

Field determination of multipollutant, open area combustion source emission factors with a hexacopter unmanned aerial vehicle[☆]



J. Aurell^a, W. Mitchell^b, V. Chirayath^c, J. Jonsson^d, D. Tabor^b, B. Gullett^{b,*}

^a University of Dayton Research Institute, Dayton, OH 45469, USA

^b U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, USA

^c National Aeronautics and Space Agency, Ames Research Center, Laboratory for Advanced Sensing, Earth Science Division, Moffett Field, CA 94305, USA

^d Stinger Ghaffarian Technologies, Inc., Moffett Field, CA 94035, USA

HIGHLIGHTS

- An unmanned hexacopter aircraft was coupled to an emission sampler.
- The system was flown into 84 combustion plumes.
- Gas and particles were sampled to determine emission factors.
- The system measured particulate matter, metals, volatile and semi-volatile organics.
- This system can safely and efficiently sample open area emission sources.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 May 2017

Received in revised form

21 July 2017

Accepted 25 July 2017

Available online 28 July 2017

Keywords:

Multicopter

Plume

Sensor

Drone

Sampler

ABSTRACT

An emission sensor/sampler system was coupled to a National Aeronautics and Space Administration (NASA) hexacopter unmanned aerial vehicle (UAV) to characterize gases and particles in the plumes emitted from open burning of military ordnance. The UAV/sampler was tested at two field sites with test and sampling flights spanning over 16 h of flight time. The battery-operated UAV was remotely maneuvered into the plumes at distances from the pilot of over 600 m and at altitudes of up to 122 m above ground level. While the flight duration could be affected by sampler payload (3.2–4.6 kg) and meteorological conditions, the 57 sampling flights, ranging from 4 to 12 min, were typically terminated when the plume concentrations of CO₂ were diluted to near ambient levels. Two sensor/sampler systems, termed “Kolibri,” were variously configured to measure particulate matter, metals, chloride, perchlorate, volatile organic compounds, chlorinated dioxins/furans, and nitrogen-based organics for determination of emission factors. Gas sensors were selected based on their applicable concentration range, light weight, freedom from interferences, and response/recovery times. Samplers were designed, constructed, and operated based on U.S. Environmental Protection Agency (EPA) methods and quality control criteria. Results show agreement with published emission factors and good reproducibility (e.g., 26% relative standard deviation for PM_{2.5}). The UAV/Kolibri represents a significant advance in multipollutant emission characterization capabilities for open area sources, safely and effectively making measurements heretofore deemed too hazardous for personnel or beyond the reach of land-based samplers.

Published by Elsevier Ltd.

[☆] This article has been through the EPA's peer and administrative review process. The views expressed in this article are those of the authors and do not necessarily reflect the views or policies of the U.S. EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

* Corresponding author.

E-mail address: gullett.brian@epa.gov (B. Gullett).

1. Introduction

Characterizing emissions from open area sources such as fires poses unique challenges to fully quantifying the release of pollutants over a wide area. Short of sampling the whole emission plume, the carbon balance method (Nelson, 1982) is often used for combustion sources. The carbon balance method relies on sampling a subset of the emissions and relating that value back to the original fuel. The method employs co-sampling the target emissions along with carbon species such as CO₂ and CO and, with knowledge of the carbon content in the combustible fuel, allows calculation of an emission factor as mass of pollutant per mass of combusted fuel. These emission factors are used in dispersion models (for example Bjorklund et al., 1998) to predict exposure and environmental deposition as well as in emission inventories to set source priorities.

The challenges of sampling open area combustion sources include representative sampling of a wind-driven, mixing, and convective plume. Proximity to the source may present hazards to personnel and equipment alike. Sampling at a distance raises challenges of securing sufficient sample to exceed detection limits from a diluted plume. Solutions to quantifying these hard to sample sources often include aerial sampling of the plume. Airplanes equipped with gas samplers (Yokelson et al., 2013; Burling et al., 2011) have used the carbon balance method and plume transects (Lavoie et al., 2017) to determine emission factors. Tethered aerostats (helium-filled balloons) equipped with gas/particle samplers have been employed for oil fires at sea (Aurell and Gullett, 2010), prescribed forest fires (Aurell et al., 2015a), and open burning and open detonation of military ordnance (Aurell et al., 2011, 2015b). Both aerial sampling technologies have disadvantages. Airplanes can be expensive and can require long lead times to schedule. The speed of airplanes can limit the transect residence time in narrow plumes, limiting the sample size, resulting in non-detects. Many emission source types preclude the use of low-flying aircraft. Aerostats solve some of these issues but present other difficulties including the presence of obstacles to tethers, the need for a large ground-based crew, safety considerations, logistical issues such as the supply of helium cylinders, and limited freedom of movement.

The confluence of developments in global positioning system (GPS) technology, battery power density, miniaturization of circuitry, small gas sensors, carbon fiber materials, 3D printers to create custom structures, and unmanned aerial system (UAV) technology have erased many of the barriers to aerial emission sampling. Recent advances have demonstrated the use of UAV for atmospheric (Peng et al., 2015), laboratory-generated (Alvarado et al., 2017), and surf zone (Brady et al., 2016) particulate matter (PM) distributions. Volcano measurements of sulfur gas species have been measured by sensor-equipped UAVs (McGonigle et al., 2008; Shinohara, 2013). Multisensor-equipped UAVs have been tested on a stationary diesel engine (Villa et al., 2016) and on a roadway tunnel (Chang et al., 2016).

