~~A~~ UAV-based sampling system~~s~~ to analyse greenhouse gases and volatile organic ~~carbons~~ compounds encompassing compound specific stable isotope analysis

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Abstract. The study herein reports on the development and testing of sampling systems (and subsequent analytical setups) that were deployed on an unmanned aerial vehicle (UAV) for the purpose of analysing greenhouse gases (GHGs) and volatile organic compounds (VOCs) in the lower atmospheric boundary layer. Two sampling devices, both of which can be mounted to an unmanned aerial vehicle (UAV) with a payload capability greater than one kg, were tested for respective sampling and analysis of GHGs (carbon dioxide (CO_2) and methane (CH_4)) and VOCs (chlorinated ethenes (CE)). The gas analyses included measurements of the molar amounts and the respective stable carbon isotope ratios. ~~The study herein reports on the development of two sampling devices and the subsequent analytical setup for the sampling and analysis of atmospheric trace gases. Both samplers can be mounted to an unmanned aerial vehicle (UAV), the targeted compounds were greenhouse gases (e.g. CO_2, CH_4) and volatile organic compounds (VOC, i.e. chlorinated ethenes), for all compounds mole fraction and the stable carbon isotope ratio were measured.~~

In addition to compound calibration in the laboratory, the functionality of the samplers and the UAV-based sampling was tested in the field. Atmospheric air was either flushed through sorbent tubes for VOC sampling or collected and sampled in glass vials for ~~greenhouse gas~~ GHG analysis.

The measurement setup for the sorbent tubes achieved analyte mass recovery rates of 63 % - 100 % (more favourable for lower chlorinated ~~VOCs~~ ethenes), when prepared from gaseous or liquid calibration standards, and reached a precision (2σ) ~~better~~ than 0.7 ‰ for $\delta^{13}C$ values in the ~~molar ratio~~ range of 0.35 – 4.45 nmol. The UAV-equipped samplers were tested over two field sampling campaigns designed to (1) compare UAV-collected and manually collected samples taken up a vertical profile at a forest site and (2) identify potential emissions of CO_2, CH_4 or VOC from a former domestic waste dump. The precision of ~~triplicate~~ CO_2 measurements from whole air sample~~s replicates~~ was < 7.3 ~~mmol~~ µmol mol^{-1} and < 0.3 ‰ for $\delta^{13}C$ values and < 0.03 µmol mol^{-1} and < 0.24‰ for CH_4 working gas standard~~s replicates~~. The results of the whole air sample analyses for methane were sufficiently accurate to detect and localize potential landfill gas emissions from a secured contaminated site using level flight. ~~The UAV-equipped samplers were tested over two field sampling campaigns designed to (1) compare UAV-~~

~~collected and manually collected samples taken up a vertical profile at a forest site and (2) identify potential emissions of CO₂, CH₄, or VOC from a former domestic waste dump.~~ Vertical CO_2 profiles from a forest location showed a causally comprehensible pattern in the molar concentrations and stable carbon isotope ratios, but also the potential falsification of the positional accuracy of an air sample due to the influence of the UAV downwash. The results demonstrate that the UAV sampling systems presented here represent a viable tool for background atmospheric monitoring, as well as for evaluating and identifying emission sources. By expanding the part of the lower atmosphere that can practicably sampled over horizontal and vertical axes, the presented UAV-capable sampling systems, which also allow for compound-specific stable isotope analysis, may facilitate improved understanding of surface-atmosphere fluxes of trace gas.~~The results emphasized the functionality of the sampling and measurement setup described, demonstrating that it a viable tool for monitoring atmospheric trace gas inventories and identifying emission sources.~~

1   Introduction

Recent technical developments, the accessibility and the low cost of small unmanned aerial vehicles (UAV) have opened up opportunities for expanded sampling of the lower troposphere ~~The popularity, ease of accessible affordable machines and engineering developments of small unmanned aerial vehicle (UAV) in the past decade has opened up opportunities for remote sampling of the lower troposphere (Burgués and Marco, 2020)~~. As a result of increased societal environmental awareness and policy making efforts (Sikora, 2021), there is a growing demand to ~~monitor and record~~enhance monitoring of the atmospheric trace gas~~es inventories~~, such as greenhouse gases (GHG) or volatile organic carbons (VOCs). Recent studies have shown that the deployment of small UAVs to sample the atmosphere for trace gases is a legitimate approach (Aurell et al., 2017; Barbieri et al., 2019; Rohi et al., 2020)~~.~~ Such UAV systems can be deployed to take air samples for subsequent laboratory analysis, as for the system presented here (Leitner et al., 2020), or can be combined with low-cost sensors for on-board measurement and monitoring (U.S. Environmental Protection Agency (EPA), 2014).~~which can contribute with low-cost sensors to monitor air quality monitoring (U.S. Environmental Protection Agency (EPA), 2014).~~

