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Development of a multicopter-carried whole air sampling apparatus and its applications in environmental studies

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HIGHLIGHTS

- A sampling device was integrated with a multicopter drone to perform aerial sampling.
- The whole air sampling can be performed at desired positions aloft with ease.
- The leak- and contamination-free properties ensured the integrity of air samples.
- Subsequent in-lab analysis of whole air samples provided a large variety of species.
- Vertical profiles of gaseous species up to 1 km height can be easily obtained.

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ABSTRACT

To advance the capabilities of probing chemical composition aloft, we designed a lightweight remote-controlled whole air sampling component (WASC) and integrated it into a multicopter drone with agile maneuverability to perform aerial whole air sampling. A field mission hovering over an exhaust shaft of a roadway tunnel to collect air samples was performed to demonstrate the applicability of the multicopter-carried WASC apparatus. Ten aerial air samples surrounding the shaft vent were collected by the multicopter-carried WASC. Additional five samples were collected manually inside the shaft for comparison. These samples were then analyzed in the laboratory for the chemical composition of 109 volatile organic compounds (VOCs), CH₄, CO, CO₂, or CO₂ isotopologues. Most of the VOCs in the upwind samples (the least affected by shaft exhaust) were low in concentrations (5.9 ppbv for total 109 VOCs), posting a strong contrast to those in the shaft exhaust (235.8 ppbv for total 109 VOCs). By comparing the aerial samples with the in-shaft samples for chemical compositions, the influence of the shaft exhaust on the surrounding natural air was estimated. Through the aerial measurements, three major advantages of the multicopter-carried WASC were demonstrated: 1. The highly maneuverable multicopter-carried WASC can be readily deployed for three-dimensional environmental studies at a local scale (0–1.5 km); 2. Aerial sampling with superior sample integrity and preservation conditions can now be performed with ease; and 3. Data with spatial resolution for a large array of gaseous species with high precision can be easily obtained.

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1. Introduction

The sources and fates of anthropogenic and biogenic compounds and their secondary products in the atmosphere are of interest to those studying anthropogenic–biogenic interaction mech-

anisms, air-sea interactions, and tropospheric chemistry of oxidants. In recent decades, light aircraft, and tethered balloons have offered a direct way of probing the lower troposphere (e.g., Toscano et al., 2011; Aurell and Gullet, 2010, 2013; Greenberg et al., 1999; Chen et al., 2002; Glaser et al., 2003; Tasi et al., 2012; Liu et al., 2013). While the advantages of light aircraft with engines include their large payloads and greater flight distances, their inability of vertical movement and hovering as well as their engine exhaust pose limits to aerial air sampling. Tethered balloons controlled by an electric capstan have proven useful when carrying

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sounding devices and Teflon bags for meteorological parameters and air pollutants without engine exhaust contamination; however, their greatest limitation is a lack of maneuverability and their short flight distances. To advance aerial investigations, a useful and novel technique using unmanned aerial vehicles (UAVs) has been developed as a flight platform in recent years and exploited in many fields, such as geological exploration, agricultural applications, military surveillance, and studies of atmosphere and climate, and early warning or subsequent monitoring before and after disasters (e.g., Patterson et al., 2006; Mak et al., 2013; Watai et al., 2006; Lin, 2006; McGonigle et al., 2008; Ramanathan et al., 2007; Gerhardt et al., 2014).

There are two types of UAVs that are most widely investigated and developed. Fixed-wing UAVs have been popular and commonly used for a variety of applications, particularly for long distance tasks (Corrigan et al., 2008; Mak et al., 2013). Rotary-wing UAVs have other unique abilities: hovering, vertical takeoff, agile movement and landing on small or limited spaces, such as on board ships or on the roofs of buildings (McGonigle et al., 2008; Saggiani and Teodorani, 2004). Rotary-wing UAVs include conventional helicopters with a single primary rotor and multi-rotor helicopters (i.e., multicopters) with multi-horizontal rotors (e.g., 4, 6, and 8). As a platform for aerial investigations, multicopters have more advantages than conventional single-rotor helicopters due to their omission of a vertical tail rotor and complex mechanical components that adjust the pitch of the fast-spinning primary blade. Additionally, the placement of rotors on the periphery of multicopters allows more room for probing devices in the center of the craft. Their simpler structure and the characteristics of stable flight make multicopters easier to operate and maintain and possibly less costly to acquire and modify. The inherent advantages associated with multicopters combined with measuring capabilities make them potentially useful for a variety of observation of different natures.

Conventional aerial observation primarily uses sensors or optical instruments. Sensors on a variety of aerial vehicles or remote sensing using optical instruments on satellites can provide valuable data with spatial resolution for some specific pollutants, such as ozone, formaldehyde, CO₂, NO_x, PM₁₀, glyoxal, etc. (Ligler et al., 1998; Chevallier et al., 2005; Emili et al., 2010; Liu et al., 2012). However, there are common limitations in precision, accuracy, and sensitivity for regular sensors and the often limited number of species that can be detected by remote sensing. For local-scale observations, air sampling accompanied by subsequent off-line analysis using more elaborate analytical instruments can be an alternative to acquire a large array of compounds with sufficiently high sensitivity. There are generally two methods for collecting air samples: one is to draw air with a pump through a tube filled with sorbents (Glaser et al., 2003; Greenberg et al., 1999; Ribes et al., 2007); the other is to collect air with an evacuated canister (e.g., electropolished stainless steel or fused silica-lined canister) or a sample bag (e.g., Teflon bag) with a sampling pump. Whole air sampling with an evacuated canister is well suited for the analysis of CH₄, CO, CO₂, N₂O, VOCs, permanent gases, and their isotopic ratios due to better preservation of the air sample.