Applications to field sources involving multiple pollutant types, particularly trace air toxics, and determination of source emission factors, are not yet demonstrated. Preliminary laboratory and field results of a UAV-based emission sampler measuring open area combustion emissions showed emission factors consistent with those from an aerostat-lofted system (Zhou et al., 2016). This current paper extends this work, describing field applications of a more comprehensive UAV-based sensor/sampling system (termed the “Kolibri”) for characterizing gas and particle emissions from open area sources. Sensors/samplers included CO, CO₂, and particulate matter (PM_{2.5}), and novel measurement of metals, chloride, perchlorate, volatile organic compounds, chlorinated dioxins/furans, and nitrogen-based organics. The system performance is

demonstrated at three military open burn campaigns at the Radford (Virginia) and McAlester (Oklahoma) Army Ammunition Plants (RFAAP and MCAAP, respectively) where hazardous, obsolete, and off-specification ordnance is demilitarized. These open area sources are particularly challenging, as the events are short in duration, typically less than 5 s, and the rapid heat release gives rise to a fast-moving, convectively-driven plume. The potential hazards to personnel and equipment require careful consideration. These challenges have been successfully addressed with the use of a highly mobile UAV coupled to an instrumented system with fast-response/recovery sensors and high throughput samplers. The performance of the UAV is characterized by its ability to maneuver into the plume, maintain position, and follow the wind-driven plume. The functioning of the Kolibri system is described in terms of concentration determinations and emission factor reproducibility.

2. Method

The Department of Defense enlisted NASA to fly their UAV into the plumes from open burning of obsolete and hazardous military ordnance while carrying a lightweight battery operated system of gas and particle samplers/sensors (termed the “Kolibri”) developed and operated by the U.S. Environmental Protection Agency (EPA) and the University of Dayton Research Institute (UDRI). The systems were used at two test sites in Virginia and Oklahoma, USA.

2.1. Test sites and materials

Both tests sites were U.S. Army ammunition facilities. The Radford Army Ammunition Plant (RFAAP) is located in the rolling hills of southwest Virginia, approximately 5 km northeast of the city of Radford, Virginia (37° 11' 35.93" N; 80° 31' 16.35" W). RFAAP lies along the New River in the relatively narrow northeastern corner of the valley. The RFAAP site consists of eight pairs of burn pans in a 420 m row. Trees and a river parallel the burn pan row, separated by approximately 15 m. On the other side of the pan row, a tree-covered ridge forms the other side boundary, approximately 65 m from the pans. The pans were loaded with off-specification rocket motor propellants and manufacturing process waste (“skid” waste).

The second sampling site is located at the McAlester Army Ammunition Plant (MCAAP). MCAAP is in central Oklahoma, approximately 220 km south of Tulsa (34° 48' 50" N; 95° 54' 28" W). The site's terrain is fairly level, surrounded by fields, and centrally located between pine forests, with the shortest distance from the pan site to the tree line being 142 m. MCAAP conducts open burning of projectile propellants that are excess, obsolete, or unserviceable.

RFAAP's rocket motor propellants consist primarily of nitrocellulose and nitroglycerin (NG); sampling targeted residual nitrocellulose and other nitroaromatics to evaluate the presence of unburned propellant and its combustion byproducts. The rocket motor propellants were bagged and placed into a 5 m × 2 m pan after which they were remotely ignited using an electric arming and ignition coil. Typically, a total of about 1300 kg of propellant was placed in the three pans which were ignited over the course of an hour. The skid waste contained a variety of waste materials from propellant manufacture totaling between 227 and 736 kg. To assist the skid waste combustion, wood pallets, corrugated cardboard sheets, and diesel fuel were added to each pan. The skid waste pans were similarly ignited remotely but in three single-pan burns per day. Eight days of testing at RFAAP in a two-week period saw 25 UAV/Kolibri plume sampling flights. The total flight time including UAV test flights was 7 h 30 min.

MCAAPs open burning material consisted of projectile propellants (155 mm, M67, and M17). The open burn (OB) grounds consist of five pad locations, each with five pans. The propellant burn is initiated by igniting a detonation cord fuse which serves as a timer. Burns consisted of 360 kg of propellant in each pan. Fourteen days of testing resulted in 32 UAV/Kolibri sampling flights at MCAAP. Including UAV tests flights, a combined flight time of 8 h 55 min was undertaken.

2.2. The unmanned aerial vehicle

NASA's UAV is a DJI Innovations Matrice 600 (M600) hexacopter with 44.5 cm arm length, 32.7 cm center frame diameter, and 55.4 cm height, including landing gear (Fig. 1). The M600 is powered by six 22.2 VDC lithium polymer batteries. The aircraft weight is 9.1 kg, and it has a 15.1 kg maximum acceptable gross take-off weight. The maximum transmission distance is 5 km with a Class G airspace maximum operating altitude of 122 m. An in-field test of transmission capability showed no loss in signal strength at a distance of 1025 m. The height accuracy is ± 0.1 m from a barometrically-corrected global position satellite (GPS) readout. The M600 is equipped with the A3 Flight Controller with ground control station and remote control stick functions, using a Lightbridge 2 link 2.4 GHz telemetry system. The A3 autopilot supplied by DJI displays voltage, GPS signal strength, and telemetry in real time. The A3 uses a multi-rotor stabilization controller for navigation, flight controls, and autopilot with an inertial measurement unit (IMU) and GPS. The M600 can fly preprogrammed flight paths or be manually controlled by the pilot. The pilot can initiate an automatic controlled or manual landing. The unit has a return-to-home function when the batteries reach a preset charge threshold. An array of automatic response actions covers all event contingencies such as loss of Command & Control signal, loss of GPS signal, geofence breach, propeller/motor failure, or low voltage. The M600 has navigational LED lights for night time, line of sight operation. The combined UAV and emission sampling payload, flight procedures, safety review, and operating procedures were certified for aircraft worthiness by NASA Ames' Air Flight Safety Review Board (AFSRB) and Flight Readiness Review Board (FRRB).

