

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

Brian Gullett¹, Johanna Aurell², William Mitchell¹, Jennifer Richardson³

Response to Referees' Comments

RC1

General Comments Gullett et al. present stack emission measurements of CO₂, CO, NO₂, NO with a UAS, using a non-dispersive infrared optical absorption sensor for CO₂ and electrochemical sensors for the other gases. They report good agreement of the measured NO_x 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 (NO_x 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 NO_x 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 NO₂ sensor (32 sec = t_{95}) still would have had minimal effect over instantaneous emission factors as the NO₂ concentration was much lower than that of NO and so had little effect upon the emission factor calculation. The NO and CO₂ sensors have similar response times (6-9 s) and would have accurately represented the instantaneous emission factor.

3) I.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 NO₂ 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 NO₂ and CO concentrations by 10 times.

6) In Fig. 2 it can be observed that the CO₂ concentration reaches the upper end of the sensor's range several times. Is this always considered in the average?

RESPONSE: CO₂ 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 NO_x 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) 1.186, 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' 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 NO_x 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 be 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 image 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 CO₂ readings were at or above the limits of the detectors, and what assumptions were made about error for such readings.

RESPONSE: CO₂ 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 NO_x 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 NO₂

RESPONSE: We scaled up the NO₂ 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

Brian Gullett¹, Johanna Aurell², William Mitchell¹, Jennifer Richardson³

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.
- The Reference list was updated to AMT format with DOI added and year moved to the end.

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

3
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10
11 **Abstract**

12 Aerial emission sampling of four natural gas boiler stack plumes was conducted using an unmanned aerial system
13 (UAS) equipped with a light-weight sensor/sampling system (the “Kolibri”) for measurement of nitrogen oxide
14 (NO), and nitrogen dioxide (NO₂), carbon dioxide (CO₂), and carbon monoxide (CO). Flights (n = 22) ranged from
15 11 to 24 minutes duration at two different sites. The UAS was maneuvered into the plumes with the aid of real-time
16 CO₂ telemetry to the ground operators and, at one location, a second UAS equipped with an infrared/visible camera.
17 Concentrations were collected and recorded at 1 Hz. The maximum CO₂, CO, NO, and NO₂ concentrations in the
18 plume measured were 10,000 ppm, 7 ppm, 27 ppm, and 1.5 ppm, respectively. Comparison of the NO_x emissions
19 between the stack continuous emission monitoring systems and the UAS/Kolibri for three boiler sets showed an
20 average of 5.6 % and 3.5 % relative percent difference for the run-weighted and carbon-weighted average emissions,
21 respectively. To our knowledge, this is the first evidence for the accuracy performance of UAS-based emission
22 factors against a source of known strength.

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



TOC Art

26 **1 Introduction**

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

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

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

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49 The feasibility of downwind plume sampling using a sensor-equipped UAS was tested on industrial boilers at the
50 Dow Chemical Company (Dow) facilities in Midland, Michigan (MI) and St. Charles, Louisiana (LA). The sensor
51 system was designed and built by the EPA’s Office of Research and Development and the UAS was owned and
52 flown by the Dow Corporate Aviation Group. To determine the comparative accuracy of the measurements, the
53 UAS-based emission factor was compared with the stack continuous emission monitoring systems (CEMS). The
54 target pollutants were nitrogen oxide (NO) and nitrogen dioxide (NO₂) to mimic the stack CEMS measurement
55 methods. Carbon as carbon dioxide (CO₂) and carbon monoxide (CO) were measured on the UAS for the carbon
56 balance method.