Coupling the advantages of multicopters with their agile maneuverability as an aerial vehicle and the canister sampling technique can open up a new dimension to perform atmospheric measurements at a local scale from aloft over locations of interest. Their swift “arrive-and-return” aerial ability permits the rapid “load-and-launch” of canisters and thus a reasonably fast sampling coverage of a target space. The whole air samples can then be brought back to laboratory for analysis with an array of elaborate analytical instruments for detailed chemical composition or isotopic information. In this study, we integrated a multicopter and the canister sampling technique into a multicopter-carried whole

air sampling apparatus. The technical details of the construction and operation of the aerial whole air sampling apparatus will be presented, accompanied by a set of test results of flight maneuverability, positioning, sampling actions and sample integrity. To demonstrate field applicability, real flights of aerial sampling above a vertical exhaust shaft of a long roadway tunnel in a mountainous area were conducted. Through these test results, three major advantages will be demonstrated: 1. Air sampling over hardly accessible locations can be performed with ease; 2. Vertical profiles of numerous gaseous species can be easily obtained to complement conventional ground-based measurements; and 3. Aerial sampling by multicopters can be easily deployed and readily performed to open up many possibilities in environmental studies or accident investigations.

2. Materials and methods

2.1. Configuration of aerial whole air sampling apparatus

The aerial whole air sampling apparatus (Fig. 1) integrates a multicopter drone with advanced UAV control techniques, the whole air sampling component (WASC) and sensors (e.g., temperature, humidity, pressure, black carbon, and CO₂). The multicopter has a deck with a surface area of 900 cm² on which lightweight probing sensors can be installed. The heavier WASC is mounted underneath the multicopter to enhance the center of gravity and thus maintain flight stability.

2.1.1. Multicopter driven by electricity

The multicopter used in the study is an octo-rotor multicopter (Spreading Wings S-1000, DJI Innovations) with a 1045 mm diagonal wheelbase and a 337.5 mm center frame diameter. The aircraft weighs 4.2 kg without payload, and its maximum takeoff mass is 11.0 kg. The octocopter is run on battery power (22.2 V, 10,000–20,000 mAh lithium polymer (Li-Po) battery) to avoid the use of a fueled engine and therefore self-contamination. With a 15,000 mAh Li-Po battery, it has a hovering time of approximately 15 min at a 2-m height for a takeoff mass of 9.5 kg. It is permissible to operate at ambient temperatures between –10 and 40 °C.

The multicopter is equipped with UAV control modules for easy flying and safety concerns. The integrated flight controllers with a high precision global positioning system (GPS) and an inertial measurement unit (IMU) can perform stable hovering at desired positions. The on-board video camera and on-screen display can provide real-time images and flight data (e.g., latitude, longitude, altitude, power voltage, and flight velocity). The multicopter can be controlled by a transmitter or set in autonomous flight mode by editing flight routes with a ground station program. In case of one-motor failure, loss of signal, or a low battery, the aircraft was equipped with an automatic return algorithm to ensure its automatic safe return.

2.1.2. Whole air sampling component (WASC)

Depending on the needs and purposes of flight studies, the multicopter drone is versatile in terms of the possible devices and sensors that can be carried. In this study, the key component of the multicopter drone was the remote-controlled WASC (Fig. 1), which consisted of a stainless steel (s.s.) sampling canister (either electropolished or fused silica-lined), a flow restrictor and a lightweight s.s. valve with a remote control circuit. A deactivated s.s. tube (1.6 mm O.D., 0.025 mm I.D.) serving as the flow restrictor was attached to the inlet of the canister to collect an integrated air sample for a duration of 1–15 min based on its length (0.5–10 cm). To remotely open and close a canister, an electric s.s. valve (TM1050S, Enteck) was used. The requirements for the electric valve used for aerial sampling should have the following

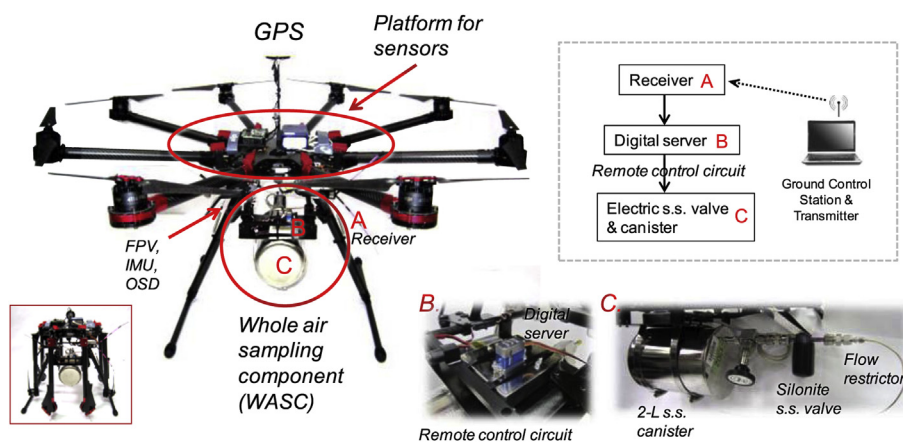


Fig. 1. Octo-rotor multicopter with advanced UAH control modules, the whole air sampling component (WASC) and sensors (temperature, humidity, pressure, CO₂, and black carbon). Whole air sampling component (WASC) consisting of a 2-L s.s. canister, a flow restrictor and a lightweight s.s. valve with a remote control circuit.

properties: 1. Minimized active adsorption sites to avoid the wall effect of target compounds; 2. Gas-tight construction to ensure that a vacuum is maintained in canister before sampling; 3. Lightweight to maximize the useable payload; 4. High torque to open an evacuated canister but low electric consumption; and 5. Remote control to open and close a canister. To execute in-flight sampling by turning on/off the electric valve from the remote ground station, a remote-control circuit was built and connected to the electric valve. Fig. 1 shows the valve with the remote control circuit linked to a receiver, which is commanded remotely by a transmitter (14SGH, Futaba) or a ground control station. The performance of the remotely controlled WASC is critical to the sampling process. As a result, assessment of robustness of WASC will also be addressed in Sect. 3.1. In the current version of WASC, which is shown in Fig. 1, the whole air sample is collected with a 2-L s.s. canister. The total weight of the remote-controlled WASC is 1515 g, consisting of a remote-control valve set of 435 g, which includes a valve rack and the remote control circuit, a canister rack of 95 g, and one 2-L s.s. canister of 985 g. The overall cost for the multicopter with the WASC was approximately \$12k.