Unmanned aerial systems (UAS), also referred to as remotely piloted aircraft system (RPAS), have a maximum take-off weight (MTOW) of < 25 kg and a maximum payload of < 4.5 kg and are defined as small UAVs. The type with a rotary-wing platform is particularly suitable for use in confined spaces, as they take off vertically, hover and have a high manoeuvrability (Burgués and Marco, 2020). When combined with on-board samplers/sensors, these features thus expand the part of lower troposphere that can be potentially sampled, and furthermore allow for sampling/measurement along vertical profiles in the lower boundary layer (< 350 m above ground level (Chang et al., 2018)), which would otherwise require building towers or using balloons. By expanding horizontal and vertical sampling of atmospheric~~These features are particularly useful to measure vertical profiles in the lower troposphere (< 350 m above ground level (Chang et al., 2018)), which would otherwise require building towers or using balloons.~~

trace gas mole fractions, UAV systems could contribute to improved monitoring of atmospheric background levels and air quality, as well as improved inverse modelling of net surface-atmosphere fluxes. Furthermore, the higher spatial resolution of

65   UAV systems could improve the evaluation of sources and sinks of trace gases, if the measurements of mole fractions include additional stable isotope analysis of the respective trace gas compounds (e.g. Bergmaschi and Harris, 1995; Keeling et al., 1979; Randazzo et al., 2020; Whiticar, 1999; Widory et al., 2012; Zazzeri et al., 2017). There is thus scope for UAV systems to contribute to improved monitoring of GHG and air pollutant emissions, which is of utmost importance, when dealing with mitigation measures (Crotwell and Steinbacher, 2018) or law enforcement.

70   ~~Gathering the site-specific trace gas mole fraction is of great interest when dealing with atmospheric background level monitoring, but does not necessarily provide the foundation to evaluate sources and sinks of the trace gases, which has implications for inventory estimates. In order to differentiate and identify sources and sinks, the application of stable isotope analysis of trace gas compounds has been proven to provide such additional information which is of utmost importance, specifically when dealing with mitigation measures (Crotwell and Steinbacher, 2018) or law enforcement.~~

75   It is of course important to point out the potential utility of UAV systems with respect to atmospheric monitoring, depends on the sampling and measurement instruments that can be carried on-board. Sampling and analysing the atmosphere for the compound specific mole fractions of GHG or VOCs can be accomplished using a broad range of sampling systems and instrumentation. Compound specific isotope analysis, mainly relies on the utilization of mass spectrometry and laser or infra-red spectroscopy (Brewer et al., 2019). Such instrumentation depends on contextual sample specifications, like sample volume,

80 sample vessel tightness and, avoidance of sample gas impurities, which are necessary for the sampling and measurement of low natural abundance, rare isotopic species of the GHG and VOCs. For VOCs, sampling efforts can be significantly eased using sorbent tubes rather than heavy-weight canisters or large volume sample bags (Woolfenden, 1997). However, sampling methodology is attendant on the targeted measurement precision. Sample pre-requisites for GHG measurements are similar to those of VOCs, often relying on large and heavy sample containers (International Atomic Energy Agency, 2002). Although,

85 There are versatile approaches using small and light ~~sampling~~ sample vessels ~~vessels as alternatives for whole-air sampling~~ (e.g. Górka and Lewicka-Szczebak, 2013). ~~Nevertheless, above-ground surface sampling often relies on the availability and access to towers and buildings~~ Notwithstanding this, the availability and access to towers and buildings imposes a limitation on spatial sampling of the near-surface atmosphere Such infrastructure is rendered potentially redundant when using UAVs equipped with versatile sensors or sampling devices. To date, most UAV-based approaches have focused on mole fraction

90 measurements of GHG (Barbieri et al., 2019; Burgués and Marco, 2020) and a few preliminary applications of UAVs to perform whole-air sampling of GHG and VOC have been documented (Chang et al., 2016). However, at the time of writing, there has been no published example of a UAV system to analyse the atmospheric mole fractions as well as the isotopologues from small sample vessel samplers. To our knowledge, there are currently no UAV-equipped sampling systems allowing for the subsequent quantification and stable isotope analysis of multiple GHGs and VOCs. ~~(Djuricin et al., 2010; Pataki et al.,~~