57 **2 Materials and Method**

58 Plume sampling tests were conducted on two natural-gas-fired industrial boilers located at Dow’s Midland,
59 Michigan and St. Charles, Louisiana facilities. The Midland boilers are firetube type boilers using low pressure
60 utility supplied natural gas. They are equipped with low NO_x burners and utilize flue gas recirculation to reduce
61 stack NO_x concentrations. The Midland facility burned natural gas with a higher heating value (HHV) of 9,697 kcal
62 m⁻³ (1089 British Thermal Unit (BTU)/ft³). The two tested stacks are 14 m above ground level and 7 m apart. To
63 avoid sampling overlapping plumes, only a single boiler was operating during the testing. The St. Charles boilers are
64 D-type water package boilers using natural gas fuels (high pressure fuel gas (HPFG) and low pressure off-gas
65 (LPOG)). They are equipped with low NO_x burners with flue gas recirculation to reduce stack NO_x concentrations.
66 The boiler stacks are about 20 m apart and reach over 20 m in height above ground level. The St. Charles facility
67 burned natural gas under steady state conditions with a composition of 77.12 % CH₄, 2.01 % C₂H₆, and 19.91 % H₂

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

70 Air sampling was accomplished with an EPA/ORD-developed sensor/sampler system termed the “Kolibri”. The
 71 Kolibri consists of real-time gas sensors and pump samplers to characterize a broad range of gaseous and particle
 72 pollutants. This self-powered system has a transceiver for data transmission and pump control (Xbee S3B, Digi
 73 International, Inc., Minnetonka, MN, USA) from the ground-based operator. For this application, gas concentrations
 74 were measured using electrochemical cells for CO, NO, and NO₂ and a non-dispersive infrared (NDIR) cell for CO₂
 75 (Table 1). All sensors were selected for their applicability to the anticipated operating conditions of concentration
 76 level and temperature as well as for their ability to rapidly respond to changing plume concentrations due to
 77 turbulence and entrainment of ambient air. Each sensor underwent extensive laboratory testing to verify
 78 performance and suitability prior to selection for the Kolibri. Tests included sensor performance (linearity, drift,
 79 response time, noise, detection limits) in response to anticipated field temperatures, pressure, humidity, and
 80 interferences. Additional information from the manufacturers on sensor performance is available from the links in
 81 Table 1. In anticipation of temperatures as low as 0°C at the Midland site and to avoid daily temperature
 82 fluctuations, insulation was added to the Kolibri frame and the sampled gases were preheated prior to the sensor
 83 with the use of a heating element and micro fan inside the Kolibri. All sensors were calibrated before each sampling
 84 day under local ambient conditions. After sampling was completed, the sensors were similarly tested to assess
 85 potential drift.

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

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 91
 92

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

93 ^aNon-dispersive infrared. ^bHz – hertz. ^cZero (0) cal gas = air.

94

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

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100 (ppm equivalent) and linearity within ± 1.5 ppm error at full scale. The NO-D4 was tested to have a response time to
101 95 % of concentration ($T_{95\%}$) of 6.3 ± 0.52 seconds and a noise level of 0.027 ppm. The temperature and relative
102 humidity (RH) operating range is 0 to +50 °C and 15 to 90 % RH, respectively.

103 The NO₂ sensor (NO2-D4) is an electrochemical gas sensor (Alphasense, Essex, UK) which likewise measures by
104 impedance changes. It has a NO₂ detection range of 0-10 ppm with resolution of 0.1 RMS noise (ppm equivalent)
105 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
106 0.015 ppm. The temperature and RH operating range is 0 to +50 °C and 15 to 90 % RH, respectively.

107 Laboratory calibration testing prior to field measurements on both the NO-D4 and NO2-D4 sensors outputs showed
108 their responses to be linearly proportional ($R^2 > 0.99$) over the range of 4- and 5-point calibration gas
109 concentrations. The response times of both sensors were derived using the maximum reference concentration of
110 47.81 ppm for NO and 10.46 ppm of NO₂. The times to reach 95% of the reference concentration, t_{95} , were 6.3 and
111 32.3 sec (RSD (8.2% and 11.8%), respectively, for the NO-D4 and NO2-D4 sensors. These response times are both
112 shorter than those measured simultaneously in the laboratory by a CEM (Ametek 9000^{RM}, Pittsburgh, PA, USA) at
113 37 and 50 sec, respectively, for NO and NO₂.