Aerial sampling with the WASC is straightforward. The sampling positions and autonomous flight routes are edited on a laptop with a flight control algorithm. Once the multicopter reaches the designated sampling position, as indicated by GPS data, the WASC is switched on to let air be drawn into the pre-evacuated canister through the flow restrictor before it is switched off by the pilot at the ground control station. The residual air left in the sampling path is estimated to be approximately 0.9 mL, which is no more than 0.05% of a 2-L canister. Therefore, depending on applications, flushing before sampling may not be necessary to simplify sampling components and to reduce payload.

2.1.3. Sensors

A variety of sensors (e.g., meteorological parameters, ozone, CO₂, NO_x, black carbon) have been widely adopted in aerial observations on light aircraft, tethered balloons, and UAVs (Pisano et al., 1997; Mak et al., 2013; Li et al., 2014; McGonigle et al., 2008; Velasco et al., 2008; Glaser et al., 2003). In addition to the WASC, in-situ sensors can also be installed on the multicopter drone to provide real-time information for specific pollutants and/or meteorological parameters and even to track plumes and guide sampling.

2.2. Flight tests and field mission of the multicopter-carried WASC

2.2.1. Flight tests

The weather conditions, particularly the wind, may affect flight stability and the accuracy of the sampling position. Three test

flights under windy conditions were conducted to evaluate flight stability, hovering time, and flight distance. The routes of the test flights were edited and controlled by a flight control algorithm (see Supplementary Materials, S1). The three test flights were individually tailored to arrive at the three target positions, including one with a vertical distance of 1 km away from the takeoff site and another with a horizontal distance of 1.5 km.

2.2.2. Field mission of aerial sampling above an exhaust shaft

To examine the performance and demonstrate the applicability of the multicopter-carried WASC, a field mission was conducted in a mountainous area under which long roadway tunnels, the Hsuehshan tunnels (in northern Taiwan ranking 5th in length worldwide), bores through. The Hsuehshan tunnels consist of eastbound and westbound tunnels; each tunnel is 12.9 km long \times 4.6 m wide \times 9.6 m high (Liu et al., 2014). Vehicles in the tunnels release a large amount of pollutants, which are accumulated in the tunnels and vented through three vertical pairs of shafts into the mountainous terrain, where it is difficult to access due to terrain restrictions (Fig. 2a). For each pair of shafts, there is one intake shaft and one exhaust shaft at every ventilation station. Among the three vertical shaft pairs, the vent of the No. 2 exhaust shaft (length = 260.1 m and internal diameter = 6.5 m) is located near the bottom of an unpopulated basin surrounded by mountains, which is an ideal location to explore the influence of anthropogenic pollutants from a single pollution source (i.e., the exhaust shaft) on natural air composition. For this purpose, the multicopter-carried WASC would be an ideal tool to perform aerial sampling near the exhaust shaft vent and its immediate surroundings.

Aerial sampling was conducted on Nov. 22, 2014 from 9:00 to 10:00 a.m. local time (GMT + 8) on a typical autumn Saturday. All operations were conducted in unpopulated mountain areas, and the flights were permitted by the Pinglin Control Center, National Freeway Bureau, which manages the Hsuehshan tunnels and shafts. Ten air samples collected above the shaft vent by the multicopter-carried WASC were for two types of measurements. Eight samples collected with the standard sampling procedure were analyzed for VOCs, CH₄, CO, and CO₂, and the other two samples with additional water removal procedures were provided for analysis of CO₂ isotopologues to avoid ¹⁸O isotope exchange with water. Water vapor was removed by drawing ambient air through a chemical trap (I.D. = 1.5 cm, length = 45 cm) filled with magnesium perchlorate to a level below 0.02% mole fraction. The sampling positions above the No. 2 shaft vent are shown in Fig. 2b, and the sampling details

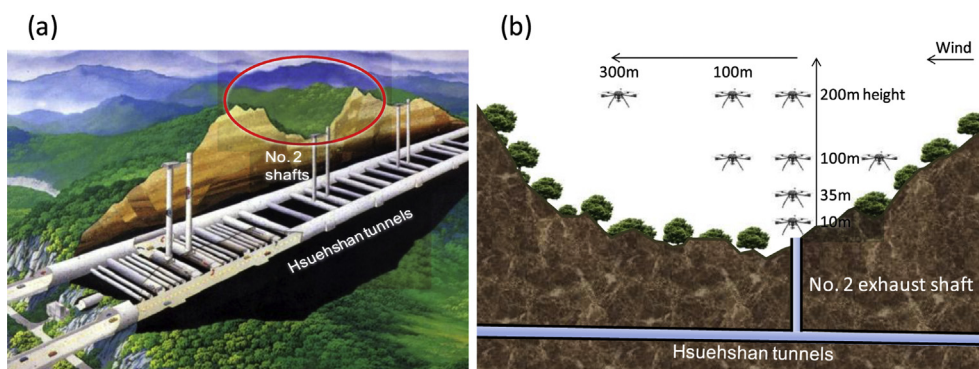


Fig. 2. Sampling locations with the geographic terrain. (a) Schematic diagram of the Hsuehshan tunnels and No. 2 shafts. (b) Aerial whole air sampling positions above the No. 2 exhaust shaft vent.

of the ten aerial samples obtained by multicopter-carried WASC are described in Table 1.