95 ~~2006; Takahashi et al., 2002). Such infrastructure is rendered redundant when using UAVs equipped with versatile sensors or sampling devices, but to date most have focused on mole fraction measurements of GHGs (Barbieri et al., 2019; Burgués and Marco, 2020). There are few preliminary applications of UAVs to perform whole-air sampling of GHG and VOCs (Chang et al., 2016), but none to analyse the mole fraction as well as the stable isotope ratios from small sample vessel samplers. To our~~

Commented [MB1]: Depends on how easily one can fly in the target region… flight permission

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~~knowledge currently there are no UAV's equipped with sampling system allowing for the subsequent quantification and stable~~
~~isotope analysis of multiple GHGs and VOCs.~~

This study documents the development and testing of practicable UAV-based sampling systems and analysis pipelines tailored to the analytical requirements for measuring multiple atmospheric trace gas species and their isotopologues. The aim was to develop gas-sampling devices that could be mounted onto small UAVs to sample atmospheric GHG and VOC, as an alternative to high-cost state-of-the art approaches typically applied at in situ monitoring stations. For GHGs, the sampling and measurement system was evaluated with respect to measurements of carbon dioxide (CO_2) and methane (CH_4). For VOCs, the focus was on measurements of chlorinated ethenes (CE), specifically Tetrachloroethene (PCE), Trichloroethene (TCE), *cis*-Dichloroethene (cDCE) and *trans*-Dichloroethene (tDCE), which are commonly found in urban and industrial areas (Ras-Mallorquí et al., 2007). ~~Therefore, a practicable sampling system tailored to the needs of the analytical measurement set-up was the goal of our study, in order to create a smooth collection and analysis pipeline. The aim was to develop gas sampling devices that could be mounted onto small UAVs to sample atmospheric GHG and VOCs, as an alternative to high-cost state-of-the art approaches. The sampling and measurement system was evaluated based on the relevant GHG gases, carbon dioxide (CO_2) and methane (CH_4) as well as important VOC, the chlorinated ethenes (CE, Tetrachloroethene (PCE), Trichloroethene (TCE), *cis* Dichloroethene (cDCE) and *trans* Dichloroethene (tDCE)). All are commonly found in urban and industrial areas. (Ras-Mallorquí et al., 2007).~~ CEs were sampled using sorbent tubes, while glass vials were used for GHG sampling and analysis. The co-developed measurement system was coordinated in such a way that it meshed with the sample vessels and ensured a correspondingly high quality measurement. GHGs can be analysed directly in the sampling vessels, which overcomes any potential issues of leakage or loss, when samples ~~aliquots~~ have to be transferred to measurement vessels, as is the case when using gasbags for example (Chang et al., 2016; Greatwood et al., 2017). Moreover, the systems described herein ~~ensures~~ ensured detection limits ~~are~~ were achieved below the current atmospheric background values of 413 mmol mol^{-1} and 1889 µmol mol^{-1} for CO_2 and CH_4 respectively (WMO - World Meteorological Organization, 2021) and allows us to obtain a reasonable recovery rate of CE in sorption tubes. Furthermore, both collection systems should allow for the measurement of compound-specific stable isotope ratios. ~~Although on~~On-board measurement (e.g. Khan et al., 2012; Martinez et al., 2020; Rohi et al., 2020) ~~have~~ has numerous advantages and can obtain similar precision in molar amount ratios when compared to laboratory analysis (Shaw et al., 2021). ~~,~~ Nevertheless, an analysis system separated from the on-board sampling device allows for the measurement of the compound specific isotope ratios of multiple species and can allow for longer operation times due to the lighter payload.

The presented sampling systems consisted of a small UAV that was equipped with two different gas samplers (whole-air samples and sorbent tubes). The sampling systems, together with processes for pre-sampling whole-air sample vessel conditioning and post-sampling laboratory analysis, were tested and evaluated over two field sampling campaigns. First, UAV-based sampling of ambient CO_2 over a vertical profile was compared to manual sampling at a forest site. ~~an analysis system separate from the sampling device enables a much more precise evaluation of the data, is less risky to fly and allows for multiple samplers to be used in swarm actions.~~

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The entire sampling system described herein, consisting of a small UAV, two gas samplers, a whole air sample vessel conditioning device and a laboratory measurement system that was tested and evaluated over two field samplings events, (1) The UAV-based sampling of ambient CO_2 collected up through a vertical profile was compared to manual sampling at forest site. (2)Second, Sspatially distributed air samples from a former domestic waste dump provided information on local GHG and CE VOC inventoriesemissions. The two sampling devices were previously tested in the laboratory in order to meet the quality assurance requirements by the subsequent measurement setup.