2.3. Emission targets and sampling method

The target emission species for both sites and associated sampling and analytical methods are included in Table 1.

2.4. The Kolibri sensor/sampler

The Kolibri system is comprised of lightweight samplers,

pumps, sensors, a GPS unit, a microcomputer, and a radio module surrounded by a carbon fiber frame (detailed in Zhou et al., 2016). The samplers and sensors were selected based on weight, power needs, and function, the latter particularly in regard to response time and recovery time, as plume sampling often involves rapid swings from ambient to elevated pollutant concentration levels. Two basic configurations of the Kolibri ("Oden" and "Loke") sample multiple pollutants; weight limitations preclude including all of the current samplers/sensors on a single model and some analytes require the same pump, precluding simultaneous sampling. Oden can be outfitted with any of the sensor/samplers except for the semivolatile sampler which is included on Loke. Both Kolibris require CO₂ and CO sensors so that pollutants can be measured in a ratio to sampled carbon. Then, with knowledge of the fuel's carbon composition, the pollutant per mass of fuel or emission factor, can be determined.

Typical Kolibri configurations for Oden weigh 3.2 kg within a 16.5 cm \times 17.8 cm \times 31.7 cm volume. Loke contains the larger pump motor for sampling air at a high flowrate (550 L min⁻¹) so its weight is 4.6 kg within a 21.6 cm \times 26.0 cm \times 45.7 cm volume. Kolibri units were secured to the base of the M600 using custom carbon fiber mounting plates and eight (8) ¼-20 stainless steel machine screws and hex nuts. Non-sampling tests for flight endurance to 20% depth of battery discharge determined flight time limits to be 17 and 25 min for the Oden and Loke Kolibri sampler payloads, respectively.

The Kolibri's data acquisition system (DAS) consists of an onboard Teensy USB-based microcontroller board (Teensy 3.2, PJRC, LLC, Sherwood, OR, USA) running an Arduino-based data acquisition and control program ("TeensyDAQ"). The main assignment for the TeensyDAQ is data logging, and data transmission (1 Hz). The Kolibri main printed circuit board (PCB) consisting of the Teensy microcontroller, connectors, and voltage regulators provides regulated voltages for all the electrical components in the sensor package. Data were stored on board the system using a Teensy universal serial bus (USB)-based microcontroller board (Teensy 3.2, PJRC, LLC, Sherwood, OR, USA) running an Arduino based data acquisition and control program ("TeensyDAQ"). Also included in the DAS is a ground-based computer that is running "KolibriDAQ", a Labview-generated data acquisition and control program, which is used to view live data and run/control the onboard TeensyDAQ via a XBee wireless network (Xbee S1B (2.4 GHz) or S3B (900 MHz), Digi International, Inc., Minnetonka, MN, USA). The XBee wireless network allowed two-way communication for control of samplers (on/off) to minimize sample dilution with ambient air. The Kolibri sampler/sensor system was controlled by a ground operator who received real time CO₂ concentrations (~4 s lag) that further helped position the UAV in the combustion plume. The KolibriDAQ plots real time CO₂ and CO data, displaying sampling time, VOC sampling volume, and performing real time calculations to estimate the total amount of gaseous carbon sampled for the energetic sample. This allows the operator to assess whether sufficient sample volume was collected for each test. Additional details are available from a previous publication (Zhou et al., 2016). During the Radford and the first McAlester campaigns, we discovered that the DJI flight control radio interfered with the Kolibri telemetry radios, causing a reduction in communication range. To address the problem, the Kolibri Digi radios were switched from the 2.4 GHz to 900 MHz bands.

The PM, CO, and CO₂ sensors/sampler (described more fully elsewhere Zhou et al., 2016) consisted of an inertial impactor (SKC, Eighty Four, PA, USA) operating at 10 L min⁻¹ with a 37 mm polytetrafluoroethylene (PTFE) filter, an electrochemical sensor (EC-4-500-CO by SGX Sensortech, High Wycombe, Buckinghamshire, UK), and a nondispersive infrared (NDIR) gas analyzer (RMT Ltd.,



Fig. 1. UAV with attached lightweight instrument sampler, Kolibri – Loke version.

Table 1
Emission targets, sampling sites, and sampling frequency.

Analyte	Instrument/Method	Site	Frequency
CO ₂	NDIR ^a , RMT Ltd. DX6220	BOTH	Continuous
CO	Electrochemical cell, SGX Sensortech EC4-500	BOTH	Continuous
PM _{2.5} ^b	Impactor/Teflon filter/ gravimetric	BOTH	Batch
Nitrocellulose	Glass fiber filter, calorimetric	BOTH	Batch
Nitroglycerin and nitroaromatics	Glass fiber filter, HPLC ^c	BOTH	Batch
Elements	Teflon Filter, XRF ^d	BOTH	Batch
Cr(VI)	Filters, NIOSH ^e 7 605-7 300/LC ^f	RFAAP	Batch
Perchlorate	MCE ^g filter/LC/MS ^h	RFAAP	Batch
Chloride	MCE filter/LC ⁱ	RFAAP	Batch
HCl	Na ₂ CO ₃ filter/LC	RFAAP	Batch
VOCs	Carbotrap 300, Supelco/TD GCMS ^j	BOTH	Batch
PCDDs/PCDFs ^k	Glass fiber filter/HRGC, HRMS ^l	RFAAP	Batch

^a Non-dispersive infrared.

^b Fine particles in the ambient air with particles less than or equal to 2.5 μm in diameter.

^c High performance liquid chromatography.

^d X-ray fluorescence.

^e National Institute for Occupational Safety and Health.

^f Liquid chromatography.

^g Mixed cellulose ester.

^h Liquid chromatography/mass spectrometry.

ⁱ Ion chromatography.