114 The CO₂ sensor (CO₂ Engine® K30 Fast Response, SenseAir, Delsbo, Sweden) is an NDIR gas sensor and the
115 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
116 % RH, respectively. The CO₂-K30 sensor was measured to have a $t_{95\%}$ response time at 6000 ppm CO₂ of 9.0 ± 0.0
117 seconds and having a noise level of 1.6 ppm. The response time was 4 sec longer than compared to CO₂ measured
118 by a portable gas analyzer (LI-820, LI-COR Biosciences, Lincoln, NE, USA). The sensor and the LI-820 showed
119 good agreement as the measurements showed a R^2 of 0.99 and a slope of 1.01.

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

127 Variations of the Kolibri sampling system allow for measurement of additional target pollutants. These include,
128 particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) including
129 carbonyls, energetics, chlorinated organics, metals from filter analyses, and perchlorate (Aurell et al., 2017; Zhou et
130 al., 2017).
131

132 At both facilities the aviation team from Dow flew their DJI Matrice 600 UAS, a six-motor multicopter
133 (hexacopter), into the plumes with EPA/ORD's Kolibri sensor/sampler system attached to the undercarriage (Figure
134 1). In this configuration of sensors, the Kolibri system weighed 2.4 kg. Typical flight elevations at Midland and St.
135 Charles were 21 and 32 m above ground level (AGL), respectively, and flight durations ranged from 9 to 24 min.
136 At the St. Charles location, the UAS pilot was approximately 100 m from the center point of the two stacks, easily
137 allowing for line of sight operation. A telemetry system on the Kolibri provided real time CO₂ concentration and
138 temperature data to the Kolibri operator who in turn advised the pilot on the optimum UAS location.

139 CEMS on the boiler stacks produced a continuous record of NO_x emission and O₂ concentrations. Stack and CEMS
140 types located at the Midland and St. Charles facilities are shown in Table 2. The stack NO_x analyzer uses a
141 chemiluminescence measurement with a photomultiplier tube and is capable of split concentration range operation:
142 Low (0-180 ppm) and High (0-500 ppm). Its response time is reported as 5 sec. The O₂ analyzer uses a zirconium
143 oxide cell with a measurement range of 0 to 25% and a reported t_{95} of < 10 sec.

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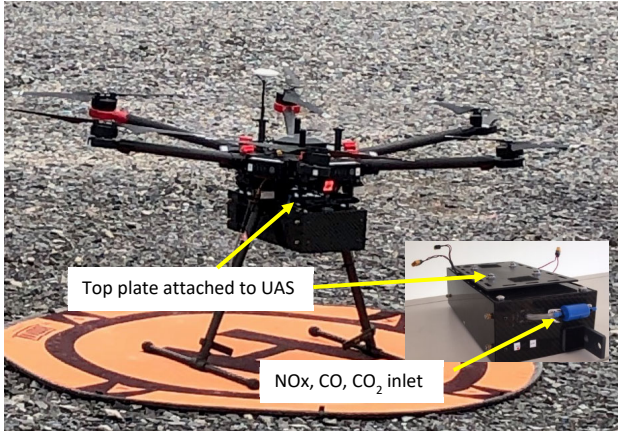


Figure 1. Dow UAS with Kolibri attached to the undercarriage.

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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

151

152 The plant CEMS undergo annual relative accuracy audit testing (NSPS Subpart Db, Part 70) using EPA Method 7E
 153 (2014) for NO_x and Method 3A (2017a) for O₂. Calculation of NO_x emissions use the appropriate F factor, a value
 154 that relates the required combustion gas volume to fuel energy input, as described in EPA Method 19 (2017b). Flue
 155 gas analysis for O₂ and CO₂ are performed in accordance with Method 3A (2017a) using an infrared analyzer to
 156 allow for calculation of the flue gas dry molecular weight.

157 The CEMS and UAS/Kolibri data were reduced to a common basis for comparison of results. Emission factors, or
 158 mass of NO_x per mass of fuel carbon burned, and emission rates, or mass of NO_x per energy content of the fuel,
 159 were calculated from the sample results. The determination of emission factors, mass of pollutant per mass of fuel
 160 burned, depends upon foreknowledge of the fuel composition, specifically its carbon concentration, and its supply
 161 rate. The carbon in the fuel is presumed for calculation purposes to proceed to either CO₂ or CO, with the minor
 162 carbon mass in hydrocarbons and PM ignored for this source type. Concurrent emission measurements of pollutant
 163 mass and carbon mass (as CO₂ + CO) can be used to calculate total emissions of the pollutant from the fuel using its
 164 carbon concentration and fuel burn rate.

