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A sampler for atmospheric volatile organic compounds by copter unmanned aerial vehicles

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Abstract. A sampler for volatile organic compounds (VOCs) was developed for deployment on a copter-technology unmanned aerial vehicle (UAV). The sampler was designed to collect VOCs on up to five commercially available VOC-adsorbent cartridges for subsequent offline analysis by thermal-desorption gas chromatography. The sampler had a mass of 0.90 kg and dimensions of 19 cm × 20 cm × 5 cm. Power consumption was <3 Wh in a typical 30 min flight, representing <3% of the total UAV battery capacity. Autonomous sampler operation and data collection in flight were accomplished with a microcontroller. Sampling flows of 100 to 400 sccm were possible, and a typical flow of 150 sccm was used to balance VOC capture efficiency with sample volume. The overall minimum detection limit for the sampling volumes and the analytical method was close to 2 ppt for isoprene and monoterpenes. The sampler was mounted to a commercially available UAV and flown in August 2017 over tropical forest in central Amazonia. Samples were collected sequentially for 10 min each at several different altitude-latitude-longitude collection points. The species identified, their concentrations, and their uncertainties are presented and discussed in the context of the sampler design and capabilities. Finally, design challenges and possibilities for next-generation samplers are addressed.

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1. Introduction

Biogenic volatile organic compound (VOC) emissions from forests vary widely across plant species, ecosystem type, season, time of day, and environmental conditions at many scales, including from 10's to 100's of m (Gu et al., 2017;Fuentes et al., 2000;Goldstein and Galbally, 2007;Alves et al., 2018;Greenberg et al., 2004;Guenther et al., 2006;Klinger et al., 1998;Kuhn et al., 2004;Pugh et al., 2011;Wang et al., 2011). These variations can have significant effects on and be affected by atmospheric chemistry, air quality, and climate (Chameides et al., 1988;Fuentes et al., 2000;Laothawornkitkul et al., 2009;Goldstein et al., 2009;Kesselmeier et al., 2013;Peñuelas and Staudt, 2010). They may also be indicators of ecosystem change, plant health, and stress (Karl et al., 2008;Kravitz et al., 2016;Niinemets, 2010;Peñuelas and Llusià, 2003). Most field observations of biogenic VOC emissions are made from fixed-location towers and tethered balloons or from aircraft flying at high velocities well above the forest canopy (see Table 1 of Alves et al., (2016) for a summary of studies in the Amazon). As such, detailed information on the spatial distribution of emissions at 10's to 100's of meters has been difficult to obtain. Thus, this scale is not represented in current VOC data sets, yet it reflects the primary scale for VOC emission and uptake and is precisely the missing link in advancing our present-day understanding of VOCs in atmospheric chemistry. This information is even more scarce in remote areas, such as the Amazon rainforest, that are very important sources of VOCs to the global atmosphere. In addition, knowledge of VOC concentrations as a function of height throughout the boundary layer is needed to better constrain emissions, chemical reactions, and atmospheric mixing of these compounds. New approaches that are suited to spatially resolved sampling at these intermediate scales is therefore needed by the atmospheric chemistry community.

Small, commercially available unmanned aerial vehicles (UAVs, commonly called drones) have the potential to fill this gap in knowledge due to their extreme maneuverability (Villa et al., 2016). UAVs are available as either fixed wing aircraft, helicopters, or multicopters. Multicopters (most often quad- or hexacopters) offer the advantages of being highly maneuverable and easy to fly, as well as offering straightforward accessory mounting options. Flight durations of up to 45 min and payload capacities of 6 kg are attainable with mid-priced, commercially available copter-type UAVs. Development or adaptation of air sensors for UAV platforms is, however, still in the early stages. To date, several researchers have utilized UAVs to carry sensors to measure atmospheric trace gases in situ (Villa et al., (2016) and references therein.) Commercially available sensors for some trace gases (e.g., CO_2, CO, and NO_x) are sufficiently compact to be carried by a UAV, but these are often limited by insufficient sensitivity or difficult calibration (Cross et al., 2017). *In situ* techniques for quantifying VOCs at the required sensitivity (< 10 ppt) are, however, large and complex instruments that exceed the payload capacity of mid-range UAVs available to most researchers (Lindinger et al., 1998;Millet et al., 2005;Blake et al., 2009;Kim et al., 2013).

