Use of an Unmanned Aircraft System to Quantify NO_x Emissions from a Natural Gas Boiler

Brian Gullett[1], Johanna Aurell[2], William Mitchell[1], Jennifer Richardson[3]

Response to Referees' Comments

RC1

General Comments Gullett et al. present stack emission measurements of CO_2, CO, NO_2, NO with a UAS, using a non-dispersive infrared optical absorption sensor for CO_2 and electrochemical sensors for the other gases. They report good agreement of the measured NOx emissions with the continuous emission monitoring system (CEMS) at the test sites. Both, CEMS and the UAV measurement determine the emission via carbon balance calculations. The authors, however, do not discuss the additional value of their measurement with the UAV over the CEMS measurement. The CEMS measures the same quantity (NOx emissions) with an up to 18 times lower error (see Tab. 7 of the manuscript). The manuscript thereby does not include the description of a scientific goal or application, like e.g. the validation of the CEMS measurement, studying the dependence of the NOx emission flux on the distance to the emitting stack, or similar. The feasibility of sampling emission plumes with a UAV was shown in the cited studies of e.g. area sources or volcanoes. In many of these works the absence of a CEMS and/or chemical conversion of the measured quantities along the emission plume motivate the studies.

Further, in my opinion, the scope of this journal demands a more detailed description of the 'extensive laboratory testing to verify performance and suitability' (l. 75, 76 of the manuscript) that was carried out. Especially, since electrochemical sensors are known for their rather unstable performance (see e.g. Jiao et al., 2016, https://amt.copernicus.org/articles/9/5281/2016/) and because the sensor calibration site and measurement site in this study have significantly different gas composition (plume and background air). Drifts, dependencies on environmental factors (e.g. temperature, humidity) and cross interferences with other trace gases in amounts that are typical for the sampled emission plume should be documented in the paper.

Without these points thoroughly addressed I advise against publishing the manuscript in AMT.

RESPONSE to general comments:

The reviewer states that the manuscript "does not include the description of a scientific goal or application" and we agree, in part, and have modified the manuscript accordingly starting with the final line in the abstract. While the advantages of a UAS platform for emission measurements are mentioned, we now explicitly stated the goal as comparison of UAS-borne emission measurements with concurrent CEM measurements (Introduction, paragraph 3). More explicit statements can lead into policy implications, for which we are unauthorized.

While we are aware of previous efforts sampling volcanoes (for example), those measurements are unable to make any comments on the accuracy of the measurements as the volcano source is an unmeasured quantity. In our work we have direct measurements of the source via the in-stack CEMS, allowing us to make definitive comparisons of our ability to determine the source strength with UAS-based measurements.

We agree with the reviewer that a detailed description of the sensor performance is important given their inherent potential for instability and inaccuracy. We place our potential sensors through rigorous in-laboratory testing covering the full range of expected target gas concentrations and then daily pre- and post-measurement calibration checks in the field. These methods are now partially mentioned in the manuscript as well as reference to manufacturers' sensor data sheets – a more extensive description of the testing is outside of the scope of this paper.

Specific Comments

1) Faivre-Pierret et al., 1980 measured volcanic gas and particle emissions with an UAV.

RESPONSE: The current authors have previously measured gases, particles, VOCs, and SVOCs with the use of UAS-born emission equipment: [Aurell et al., 2017 – Atm Env 166]. However, questions about accuracy based upon known source strength and about the potential effects of rotor wash on emission measurements have been incompletely addressed in the literature; this paper answers some of those questions.

2) The influence of the different time constants (response times) of the sensors on the comparability of the individual measurements should be shortly discussed.

RESPONSE: Each sensor has a different response time to changes in concentration; this could be a consideration, depending on how the measurements are used. If comparisons are to be made instantaneously between pollutants, this could have a significant effect, and can be partially mitigated through use of time-averaging of concentrations. Our work took this approach in reporting concentrations, however, this was not critical, as our emission factor calculations were based upon the time-integrated sum of the concentrations over many minutes of sampling.

If we had relied upon and reported instantaneous data, the longer response time of the NO_2 sensor (32 sec = t_{95}) still would have had minimal effect over instantaneous emission factors as the NO_2 concentration was much lower than that of NO and so had little effect upon the emission factor calculation. The NO and CO_2 sensors have similar response times (6-9 s) and would have accurately represented the instantaneous emission factor.

3) l.113: The underlying detection techniques of the CEMS measurements should at least be mentioned.

RESPONSE: These are now mentioned in the revised text.

4) A schematic drawing or photograph of the Kolibri setup would be illustrative.

RESPONSE: A close up photo of the Kolibri with text explanations was inserted to Figure 1.

5) The CO and NO_2 values in Fig. 2 should be scaled up by at least a factor of 10 in order to be clearly visible.

RESPONSE: We scaled up the NO_2 and CO concentrations by 10 times.

6) In Fig. 2 it can be observed that the CO_2 concentration reaches the upper end of the sensor's range several times. Is this always considered in the average?

RESPONSE: CO_2 peaks exceeded the range of the sensor for 1,108 seconds out of the 16,500 seconds total sampling duration for the 14-run test, or 6.7% of the sampling time. These concentrations, at their range limit, are included in the average emission factor calculations. Exclusion of the NOx and C data during those 1,108 seconds only affects the EFs by 3 %. When the sensors' ranges are exceeded, the UAS pilot is instructed to back off from the source toward a more dilute airstream.