In addition to aerial sampling, five exhaust samples of the No. 2 shaft were manually collected into evacuated canisters through a 1/4 inch Teflon tube, extending into 5 m of the exhaust shaft. Of the five samples, two samples with water removal were provided for CO₂ isotopologues, while the other three without water removal were collected for VOCs, CH₄, CO, and CO₂ (summarized in Table 1). During the sampling period, the mean traffic volume and fleet speed in Hsuehshan tunnels were approximately 1890 vehicles/h and 70 km h⁻¹, respectively. Meteorological data such as wind speed, wind direction, ambient temperature, and humidity were collected with a compact weather station (WXT520, Vaisala, Finland) at the exhaust shaft. The mean wind speed and temperature during aerial sampling were 1.0 ± 0.6 m/s and 22–24 °C, respectively.

2.3. Analysis of gaseous composition by off-line instruments

The canisters were humidified and evacuated to <0.05 Torr prior to aerial and shaft sampling; cleaning procedures were in accordance with the U.S. EPA compendium method TO-15 (Center for Environmental Research Information, 1999). The filled samples were analyzed within one week in the laboratory. The in-lab instruments are described as follows.

An automated GC–MS/FID (450-GC and 240-MS, Varian, Walnut Creek, CA) system was used to simultaneously analyze 109 VOCs over a wide range of species including C₂–C₁₁ non-methane hydrocarbons (NMHCs), ≥C₁ halocarbons, toxic chlorinated compounds, isoprene, monoterpenes, and some esters, ethers, and ketones. The

automated GC–MS/FID for VOC analysis is an upgrade of the one described in the reference (Wang et al., 2012). In brief, the air sample collected in the canister was drawn through a cryo-trap packed with fine glass beads and cooled with liquid nitrogen controlled at –170 °C at 60 mL/min for 3 min to yield an aliquot of 180 mL. Desorption was performed by flash heating the trap to 100 °C, and a stream of ultra-high purity helium (99.9999%) was then used to back-flush the analytes from the trap onto two parallel columns, i.e., a PLOT Al₂O₃/KCl column (J&W; 30 m × 0.32 mm; df = 5.0 μm) connected to FID for the separation and detection of the extremely volatile C₂–C₄ NMHCs, and a DB-1 column (J&W; 60 m × 0.32 mm; df = 1.0 μm) connected to MS for separation and detection of the remaining heavier VOCs.

Two certified standard gas mixtures of 66C₂–C₁₁ NMHCs (Linde Electronic and Specialty Gases, USA) and 61C₁–C₁₀ VOCs (Air Liquide America Specialty Gases LLC/SCOTT, USA) were used for the concentration calibration and quality control purposes. Calibration curves were made by injecting the standard gas mixtures of six different concentrations in the range of 0.03–25 ppbv. The linearities (R²) of the calibration curves for all the target compounds were greater than 0.999. Based on the seven repeated analyses of the standard gas mixtures, the repeatability of most target species was 0.3–2%, and the limits of detection for most species were 1–30 pptv (summarized in Table 2).

The technique of analyzing canister samples for CO₂, CH₄, and CO involved a self-constructed gas manifold connected to a CRDS analyzer (G2401, Picarro Inc., Santa Clara, CA, US). The repeatability (1σ) based on the nine repeated analyses was 0.03 ppmv, 0.9 ppbv, and 1.3 ppbv for CO₂, CH₄, and CO, respectively. Further information on the flask-CRDS method can be found in Wang et al. (2013).

Table 1
Description of sampling positions, methods, and numbers.

Targets	Position ^a and description		Sampling method and number of samples ^b
109 VOCs, CH ₄ , CO, and CO ₂	Exhaust shaft	inside the No. 2 exhaust shaft	Manual ^d (3)
	Upwind shaft	100 m away at 100-m height of the exhaust shaft vent ^a	WASC ^c (1)
	Above shaft	10 m above	WASC (1)
		35 m above	WASC (1)
		100 m above	WASC (1)
		200 m above	WASC (1)
	Downwind shaft	100 m away at 100-m height	WASC (1)
		100 m away at 200-m height	WASC (1)
		300 m away at 200-m height	WASC (1)
			WASC (1)
CO ₂ isotopologues	Exhaust shaft	inside the No. 2 exhaust shaft	Manual (2)
	Upwind shaft	100 m away at 100-m height	WASC (1)
	Above shaft	35 m above	WASC (1)

^a Refer to Fig. 2b.

^b Number in parentheses denotes number of samples at each position.

^c Aerial sampling by multicopter-carried WASC.

^d Manual sampling through a Teflon tube.

Table 2
Quality criteria for the 109 target VOCs.

