar scattering would be such it could only induce an overestimation of the transmissivity, and as such could only lead to an underestimation of the soot emission rate. An approach to correcting for this potential uncertainty in bright sun conditions is currently being investigated in related work (41). This issue would not be faced for overcast or cloudy conditions or during measurements at dawn or dusk since the sun is effectively blocked.

The sensitivity of the sky-LOSA method is principally limited by the sky interpolation uncertainty. Soot emission rates cannot be measured for κ values below κ_{interp} (approximately 0.0006 for all sky conditions). This corresponds to a sensitivity limit of 0.5 mg/s for a 2-m-diameter plume with a constant wind speed of 4 m/s (eq 9). In terms of mass flow of soot, sensitivities improve as either the velocity or plume diameter is decreased.

Perhaps due to the lack of existing practical techniques for making quantitative measurements of soot mass emission rate in operating flares, there are very limited data in the literature with which to compare the capabilities of the sky-LOSA diagnostic. Only refs 17 and 45 are known to have specifically considered soot emissions from large scale flares, although neither reported direct data on mass emission rates of soot. However, the available information in these sources suggests that κ values even larger than those of case #1 could be expected from full-scale flares. For a conservative example field measurement of a 2-m-diameter plume moving at 4 m/s with a κ value ten times the sensitivity limit (i.e., 0.006), and allowing for a 25% uncertainty in the plume velocity (whether measured based on wind anemometers or image correlation velocimetry from the motion of the plume itself), the present analysis suggests an overall uncertainty of 29–32% would be achievable depending on the sky condition. Relative to existing opacity based methods, the potential for quantitative measurement of soot mass emission rates using sky-LOSA represents a significant advance.

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Literature Cited

- Peters, A.; Dockery, D.; Muller, J.; Mittleman, M. Increased particulate air pollution and the triggering of myocardial infarction. *Circulation* **2001**, *103*, 2810–2815.
- Pope, C., III; Burnett, R.; Thun, M.; Eugenia, E.; Krewski, D.; Ito, K.; Thurston, G. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *JAMA* **2002**, *287*, 1132–1141.
- U.S. Environmental Protection Agency. *Air Quality Criteria for Particulate Matter, Vol. II*; EPA/600/P-99/002aF; EPA: Washington, DC, 2004.
- Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K.; Tignor, M.; Miller, H. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, UK and New York, 2007.
- Ramanathan, V.; Carmichael, G. Global and regional climate changes due to black carbon. *Nat. Geosci.* **2008**, *1*, 221–227.
- Elvidge, C.; Ziskin, D.; Baugh, K.; Tuttle, B.; Ghosh, T.; Pack, D.; Erwin, E.; Zhizhin, M. A fifteen year record of global natural gas flaring derived from satellite data. *Energies* **2009**, *2*, 595–622.
- Poudenx, P. Plume sampling of a flare in crosswind: structure and combustion efficiency. M.Sc. Thesis, University of Alberta, Edmonton, AB, 2000.
- U.S. Environmental Protection Agency. Method 9 - Visual determination of the opacity of emissions from stationary sources. *Code of Federal Regulations* Part 60, Title 40, 1991.
- McFarland, M.; Terry, S.; Calidonna, M.; Stone, D.; Kerch, P.; Rasmussen, S. Measuring visual opacity using digital imaging technology. *J. Air Waste Manage. Assoc.* **2004**, *54*, 296–306.
- McFarland, M.; Terry, S.; Stone, D.; Rasmussen, S.; Calidonna, M. Evaluation of the digital opacity compliance system in high mountain desert environments. *J. Air Waste Manage. Assoc.* **2003**, *53*, 724–730.
- Du, K.; Rood, M. J.; Kim, B. J.; Kemme, M. R.; Franek, B.; Mattison, K. Quantification of plume opacity by digital photography. *Environ. Sci. Technol.* **2007**, *41*, 928–35.
- Greenberg, P.; Ku, J. Soot volume fraction imaging. *Appl. Opt.* **1997**, *36*, 5514–5522.
- Snelling, D.; Thomson, K.; Smallwood, G.; Gülder, O. Two-dimensional imaging of soot volume fraction in laminar diffusion flames. *Appl. Opt.* **1999**, *38*, 2478–85.
- Thomson, K.; Johnson, M.; Snelling, D.; Smallwood, G. Diffuse-light two-dimensional line-of-sight attenuation for soot concentration measurements. *Appl. Opt.* **2008**, *47*, 694–703.
- Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1983.
- Siegel, R.; Howell, J. R. *Thermal Radiation Heat Transfer*, 3rd ed.; Hemisphere Publishing Corp.: Washington, DC, 1992.
- Pohl, J.; Lee, J.; Payne, R.; Tichenor, B. Combustion efficiency of flares. *Combust. Sci. Technol.* **1986**, *50*, 217–231.
- Stroscher, M. Characterization of emissions from diffusion flare systems. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1723–1733.
- Johnson, M.; Kostiuik, L. Efficiencies of low-momentum jet diffusion flames in crosswinds. *Combust. Flame* **2000**, *123*, 189–200.
- Johnson, M.; Wilson, D.; Kostiuik, L. A fuel stripping mechanism for wake-stabilized jet diffusion flames in crossflow. *Combust. Sci. Technol.* **2001**, *169*, 155–174.
- Johnson, M.; Kostiuik, L. A parametric model for the efficiency of a flare in crosswind. *Proc. Combust. Inst.* **2002**, *29*, 1943–1950.
- Yang, C. Sky-scattered solar radiation based plume transmissivity measurements. M.A.Sc. Thesis, Carleton University, Ottawa, ON, 2008.
- Hewitt, C. The atmospheric chemistry of sulphur and nitrogen in power station plumes. *Atmos. Environ.* **2001**, *35*, 1155–1170.
- Köylü, Ü.; Faeth, G. Optical-properties of overfire soot in buoyant turbulent-diffusion flames at long residence times. *J. Heat Transfer* **1994**, *116*, 152–159.
- Farias, T.; Carvalho, M.; Köylü, Ü.; Faeth, G. Computational evaluation of approximate Rayleigh-Debye-Gans/fractal-aggregate theory for the absorption and scattering properties of soot. *J. Heat Transfer* **1995**, *117*, 152–159.
- Liu, F.; Snelling, D. R. Evaluation of the accuracy of the RDG approximation for the absorption and scattering properties of fractal aggregates of flame-generated soot. *Proceedings of the 40th AIAA Thermophysics Conference*, Seattle, WA, June 23–26, 2008.
- Sorensen, C.; Cai, J.; Lu, N. Light-scattering measurements of monomer size, monomers per aggregate, and fractal dimension for soot aggregates in flames. *Appl. Opt.* **1992**, *31*, 6547–6557.
- Coderre, A. Spectrally-resolved light absorption properties of cooled soot from a methane flame. M.A.Sc. Thesis, Carleton University, Ottawa, ON, 2009.
- Dobbins, R.; Mulholland, G.; Bryner, N. Comparison of a fractal smoke optics model with light extinction measurements. *Atmos. Environ.* **1994**, *28*, 889–897.