2   Material and Methods

2.1   Gas sampling with sorbent tubes

2.1.1   Sorbent tube preparation

Stainless steel tubes with an outer diameter of 6 mm and a length of 70.4 mm were used as sorbent tubes. They were filled with sorbent material over a maximum length of 56 mm (equivalent volume of 1 mL), which was held in place by two pieces of 70 μm mesh stainless steel gauzes. The sorbent tubes were filled at the bottom with a gas stream top-down during sampling and bottom-up during desorption. A number of sorbent materials were tested, these were Carboxen 1016 60/80 mesh (Merck KGaA, Darmstadt, Germany), Molecular Sieve 5 Å 60/80 mesh (Sigma Aldrich Co., MO, USA), Porapak N 50/80 mesh (Waters Corporation, MA, USA), HayeSep D 60/80 mesh (Hayes Separation Inc., Texas, USA) and Tenax GR 60/80 mesh (OHIO Valley Speciality, Ohio, USA). The adequate CE mass recovery potential ((Brown and Purnell, 1979; Ras-Mallorquí et al., 2007)), ghost peaks appearing in blank-chromatograms and a maximum desorption temperature of 280°C of the available autosampler were decisive factors in choosing the Tenax GR for the presented study (Ras-Mallorquí et al., 2007; Restek Corporation, 2003; Shirey, n.d.). Tenax GR is a weak VOC adsorbent and therefore can be desorbed at much lower temperatures when compared to very strongly sorbent materials such as Carboxene 1016 (Ras et al., 2009).

Prior to gas sampling, the sorbent tubes were conditioned at 300°C for 3 hours under a 20 mL min^{-1} stream of nitrogen (5.0 purity) and then stored in glass tubes sealed with PTFE-caps. Tube conditioning was conducted using the TubeCon2 device (Envea GmbH, Vohenstrauß, Germany), which is a supplementary device to the purge and trap autosampler (VSP4000, Envea GmbH, Vohenstrauß, Germany), which is discussed further later-on in the text.

2.1.2   Preparation of calibration standards.

The TubeCon2 device (D of Figure 1) was subsequently used to load sorption tubes with either liquid or gaseous calibration standard aliquots. 15 cm long stainless steel pipes, bent upwards by 60°, substituted the sorbent tubes on the heating block which was maintained at 80°C. The sorbent tubes were connected to the top of the bent pipes at the opposite end of a T connector sealed with 6 mm PEEK-fittings. The perpendicular end of the T, facing downwards at an angle of 30°, was used as injection port for liquid or gaseous calibration standard aliquots and was sealed with a 3 mm PTFE coated silicon septa. Injected

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aliquots were directed through the sorbent tubes providing a continuous nitrogen flow (5.0 purity) of 20 mL min^{-1} for 25 minutes, similar to the approaches previously described ((Hartwig, 2017; U.S. Environmental Protection Agency (EPA),
165   1999b). Gaseous aliquots were injected using a 100 µL gastight microliter syringe with a G26 side-port needle (SGE, BGB Analytik Vertrieb GmbH, Lörrach, Germany) and liquid aliquots were injected using a 10 µL gastight microliter syringe with a G26 bevel tip needle (SGE).