7) l.186, 189: If the progressions of the time series as plotted in Fig. 2 were mostly determined by leaving and entering the plume with the UAV, the standard deviation of this time series would not be a good measure for the measurement error.

RESPONSE: The authors are not clear if the reviewer is referring to the RSD values cited just below Figure 2. If so, we've clarified that the cited RSDs are for flight durations and not for the observed concentrations. In any case, the reviewer is correct regarding his/her observation. Because the plume is mixing and entraining ambient air, there is considerable fluctuation in concentrations even for the stationary UAS, necessitating time-averaged values. While this is less of an issue for the more homogeneous gas measurements in the stack, the CEMs also use an averaged display value with a rolling average of 60 seconds which further smooths out any fluctuations in concentration.

Referee's References

Jiao, W., Hagler, G., Williams, R., Sharpe, R., Brown, R., Garver, D., Judge, R., Caudill, M., Rickard, J., Davis, M., Weinstock, L., Zimmer-Dauphinee, S., and Buckley, K.: Community Air Sensor Network (CAIRSENSE) project: evaluation of low-cost sensor performance in a suburban environment in the southeastern United States, Atmos. Meas. Tech., 9, 5281–5292, https://doi.org/10.5194/amt-9-5281-2016, 2016.

Faivre-Pierret, R., Martin, D. & Sabroux, J.C., Contribution des Sondes Aérologiques Motorisées à l'Etude de la Physico-Chimie des Panaches Volcaniques, Bull Volcanol (1980) 43: 473. https://doi.org/10.1007/BF02597686

Our References:

Aurell, J.; Mitchell, W.; Chirayath, V.; Jonsson, J.; Tabor, D.; Gullett, B., Field determination of multipollutant, open area combustion source emission factors with a hexacopter unmanned aerial vehicle. *Atmospheric Environment* **2017,** *166*, 433-440.

Reply

The authors recognize that electrochemical sensors do not have the same performance as CEMs. The referees cite Jiao et al. that tested electrochemical sensors under ambient conditions (measurement range of ppb), for a minimum 30-day testing period, and without any calibrations of the sensors. Our manuscript performed calibrations just before the testing and checked the against the same calibration gases just after the test period to establish if the sensors had drifted during the testing period. For clarification we have added sensor calibration information as well as references to more extensive characterization data. The objective of conducting calibration is to ensure that the sensor measures the gas in question within acceptable levels. Calibrations of sensors and CEMs must be performed using certified gases with a known percentage of the gas tested. As such, the calibration gas mixture will always differ from the plume or stack gas mixtures. References to manufactures's technical specification sheets for each sensor have been added; these data sheets include the sensors performance and cross sensitivity to other gases.

Comment from Referee #1 on Referee #2 comments, RC3

Agreed [with Referee #1], but suggest this can be addressed by brief reference to other publications by the authors (if available) or through the use of supplemental material and data (i.e., inclusion in body of paper will distract from focus of research).

RESPONSE: The authors assume that Referee #1 agrees to Referee #2 comment about "extensive testing" as described in RC2 below. We have added this in the text.

RC2

General Comments:

Gullett et al. describe the methods and results for a novel UASbased sampling approach for stack emissions relative to standard stack continuous emission monitoring system (CEMS). Results indicate good agreement (within 9 percent) for Run-Averaged NOx Emission Factor between UAS and CEMS systems. Error values for UAS-based measurements range from 3 times greater to more than an order of magnitude greater than for CEMS measurement.

The paper would be strengthened by discussion of the implications of differences between methods and the greater error associated with UAS-based measurement. Such a discussion, in turn, may aided by addressing in the Introduction and Conclusions sections, the potential applications of UAS-based measurement for future research or regulatory purposes. The paper could benefit from additional background and discussion of observed sensor performance in the context of known issues relating to sensor performance as affected by atmospheric conditions.

The comment from Referee #2 asking for more detail on "extensive testing" is germane, and can be addressed by reference to other publications by the authors (if available) or through the inclusion of descriptions of such testing and data as supplemental materials. Suggestion for reconsideration after "major" revisions is based on author's ability to address above issues.

RESPONSE to general comments:

The authors believe that the standard deviation values don't reflect "error" – our error measures are based on the test runs' emission factor calculations, not the instantaneous variation of the measured concentrations. These run-specific variations in emission factors are quite modest: average of 5.6% (3.5% for carbon-weighted values) for the three boilers. The significant variation in concentrations observed by the sensors within the plume due to mixing of ambient air is compensated for by reliance on whole-run, integrated values of concentrations for determinations of emission factors. Thus, use of UAS for emission determination, much like annual compliance tests with CEMS, would require a series of measurements to arrive at a final value.

The authors are limited to speculate on regulatory prospects due to the policy implications.

Additional information on sensor sensitivities is now included in the body.

Specific comments:

1. Suggestion to include closer imager of mounted Kolibri to illustrate location of intake ports

RESPONSE: We have added a labelled photo of the Kolibri.

2. Suggestion to include schematic of Kolibri as flown

RESPONSE: Labelled photo is added.

3. How did the authors treat data values where CO_2 readings were at or above the limits of the detectors, and what assumptions were made about error for such readings.

RESPONSE: CO_2 peaks exceeded the range of the sensor for 1,108 seconds out of the 16,500 seconds total sampling duration for the St. Charles location (not Midland), or a total of 6.7%. These are included in the average. Exclusion of the NOx and C data during those 1,108 seconds only affects the EFs by 3 %. When the sensors' ranges are exceeded, the UAS pilot is instructed to back off from the source toward a more dilute airstream.