^j Thermal desorption gas chromatography mass spectrometry (GCMS).

^k Polychlorinated dibenzo-*p*-dioxin/polychlorinated dibenzofuran.

^l High resolution gas chromatography/high resolution mass spectrometry.

Moscow, Russia), respectively. The system CO₂ sensor (DX62210/DX6220 OEM Model, RMT Ltd., Moscow, Russia) measures CO₂ concentration by means of NDIR. The sensor underwent a daily four-point calibration in accordance with EPA Method 3A (U.S. EPA Method 3A, 1989) using National Institute of Standards and Technology (NIST)-traceable standards and a precision dilution calibrator (Serinus Cal 2000, American ECOTECH L.C., Warren, RI, USA). The CO sensor (e2V EC4-500-CO) is an electrochemical gas sensor (SGX Sensortech Ltd., High Wycombe, Buckinghamshire, United Kingdom) which measures CO oxidation and changing impedance. A calibration curve calculated in the EPA Metrology Laboratory from 0 to 100 ppm resulted in ±2 ppm error using U.S. EPA Method 3A (U.S. EPA Method 3A, 1989). As with the CO₂ sensor, CO was calibrated on a daily basis. Both the CO and CO₂ concentrations were recorded on the Teensy a USB-based microcontroller board using an Arduino-generated data program. PM_{2.5} was sampled with SKC impactors (761-203B) using a 37 mm tared Teflon filter with a pore size of 2.0 μm via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) of 10 L min⁻¹. Gravimetric measurements were made following the procedures described in 40 CFR Part 50 (40 CFR Part 50, 1987). The constant flow pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg, FL, USA).

A VOC sampler consisted of a Carbotrap 300 stainless steel TD Tube (Supelco Inc., Bellefonte, PA, USA) through which gas was sampled via a constant micro air pump at 160 mL min⁻¹ (3A120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) in accordance with U.S. EPA Method TO-17 (U.S. EPA Method TO-17, 1997). The constant flow pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg, FL, USA) and is turned on and off by the operator or automatically with a user-set CO₂ concentration trigger. The Carbotrap tubes are sampled using thermal desorption coupled to gas chromatography/mass spectrometry methods as per U.S. EPA Method TO-17 (U.S. EPA Method TO-17, 1997).

Plumes were sampled for nitrogen-based energetics through two 15 cm glass fiber filters (Fisher Scientific) with a nominal rate of

500 L min⁻¹ powered by a low voltage MINIJammer brushless blower (Amtek Technology Co., Ltd., Arnold, MD, USA). The blower is triggered by the CO₂ concentration set points using the Kolibri's data acquisition program. The flow rate is measured by a ±5" H₂O Model ASDX pressure differential transducer (Honeywell, Wabash, Indiana, USA) across a Herschel Standard Venturi tube (EPA in-house made). The Venturi tube is specially designed to PCDDmeet the desired sampling rate for the target compound. The Venturi tube is mounted on the outlet of the MINIJammer blower Model 119378-52 (Amtek). The voltage equivalent to this pressure differential is recorded on the onboard Teensy USB microcontroller board, which is calibrated with a Roots meter (Model 5M, Dresser Measurement, Santa Ana, CA USA). A K-type temperature thermistor (Adafruit, New York, NY USA) measures the air temperature exiting the Venturi as well as the ambient temperature. Analytical methods include EPA Method 8330b (U.S. EPA Method 8330B, 2006) for nitroglycerin and possible degradation products and EPA Method 353.2 (U.S. EPA Method 353.2, 1993) (a nitrate-nitrite colorimetric method) for nitrocellulose.

PCDD/PCDF sampling was done by adding a polyurethane foam plug (PUF) inside a glass fiber thimble to the energetic setup. With the pre-filter the sampler flow rate is 450 L min⁻¹. Samples were cleaned up and analyzed using an isotope dilution method based on U.S. EPA Method 23 (U.S. EPA Method 23, 1991). Concentrations were determined using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) with a Hewlett-Packard gas chromatograph 6 890 Series coupled to a Micromass Premier mass spectrometer (Waters Corp., Milford, MA, USA) with an RTX-Dioxin 2, 60 m × 0.25 mm × 0.25 μm film thickness column (Restek Corp., Bellefonte, PA, USA). For analysis of tetra-through octa-CDDs/Fs, Method 8290a (U.S. EPA Method 8290A, 2007) was followed using the isotope dilution method with standards from Cambridge Isotope Laboratories Inc. (Cambridge, MA, USA).

Metal/elemental species are analyzed from the PM collected on the filters. X-ray fluorescence spectrometry (XRF) analysis of the Teflon PM_{2.5} filters used EPA Compendium Method IO-3.3 (U.S. EPA Compendium Method IO-3.3, 1999) and inductively coupled