As an alternative, the UAV platform offers the possibility to collect air samples for later laboratory analysis. Black et al. (2018) used a commercial quadcopter to collect samples of airborne mercury by drawing air through gold-coated quartz cartridges for later analysis by cold vapor atomic fluorescence spectroscopy. The results showed the ability to resolve vertical concentration profiles above a source and to differentiate between urban and rural mercury concentrations. Although remote control of the sampler was not implemented, the authors suggested this as a possible future improvement. Chang et al. (2016) demonstrated the use of a whole air sampling apparatus mounted on a multicopter UAV platform to collect air samples for off-line analysis. The sampler consisted of a single evacuated 2-L canister with a remote-controlled valve actuated by a separate remote control unit independent of the UAV controller. The flow rate and total sample volume was not monitored during flight. The authors successfully detected VOCs, CO, CO_2, and CH_4 in the collected air samples and were able to distinguish between samples collected upwind and downwind of an exhaust shaft. Both studies cite maneuverability in three dimensions, spatial resolution, and the ability to evaluate emissions from otherwise inaccessible locations as key advantages of UAV-based atmospheric sampling. They also point out flight stability, an easily accessed and symmetrically positioned mounting location, low cost, and lack of engine exhaust as features of battery-powered multicopters that make them particularly well suited for environmental applications. While the ability to detect atmospheric trace species and to map spatial gradients depends strongly upon the target species, including its atmospheric variability and the detection threshold of the analytical method, these several studies suggest that UAV-based sample collection is a viable approach that promises to greatly expand access to previously inaccessible locations and to provide a means to map spatial patterns in atmospheric trace species concentrations.

The use of VOC-adsorbent cartridges to capture VOCs from air with subsequent analysis by thermal-desorption gas-chromatography mass spectrometry (TD-GC-MS) is well established (Woolfenden, 2010a;Pankow et al., 2012). The adsorbent cartridges are small glass or metal tubes, typically 9 cm in length and 0.64 cm in diameter. The cartridges are filled with a sorbent material with a high affinity for VOCs. The cartridges provide a lightweight (10 g), simple, sensitive, and quantitative approach for determining a wide range of VOCs at ambient atmospheric levels. The challenge is to design and construct an automated sample collection system for cartridges suited to deployment on a multicopter UAV.

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The primary scientific requirement of the sampler is that the total mass of analyte collected be greater than the detection limit of the analytical system for that compound. In the case of a volatile organic compounds detected by GC-MS, the detection limit has typically been ca. 10 pg. For a sample volume of a few liters of air, which can be collected in 5 to 15 min by typical flow rates through adsorbent cartridges, this corresponds to a VOC detection limit of less than 10 pptv (Pankow et al., 2012). Commercial detectors are now available with detection limits of < 1 pg, including the GC-ToF-MS used for this study (Hoker et al., 2015), implying an order of magnitude lower detectable VOC mixing ratios. This suggests that detection of VOCs in cartridge samples collected within current multicopter flight durations is feasible. Automated operation of the sampler, controlled either algorithmically based on elapsed time or position, or remotely by sending commands to the sampler during flight, is desirable. Furthermore, the mass and dimensions of the sampler must fit within the payload capacity of available UAV platforms. Herein, the design, operation, and field validation of a VOC sampler using adsorption/thermal desorption cartridges on a mid-size copter-technology UAV that meets these requirements is described, and an example data set collected in central Amazonia including a discussion of uncertainties is presented.

2. Experimental

2.1. Flight platform

The UAV platform was a DJI Matrice 600 Professional Grade (Figure 1), which is a hexacopter design with onboard stabilization. With propeller arms extended, the UAV measured 1.668 m across by 0.759 m high. Without the sampler attached, it weighed 9.6 kg with its six batteries installed (model TB48S; 130 Wh, 18 V). The maximum ascent rate was 5 m s^{-1}, and the maximum horizontal speed was 18 m s^{-1}. It had GPS positioning and maintained two-way

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communication with DJI programs developed for iPad and Android tablet systems. The positioning accuracy was ±0.5 m in the vertical and ±1.5 m in the horizontal. The maximum flight time specified by the manufacturer was 40 min without a payload and 18 min for the maximum payload mass of 5.5 kg at sea level. The VOC sampler was mounted to a mounting frame underneath the UAV platform (DJI Matrice 600 Series Z15 Gimbal Mounting Connector kit). Testing for the sampler load of this study indicated 25 min of flight time with a margin of security of an additional 5 min. Actual battery use in each flight depended on the flight plan and strength of local winds during the flight. The UAV was tested to a horizontal flight distance of 1000 m and a height of 150 m. A ceiling of 500 m above local ground level is hard-wired into the device by the manufacturer.