165 The UAS/Kolibri emission factors were calculated from the mass ratio of NO + NO₂ with the mass of CO + CO₂
 166 resulting in a value with units of mg NO_x kg⁻¹ C. CO₂ concentrations were corrected for upwind background
 167 concentrations. CEMS values of O₂ and fuel flowrate were used to calculate stack flowrate using US EPA Method
 168 19 (2017b). This Method requires the fuel higher heating value and an F factor (gas volume per fuel energy content,
 169 e.g., m³ kcal⁻¹ (ft³ BTU⁻¹)) to complete this calculation. For natural gas, the F factor is 967 m³ 10⁻⁶ kcal (8,710 ft³ 10⁻⁶

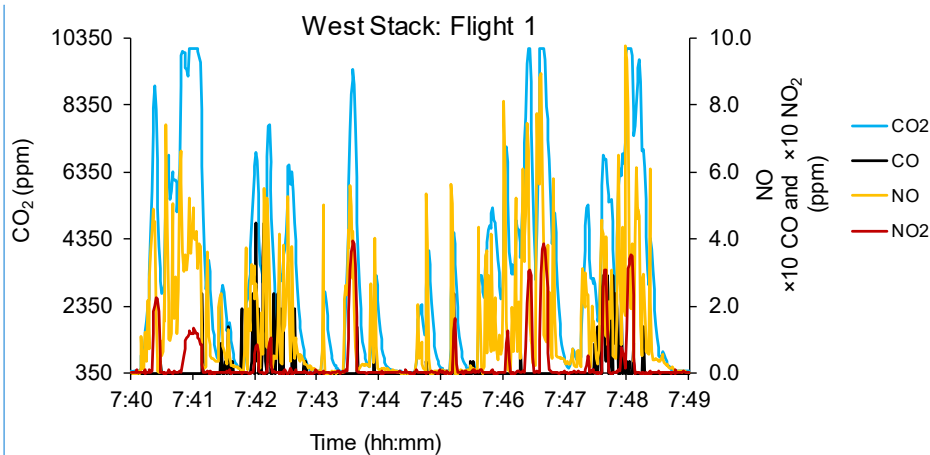
171 ⁶ BTU) (Table 19-2, EPA Method 19 (2017b)). The concentration, stack flowrate, and fuel flowrate data allow
172 determination of NO_x and C emission rates.

173 3 Results and Discussion

174 The UAS/Kolibri team easily found the stack plumes at both locations using the wind direction and CO₂ telemetry
175 data transmitted to the ground operator. Use of an infra-red (IR)/visible camera on a second UAS at St. Charles for
176 some of the flights aided more rapid location of the plume and positioning of the UAS/Kolibri. Gas concentration
177 fluctuations were rapid and of high magnitude as observed in a representative trace in Figure 2. CO₂ concentrations
178 to 10,000 ppm were observed; the relatively lower average CO₂ concentrations reflect the rapid mixing and
179 entrainment of ambient air causing dilution.

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180

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

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183 Sampling data and emission factors from the UAS/Kolibri are shown in Tables 3, 4, and 5 for the Midland, St.
184 Charles east stack, and St. Charles west stack, respectively. Eight sampling flights were conducted at the Midland
185 site, five on the St. Charles East boiler, and nine on the St. Charles West boiler. Both boilers at the Midland site
186 were operated under the same conditions, so their results have been presented together. Flight times averaged 14 min
187 (10 % relative standard deviation (RSD)) at the Midland facility and just over 20 min (10 % RSD) at the St. Charles
188 facility. The shorter flight times in Midland were due to lower UAS battery capacity caused by colder temperatures
189 (the sampling temperatures in the plume averaged 10±3°C). The average, multi-concentration drift for each of the
190 sensors, tested at both locations after each sampling day, was less than ±3%. The NO₂-D4 sensor showed higher
191 drift (average 8.6%) at one location for the highest concentration of its calibration gas (10.4 ppm). This had minimal
192 effect on the emission factor calibrations as the measured NO₂ in the plume was actually less than 1 ppm, a range
193 where the drift was much lower, and NO₂ is a minor contributor to the measured NO_x species.