Calibrated compounds comprised of *trans*-1,2-Dichloroethene (tDCE), *cis*-1,2-Dichloroethene (cDCE), Trichloroethene (TCE) and Tetrachloroethene (PCE) (as pure substances, Sigma-Aldrich Handels Gmbh, Vienna, Austria). According to
170   Woolfenden (1997) the use of organic solvents such as methanol is not suitable for Tenax GR because methanol would also be retained causing instrumental issues at loading, desorption and analysis. The liquid calibration standard was prepared by injecting pure compounds into a 65 mL glass vessel filled with Millipore water, sealed with a Mininert cap and stored at 5 °C (to give a final molar ratio of 400 µmol L^{-1} each). Sorbent tubes were loaded with liquid standard aliquots of 1-10 µL (10-110 ngC), which was also applied in recent studies (Woolfenden, 1997).
175   The gaseous calibration standard was prepared by injecting liquid aliquots of tDCE, cDCE, TCE and PCE to a molar ratio of 1000 µmol mol^{-1} made up in a 350 mL gas mouse (sealed with PTFE valves and a PTFE coated silicon septa), which had been equilibrated at 60°C for 30 min after flushing with Helium 5.0 (U.S. Environmental Protection Agency (EPA), 1999b). After an initial equilibration time of 30 min a gaseous calibration standard could be successively used over a period of two days, when stored at 60 °C. Gaseous aliquots of 10 to 100 µL (10-110 ngC) were transferred to the TubeCon2 device at a gas mouse
180   and syringe temperature of 60 °C. The calibration range was designed to the manufacturer's (Thermo Fisher Scientific) recommendation of linear IRMS analyser readings of 2 – 8 Volts, but can be adjusted using the sample split option of the used purge and trap autosampler.

2.1.3   Gas sampler using sorbent tubes

The sorbent tube gas sampler (C in Figure 1) was loaded with four sorbent tubes (weight: 1200 grams; dimensions:
185   180x155x130 mm (LxWxH) with installed sorbent tubes). The sample gas inlet was adjusted with a manually adjustable pinch valve, and maintained at 50 mL min^{-1} when using 6 mm thick Tenax GR packed sorbent tubes (Brown and Purnell, 1979). All tubing was made out of 4/6 mm PTFE-tubing and tube connections were made out of polyethylene terephthalate (PEBT) or metal.

Passing the restriction valve at the sampler inlet the flow is split in two using a Y-connector and forwarded to the two inlet
190   ports of an electric four-port gas distribution manifold. The gas manifold enables switching between different sampling modes, either loading all four tubes simultaneously or individually or allows for collection of subsequent duplicates. The sorbent tubes are installed at the outlets of the gas manifold using straight push-in connections. At the outlet of the four sorbent tubes the gas flow is merged into two streams using a 90° push-in Y-connector. Each stream then passes through a flow sensor, recording the actual flow rate. The gas streams are finally united and directed to the suction pump. To circumvent the non-regulated

195 suction power of the pump a tee piece was installed prior to the pump feed to equalize the different flow rates set at the restriction valve of the sample inlet. Thereby the exposure to under pressures resulting in altered flow readings and the overuse of sampler components could be prevented.

The sorbent tube sampler was equipped with an SD card which besides measuring the actual flow rate, collected and logged temperature, air pressure, humidity, the activated sample port number and time data over the sampling event. The sorbent tube
200 sampler was connected via a quick release dovetail mount to the bottom of the UAV.

2.2 Gas sampling with glass vials

2.2.1 Vial preparation and conditioning

~~20~~ Twenty mL crimp-top glass vials were used as sample vessels, which were sealed with 5 mm thick PTFE-lined grey butyl-rubber stoppers and aluminium crimp caps. The developed vial conditioning device (A in Figure 1) can be loaded with up to
205 12 glass vials and conditions the vials via flushing and evacuation. First, crimp sealed vials were flushed ~~Flushing of closed vials was either done~~ with synthetic air or helium for 1 min at 200 mL min^{-1} using two G26 side-port needles. Second, flushed vials were ~~before being~~ evacuated through a single G26 side-port needle to a final pressure of approx. 0.5 Pa using a rotary vane pump (Edwards E2M-1.5, Sussex, UK). In order to follow the identical-treatment principle ~~approach~~ (Werner et al., 2001) vials used in the field sampling campaigns and for preparing compound calibration standards were all flushed with synthetic
210 air. ~~We recommend to flush the vials with synthetic air when preparing calibration standards vials measured with atmospheric air samples in order to follow the identical-treatment approach (Werner et al., 2001).~~