2.2. Sampler description

Figure 2 shows the full system schematic, including the pump system flow paths and the major power and signal connections within the sampler casing. The sampler requires a pump to draw air flow through the sorbent cartridge, flow and pressure sensors, a flow regulation valve, and a cartridge selection manifold to allow for multiple samples, as well as electronics to provide power, issue commands, and collect data from the sensors during flight. The overall system layout of the sampler is designed to fit a standalone, modular form factor in order to simplify installation and troubleshooting as well as to maximize electromechanical compatibility with multiple UAV platforms in the field. A table with a complete list of the sampler components is provided in the Supplement.

Casing. The sampling system resides in a rectangular acrylic casing that can be opened for easy access for repairs and software updates to the onboard microcontroller. The completed sampler measures 19 cm × 20 cm × 5 cm. The casing remains closed and attached to the chassis of the UAV platform for exchanging sorbent cartridges between flights. The sampler casing is directly integrated to the underside of the UAV chassis and does not interfere with standard flight operations, including the functionality of the Matrice 600's automatically retracting landing legs. The total sampler mass is 0.90 kg. The flight time decreases approximately linearly with increasing payload mass below 5 kg. Based on the relationship between payload mass and flight time provided by the UAV manufacturer, the decrease in flight time for a 1-kg payload is estimated as 3.4 min (DJI.com).

Flow system. The cartridge sampling requires a sample stream at a calibrated flow rate in order to determine the volume captured over the sampling period. The sample flow is drawn through the system by a Parker CTS Micro Diaphragm pump, which can pull between 100 and 600 sccm of flow in a compact form factor. The volumetric flow of the pump is a function of the pressure drop across the inlet and outlet, and is controlled via an adjustable pinch valve (Model 44560; US Plastic Corp.) at the output of the flow system. The pump is driven by a 5.0 VDC brush-sleeve bearing motor. A mass flow sensor (Model D6F-P; Omron) was installed upstream of the pump to provide a continuous analog output signal corresponding to the mass flow at standard temperature and pressure. The flow sensor supports a flow range of 0 to 1000 sccm and includes a built-in cyclone dust segregation system, which diverts particulates from the sensor element. The mass flow sensor was calibrated periodically against a reference standard in the lab. The mass flow rate is converted into a volumetric flow rate using the measured pressure at the flow sensor and atmospheric temperature. The sample volume is obtained by integrating the volumetric flow rate over time. The flow sensor also serves as an indicator of sampler malfunction due to factors such as valve failure or obstruction of the flow by debris during flight.

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Pressure system. An absolute pressure transducer (MX4100AP; NXP) is positioned adjacent to the flow sensor in order to measure the pressure in the flow path. The measured pressure is also used with atmospheric temperature to convert mass flow rate to volumetric flow rate as UAV altitude changes. The device operates across a pressure range of 20 to 10^5 kPa. It outputs an analog voltage signal recorded by the microcontroller that can be converted to a pressure value.

Manifold. Activation of each sample cartridge is achieved with a solenoid valve manifold (Model 161T102; NResearch Inc.) consisting of five independently actuated two-way, normally-closed solenoid valves. All five valves have a nominal orifice of 1.0 mm and share a common output port. The manifold is controlled by a valve driver board (CoolDrive Model 161D5X24; NResearch Inc.). Valve actuation requires 200 mA at 24 V. The board uses a holding voltage that is one third of the actuation voltage and is automatically achieved within 100 ms of activating the solenoid. The five solenoid valves are independently controlled using 5 V logic level signals.

Control system. Autonomous sampler operation and data collection in flight is accomplished with an Arduino Uno microcontroller. The microcontroller coordinates the activation and operation of the pump and valves using a pre-programmed algorithm based on elapsed flight time and collects data from the sensors.

Electrical system. The sampling system is powered by the 18 VDC output provided by the UAV batteries via the power distribution board onboard the Matrice 600. Voltage regulators provide 5 VDC output for the pump, sensors, and Arduino Uno driver boards, as well as 24 VDC output for the valve manifold. The system consumes 2.5 Wh of electricity during a 30-min flight (25 min of sample time), which is less than 2% of the total UAV battery capacity. The remaining 98% of battery capacity is available for UAV flight operations. The use of a separate onboard battery to power the sampler was considered; however, the extra power capacity was more than offset by the effect of the weight of an additional battery on total available flight time.