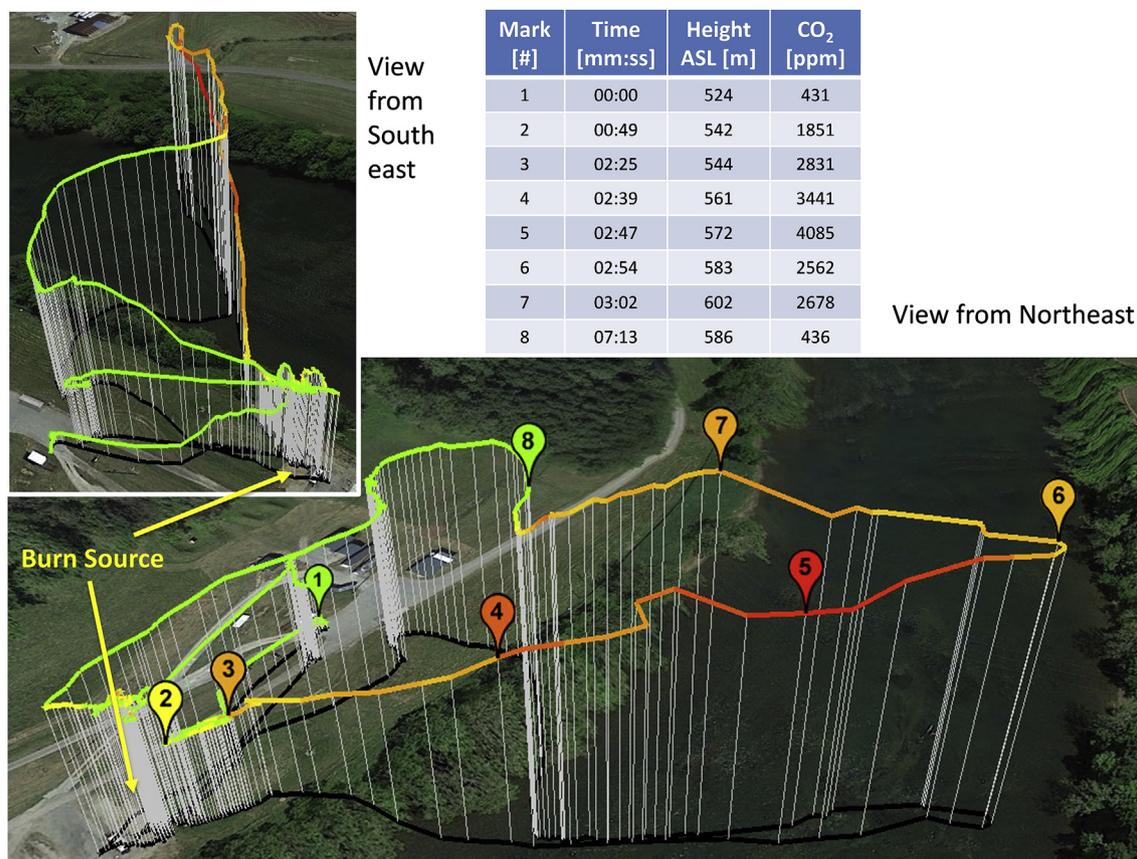


Fig. 2. Two views of a typical UAV/Kolibri flight path at RFAAP while sampling burn emissions. Multicolor flight path indicates CO₂ concentration (plume concentration). Projection downward indicates the ground path as a black line. ASL = Above sea level.

plasma (ICP) using EPA Compendium Method IO-3.4 (U.S. EPA Compendium Method IO-3.4, 1999) were used to identify metals. Specialty analyses for Chrome VI were conducted based on an EPA standard operating procedure (U.S. EPA SOP, 2006). Samples were captured on a bicarbonate-impregnated “acid hardened” cellulose filter through a filter cartridge (Chester LabNet, Tigard, OR, USA) via a constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA) at 9 L min^{-1} .

A similar sampling method was used for the collection of HCl, perchlorate, chlorate, and chloride. Methods for sampling HCl are derived primarily from the methods intended for sampling inhalable HCl to relate to exposure risk. A filter “sandwich” cassette used alkali-impregnated filters following a solid perchlorate and chloride filter (International standard ISO 21438-2:2009, 2009). HCl gas is expected to pass through the first perchlorate/chloride filter and be adsorbed by a second filter coated with Na_2CO_3 . This second filter was analyzed for HCl by ion chromatographic methods specified in U.S. EPA Method 26. Perchlorate was sampled at 5 L min^{-1} through a 37 mm mixed cellulose ester (MCE) filter ($0.8 \mu\text{m}$ pore size) enclosed in a closed-face cassette (SKC Corporation) using a calibrated, constant micro air pump (C120CNSN, Sensidyne, LP, St. Petersburg, FL, USA). The constant flow pump was calibrated with a Gilibrator Air Flow Calibration System (Sensidyne LP, St. Petersburg, FL, USA). Perchlorate salts are captured as a solid on the filter, which assumes no perchloric acid formation. Cassette samples were dissolved/extracted in water, an internal standard added, and then analyzed for perchlorate and chlorate with liquid chromatography/mass spectrometry (LC/MS) and for chloride with ion chromatography.

2.5. Plume sampling operations

Air sampling was accomplished by maneuvering the NASA UAV hexacopter into the plume with the EPA/ORD sampling system called the “Kolibri” straddled underneath the central axis. The UAV was launched approximately 1 min prior to the burn ignitions, set to a safe altitude, and hovered over the expected path of the plume. Heights for the UAV throughout the sampling process were 10–122 m; the UAV was made to follow the plume and, if residual smoldering was observed, brought closer to the source to capture any remaining emissions. Typical downwind distances from the UAV to the source were 50–200 m; visual contact with the UAV was maintained at all times. Optimal contact with the plume was achieved by positioning radio-equipped observers in an orthogonal position to each other and by use of a visible camera with live video transmitted to the UAV operator via the DJI Lightbridge system. The pilot was aided by a Google Earth® screen image tracking the UAV position, orthogonally-positioned spotters in radio communication, and feedback from the Kolibri system’s CO₂ concentration.