4. Vertical axis scale adjustment for CO and NO_2

RESPONSE: We scaled up the NO_2 and CO concentrations by 10 times for improved visibility.

Technical comments:

1. In Table 3, flight 4 is excluded from the table entirely and an explanatory note provided; however, in Table 4, Flight 5 is excluded from calculations (for reasons that appear similar to flight 4's exclusion from the previous table), but its data is retained in the table. Recommendation to leave flight 4 data in table 3 and use common language (e.g. "excluded from calculations") between tables.

RESPONSE: We added the data for flight 4 in the revised table 5.

Authors' comments

Data had been erroneously been moved around in Table 5. We have corrected this in the updated table.

Date	Flight	Flight time (hh:mm:ss)			NO_2	NO	NO_x	Avg. CO_2
	#	Up	Down	Total	mg/kg C	mg/kg C	mg/kg C	ppm
07/24/2019	1	07:31:00	07:49:00	00:18:00	25	1366	1391	3221
07/24/2019	2	07:52:00	08:16:00	00:24:00	49	1263	1312	3503
07/24/2019	3	08:19:00	08:38:00	00:19:00	87	1420	1507	3415
07/24/2019	4	09:23:00	09:46:00	00:23:00	65	1341	1406	4509
07/24/2019	5	09:49:00	10:11:00	00:22:00	47	1296	1343	4813
07/24/2019	6	10:16:00	10:36:00	00:20:00	52	1299	1351	3773
07/24/2019	7	10:38:00	11:00:00	00:22:00	53	1316	1369	4194
07/24/2019	8	11:51:00	12:13:00	00:22:00	90	1460	1549	3129
07/24/2019	9	13:17:00	13:39:00	00:22:00	47	1464	1511	3606
Average				**00:21:20**	**57**	**1358**	**1416**	**3796**
Stand. Dev.				**00:01:56**	**21**	**74**	**86**	**586**
RSD (%)				**9**	**36**	**5.5**	**6.0**	**15**

Use of an Unmanned Aircraft System to Quantify NO_x Emissions from a Natural Gas Boiler

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List of Relevant Changes Made in the Manuscript

- Addition of sensor characterization and performance data were added to the manuscript.
- Implications for sensor response time were addressed.
- A photo of the Kolibri sensor system was inset to Figure 1 to better explain the inlets.
- Figure 2 was improved for better visibility.
- The goal of the overall effort was stated and emphasized.
- The effect of exceedances of the sensor ranges was discussed.
- Table 5 was revised.

Use of an Unmanned Aircraft System to Quantify NO_x Emissions from a Natural Gas Boiler

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Abstract

Aerial emission sampling of four natural gas boiler stack plumes was conducted using an unmanned aerial system (UAS) equipped with a light-weight sensor/sampling system (the "Kolibri") for measurement of nitrogen oxide (NO), and nitrogen dioxide (NO_2), carbon dioxide (CO_2), and carbon monoxide (CO). Flights (n = 22) ranged from 11 to 24 minutes duration at two different sites. The UAS was maneuvered into the plumes with the aid of real-time CO_2 telemetry to the ground operators and, at one location, a second UAS equipped with an infrared/visible camera. Concentrations were collected and recorded at 1 Hz. The maximum CO_2, CO, NO, and NO_2 concentrations in the plume measured were 10,000 ppm, 7 ppm, 27 ppm, and 1.5 ppm, respectively. Comparison of the NO_x emissions between the stack continuous emission monitoring systems and the UAS/Kolibri for three boiler sets showed an average of 5.6 % and 3.5 % relative percent difference for the run-weighted and carbon-weighted average emissions, respectively. To our knowledge, this is the first evidence for the accuracy performance of UAS-based emission factors against a source of known strength.

Keywords: Emissions, natural gas, boiler, unmanned aircraft system, drone, continuous emission monitoring

TOC Art

1 Introduction

Aerial measurement of plume concentrations is a new field made possible by advances in Unmanned Aircraft Systems (UAS, or "drones"), miniature sensors, computers, and small batteries. The use of a UAS platform for environmental sampling has significant advantages in many scenarios in which access to environmental samples are limited by location or accessibility. Hazards to equipment and personnel can also be minimized by the mobility of the UAS as well as their ability to be remotely operated away from hazardous sources. UAS-based emission samplers have been used for measurement of area source gases (Neumann et al., 2013; Rosser et al., 2015; Chang et al., 2016; Li et al., 2018), point source gases (Villa et al., 2016), aerosols (Brady et al., 2016), black carbon particles (Craft, 2014), volcanic pollutants (Mori et al., 2016), particle mass (Peng et al., 2015), and particle number concentrations (Villa et al., 2016).

UAS-based emission measurements are particularly suited for area source measurements of fires and can be used to determine emission factors, or the mass amount of a pollutant per unit of source operation, such as mass of particulate matter (PM) per mass of fuel (e.g., biomass) burned. These values can be converted into emission rates, such as mass of pollutant per unit of energy (e.g., g NO_x kJ^{-1}). These determinations typically rely on the carbon balance method in which the target pollutant is co-sampled with the major carbon species present and, with knowledge of the source's fuel (carbon) composition, the pollutant to fuel ratio or an emission rate/factor, can be calculated.