2.2.2 Whole air sampler

The whole air sampler ~~developed~~ (B in Figure 1) weighed less than one kg (200x200x200 mm) and could be loaded with up to 12 glass vials positioned in a rotating barrel. The sample gas inlet was positioned at a vertical offset of 40 cm to the centre
215 of the UAV rotor-plane in order to minimize the impact of the airflow from the UAV rotors ((Alvarado et al., 2017; Palomaki et al., 2017; Poyi et al., 2016; Zhou et al., 2018)). A 0.5 mm ID PEEK-tubing (length of approx. 70 cm) was used as transfer line to connect the downwards facing sample inlet to the whole air sampler inlet. The transfer line was connected to a G23 side-port needle (Hamilton Bonaduz AG) mounted to a moving cantilever of the whole air sampler. At a sampling event the cantilever pushes the needle through the glass vial septa and thereby enables the evacuated vial to ~~'s negative pressure to~~
220 equilibrate with the surrounding environment, sucking in a sample of approx. 20 mL (equilibration time of 25 sec). The dead-volume of the transfer line was (100 µL) and the residual flush- ~~gas volume~~ gas volume inside the evacuated glass vial was <0.5 mL. Analysis of evacuated glass vials, filled thereafter with synthetic air only, did not reveal any chromatographic peak for CH_4 and a reproducible blank peak of approx. 30 µmol mol^{-1}. The consistent blank peak was either due to the impurity of the flushing gas bottles ($CO_2 \leq 0.5$ µmol mol^{-1}, Synthetische Lut 5.0 KW-frei, Messer Austria GmbH, Gumpoldskirchen, Austria)

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225 or a leak somewhere in the buildings gas pipe system, because blank vials prepared and flushed with Helium (purity 5.0) did not show chromatographic peaks at the retention time of CO_2. ~~inside the evacuated glass vial did not show any significant influence to follow-up measurement setup.~~

2.3 UAV description

The UAV used during the field sampling campaigns was a Hermes V2 RPAS (Figure 1, M3 Agriculture Technologies, Dayton,
230 OH, USA), which is a 1000 mm (motor to opposing motor) scale hexacopter utilizing an ArduPilot supported autopilot and associated hardware. The Hermes V2 is capable of operating in conditions such as high wind (< 20 knots) and light rain due to its design, which places sensitive electronic components inside a fuselage protected from rain.

ArduPilot is a community supported open source autopilot software suite supporting a variety of autonomous ground, water and air vehicles. The user interface or Ground Control Station (GCS) utilized to plan the sampling operations and interface
235 with the Hermes V2 is MissionPlanner, an open source GSC software which supports ArduPilot. The Hermes V2 can lift up to five kilograms of payload and operate for up to 25 minutes when equipped with zero payload, while drawing energy from a 17,000 mAh 6S lithium polymer (LIPO) High Voltage battery. The time aloft of any RPAS (remotely piloted aircraft system) is inversely proportional to the mass of the payload. The Hermes V2 weighs 7.25 kg when ready to fly. The atmospheric samplers utilized during the sampling campaign each weighed less than 1.5 kg and allowed maximum flight times up to 22
240 minutes, depending upon environmental and mission planning requirements. Technical details of the Hermes V2 RPAS are provided in the supplementary material (Table S1).

The gas samplers were triggered to gather a sample utilizing a 5 V DC relay connected to the open source autopilot. The relay was autonomously triggered with missions created using MissionPlanner GCS. Sample collection was initiated by approaching within 2 meters of a designated point, where the relay would be triggered. The sampling mission was programmed to delay
245 and gather a sample at the designated point for 25 (to glass vessels) or 600 seconds (to sorption tubes). The RPAS could then move to another sampling location or return and land at the take-off location. A sample could alternatively be collected manually utilizing the pilots console transmitter. The samplers were mounted underneath the RPAS fuselage between the landing gear legs using a quick release dovetail mount. ~~12~~ Twelve V DC power was supplied to the atmospheric samplers from the RPAS. Flight logs were available to be downloaded from the autopilot and analysed post flight using the MissionPlanner
250 GCS software. Flight profiles could be visually appreciated by viewing a .kmz file and other data such as sampling heights and GPS coordinate locations could be confirmed.

Figure 1: Overview of the sampling system comprising of the vial preparation device (A), the whole-air sampler (B), the gas sampler for adsorbent tubes (C), the sorbent tube conditioning device (TubeCon2, D) and the UAV applied in field test equipped with the whole-air sampler. ~~Sampling system overview comprising of the vial preparation device (A), the whole-air sampler (B), the gas~~
255 ~~sampler for adsorbent tubes (C), the sorbent tube conditioning device (TubeCon2, D) and the UAV applied in field test equipped with the whole-air sampler.~~

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2.4   Referencing and calibration of stable carbon isotope ratios

Stable isotope ratios of carbon in CO_2, CH_4, PCE, TCE, cDCE and tDCE are reported in the δ-notation (‰) and were referenced to the Vienna Pee Dee Belemnite (VPDP) scale. The normalization of measured stable isotopic compositions to isotope reference scales followed the procedures of Paul and Skrzypek (2007). The δ-values were calculated as

$$\delta^{13}C \quad = \frac{R_P}{R_{Std}} - 1,$$

where R is the ratio of the abundance of ^{13}C to ^{12}C of a sample (P) and a measurement standard (Std) (Coplen, 2011).