- (30) Köylü, Ü.; Faeth, G. Spectral extinction coefficients of soot aggregates from turbulent diffusion flames. *J. Heat Transfer* **1996**, *118*, 415–421.
- (31) Krishnan, S. S.; Lin, K.; Faeth, G. Optical properties in the visible of overfire soot in large buoyant turbulent diffusion flames. *J. Heat Transfer* **2000**, *122*, 517.
- (32) Schnaiter, M.; Horvath, H.; Mohler, O.; Naumann, K.; Saathoff, H.; Schöck, O. UV-VIS-NIR spectral optical properties of soot and soot-containing aerosols. *J. Aerosol Sci.* **2003**, *34*, 1421–1444.
- (33) Snelling, D.; Liu, F.; Smallwood, G.; Gülder, O. Determination of the soot absorption function and thermal accommodation coefficient using low-fluence LII in a laminar coflow ethylene diffusion flame. *Combust. Flame* **2004**, *136*, 180–190.
- (34) Hashmonay, R. A.; Varma, R. M.; Modrak, M. T.; Kagann, R. H.; Segall, R. R.; Sullivan, P. D. Radial plume mapping: a US EPA test method for area and fugitive source emission monitoring using optical remote sensing. In *Advanced Environmental Monitoring*; Kim, Y. J., Platt, U., Eds.; Springer Netherlands: Dordrecht, 2008; pp 21–36.
- (35) Vogt, S.; Thomas, P. Test of a phased array SODAR by intercomparison with tower data. *J. Atmos. Oceanic Technol.* **1994**, *11*, 94–102.
- (36) Werner, C.; Haus, R.; Köpp, F.; Schäfer, K. Remote sensing of mass fluxes of trace gases in the boundary layer. *Appl. Phys., B* **1995**, *61*, 249–251.
- (37) Johnson, M. R.; Devillers, R. W.; Thomson, K. A. Quantitative field measurement of soot emission from a large gas flare using sky-LOSA. *Environ. Sci. Technol.* 2010. submitted for publication.
- (38) Weibring, P.; Andersson, M.; Edner, H.; Svanberg, S. Remote monitoring of industrial emissions by combination of LIDAR and plume velocity measurements. *Appl. Phys., B* **1998**, *66*, 383–388.
- (39) Stipe, C. B.; Higgins, B. S.; Lucas, D.; Koshland, C. P.; Sawyer, R. F. Inverted co-flow diffusion flame for producing soot. *Rev. Sci. Instrum.* **2005**, *76*, 023908.
- (40) Cleveland, W. S.; Devlin, S. J. Locally weighted regression: an approach to regression analysis by local fitting. *J. Am. Stat. Assoc.* **1988**, *83*, 596–610.
- (41) Devillers, R. W.; Thomson, K. A.; Johnson, M. R. Polarization correction of sun-light scattering in sky-scattered solar radiation based plume transmissivity measurements. *Proceedings of the Air & Waste Management Association 103rd Annual Conference & Exhibition*, Calgary, AB, June 22–25, 2010.
- (42) Choi, M.; Mulholland, G.; Hamins, A.; Kashiwagi, T. Comparisons of the soot volume fraction using gravimetric and light extinction techniques. *Combust. Flame* **1995**, *102*, 161–169.
- (43) Choi, M.; Hamins, A.; Mulholland, G.; Kashiwagi, T. Simultaneous optical measurement of soot volume fraction and temperature in premixed flames. *Combust. Flame* **1994**, *99*, 174–186.
- (44) Wu, J.; Krishnan, S.; Faeth, G. Refractive indices at visible wavelengths of soot emitted from buoyant turbulent diffusion flames. *J. Heat Transfer* **1997**, *119*, 230–238.
- (45) McDaniel, M. *Flare Efficiency Study*; EPA-600/2-83-052; U.S. Environmental Protection Agency: Washington, DC, 1983.

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