For internal combustion sources that have a process emission stack, downwind plume sampling can use the same method. When combined with the source fuel supply rate and stack flow rates (to determine the dilution rate), measurements comparable to extractive stack sampling may be possible. To our knowledge, determination of emission factors from a stack plume using a UAS-borne sampling system has not previously been demonstrated. The goal of this effort was to compare NO_x measurements obtained by UAS-borne emission samplers with those from concurrent CEM measurements.

The feasibility of downwind plume sampling using a sensor-equipped UAS was tested on industrial boilers at the Dow Chemical Company (Dow) facilities in Midland, Michigan (MI) and St. Charles, Louisiana (LA). The sensor system was designed and built by the EPA's Office of Research and Development and the UAS was owned and flown by the Dow Corporate Aviation Group. To determine the comparative accuracy of the measurements, the UAS-based emission factor was compared with the stack continuous emission monitoring systems (CEMS). The target pollutants were nitrogen oxide (NO) and nitrogen dioxide (NO_2) to mimic the stack CEMS measurement methods. Carbon as carbon dioxide (CO_2) and carbon monoxide (CO) were measured on the UAS for the carbon balance method.

2 Materials and Method

Plume sampling tests were conducted on two natural-gas-fired industrial boilers located at Dow's Midland, Michigan and St. Charles, Louisiana facilities. The Midland boilers are firetube type boilers using low pressure utility supplied natural gas. They are equipped with low NO_x burners and utilize flue gas recirculation to reduce stack NO_x concentrations. The Midland facility burned natural gas with a higher heating value (HHV) of 9,697 kcal m^{-3} (1089 British Thermal Unit (BTU)/ft^{-3}). The two tested stacks are 14 m above ground level and 7 m apart. To avoid sampling overlapping plumes, only a single boiler was operating during the testing. The St. Charles boilers are D-type water package boilers using natural gas fuels (high pressure fuel gas (HPFG) and low pressure off-gas (LPOG)). They are equipped with low NO_x burners with flue gas recirculation to reduce stack NO_x concentrations. The boiler stacks are about 20 m apart and reach over 20 m in height above ground level. The St. Charles facility burned natural gas under steady state conditions with a composition of 77.12 % CH_4, 2.01 % C_2H_6, and 19.91 % H_2

and a HHV of 7,845 kcal m^{-3} (881 BTU ft^{-3}). Both boilers were operational during aerial sampling, but the wind direction and UAS proximity to the target stack precluded co-mingling of the plumes.

Air sampling was accomplished with an EPA/ORD-developed sensor/sampler system termed the "Kolibri". The Kolibri consists of real-time gas sensors and pump samplers to characterize a broad range of gaseous and particle pollutants. This self-powered system has a transceiver for data transmission and pump control (Xbee S3B, Digi International, Inc., Minnetonka, MN, USA) from the ground-based operator. For this application, gas concentrations were measured using electrochemical cells for CO, NO, and NO_2 and a non-dispersive infrared (NDIR) cell for CO_2 (Table 1). All sensors were selected for their applicability to the anticipated operating conditions of concentration level and temperature as well as for their ability to rapidly respond to changing plume concentrations due to turbulence and entrainment of ambient air. Each sensor underwent extensive laboratory testing to verify performance and suitability prior to selection for the Kolibri. Tests included sensor performance (linearity, drift, response time, noise, detection limits) in response to anticipated field temperatures, pressure, humidity, and interferences. Additional information from the manufacturers on sensor performance is available from the links in Table 1. In anticipation of temperatures as low as 0°C at the Midland site and to avoid daily temperature fluctuations, insulation was added to the Kolibri frame and the sampled gases were preheated prior to the sensor with the use of a heating element and micro fan inside the Kolibri. All sensors were calibrated before each sampling day under local ambient conditions. After sampling was completed, the sensors were similarly tested to assess potential drift.

Concentration data were stored by the Kolibri using a Teensy USB-based microcontroller board (Teensy 3.2, PJRC, LLC., Sherwood, OR, USA) with an Arduino-generated data program and SD data card. All four sensors underwent pre- and post-sampling two- or three-point calibration using gases (Calgasdirect Inc., Huntington Beach, CA, USA) traceable to National Institute of Standards and Technology (NIST) standards.

Table 1. UAS/Kolibri Target Analytes and Methods

Analyte	Instrument, Manufacturer's Data Link	Frequency	Cal. Gases (ppm) Midland	Cal Gases (ppm) St. Charles
CO_2	SenseAir CO_2 Engine K30, NDIR[a] https://www.co2meter.com/products/k-30-co2-sensor-module	Continuous, 1 Hz[b]	408, 990	392, 996, 5890
CO	E2v EC4-500-CO, Electrochemical cell https://www.sgxsensortech.com/content/uploads/2014/07/EC4-500-CO1.pdf	Continuous, 1 Hz	0[c], 9.67, 50.6	0, 9.9, 51.8
NO	NO-D4, Electrochemical cell http://www.alphasense.com/WEB1213/wp-content/uploads/2013/10/NOD4.pdf	Continuous, 1 Hz	0, 2.1, 41.4	0, 2.1, 40.4
NO_2	NO2-D4, Electrochemical cell http://www.alphasense.com/WEB1213/wp-content/uploads/2020/09/NO2-D4.pdf	Continuous, 1 Hz	0, 2.1, 10.4	0, 1.9, 10.4

[a]Non-dispersive infrared. [b]Hz – hertz. [c]Zero (0) cal gas = air.