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194 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.
195 Charles boilers with an average RSD of 37 %, 36 %, and 12 %, respectively. The NO emission factor was typically
196 97 % of the total NO_x, with the NO₂ providing the minor balance.

201

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

Date	Flight #	Flight time (hh:mm:ss)			NO ₂ mg kg ⁻¹ C	NO mg kg ⁻¹ C	NO _x mg kg ⁻¹ C	Avg. CO ₂ ppm
		Up	Down	Total				
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

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

204

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

Date	Flight #	Flight time (hh:mm:ss)			NO ₂ mg kg ⁻¹ C	NO mg kg ⁻¹ C	NO _x mg kg ⁻¹ C	Avg. CO ₂ ppm
		Up	Down	Total				
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

206 *Flight # 5 was not included in the average as elevated CO concentrations were detected, likely from other sources*
207 *in the facility.*208 **Table 5. St. Charles West Stack UAS/Kolibri Sampling Data and Emission Factors.**

Date	Flight #	Flight time (hh:mm:ss)			NO ₂ mg/kg C	NO mg/kg C	NO _x mg/kg C	Avg. CO ₂ ppm
		Up	Down	Total				
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

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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

209

210 Table 6 presents the average O₂ and NO_x measurement results and the fuel supply rate at both locations. Values for
 211 natural gas supply, adjusted for the C₂H₆ and H₂ composition of the St. Charles fuel, were used to calculate the fuel
 212 carbon supply rate. These data allow calculation of the emission factor, mass of NO_x to the mass of carbon, reported
 213 in [Table 7](#).

214

215 **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

216

217 **Table 7. Comparison of Average NO_x Emission Factors from CEMS and UAS/Kolibri**

	Run-Averaged NO _x 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

218

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

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230 The emission rates calculated from the UAS/Kolibri data are 5.6 kg NO_x •10⁻³ kJ, 14.6 kg NO_x •10⁻³ kJ, and 13.3 kg
231 NO_x •10⁻³ kJ (0.013, 0.034, and 0.031 lbs NO_x •10⁻⁶ BTU), respectively, for the Midland, East St. Charles, and West
232 St. Charles boilers, below the regulatory standard of 15.5 kg NO_x •10⁻³ kJ (0.036 lbs NO_x •10⁻⁶ BTU). The emission
233 factors were also calculated as carbon-weighted values to reflect potential differences in plume sampling efficiency
234 between runs. The Midland, East St. Charles, and West St. Charles UAS/Kolibri emission factors were, respectively,
235 607, 1525, and 1409 mg NO_x kg⁻¹ C. These amounted to relative percent differences of 0.8, 1.9, and 7.8 % between
236 the CEM and UAS/Kolibri values, for an overall run-weighted average difference of 5.6 %. The difference between
237 the CEM readings and those from the Kolibri weighted by the carbon collection amounts, reflecting the success at
238 being within the higher plume concentrations, was 3.5 %.

239 4 Conclusions

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

242 The UAS/Kolibri system was easily able to find and take measurements from the downwind plume of a natural gas
243 boiler despite lack of any visible plume signature. The telemetry system aboard the Kolibri system reported real time
244 CO₂ concentrations to the operator on the ground, allowing the operator to provide immediate feedback to the UAS
245 pilot on plume location. Comparison of the CEM data with the UAS/Kolibri data from field measurements at two
246 locations showed agreement of NO_x emission factors within 5.6 % and 3.5 % for time-weighted and carbon-
247 collection-weighted measurements, respectively.

248

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

251

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

255

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

257

258 Disclaimer. The views expressed in this article are those of the authors and do not necessarily represent the views or
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260

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265

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