Compound	Repeatability ^a (RSD%)	Limit of detection (ppbv)	Adsorption check (%) ^b	Compound	Repeatability ^a (RSD%)	Limit of detection (ppbv)	Adsorption check (%) ^b
<i>Alkanes</i>				<i>Aromatics</i>			
ethane	1.4	0.043	2.1	<i>o</i> -xylene	0.5	0.002	2.8
propane	1.1	0.035	1.3	isopropylbenzene	0.6	0.002	−0.6
isobutane	1.2	0.027	2.5	<i>n</i> -propylbenzene	1.3	0.002	3.0
<i>n</i> -butane	1.2	0.030	0.3	<i>m</i> -ethyltoluene	1.0	0.002	3.3
isopentane	0.3	0.007	−0.2	<i>p</i> -ethyltoluene	0.8	0.002	3.0
<i>n</i> -pentane	1.2	0.007	−1.5	1,3,5-trimethylbenzene	1.8	0.002	0.3
2,2-dimethylbutane	1.4	0.007	0.0	<i>o</i> -ethyltoluene	1.5	0.002	1.6
cyclopentane	0.6	0.009	−0.8	1,2,4-trimethylbenzene	1.3	0.001	4.2
2-methylpentane	0.3	0.010	1.8	1,2,3-trimethylbenzene	1.4	0.002	2.9
3-methylpentane	0.7	0.005	−1.9	<i>m</i> -diethylbenzene	1.5	0.008	4.6
<i>n</i> -hexane	0.5	0.006	2.7	<i>p</i> -diethylbenzene	2.3	0.007	4.4
methylcyclopentane	0.4	0.003	4.6	<i>o</i> -diethylbenzene	2.4	0.007	0.8
2,4-dimethylpentane	1.0	0.003	−0.7	<i>Halogenated</i>			
cyclohexane	1.0	0.003	−0.3	CFC-12	1.6	0.002	−0.2
2-methylhexane	0.6	0.007	1.3	chloromethane	2.1	0.017	−4.3
2,3-dimethylpentane	1.0	0.005	1.5	CFC-114	1.2	0.001	−1.9
3-methylhexane	0.5	0.004	1.2	CFC-11	1.3	0.001	1.6
2,2,4-trimethylpentane	1.0	0.002	2.8	CFC-113	1.2	0.001	−3.8
<i>n</i> -heptane	1.0	0.007	0.7	1,1,1-trichloroethane	0.6	0.001	−0.7
methylcyclohexane	0.6	0.002	1.3	carbon tetrachloride	0.6	0.002	−0.4
2,3,4-trimethylpentane	0.8	0.003	2.4	trichloroethene	1.7	0.002	2.5
2-methylheptane	0.3	0.008	−0.5	tetrachloroethene	0.9	0.001	−0.4
3-methylheptane	1.2	0.005	2.0	vinyl chloride	1.2	0.004	−0.5
<i>n</i> -octane	1.0	0.004	−0.3	bromomethane	1.1	0.002	0.1
<i>n</i> -nonane	1.3	0.005	2.9	chloroethane	1.7	0.012	−1.3
<i>n</i> -decane	1.5	0.005	6.4	1,1-dichloroethene	2.0	0.003	−2.9
<i>n</i> -undecane	2.4	0.008	6.2	methylene chloride	1.4	0.007	−9.5
<i>Alkenes</i>				trans-1,2-dichloroethene	1.4	0.007	−1.4
ethene	1.1	0.042	1.6	1,1-dichloroethane	0.3	0.003	−0.7
propene	0.9	0.030	1.2	cis-1,2-dichloroethene	0.7	0.004	0.7
trans-2-butene	1.1	0.027	4.0	chloroform	0.6	0.003	−0.1
1-butene	1.6	0.023	−0.5	1,2-dichloroethane	0.3	0.001	−0.3
isobutene	1.6	0.026	1.0	1,2-dichloropropane	0.7	0.005	0.2
cis-2-butene	0.5	0.020	3.1	bromodichloromethane	1.2	0.001	−2.2
3-methyl-1-butene	0.8	0.006	−0.1	cis-1,3-dichloropropene	1.1	0.002	−0.9
1-pentene	1.0	0.010	−0.3	trans-1,3-dichloropropene	1.2	0.002	−1.3
1,3-butadiene	0.6	0.010	−0.4	1,1,2-trichloroethane	0.9	0.002	0.0
isoprene	0.5	0.003	−0.8	dibromochloromethane	0.5	0.001	−0.5
trans-2-pentene	0.9	0.005	1.2	1,2-dibromoethane	1.3	0.004	−0.5
cis-2-pentene	0.6	0.005	2.0	chlorobenzene	1.1	0.003	−1.5
2-methyl-2-butene	1.5	0.005	−1.7	bromoform	1.0	0.002	−3.7
cyclopentene	0.9	0.002	−0.7	benzyl chloride	1.7	0.005	−3.8
4-methyl-1-pentene	1.1	0.015	−1.8	1,3-dichlorobenzene	0.5	0.001	−5.3
2-methyl-1-pentene	1.0	0.008	1.9	1,4-dichlorobenzene	1.0	0.002	−3.2
trans-2-hexene	0.9	0.005	2.8	1,2-dichlorobenzene	0.7	0.002	−6.6
cis-2-hexene	0.8	0.005	3.5	<i>Oxygenated</i>			
α -pinene	0.4	0.002	−2.1	acetone	1.7	0.029	1.3
camphene	0.9	0.002	0.6	methyl ethyl ketone	0.4	0.065	1.7
β -pinene	0.7	0.002	−0.3	methyl isobutyl ketone	1.3	0.015	−1.9
limonene	0.6	0.005	0.6	methyl butyl ketone	2.4	0.020	−4.2
<i>Alkyne</i>				isopropanol	3.5	0.034	−4.4
ethyne	0.4	0.060	−0.5	ethyl acetate	0.5	0.012	−0.3
<i>Aromatics</i>				vinyl acetate	1.4	0.016	−0.9
benzene	0.8	0.002	4.3	methyl tert-butyl ether	0.6	0.003	−0.9
styrene	0.9	0.003	4.2	<i>Others</i>			
toluene	0.8	0.001	1.8	tetrahydrofuran	0.9	0.003	−1.7
ethylbenzene	0.7	0.002	1.4	carbon disulfide	1.6	0.012	−6.9
<i>m,p</i> -xylene	0.5	0.003	0.7				

The details of the target VOCs can be found via the link <http://webbook.nist.gov/chemistry/name-ser.html> (NIST Chemistry WebBook).

^a N = 7, concentrations of standard gas mixtures at around 1 ppbv.

^b Difference (%) = (with WASC −bypassing WASC)/bypassing WASC.