2.6. Emission factor calculations

The determination of emission factors, mass of pollutant per mass of fuel burned, depends upon foreknowledge of the fuel composition, specifically its carbon concentration. The carbon in the fuel is presumed for calculation purposes to proceed to either CO₂ or CO, with the minor carbon mass in hydrocarbons, and PM is ignored. Concurrent emission measurements of pollutant mass per

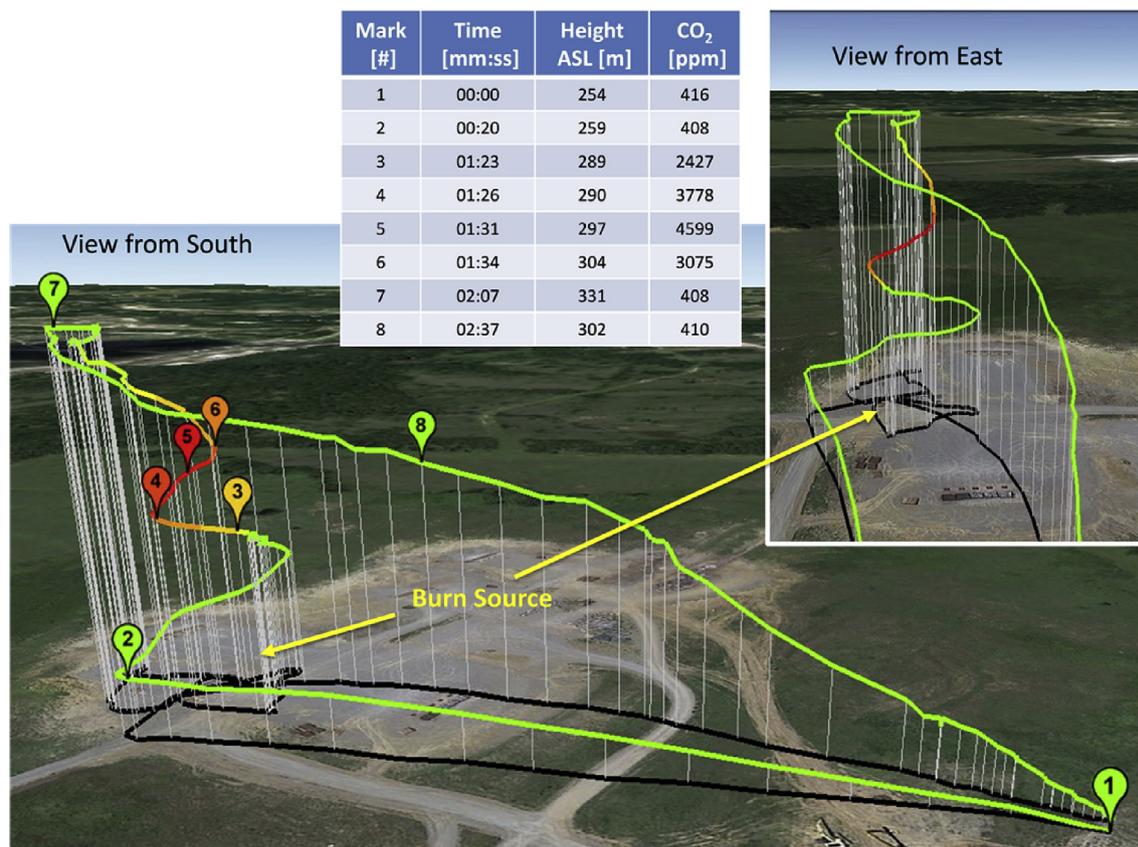


Fig. 3. Two views of a typical UAV/Kolibri flight path at MCAAP while sampling burn emissions. Multicolor flight path indicates CO₂ concentration (plume concentration). Projection downward indicates the ground path as a black line. ASL = Above sea level.

carbon (as CO₂ + CO) can be used to calculate total emissions of the pollutant from the fuel using its carbon concentration.

3. Results and discussion

Typical UAV/Kolibri flight paths at RFAAP and MCAAP are shown in Figs. 2 and 3, respectively. Each figure illustrates the elevation and flight time. At both sites, the Matrice pilot positioned the UAV at a safe height above and slightly downwind of the burn site prior to ignition. After ignition, the UAV was maneuvered into the plume to maximize sample collection efficiency, successfully sampling every plume. The altitude stability in the turbulent convective plumes created typical altitude variations of 1–3 m due to flow instability (qualitative observation).

For plume sampling of an OB, the mobility and positional flexibility of the UAV/Kolibri system had significant advantages over more static sampling systems, such as the tethered balloon system (the Aerostat/Flyer) documented in Aurell et al. (2011, 2015b), or highly mobile systems such as airplanes running plume transects (Lavoie et al., 2017). The mobility of the UAV/Kolibri system allowed the operator to set up a takeoff zone independent of wind direction and at a safe standoff distance for personnel, saving considerable time in predicting wind direction, positioning samplers downwind of the source, and moving personnel from equipment to safe zones. The UAV/Kolibri also showed considerable x-y-z positional flexibility, allowing the operator to adjust to wind shifts and plume rise, maximizing the sampling period within the concentrated portion of the plume. The ability of the UAV/Kolibri to loiter in the plume increased the plume sampling time considerably over use of fixed wing airplanes that must deal with a few seconds of sampling

through the plume before a long, looping return flight.

The performance of the UAV/Kolibri system can be assessed by comparing results with published emission factors and noting the relative standard deviation (precision) of the measurements. While limited data are available to compare the same energetic material and emissions obtained via aerial sampling, some comparisons can be made. One of the critical measures of sampling system performance is the carbon collection efficiency. The carbon collection efficiency measure reflects the ability of the UAV to be in the highest concentration of the combustion plume, measuring carbon as predominantly CO and CO₂. We compared the performance of the UAV/Kolibri system with that of the balloon-lofted instrument package (Aurell et al., 2011) measuring the same propellant type during an open burn. The UAV/Kolibri system for sampling PM_{2.5} doubled the carbon collection rate of the Aerostat/Flyer, collecting 5.2 mg carbon as CO + CO₂ per minute for the McAlester tests. Collection rates of 5.1 mg carbon per min were obtained at Radford on the skid waste. These higher carbon collection rates indicate that the sampler is in a more concentrated part of the plume, increasing the sampling effectiveness.