2.3. Sampling methods

Air samples are collected using cartridge tubes packed with Tenax TA and Carbograph 5TD (Markes International, Inc. C2 -AXXX-5149). Tenax TA is a relatively weak sorbent that collects components with volatility less than benzene (e.g., monoterpenes and sesquiterpenes), whereas Carbograph 5TD shows strong sorbate affinity and captures low-molecular-weight VOCs with carbon number of C_3 to C_8 (Woolfenden, 2010a). The combination of these sorbent materials enables sampling of VOCs with carbon number from C_3 to C_{30}. Both of the sorbent materials are hydrophobic and suitable for air sampling at high RH conditions. Prior to sampling, tubes are preconditioned at 320 °C for 2 h, then at 4 h at 330 °C for 4 h, and are then capped using 0.25-inch (6.35-mm) Swagelok fittings with PTFE ferrules and kept sealed until they are installed on the sampler just prior to flight.

The sorbent cartridges are mounted at the sampler inlet to ensure that the sample gas that passes through the cartridges has not contacted other surfaces in the flow system, thus preventing potential analyte losses or contamination from the flow system tubing. The cartridges are oriented in a vertical position for sampling since horizontal installation can cause “channeling” to occur as a result of sorbent falling away from the walls of the cartridge (ASTM International, 2015). No particle or ozone filter was used upstream of the cartridges to prevent loss of analytes on the filter surfaces.

A constant low volumetric flow rate is required to allow for optimal sorbent-sorbate interaction and uptake onto the sorbent matrix. A target flow rate of 150 sccm was defined to maximize both VOC capture efficiency and sample volume (Woolfenden, 2010b;Markes

International Ltd., 2014). Based on the relationship between sample volume and minimum detection limit reported by past studies (Pankow et al., 2012), a minimum sampling volume of 1.5 L per adsorbent cartridge collected is targeted. This results in 10 min of sampling time per cartridge. Two to three cartridge samples of this volume can be collected in a single flight while also carrying out take-off/landing and transits between sampling locations. The Arduino Uno microcontroller provides the operational flexibility to obtain smaller or larger sample volumes by utilizing either more tubes and shorter collection times or fewer tubes and longer collection times, respectively, during a single flight.

Alongside the sampling, blanks are collected to examine sampling artifacts such as passive diffusion of VOCs into the tube. For the blanks, a sorption cartridge is installed on the UAV and uncapped, but the sampling valve is not opened during flight. After sample collection, the sample tubes and blanks are capped using the Swagelok fittings with PTFE ferrules, and stored at room temperature. The collected tubes are transported from Brazil to USA for chromatographic analysis. Tubes were analyzed within 1 week after collection. Under proper transport and storage, sample artifacts were minimal and did not influence the results (Pollmann et al., 2005).

2.4. Analysis by thermal desorption gas chromatography mass spectrometry (TD-GC-MS)

The cartridge tubes are mounted into a thermally desorbing autosampler (TD-100, Markes International, Inc). The VOCs are pre-concentrated at 10 °C followed by injection into a gas chromatograph (GC, model 7890B, Agilent Technologies, Inc) equipped with time-of-flight mass spectrometer (Markes BenchTOF-SeV) and flame ionization detector (TD-GC-FID/TOFMS) (Woolfenden and McClenny, 1999;ASTM International, 2015). Internal standards tetramethylethylene and decahydronaphtalene are injected into each sample prior to analysis. The system is calibrated daily with a commercial standard from Apel-Riemer Environmental Inc. (c.f. Supplement). The external gas standard is prepared using a dynamic dilution system and the effluent is added to sorbent cartridges under conditions similar to those used for sampling. The calibration cartridges are then analyzed using the same thermal desorption GC analysis method. Response factors for additional VOCs are determined using liquid standards injected on the cartridges or using FID signals by effective carbon number (Faiola et al., 2012).

The mixing ratio X_{VOC} of VOCs is calculated from the measured mass of each compound in the sample and the volumetric flow rate according to the following governing equation:

$$X_{\mathrm{VOC}} = \text{moles VOC} / \text{moles air} = (m_{\mathrm{VOC}}\, R\, T) / (M_{\mathrm{VOC}}\, P\, Q\, \tau) \qquad \text{(Eq. 1)}$$

where m_{VOC} is the mass of the VOC measured in the sample, M_{VOC} is the molar mass, R is the gas constant, T is the temperature, P is the pressure, Q is the volumetric flow rate, and τ is the sampling time.