The NO sensor (NO-D4) is an electrochemical gas sensor (Alphasense, Essex, UK) which measures concentration by changes in impedance. The sensor has a detection range of 0 to 100 ppm with resolution of < 0.1 RMS noise

(ppm equivalent) and linearity within ±1.5 ppm error at full scale. The NO-D4 was tested to have a response time to 95 % of concentration ($T_{95\%}$) of 6.3±0.52 seconds and a noise level of 0.027 ppm. The temperature and relative humidity (RH) operating range is 0 to +50 °C and 15 to 90 % RH, respectively.

The NO_2 sensor (NO2-D4) is an electrochemical gas sensor (Alphasense, Essex, UK) which likewise measures by impedance changes. It has a NO_2 detection range of 0-10 ppm with resolution of 0.1 RMS noise (ppm equivalent) and linearity error of 0 to 0.6 ppm at full scale. Its $T_{95\%}$ was measured as 32.3±3.8 seconds with a noise level of 0.015 ppm. The temperature and RH operating range is 0 to +50 °C and 15 to 90 % RH, respectively.

Laboratory calibration testing prior to field measurements on both the NO-D4 and NO2-D4 sensors outputs showed their responses to be linearly proportional ($R^2 > 0.99$) over the range of 4- and 5-point calibration gas concentrations. The response times of both sensors were derived using the maximum reference concentration of 47.81 ppm for NO and 10.46 ppm of NO_2. The times to reach 95% of the reference concentration, t_{95}, were 6.3 and 32.3 sec (RSD (8.2% and 11.8%), respectively, for the NO-D4 and NO2-D4 sensors. These response times are both shorter than those measured simultaneously in the laboratory by a CEM (Ametek 9000^{RM}, Pittsburgh, PA, USA) at 37 and 50 sec, respectively, for NO and NO_2.

The CO_2 sensor (CO_2 Engine® K30 Fast Response, SenseAir, Delsbo, Sweden) is an NDIR gas sensor and the voltage output is linear from 400 to 10,000 ppm. The temperature and RH operating range is 0 to +50 °C and 0 to 90 % RH, respectively. The CO_2-K30 sensor was measured to have a $t_{95\%}$ response time at 6000 ppm CO_2 of 9.0 ± 0.0 seconds and having a noise level of 1.6 ppm. The response time was 4 sec longer than compared to CO_2 measured by a portable gas analyzer (LI-820, LI-COR Biosciences, Lincoln, NE, USA). The sensor and the LI-820 showed good agreement as the measurements showed a R^2 of 0.99 and a slope of 1.01.

The CO sensor (e2V EC4-500-CO, SGX Sensortech Ltd, High Wycombe, Buckinghamshire UK) is described more fully elsewhere (Aurell et al., 2017; Zhou et al., 2017). In previous sensor evaluation tests with laboratory biomass burns (Zhou et al., 2017) with CO ranging between 0 and 250 ppm, the sensor was compared to simultaneous measurements by a CO CEM (CAI Model 200, California Analytical Instruments Inc., Orange, CA, USA). The concentration measurements had an $R^2 = 0.98$ and a slope of 1.04, indicating the level of agreement between the two devices. The t_{90} was measured as 18 s while comparison of the time-integrated CO concentration differences with the CAI-200, rated at $t_{90} < 1$ s, were only 4.9%.

Variations of the Kolibri sampling system allow for measurement of additional target pollutants. These include particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) including carbonyls, energetics, chlorinated organics, metals from filter analyses, and perchlorate (Aurell et al., 2017; Zhou et al., 2017).

At both facilities the aviation team from Dow flew their DJI Matrice 600 UAS, a six-motor multicopter (hexacopter), into the plumes with EPA/ORD's Kolibri sensor/sampler system attached to the undercarriage (Figure 1). In this configuration of sensors, the Kolibri system weighed 2.4 kg. Typical flight elevations at Midland and St. Charles were 21 and 32 m above ground level (AGL), respectively, and flight durations ranged from 9 to 24 min. At the St. Charles location, the UAS pilot was approximately 100 m from the center point of the two stacks, easily allowing for line of sight operation. A telemetry system on the Kolibri provided real time CO_2 concentration and temperature data to the Kolibri operator who in turn advised the pilot on the optimum UAS location.

CEMS on the boiler stacks produced a continuous record of NO_x emission and O_2 concentrations. Stack and CEMS types located at the Midland and St. Charles facilities are shown in Table 2. The stack NO_x analyzer uses a chemiluminescence measurement with a photomultiplier tube and is capable of split concentration range operation: Low (0-180 ppm) and High (0-500 ppm). Its response time is reported as 5 sec. The O_2 analyzer uses a zirconium oxide cell with a measurement range of 0 to 25% and a reported t_{95} of < 10 sec.