The UAV/Kolibri system performance can also be assessed by comparing previous emission factors determined by the aforementioned Aerostat/Flyer to those determined using the UAV. Comparisons are made using propellants with identical composition: M67 from this work and M1 from Aurell et al. (2011). PM_{2.5} measurements (this work) are compared with PM₁₀ measurements in previous work (Aurell et al., 2011) without compromise as previous OB sampling has shown that these measurements are indistinct (Aurell et al., 2015b), meaning that all of the particles are of mass median diameter PM_{2.5} or less. We compared M67 propellant

emission factors for PM_{2.5} at McAlester versus M1 propellant emission factors for PM₁₀ at Tooele (Aurell et al., 2011) and versus published airplane-based sampling data (U.S. Army AMMCOM, 1992). The airplane-based plume sampling resulted in a PM₁₀ emission factor of 6.9 g PM₁₀ kg⁻¹ M1 (n = 2, U.S. Army AMMCOM, 1992) while the Aerostat/Flyer had a value of 5.7 g PM₁₀ kg⁻¹ M1 (n = 1, Aurell et al., 2011). In comparison, the UAV/Kolibri at McAlester resulted in an M67 emission factor of 4.0 g PM_{2.5} kg⁻¹ M67 (±1.2 std. dev., n = 9) and 4.8 g PM_{TOT} kg⁻¹ M67 (±2.8 std. dev., n = 4), values statistically consistent with the limited previous data. This agreement is reasonable, given uncertainties in comparable burn methods and the limited number of historical samples, but should be further compared with additional measurements. The PM_{2.5} emission factor is similar to that from the UAV also suggesting that the rotor wash does not reduce the particle sampling by the inertial impactor.

Comparisons of the measurements can also be made with lead, Pb. The UAV/Kolibri emission factor is 2.4 g Pb kg⁻¹ M67 (±0.8 std. dev., n = 9, PM_{2.5}), whereas the Aerostat/Flyer resulted in a value of 4.3 g Pb kg⁻¹ M1 (n = 1, PM₁₀, Aurell et al., 2011). The airplane-based data were below detection limit for Pb (U.S. Army AMMCOM, 1992). Given differences in the propellant amounts and the limited number of data points, these values are tentatively comparable, pending additional data.

Measurement precision can also be used to assess the performance of the sampling system. At McAlester, a total of 20 samples for PM_{2.5} resulted in a sample-number-weighted relative standard deviation of 26.2%. Six samples of PM_{TOT} resulted in a 50% RSD. Likewise, lead (Pb) emissions, determined by analysis of the PM_{2.5} filters (n = 17) at McAlester, resulted in emission factors with a sample-number-weighted relative standard deviation of 32.2%. VOC concentrations, sampled by a sorbent/pump system at McAlester, were measured with an average relative standard deviation of 46% whereas an evacuated canister sampler on the Aerostat/Flyer system got 54% (Aurell et al., 2011), indicating good precision for replicates.

Acknowledgments

This work was sponsored by the Department of the Army, PD Joint Services, Picatinny Arsenal, through Interagency Agreements RW-97-92434401-0/1 and RW-021-92455501-0 with U.S. EPA and Interagency Agreement PDJSFY15PIF-NASA with NASA. J. Aurell was supported by Army Contracting Command, Rock Island Arsenal (Radford) through BAE Ordnance Systems, Inc. (PO #NDF-041116-01) and PD Joint Services (McAlester) through an EPA Interagency Agreement (DW-47-92445401-0/1) with US General Services Administration (Task Order 018 GS05T13BMD001). The authors acknowledge the assistance of Michele Gehring (Coterie Environmental), subcontractor to BAE, with the Radford composition data and Angela Hutten and Joey Hutten, U.S. Army Demilitarization Capabilities Division (AMSJM-ICD), Joint Munitions Command, McAlester AAP with the McAlester logistics and composition data. David Satterfield (NASA) provided expert assistance as the Range Safety Officer in both locations.

References

40 CFR Part 50, 1987. Appendix L. Reference Method for the Determination of Particulate Matter as PM_{2.5} in the Atmosphere. <https://www.gpo.gov/fdsys/pkg/CFR-2014-title40-vol2/pdf/CFR-2014-title40-vol2-part50-appL.pdf>. (Accessed 22 November 2016).

Alvarado, M., Gonzalez, F., Erskine, P., Cliff, D., Heuff, D., 2017. A methodology to monitor airborne PM₁₀ dust particles using a small unmanned aerial vehicle. *Sensors* 17, 343.

Aurell, J., Gullett, B.K., 2010. Aerostat sampling of PCDD/PCDF emissions from the gulf oil spill in situ burns. *Environ. Sci. Technol.* 44, 9431–9437.

Aurell, J., Gullett, B.K., Pressley, C., Tabor, D., Gribble, R., 2011. Aerostat-lofted instrument and sampling method for determination of emissions from open area sources. *Chemosphere* 85, 806–811.

Aurell, J., Gullett, B.K., Tabor, D., 2015. Emissions from southeastern U.S. Grasslands and pine savannas: comparison of aerial and ground field measurements with laboratory burns. *Atmos. Environ.* 111, 170–178.

Aurell, J., Gullett, B.K., Tabor, D., Williams, R.K., Mitchell, W., Kemme, M.R., 2015. Aerostat-based sampling of emissions from open burning and open detonation of military ordnance. *J. Hazard Mater* 284, 108–120.

Bjorklund, J., Bowers, J., Dodd, G., White, J., 1998. Open Burzzning/Open Detonation (OBODM) User's Guide. DPG Document No. DPG-TR-96-008b. U. S. Army Dugway Proving Ground, Dugway, UT. <http://www.epa.gov/ttn/scram/userg/nonepa/obodmvol2.pdf>. (Accessed 14 July 2017).