The detection limit of the GC-TOFMS analysis for isoprene is 1 pg, which is 0.25 ppt for a 1.5-L sample. The detection limit of the measurement is, however, limited by the uncertainty in the background (blank), which is typically ca. 10 pg, equivalent to 2.5 ppt or 5%, whichever is greater, for a 1.5-L sample, and by the uncertainty in the in-flight flow rate measurement, which is 15%. Combining these factors, the overall uncertainty in the measured mixing ratio is then the greater of 3 ppt or 20%.

2.5. Computational fluid dynamics (CFD) simulation

CFD simulations are carried out using SOLIDWORKS Flow Simulation (Ver. 2017 SP3.0) (Waltham, USA). Dimensions and an input geometric model of the UAV are obtained from the DJI company (DJI Downloads). A box with the dimensions and location of the sampler is added to the geometry file. The propellers are simulated by discs of the same diameter, and to simulate a hovering UAV a downward velocity of 11 m s^{-1} is imposed through each disc so that the lift produced by the motors balanced the system weight. Boundary conditions include atmospheric pressure far from the UAV. The pressure is used for a basis of simulation and comparison, and it may not represent the actual value during the sampling. The results are optimized by performing iterations until the pressure difference between the last two iterations was within 2 Pa.

3. Results and discussion

Samples were collected on August 2, 2017 of the dry season in central Amazonia at the Manaus Botanical Gardens ("MUSA") of the Adolfo Ducke Forest Reserve. It is a 10 km × 10 km area set aside since 1963 to the north of Manaus, Amazonas, Brazil, and it has served as a study site for several thousand publications. Three major terra firme forest classifications describe the forest, including valley, slope, and plateau forests (Ribeiro et al., 1994;Oliveira et al., 2008). The tree canopy height is typically in the range of 25 to 30 m. The UAV equipped with the sample collector was launched and recovered from a platform of 3.5 m × 3.5 m atop a 42-m tower (3.0032° S, 59.9397° W, 120 m above sea level). Samples were collected on the UAV at point A (3.0030° S, 59.9333° W, 122 m above sea level; Figure S1). The collection point was 711 m from the launch point. The UAV successfully flew to the sample location repeatedly based on pre-programmed GPS coordinates. Three samples were collected in separate flights at heights of 60 m, 75 m, and 100 m relative to the ground level at the tower location. A sample flow rate of 150 sccm and duration of 10 min duration were used to collect a total sample volume of 1.5 L. For comparison, VOC collections were performed concurrently atop the MUSA Tower with a hand-held motorized pump (Model 210-1002, SKC). These samples were collected using a flow rate of 200 sccm and sampling time of 20 min for a total sample volume of 2.0 L.

Data from the sampler showing flow and pressure for the three in-flight samples are shown in Figure 3. To conserve battery power, the pump is turned off between samples and no data are recorded. The results show that each valve successfully activated. After the initial start up, a uniform flow rate of 150 sccm and a pressure of 1 atm is maintained during each sampling period. The measured flow rate is used to calculate the volume of each sample to account for small variations in flow.

VOC mixing ratios determined from the samples collected by the UAV sampler and from atop the tower are presented in Table 1. VOC concentrations depend on many conditions, including season, time of day, temperature, light levels (i.e., cloudiness), height above the canopy, and canopy composition, which can vary on spatial scales of 10's of meters. Nevertheless, the results demonstrate reasonable consistency between samples collected by the UAV and on the tower, separated by 711 m. They also suggest that vertical concentration gradients can be assessed using this method. Further analysis and scientific interpretation of these results and a larger data set are the subject of a separate publication (Batista et al., 2018).

The possible effects of air circulation created by the UAV multicopter rotors on the sampling was considered. The flow field is also a factor in determining the sampler placement. As there are no published computational fluid dynamics (CFD) studies specifically of the DJI Matrice 600, CFD simulations of the UAV were performed. As shown in Fig. 4a, the pressure difference between the area underneath the sampling box and the area under the propellers was calculated as <100 Pa, indicating that the effect of the UAV on the pressure in the sampling region is minimal. This suggests that any possible effects of UAV pressure fields on any pressure sensitive sensor mounted in this area would be small.