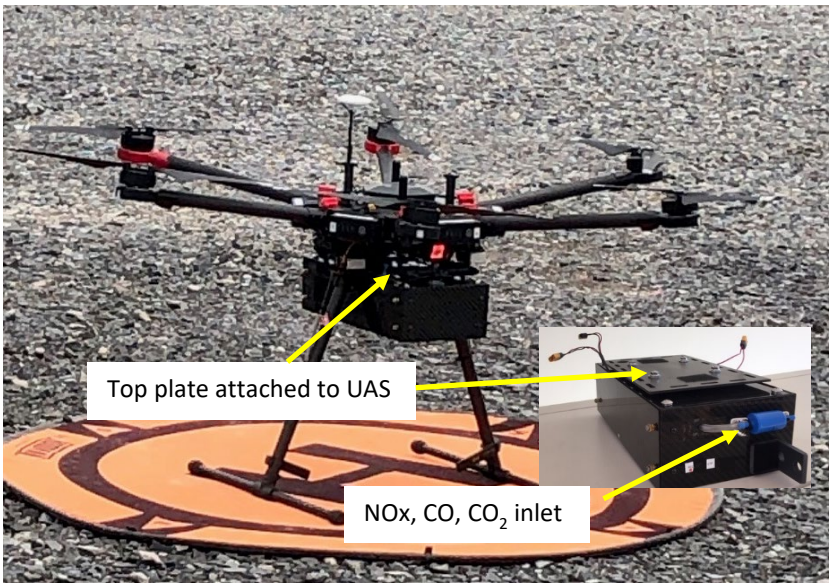

Figure 1. Dow UAS with Kolibri attached to the undercarriage.

Table 2. CEMS Instruments at both Dow locations.

Gas Measured	Midland CEMS	St. Charles CEMS
O_2	Gaus Model 4705	ABB/Magnos 106
NO_x	Thermo Model 42i-HL	ABB/Limas 11

The plant CEMS undergo annual relative accuracy audit testing (NSPS Subpart Db, Part 70) using EPA Method 7E (2014) for NO_x and Method 3A (2017a) for O_2. Calculation of NO_x emissions use the appropriate F factor, a value that relates the required combustion gas volume to fuel energy input, as described in EPA Method 19 (2017b). Flue gas analysis for O_2 and CO_2 are performed in accordance with Method 3A (2017a) using an infrared analyzer to allow for calculation of the flue gas dry molecular weight.

The CEMS and UAS/Kolibri data were reduced to a common basis for comparison of results. Emission factors, or mass of NO_x per mass of fuel carbon burned, and emission rates, or mass of NO_x per energy content of the fuel, were calculated from the sample results. The determination of emission factors, mass of pollutant per mass of fuel burned, depends upon foreknowledge of the fuel composition, specifically its carbon concentration, and its supply rate. The carbon in the fuel is presumed for calculation purposes to proceed to either CO_2 or CO, with the minor carbon mass in hydrocarbons and PM ignored for this source type. Concurrent emission measurements of pollutant mass and carbon mass (as CO_2 + CO) can be used to calculate total emissions of the pollutant from the fuel using its carbon concentration and fuel burn rate.

The UAS/Kolibri emission factors were calculated from the mass ratio of NO + NO_2 with the mass of CO + CO_2 resulting in a value with units of mg NO_x kg^{-1} C. CO_2 concentrations were corrected for upwind background concentrations. CEMS values of O_2 and fuel flowrate were used to calculate stack flowrate using US EPA Method 19 (2017b). This Method requires the fuel higher heating value and an F factor (gas volume per fuel energy content, e.g., m^3 $kcal^{-1}$ (ft^3 BTU^{-1})) to complete this calculation. For natural gas, the F factor is 967 m^3 10^{-6} kcal (8,710 ft^3 10^{-}

^{6} BTU) (Table 19-2, EPA Method 19 (2017b)). The concentration, stack flowrate, and fuel flowrate data allow determination of NO_x and C emission rates.

3 Results and Discussion

The UAS/Kolibri team easily found the stack plumes at both locations using the wind direction and CO_2 telemetry data transmitted to the ground operator. Use of an infra-red (IR)/visible camera on a second UAS at St. Charles for some of the flights aided more rapid location of the plume and positioning of the UAS/Kolibri. Gas concentration fluctuations were rapid and of high magnitude as observed in a representative trace in Figure 2. CO_2 concentrations to 10,000 ppm were observed; the relatively lower average CO_2 concentrations reflect the rapid mixing and entrainment of ambient air causing dilution.