Brady, J.M., Stokes, M.D., Bonnardel, J., Bertram, T.H., 2016. Characterization of a quadrotor unmanned aircraft system for aerosol-particle-concentration measurements. *Environ. Sci. Technol.* 50, 1376–1383.

Burling, I.R., Yokelson, R.J., Akagi, S.K., Urbanski, S.P., Wold, C.E., Griffith, D.W.T., Johnson, T.J., Reardon, J., Weise, D.R., 2011. Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States. *Atmos. Chem. Phys.* 11, 12197–12216.

Chang, C.-C., Wang, J.-L., Chang, C.-Y., Liang, M.-C., Lin, M.-R., 2016. Development of a multicopter-carried whole air sampling apparatus and its applications in environmental studies. *Chemosphere* 144, 484–492.

International standard ISO 21438-2:2009, 2009. *Workplace Atmospheres — Determination of Inorganic Acids by Ion Chromatography — Part 2: Volatile Acids, except Hydrofluoric Acid (Hydrochloric Acid, Hydrobromic Acid and Nitric Acid)*.

Lavoie, T.N., Shepson, P.B., Gore, C.A., Stirm, B.H., Kaeser, R., Wulle, B., Lyon, D., Rudek, J., 2017. Assessing the methane emissions from natural gas-fired power plants and oil refineries. *Environ. Sci. Technol.* 51, 3373–3381.

McGonigle, A.J.S., Aiuppa, A., Giudice, G., Tamburello, G., Hodson, A.J., Gurrieri, S., 2008. Unmanned aerial vehicle measurements of volcanic carbon dioxide fluxes. *Geophys. Res. Lett.* 35.

Nelson Jr., R.M., 1982. An Evaluation of the Carbon Balance Technique for Estimating Emission Factors and Fuel Consumption in Forest Fires. US Department of Agriculture, Forest Service, Southeastern Forest Experiment Station, Asheville, NC, USA. Research Paper SE-231.

Peng, Z.-R., Wang, D., Wang, Z., Gao, Y., Lu, S., 2015. A study of vertical distribution patterns of PM_{2.5} concentrations based on ambient monitoring with unmanned aerial vehicles: a case in Hangzhou, China. *Atmos. Environ.* 123, 357–369.

Shinohara, H., 2013. Composition of volcanic gases emitted during repeating Vulcanian eruption stage of Shinmoedake, Kirishima volcano. *Jpn. Earth Planet Space* 65, 667–675.

U.S. Army, AMMCOM, January 1992. *Development of Methodology and Techniques for Identifying and Quantifying Products from Open Burning and Open Detonation Thermal Treatment Methods - Field Test Series a, B and C. AD-A250735. Volume 1, Test Summary.* U.S. Army, AMMCOM, Rock Island, IL 61299–66000.

U.S. EPA Compendium Method IO-3.3, 1999. Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy. <http://www.epa.gov/ttnamt1/files/ambient/inorganic/mthd-3-3.pdf>. (Accessed 5 May 2014).

U.S. EPA Compendium Method IO-3.4, 1999. Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy. <http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-4.pdf>. (Accessed 5 May 2014).

U.S. EPA Method 23, 1991. Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources, 40 CFR Part 60, Appendix A. <http://www.epa.gov/ttn/emc/promgate/m-23.pdf>. (Accessed 10 November 2015).

U.S. EPA Method 26. Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Non-Isokinetic Method. <https://www3.epa.gov/ttnemc01/promgate/m-26.pdf> (Accessed 15 July 2016).

U.S. EPA Method 353.2, 1993. Determination of Nitrate-nitrite Nitrogen by Automated Colorimetry. https://www.epa.gov/sites/production/files/2015-08/documents/method_353-2_1993.pdf. (Accessed 18 July 2016).

U.S. EPA Method 3A, 1989. Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure). <http://www.epa.gov/ttn/emc/promgate/m-03a.pdf>. (Accessed 5 May 2014).

U.S. EPA Method 8290A, 2007. Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-resolution Gas Chromatography/high-resolution Mass Spectrometry (HRGC/HRMS). <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8290a.pdf>. (Accessed 21 November 2012).

U.S. EPA Method 8330B, 2006. Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatograph (HPLC). <https://www.epa.gov/sites/production/files/2015-07/documents/epa-8330b.pdf>. (Accessed 18 July 2016).

U.S. EPA Method TO-17, 1997. Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes. <http://www.epa.gov/ttnamt1/files/ambient/airtox/to-17r.pdf>. (Accessed 25 July 2013).

U.S. EPA SOP, 2006. Standard Operating Procedure for the Determination of Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC). <https://www3.epa.gov/ttnamt1/files/ambient/airtox/hexchromsop.pdf>. (Accessed 4 April 2017).

- Villa, T.F., Salimi, F., Morton, K., Morawska, L., Gonzalez, F., 2016. Development and validation of a UAV based system for air pollution measurements. *Sensors* 16.
- Yokelson, R.J., Burling, I.R., Gilman, J.B., Warneke, C., Stockwell, C.E., de Gouw, J., Akagi, S.K., Urbanski, S.P., Veres, P., Roberts, J.M., Kuster, W.C., Reardon, J., Griffith, D.W.T., Johnson, T.J., Hosseini, S., Miller, J.W., Cocker III, D.R., Jung, H., Weise, D.R., 2013. Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires. *Atmos. Chem. Phys.* 13, 89–116. <https://doi.org/10.5194/acp-13-89-2013>.
- Zhou, X., Aurell, J., Mitchell, W., Tabor, D., Gullett, B., 2016. A small, lightweight multipollutant sensor system for ground-mobile and aerial emission sampling from open area sources. *Atm. Env.* 154, 31–41.