Figure 4b shows the calculated air velocity distribution around the UAV. The simulation suggests that air enters the sampling region from above the propellers, undergoes turbulent recirculation to the UAV sampling region, and then is ejected below the UAV. This is consistent with the CFD study by Ventura Diaz and Yoon (2018), which suggested the sample represented an air parcel extending approximately 1 m above the UAV. In addition, the simulation shows that the air flushing time in the sample region is fast (i.e., several seconds) compared to the timescale of VOC sampling (i.e., 5-10 min). The simulations thus indicate that the sampler performs representative real-time sampling of ambient VOC concentrations averaged across several meters around the UAV.

Several other studies investigated the effects of a multicopter on air sampling and reached similar conclusions. Roldan et al. (2015) simulated flow around a quadcopter and validated the simulations with air velocity measurements. The results showed that air speeds were greatest near the propellers and smallest near the center of the UAV. The optimal location for air sensors was at the center of the vehicle. Further testing involved measurements of CO_2 concentrations with an onboard sensor near a CO_2 source, with and without the propellers rotating. There were small differences (<5%) in the measured CO_2 concentrations, supporting the conclusions of the simulations. Similarly, Black et al. (2018) demonstrated that no difference was observed in the measured atmospheric mercury concentrations using a copter-based sampler when the UAV was powered as compared to when it was unpowered. Together with the results of the current simulations, these studies suggest that valid measurements of many atmospheric gas concentrations can be obtained from multicopter platforms.

One of the key constraints on VOC sample collection by UAVs is the flight duration. Although the manufacturer specifies a maximum flight time of 40 min, when carrying the sampler under tested flight conditions and factoring in a margin of safety, the maximum flight duration is limited to 25 min. Because the volumetric flow rate is also constrained to <200 sccm for the manufacturer-recommended operation of the cartridges to avoid breakthrough, the maximum air volume that can be collected during a flight is 5.0 L. Equation 1 in conjunction with the method detection limit of 10 pg suggests a minimum detectable atmospheric mixing ratio of 1 ppt for this sample volume at standard temperature and pressure. This sensitivity is sufficient for abundant primary emissions such as isoprene and monoterpenes, which can have mixing ratios of 10^2 to 10^4 ppt in tropical forests (Yáñez-Serrano et al., 2018). It may not, however, be sufficient for quantifying primary compounds in other ecosystems with low-emitting flora species, such as forests at higher latitudes or other ecosystem types such as grasslands. It may also not allow for the detection of species of lower concentrations such as sesquiterpenes. Characterization of these compounds is needed to fully understand the reactive chemistry and aerosol formation potential of VOCs in forest environments. Additional strategies to be explored for these compounds include more-rapid flow through the cartridge for low-volatility compounds for which breakthrough is less of a concern or parallel sampling with several cartridges simultaneously followed by common desorption at the TD-GC/MS.

There is a trade-off between the number of samples collected per flight and the individual sample volume. Collecting multiple samples in one flight necessitates smaller volumes for each sample and thus higher detection limits. Subject to the overall flight time limitation, the design of the sampler allows flexibility in the sample count and duration to best achieve the experimental objectives. For each individual flight, scientific choices can be made whether to collect a single, large volume sample to target less-abundant species or multiple smaller samples for surveying the major VOC components.

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A number of strategies can ameliorate these limitations. To facilitate the continuous operation of the UAV, multiple sets of batteries can be used. One set is charged while another set is in use. After each flight, the depleted batteries can be replaced with the spare fully charged set and the UAV launched immediately instead of waiting for the batteries to charge. This allows the number of samples collected to be maximized. Extension of the sample time can also be achieved by initiating a sample on one flight, pausing while the UAV returns for battery replacement, then returning to the same location and resuming collection with the same cartridge. A modification on this approach would be to use a single cartridge to collect air at the same location and time of day over multiple days, resulting in an average for that time period.

A major goal of ongoing development of the sampler is to enable operation either remotely through tablet-based software or with a pre-programmed GPS-based flight trajectory. Both of these operational modes require real-time communication among the sampler, the UAV on-board computer, and the user control interface on the tablet. The Arduino Uno microcontroller is unable to communicate with the UAV on-board computer. To address this issue, an ongoing step in the development is the replacement the Arduino Uno microcontroller with a Raspberry Pi miniature computer. Communication between the sampler and user interface also can enable development of custom software as a diagnostic tool that enables monitoring the status of the valves and pump during the flight. This capability can be important to alert the user to problems during flight, such as the failure of valves or the pump to be activated, as has occurred occasionally on windy days due to strong vibration.