For CO₂ isotopologues, trace amounts of water vapor and other gases in the air samples that could potentially interfere with the CO₂ isotope analysis were removed cryogenically while pumping away the major gases using a glass vacuum system with five traps; this is a slight modification of Mahata et al. (2012). Two traps were used at dry ice temperature (−77 °C) for removing water and VOCs while the remaining three were used for CO₂ collection at

the temperature of liquid nitrogen (−196 °C). The flow rate was maintained at 100 mL/min during pumping at a pressure of approximately 10–15 Torr. The above process was checked by several control experiments to ensure that there is no escape of CO₂ and attendant isotope fractionation. Isotopic analyses for CO₂ were performed using a FINIGAN MAT 253 mass spectrometer in dual inlet mode (Mahata et al., 2012).

3. Results and discussion

3.1. Performance of the multicopter-carried WASC

The key component of the aerial whole air sampling apparatus was the remote-controlled WASC. To maximize the available flight time, the remote-controlled WASC was designed to be lightweight. As the critical part of WASC, the ultraclean s.s. valve weighs only 295 g. The electric actuator for the valve is operated by a 5–9 V DC but produces a high torque force for the open/close actions and to hold the vacuum of the canister (<0.05 Torr). Power consumption of approximately 5 W only occurs when switching on/off the valve. To test the gas tightness of the valve, an evacuated canister (0.03 Torr) was connected to the valve. After 24 h, the pressure inside the canister was maintained at 0.03 Torr.

The inner surface of the valve is treated with fused silica (Silonite®) to minimize active adsorption sites. To examine the possible adsorption losses of the analytes onto the surface of WASC, including the Silonite valve, a connector (1/4 inch I.D., Ultra-Torr, Swagelok), and an electropolished s.s. canister (Fig. 1); a gas standard mixture, containing 109 VOCs (0.2–1.8 ppbv) mixed with 20 Torr of water vapor was analyzed using two procedures. In one procedure, the standard mixture was directly connected to GC–MS for analysis, while bypassing WASC to serve as a reference. In the other procedure, the standard mixture was fed into WASC, and then the canister with the standard mixture was removed from WASC and connected to the GC–MS for analysis. The two results were comparable with differences within 5% for most species (Table 2), affirming the negligible loss of target compounds.

Three test flights under moderate windy conditions were conducted to evaluate the flight stability, hovering time, and maximum flight distance of the aerial sampling apparatus (see Supplementary materials, S1). The tested multicopter equipped with WASC was supported by a 16,500 mAh Li–Po battery (22.2 V) with a takeoff mass of 7.8 kg. The maximum wind speeds during these test flights were 7.7–10.8 m/s, and the mean wind speed was 4.1 ± 0.5 m/s. In all three cases, the GPS data showed that the multicopter with WASC accurately arrived the designated sampling positions, and the hovering of multicopter-carried WASC at the designated sampling positions remained stable within ± 1 m. The results of the three test flights showed that the multicopter-carried WASC apparatus can readily carry out sampling tasks under moderately windy conditions and can be reliably controlled within 1 km vertically and 1.5 km horizontally away from the ground control station (i.e., the takeoff site). With a takeoff weight of 7.8 kg, the hovering time available for sampling at 200 m and 1000 m heights were approximately 15 and 3 min, respectively.

Aerial sampling over the No. 2 shaft led to collection of 10 aerial samples upwind, overhead, and downwind of the exhaust shaft vent (Fig. 2b and Table 1). The outcome demonstrated that the multicopter-carried WASC apparatus can readily sample in a target aerial space by the virtues of vertical takeoff/landing capabilities, agile maneuverability, and stable hovering. The ten aerial samples and five in-shaft samples were then returned to the laboratory for analyses of 109 VOCs using GC–MS/FID, CH₄, CO and CO₂ using CRDS, or CO₂ isotopologues using IRMS. The integrity of the aerial samples plus high-quality in-laboratory analysis greatly facilitated meaningful interpretation of the data, which will be discussed in the next section.

3.2. Results of the field missions

In order to assess the influence of pollutants from the exhaust shaft on the surrounding atmosphere, knowing the source composition of the shaft exhaust is essential. Three in-shaft samples were analyzed to acquire the composition of 109 VOCs, CH₄, CO, and CO₂

(detailed numeric data are shown in Supplementary Materials, S2). Of the measured 109 VOCs, ethene and *m,p*-xylene were the most abundant species, accounting for 15.7% and 13.1% of the total VOC abundance in shaft exhaust, followed by *o*-xylene, ethyne, propene, isopentane, and toluene, accounting for 7.1%, 6.0%, 5.5%, 5.1%, and 3.5%, respectively.

To investigate the spread of anthropogenic pollutants from the exhaust shaft into surrounding areas, the levels of pollutants at different heights above the exhaust shaft as well as upwind and downwind of the exhaust shaft vent are compared. The sample collected upwind (100 m away at 100-m height) of the exhaust shaft is designated as the baseline sample (i.e., least affected by shaft exhaust) for the area, serving as a reference of comparison for the other samples.

Fig. 3 shows the composition of the baseline sample and a sample downwind of the exhaust shaft vent (100 m away at 100-m height) for comparison. The concentrations of most VOC species in the two samples were very low, ranging from below detection limits to hundreds of pptv (detailed numeric data in Supplementary Materials, S2). In both samples, acetone and ethane were the most abundant species, followed by chloromethane, dichlorodifluoromethane (CFC-12), ethene, ethyne, etc. Although the compositional profiles of the two samples are similar, the concentrations of most exhaust related species, such as ethene, propene, *m,p*-xylene, and *o*-xylene, in the downwind sample were higher than those in the baseline sample, suggesting influence by the shaft exhaust. The concentration of total VOCs of the downwind sample is 7.9 ppbv, which is 1.3 times that of the baseline sample (5.9 ppbv for total VOCs). Despite the low concentrations, aerial sampling plus in-laboratory analysis can still reveal the contribution from the exhaust shaft.