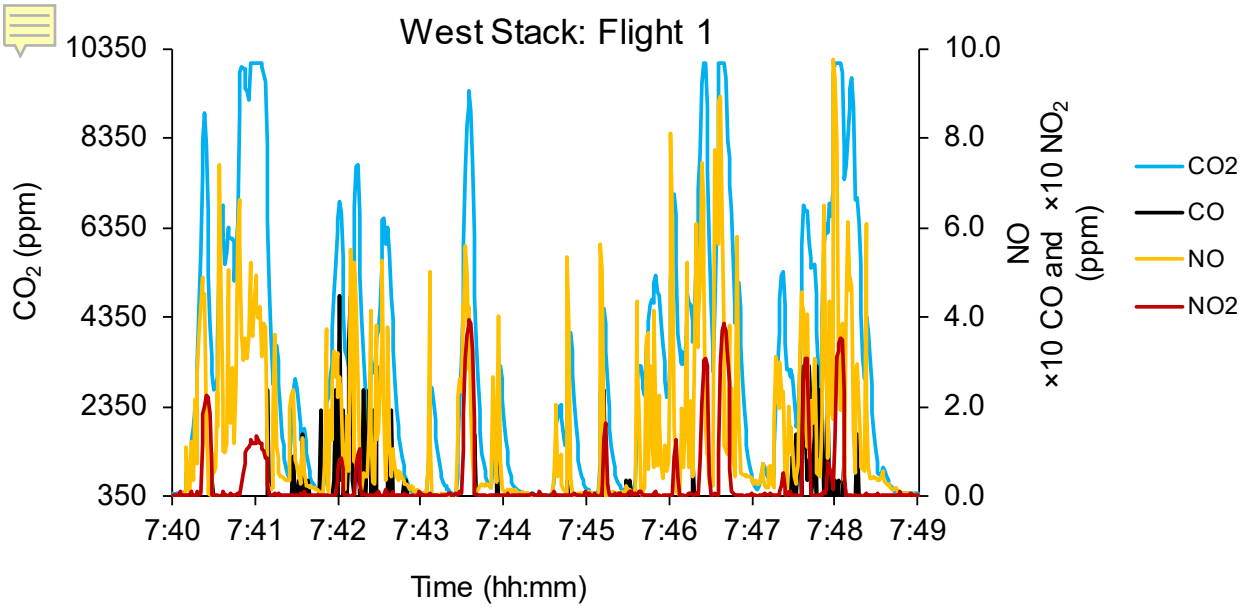

Figure 2. Example of UAS/Kolibri-measured plume concentrations from the St. Charles West Boiler. Data reported at 1 Hz.

Sampling data and emission factors from the UAS/Kolibri are shown in Tables 3, 4, and 5 for the Midland, St. Charles east stack, and St. Charles west stack, respectively. Eight sampling flights were conducted at the Midland site, five on the St. Charles East boiler, and nine on the St. Charles West boiler. Both boilers at the Midland site were operated under the same conditions, so their results have been presented together. Flight times averaged 14 min (10 % relative standard deviation (RSD)) at the Midland facility and just over 20 min (10 % RSD) at the St. Charles facility. The shorter flight times in Midland were due to lower UAS battery capacity caused by colder temperatures (the sampling temperatures in the plume averaged 10±3°C). The average, multi-concentration drift for each of the sensors, tested at both locations after each sampling day, was less than ±3%. The NO2-D4 sensor showed higher drift (average 8.6%) at one location for the highest concentration of its calibration gas (10.4 ppm). This had minimal effect on the emission factor calibrations as the measured NO_2 in the plume was actually less than 1 ppm, a range where the drift was much lower, and NO_2 is a minor contributor to the measured NO_x species.

Average plume NO_x concentrations were 0.88±0.32 ppm at Midland and 1.22 ppm and 2.41 ppm at the two St. Charles boilers with an average RSD of 37 %, 36 %, and 12 %, respectively. The NO emission factor was typically 97 % of the total NO_x, with the NO_2 providing the minor balance.

Table 3. Midland UAS/Kolibri Sampling Data and Emission Factors.

Date	Flight	Flight time (hh:mm:ss)			NO_2	NO	NO_x	Avg. CO_2
	#	Up	Down	Total	mg kg^{-1} C	mg kg^{-1} C	mg kg^{-1} C	ppm
11/14/2018	1	10:29:00	10:43:00	00:14:00	201	618	819	1213
11/14/2018	2	11:13:04	11:28:28	00:15:24	186	624	810	1138
11/14/2018	3	12:54:17	13:08:47	00:14:30	230	659	889	2948
11/14/2018	5	13:27:40	13:42:05	00:14:25	99	570	669	4658
11/15/2018	6	10:24:20	10:39:30	00:15:10	61	394	454	3703
11/15/2018	7	10:41:36	10:52:40	00:11:04	84	397	481	3983
11/15/2018	8	10:55:10	11:10:10	00:15:00	126	398	524	4781
Average				**00:14:13**	**141**	**523**	**664**	**3203**
Stand. Dev.				**00:01:28**	**65**	**121**	**179**	**1514**
RSD (%)				**10**	**46**	**23**	**27**	**47**

Flight # 4 excluded from calculations as CO was observed, which originated from a cycling second boiler.

Table 4. St. Charles East Stack UAS/Kolibri Sampling Data and Emission Factors.

Date	Flight	Flight time (hh:mm:ss)			NO_2	NO	NO_x	Avg. CO_2
	#	Up	Down	Total	mg kg^{-1} C	mg kg^{-1} C	mg kg^{-1} C	ppm
07/23/2019	1	09:49:00	10:07:00	00:18:00	1	1442	1442	2305
07/23/2019	2	10:12:00	10:34:00	00:22:00	15	1461	1476	2526
07/23/2019	3	10:45:00	11:08:00	00:23:00	5	1534	1539	785
07/23/2019	4	11:11:00	11:31:00	00:20:00	101	1684	1785	1082
07/23/2019	5	11:52:00	12:01:00	00:09:00	107	2110	2217	1923
Average				**00:20:45**	**30**	**1530**	**1560**	**1675**
Stand. Dev.				**00:02:13**	**47**	**110**	**155**	**869**
RSD (%)				**11**	**155**	**7.2**	**9.9**	**52**

Flight # 5 was not included in the average as elevated CO concentrations were detected, likely from other sources in the facility.

Table 5. St. Charles West Stack UAS/Kolibri Sampling Data and Emission Factors.