Together with the flight capabilities offered by modern day UAV platforms, this sampler opens the door to studying VOC emission and uptake at previously inaccessible scales. In the

358 long term, data from this project will shed light on atmospheric chemistry, biodiversity, and
359 ecosystem stress within the context of global climate change.

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Table 1. Summary of biogenic VOC types and concentrations collected on 2 August 2017. Results are shown for sample collection by the UAV-based sampler at 711 m from the tower launch location as well as by use of a hand-held pump at the top of the tower. Local time is -4 h to UTC. [a]Samping height as relative to ground level at the MUSA tower. [b]Only major monoterpenes are listed here. In addition to isoprene and monoterpenes, four sesquiterpenes including β-caryophyllene were detected. [c]"n.d." denotes that the VOC concentration was below the detection limit of the instrument.

Sample	Local time	Location (Distance to Tower, m)	Sampling height[a] (m)	Isoprene (ppt)	α-Pinene (ppt)	β-Pinene (ppt)	d-Limonene (ppt)	α-thujene (ppt)	Tricyclene (ppt)	Camphene (ppt)	Total Monoterpenes[b] (ppt)
1	11:15 - 11:35	711 m	75	429.3 ± 68.7	33.7 ± 5.4	7.0 ± 1.1	n.d.[c]	1.4 ± 0.2	0.7 ± 0.1	0.5 ± 0.1	43.6 ± 7.0
2	11:15 - 11:35	Tower top	42	622.0 ± 99.5	65.7 ± 10.5	12.7 ± 2.0	n.d.	1.6 ± 0.3	1.1 ± 0.2	n.d.	82.0 ± 13.1
3	13:15 - 13:35	711 m	100	912.7 ± 146.0	41.6 ± 6.7	9.2 ± 1.5	3.2 ± 0.5	0.5 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	56.2 ± 9.0
4	15:15 - 15:35	711 m	60	579.7 ± 92.8	37.0 ± 5.9	8.6 ± 1.4	n.d.	2.2 ± 0.4	1.4 ± 0.2	1.8 ± 0.3	51.1 ± 8.2
5	15:15 - 15:35	Tower top	42	784.3 ± 125.5	39.8 ± 6.4	7.5 ± 1.2	0.5 ± 0.1	2.5 ± 0.4	0.2 ± 0.1	0.4 ± 0.1	51.3 ± 8.2

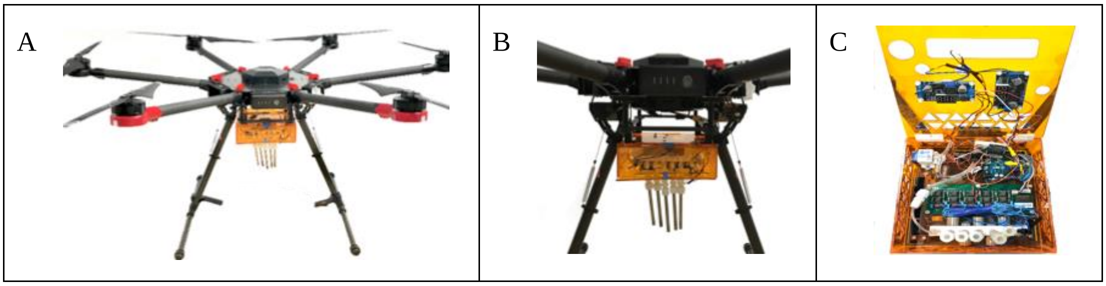

Figure 1. UAV equipped with VOC sampler: (A) DJI Matrice 600 hexacopter UAV. (B) Custom-built sampler visible in orange mounted to UAV. Five VOC sorbent cartridges (Markes International, Inc) are seen on the undercarriage. (C) Sampler with lid open to show pump and electronics package seen in panel B for differentially actuating sample flow through the sorbent cartridges.