Fig. 4 shows the concentrations of VOCs, CO, CO₂, and CH₄ in the samples upwind, inside, overhead, and downwind of the exhaust shaft vent. To simplify the data interpretation of numerous VOC composition, the measured VOCs are divided into the six categories of halogenated VOCs, oxygenated VOCs (OVOCs), alkanes, alkenes, aromatics, and ethyne. As illustrated in Fig. 4a, the levels of halogenated compounds at different heights and inside the shaft were found to be similar and near the baseline concentration of 1.8 ppbv in the mountain area, indicating negligible contribution of halocarbons from the shaft vent to the surroundings. The homogeneity of halocarbons across all samples also safe-guarded the quality of aerial sampling and in-laboratory analysis (Wang et al., 2000). Oxygenated VOCs revealed a small concentration difference of approximately 5–7 ppbv between the aerial and in-shaft samples, suggesting only minor inputs of oxygenated VOCs from the shaft to the surrounding air. In contrast to halogenated and oxygenated VOCs, other VOCs of vehicular emissions (e.g., alkanes, alkenes, aromatics, and ethyne) as well as CO show considerable differences in concentrations between the aerial and in-shaft exhaust samples (Fig. 4a and 4b). For instance, the concentrations of alkanes, alkenes, aromatics, ethyne, and CO in shaft exhaust were 41, 94, 93, 48, and 48 times the concentrations in the baseline sample. However, among the aerial samples, only the sample collected 10 m above the vent revealed significantly elevated concentrations for these species, whereas the air samples collected 35 m above the shaft opening as well as 100 m and 300 m downwind of the exhaust shaft showed close-to-baseline concentrations, indicating exhaust was rapidly diluted by the surrounding air after venting from the shaft.

To further investigate the dissipation of anthropogenic pollutants from the exhaust shaft into the surrounding environment, a vehicular tracer, methyl tert-butyl ether (MTBE), one of oxygenated VOCs included in the 109 measured compounds, was used. MTBE is an octane-enhancing gasoline additive and originates exclusively from vehicle-related emissions (Chang et al., 2003). As shown in

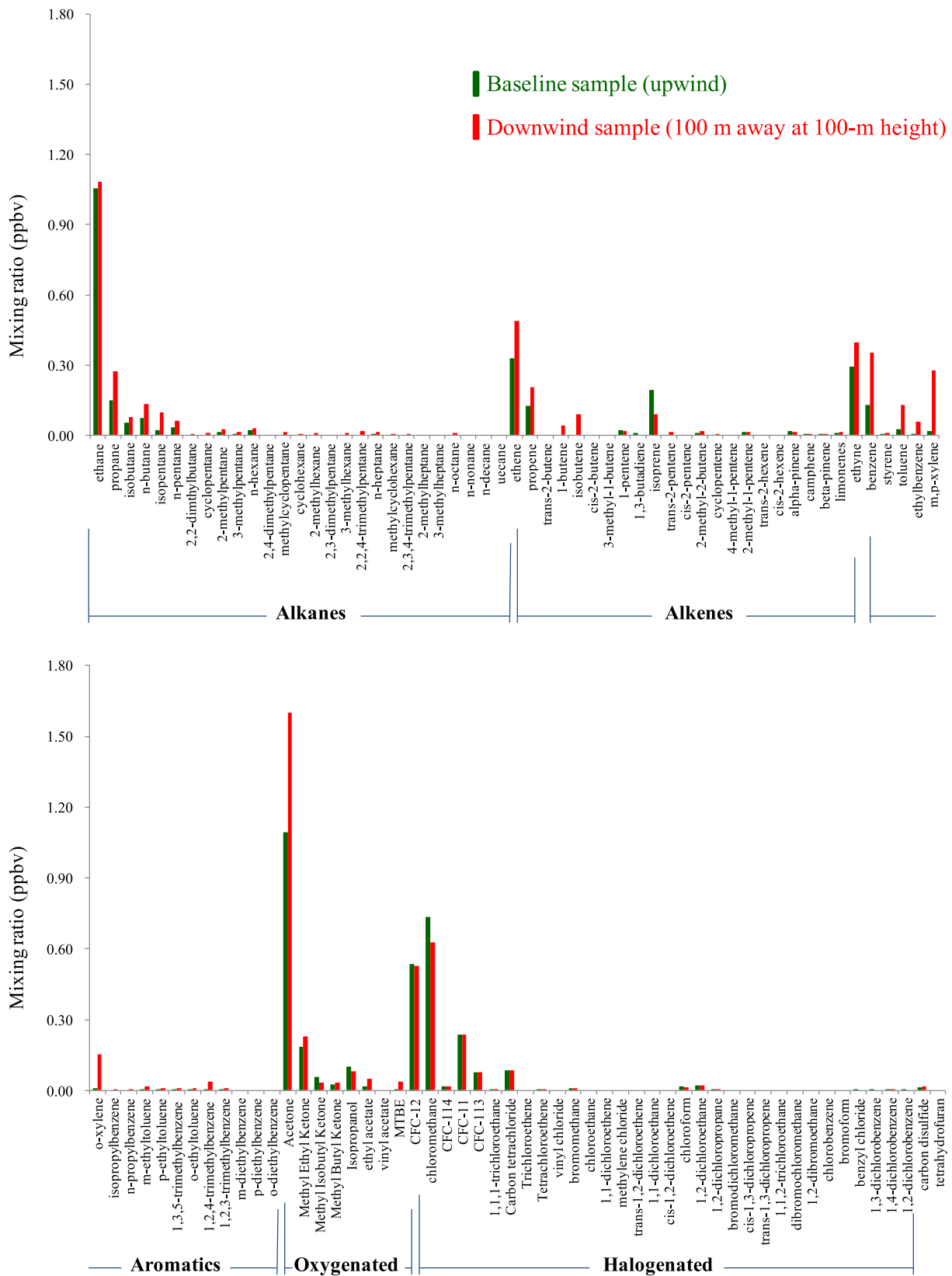


Fig. 3. Comparison of 109 VOCs between the baseline sample and a sample downwind of the exhaust shaft vent (100 m away at 100-m height).