$\delta^{13}C$ values of CE were calibrated against three international reference materials (USGS 87, NBS 22, IAEA CH-3) using an elemental analyser connected to a DeltaV Advantage IRMS (EA-IRMS, Thermo Fisher Scientific, Bremen Germany). Assigned $\delta^{13}C$ values of CE were -27.51‰ ± 0.13‰ (n=5), -29.81‰ ± 0.08‰ (n=3), -25.94‰ ± 0.02‰ (n=5), -12.22‰ ± 0.02‰ (n=5) for PCE, TCE, cDCE and tDCE, respectively. Both, CE and reference materials, were ~~both~~ sampled in tin cups designed for sampling liquids. The CO_2 and CH_4 working gas was calibrated against two isotope certified CO_2 gas standards (-6.7‰ ± 0.2‰, -39.0‰ ± 0.2‰, ISO-TOP, Messer Austria GmbH) after direct injection to a GC-C-IRMS measurement setup, as presented elsewhere (Leitner et al., 2020). Obtained $\delta^{13}C$ values ± 1 σ were -4.34‰ ± 0.2‰ (n=17) and -40.3‰ ± 0.2‰ (n=38) for the CO_2 and CH_4 working gases respectively.

2.5   Measurement setup for sorbent tubes

The measurement system (purge&trap GC-qMS/C-IRMS) comprised ~~of~~ a purge and trap autosampler (VSP4000, Envea GmbH, Vohenstrauß, Germany) connected to a gas chromatograph (GC, Trace GC, Thermo Scientific, Bologna, Italy) linked at a 10:1 gas flow split ratio to a gas conversion system (GC-Isolink, Thermo Fisher Scientific, Bremen, Germany) and a single-quadrupole mass spectrometer (qMS, ISQ, Thermo Fisher Scientific, MA, USA). The qMS was in electron~~ic~~ ionization mode with the filament emission at 70 eV and a source temperature of 230 °C to detect the *m/z* ratios of mass 12 to 166 at a scan time rate of 0.2 sec. The GC-Isolink is further connected to a gas distribution system (Conflo IV, Thermo Fisher Scientific, Bremen, Germany) introducing the CO_2-converted gaseous analytes together with CO_2 working gas spikes to an isotope ratio mass spectrometer (IRMS, Delta V Advantage, Thermo Fisher Scientific, Bremen, Germany). The mass-to-charge rations (*m/z*) of mass 44, 45 and 46 were continuously monitored to quantify the amounts of each analyte and determine its stable carbon isotope ratio ($\delta^{13}C$).

Sorbent tubes were analysed using the purge and trap autosampler set to thermal desorption mode. Thereafter, sorbent tubes were heated to 200 °C to desorb analytes during a period of 10 min and transferred with a Helium flow of 20 mL min^{-1}. Adsorbed water vapour was removed by a membrane water trap (purged with N2 at 200 mL min^{-1}). Desorbed analytes were trapped at -50 °C inside a Tenax GR-packed cryotrap cooled with liquid nitrogen (LN$_2$) and then released by heating the cryotrap to 200°C to be transferred with the He carrier flow (inlet pressure of 1200 mbar) to the GC, equipped with a 30m,

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0.25 mm ID, 0.25 μm film thickness TG-5MS column (Thermo Fisher Scientific, Bremen, Germany). The temperature program started at an initial temperature of 35 °C, held for 1 min, then heating- up to 70 °C by 5 °C min^{-1}, before reaching the final temperature of 260 °C after heated-up by 60 °C min^{-1}.

2.6   Measurement setup for glass vials

The measurement procedure and the calibration standard preparation for the analysis of CO_2 and CH_4 (molar ratio and $^{13}C/^{12}C$ ratio) is reported in details in a preceding publication of Leitner et al. (2020). The analysis of CO_2 (detection limit of 100 μmol mol^{-1}) was carried out with head-space (HS) GC-C-IRMS analysis. A 300 uL sample aliquot was injected via an autosampler (CTC Combi PAL, Switzerland) to a ShinCarbonST 80/100 mesh 2m x 1mm ID packed GC-Column (Restek Corporation, BGB Analytik AG, Rheinfelden, Switzerland). The temperature programme of the GC starting at 40°C, heated up by 20 °C min^{-1} to 150 °C, held for 5 min, before heated up by 50 °C min^{-1} to the final temperature of 180 °C. CO_2 was then passed the non-active (400 °C) high-temperature-conversion unit inside the GC Isolink, to assure an unchanged state of CO_2 before being sent to the Delta V Advantage.