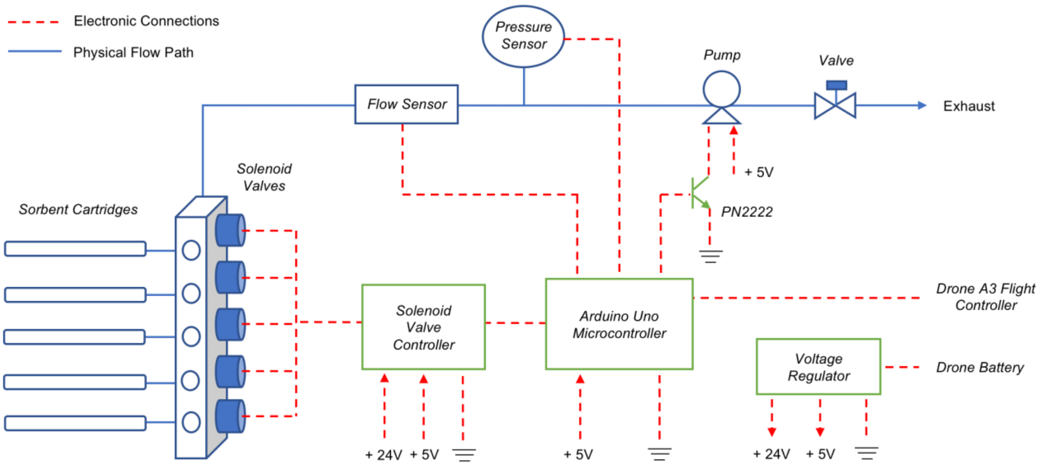

Figure 2. Schematic diagram of sampling device. All components are powered by onboard batteries on the UAV and are controlled by an Arduino Uno microcontroller. Gas flows from the ambient atmosphere through the sorbent cartridges and out to the pump and exhaust.

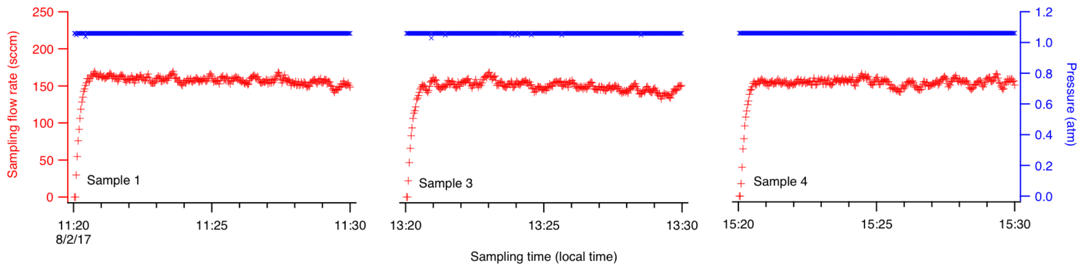

Figure 3. Time series of diagnostic data collected during the VOC-sampling UAV flights.

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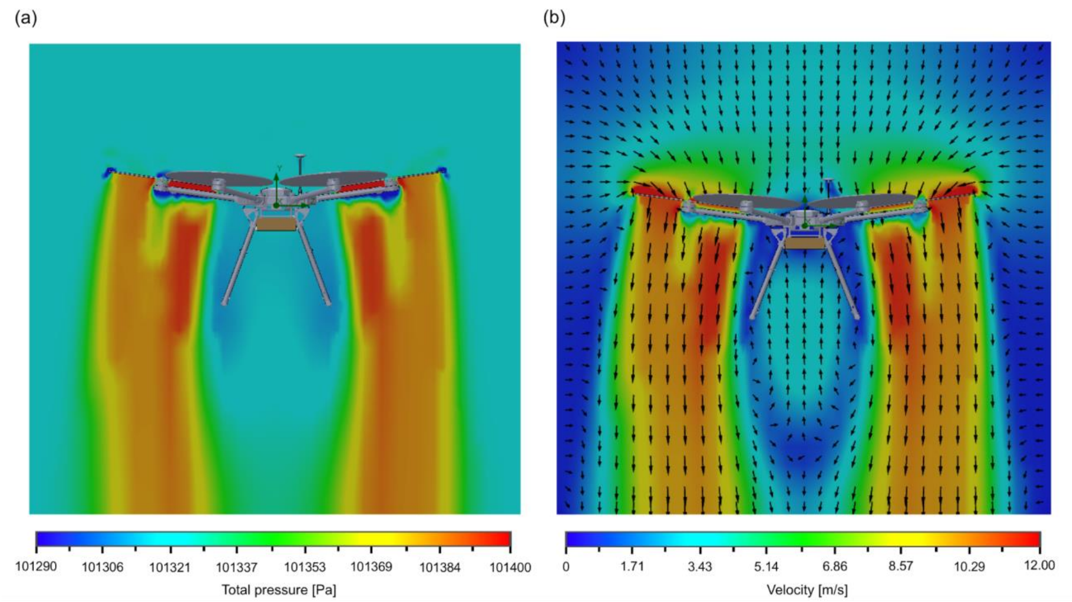

Figure 4.