Date	Flight	Flight time (hh:mm:ss)			NO_2	NO	NO_x	Avg. CO_2
	#	Up	Down	Total	mg/kg C	mg/kg C	mg/kg C	ppm
07/24/2019	1	07:31:00	07:49:00	00:18:00	25	1366	1391	3221
07/24/2019	2	07:52:00	08:16:00	00:24:00	49	1263	1312	3503
07/24/2019	3	08:19:00	08:38:00	00:19:00	87	1420	1507	3415
07/24/2019	4	09:23:00	09:46:00	00:23:00	65	1341	1406	4509
07/24/2019	5	09:49:00	10:11:00	00:22:00	47	1296	1343	4813

07/24/2019	6	10:16:00	10:36:00	00:20:00	52	1299	1351	3773
07/24/2019	7	10:38:00	11:00:00	00:22:00	53	1316	1369	4194
07/24/2019	8	11:51:00	12:13:00	00:22:00	90	1460	1549	3129
07/24/2019	9	13:17:00	13:39:00	00:22:00	47	1464	1511	3606
Average				**00:21:20**	**57**	**1358**	**1416**	**3796**
Stand. Dev.				**00:01:56**	**21**	**74**	**86**	**586**
RSD (%)				**9**	**36**	**5.5**	**6.0**	**15**

Table 6 presents the average O_2 and NO_x measurement results and the fuel supply rate at both locations. Values for natural gas supply, adjusted for the C_2H_6 and H_2 composition of the St. Charles fuel, were used to calculate the fuel carbon supply rate. These data allow calculation of the emission factor, mass of NO_x to the mass of carbon, reported in Table 7.

Table 6. Multi-Run Average Stack CEMS Data

	Midland	St. Charles	
	Both Boilers	East Boiler	West Boiler
O_2 (%)	8.2	4.9	4.5
NO_x (ppm)	15.7	50.4	42.9
Fuel rate	39.3 10^6 kJ h^{-1}	155.2 10^6 kJ h^{-1}	177.8 10^6 kJ h^{-1}

Table 7. Comparison of Average NOx Emission Factors from CEMS and UAS/Kolibri

Run-Averaged NOx Emission Factor, mg NO_x kg^{-1} C (± 1 std dev)			
	Midland	St. Charles	
	Both Boilers	East Boiler	West Boiler
CEMS	612 ± 10	1555 ± 50	1303 ± 29
UAS/Kolibri	664 ± 179	1560 ± 155	1416 ± 86
RPD: CEM & UAS/Kolibri, %	8.2	0.3	8.3

The UAS/Kolibri NO_x emission factor for Midland is 8 % higher than the simultaneous CEMS value. For the East and West boilers at St. Charles, the UAS/Kolibri NO_x emission factor value is <1 % and 8 % higher, respectively, than the CEMS values. The difference for the UAS/Kolibri in Midland may be attributed in part to the extremely cold temperature affecting the performance of the electrochemical sensors. The standard deviations for the CEMS data are based on the run-average NO_x values for each test. These values were calculated based on 10 sec averaging for the Midland tests, 60 sec averaging in St. Charles, and 1 sec averaging for the UAS/Kolibri. Higher standard deviations for the UAS/Kolibri are predictable given the rapidly changing values and wide range (~0-10 ppm) of NO_x data observed in Figure 2. Difference testing for the CEMS and UAS/Kolibri using $\alpha = 0.05$ and assumed unequal variances indicate that only the West Boiler and UAS/Kolibri are statistically distinct.

The emission rates calculated from the UAS/Kolibri data are 5.6 kg NO_x $\bullet 10^{-3}$ kJ, 14.6 kg NO_x $\bullet 10^{-3}$ kJ, and 13.3 kg NO_x $\bullet 10^{-3}$ kJ (0.013, 0.034, and 0.031 lbs NO_x $\bullet 10^{-6}$ BTU), respectively, for the Midland, East St. Charles, and West St. Charles boilers, below the regulatory standard of 15.5 kg NO_x $\bullet 10^{-3}$ kJ (0.036 lbs NO_x $\bullet 10^{-6}$ BTU). The emission factors were also calculated as carbon-weighted values to reflect potential differences in plume sampling efficiency between runs. The Midland, East St. Charles, and West St. Charles UAS/Kolibri emission factors were, respectively, 607, 1525, and 1409 mg NO_x kg^{-1} C. These amounted to relative percent differences of 0.8, 1.9, and 7.8 % between the CEM and UAS/Kolibri values, for an overall run-weighted average difference of 5.6 %. The difference between the CEM readings and those from the Kolibri weighted by the carbon collection amounts, reflecting the success at being within the higher plume concentrations, was 3.5 %.

4 Conclusions

This work reports, to our knowledge, the first known comparison of continuous emission monitoring measurements made in a stack with downwind plume measurements made using a UAS equipped with emission sensors.

The UAS/Kolibri system was easily able to find and take measurements from the downwind plume of a natural gas boiler despite lack of any visible plume signature. The telemetry system aboard the Kolibri system reported real time CO_2 concentrations to the operator on the ground, allowing the operator to provide immediate feedback to the UAS pilot on plume location. Comparison of the CEM data with the UAS/Kolibri data from field measurements at two locations showed agreement of NO_x emission factors within 5.6 % and 3.5 % for time-weighted and carbon-collection-weighted measurements, respectively.

Data availability. The tabular and figure data are available at the Environmental Dataset Gateway https://edg.epa.gov/metadata/catalog/main/home.page.

Author contributions. BG was the prime author of the paper and the project lead. JA conducted the Kolibri field testing and data analysis. WM designed the instrument electronics. JR led the UAS group and field test arrangements.

Competing interests. The authors declare that they have no conflict of interest.

Disclaimer. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

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