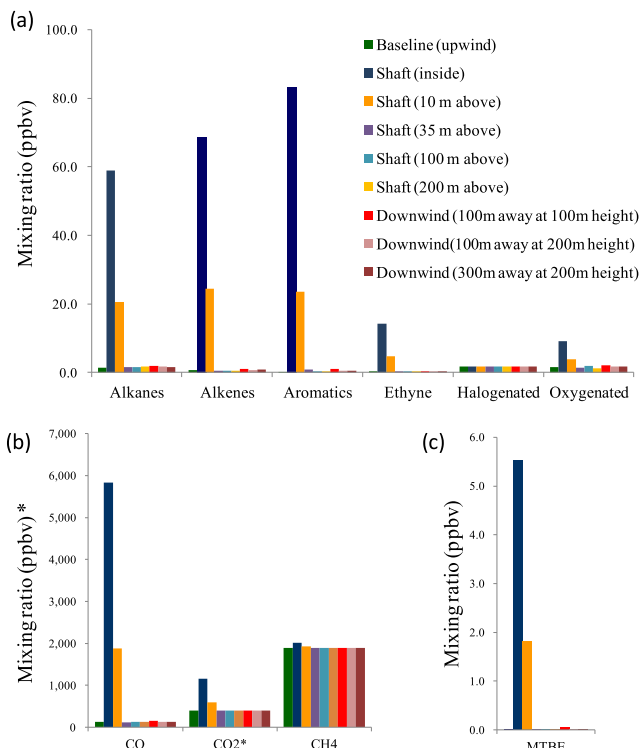


Fig. 4. Concentrations of (a) alkanes, alkenes, aromatics, ethyne, halogenated VOCs, and oxygenated VOCs; (b) CO, CO₂, and CH₄; (c) MTBE in the samples upwind, inside, above, and downwind of the exhaust shaft vent. Note: CO₂ is in ppmv.

Fig. 3, the level of MTBE in natural background air (baseline sample) is near zero and is thus suitable for use as a tracer to examine the influence of shaft exhaust on the surrounding environment. Fig. 4c demonstrates that, as expected, the air 10 m above the exhaust shaft with MTBE of 1.8 ppbv was most affected by the exhaust (5.5 ppbv for MTBE). When the sampling position moved higher and farther away from the exhaust shaft opening, the MTBE levels decreased to near the measurement detection limit. The tracer results are consistent with the bulk results of the compound groups of alkanes, alkenes, aromatics, ethyne, and CO.

The isotope analysis for the collected CO₂ is summarized in Fig. 5 along with the CO₂ collected in the Hsuehsan tunnels (Laskar et al., 2015, submitted) to enhance the correlation for source identification. The carbon and oxygen Keeling approaches show that CO₂ collected in the exhaust shaft is significantly affected by fossil fuel combustion processes. The intercept for $\delta^{13}\text{C}$ is -27.0% (V-PDB), which is indicative of fossil fuel signal (Newman et al., 2008). Similarly, the $\delta^{18}\text{O}$ intercept is $+24.2\%$ (V-SMOW), which is similar to air O₂, suggesting combustive origins (Horvath et al., 2013). Away from the tunnel, CO₂ biogeochemistry becomes important, leading to an elevated $\delta^{18}\text{O}$ value ($+25.6\%$).

This example of exploiting the multicopter-carried WASC for aerial whole air sampling in the field demonstrated the applicability and usefulness in obtaining spatially resolved results for numerous pivotal gaseous species that are relevant to the environment and climate. Future studies that integrate more devices or sensors into multicopter-carried WASC for simultaneous sampling and observation of other airborne species are planned.

4. Conclusion

We designed a lightweight remote-controlled WASC attached to a multicopter drone to perform aerial whole air sampling. The leak- and contamination-free properties of the WASC ensured the

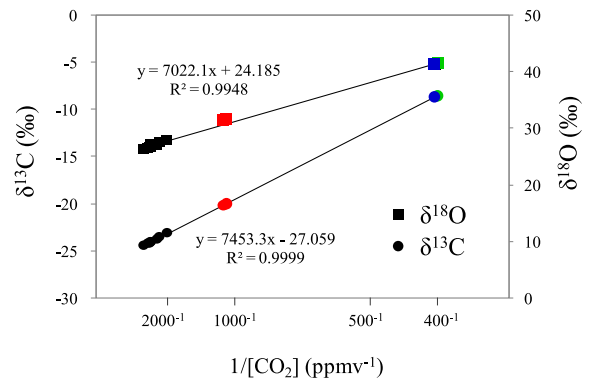


Fig. 5. Keeling plots for bulk isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of CO₂ collected in No. 2 exhaust shaft (in red), at 35 m above exhaust shaft vent (in blue) and in upwind baseline sample (in green) along with CO₂ collected in the Hsuehsan tunnels (in black). Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are referenced with respect to V-PDB and V-SMOW scales, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

integrity of the collected air samples. The flight tests under windy conditions and field missions of aerial sampling above an exhaust shaft demonstrated the robustness and effectiveness of the multicopter-carried WASC in collecting air samples at desired positions aloft. Fast and accurate sampling followed by subsequent whole air analysis provided high-quality data for a variety of trace level gaseous constituents (e.g., 109 VOCs, CO, CO₂, CH₄, or CO₂ isotopologues in this study). The multicopter-carried WASC is simple in configuration, lightweight, highly maneuverable and can be easily built and readily deployed for aerial studies at a local scale (0–1.5 km in the current version). In future plans, the multicopter-carried WASC will further combine with other devices and sensors to enhance its versatility in applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.08.028>.

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