The analysis of CH_4 for atmospheric background levels (~1.9 μmol mol^{-1}) was carried out using a different measurement setup. Analysis of CH_4 (detection limit of 0.7 μmol mol^{-1}) followed a purge and trap autosampling routine using a VSP4000 equipped with a HayeSep-D (60/80 mesh) packed cryotrap maintained at -140 °C using LN2 and subsequent cryogenic trapping at the initial section of a Poraplot Q (30 m, 0.32 mm ID) GC-column (Agilent Technologies Austria GmbH, Vienna, Austria), inside a LN$_2$ dewar, which is otherwise maintained at 35 °C inside the GC. CH_4 which was thereby separated from the interfering atmospheric air components (e.g. N_2, CO_2 and N_2O) and was then oxidized to the measurement gas CO_2 by passing through a combustion/reduction reactor or to H_2 inside a high temperature conversion reactor (GC Isolink) before being forwarded to a ConfloIV linked to a Delta V Advantage to measure the stable isotopic composition of either carbon or hydrogen.

2.7   Field site descriptionDescription of field sites

The gas-sampling system was tested at two field sites, which were representative for the application of the sorbent tube and/or whole air sampling system. Target compounds using the sorbent tube sampler were VOCs such as chlorinated ethenes (CE), which are a prominent constituent of encapsulated and secured former domestic waste dumps across Europe. The whole air sampler was designed to specifically sample the atmosphere for greenhouse gases.

The former domestic waste dump at Kapellerfeld (Lower Austria, Austria, https://www.altlasten.gv.at/atlas/verzeichnis/Niederoesterreich/Niederoesterreich-N12.html), where CE and BTEX (benzene, toluene, ethylbenzene, xylenes) had been identified as part of the pool of potential local contaminants, was chosen for testing the sorbent tube sampler. Due to the formation of landfill gas at Kapellerfeld local authorities had installed a landfill gas extraction system to prevent emission, which mostly consist of CH_4 and CO_2. In order to test whether the sampling system

was capable of detecting potential leakage through encapsulated landfills or piping systems the whole air sampler was also used at Kapellerfeld.

320 The whole air sampler was tested along a horizontal sampling profile above the interconnecting pipelines of two landfill gas suction system units. Each unit consisted of an above-ground pipeline with alternate gas extraction wells connected to the pipeline at right angles. The above-ground pipelines of both units were aligned to each other, but were also broken half-way in between at a perpendicular transfer pipeline. At the sampling event, only one unit was operating and there was a total of 23 gas extraction wells. The flight path started 3 m above the gas extraction wells on one side of the operating unit and continued

325 until the unit in "stand-by" before reversing over the opposite sided extractions wells back to the starting point. Independent single samples were taken, which were analysed for the carbon isotope ratio and mole fraction of CO_2 and CH_4. Each compound was measured sequentially from the same sample vessel filled at the waste dump using two different measurement setups (Leitner et al., 2020). First, CO_2 was analysed from three measurements of 300 µL sample volume aliquots each, before analysing the entire residual volume (~19.6 mL) for CH_4.

330 The former domestic waste dump at Kapellerfeld (Lower Austria, Austria, https://www.altlasten.gv.at/atlas/verzeichnis/Niederoesterreich/Niederoesterreich-N12.html), where CE had been identified as part of the pool of potential local contaminants was chosen for testing the sorbent tube sampler. Due to the formation of landfill gas at Kapellerfeld local authorities had installed a landfill gas extraction system to prevent emission, which mostly consist of CH_4 and CO_2. In order to test whether the sampling system was capable of detecting potential leakage through encapsulated

335 landfills or piping systems the whole air sampler was also used at Kapellerfeld.
The whole air sampler was tested along a horizontal sampling profile above the interconnecting pipeline of two landfill gas suction system units. The units were broken half-way in between at a transfer pipeline and only one unit was operating during sampling. There were 23 inspection wells opposite to each other and perpendicular to another along the pipeline. The flight path started 3 m above the inspection wells of the operating unit and continued until the unit in "stand-by" before reversing

340 over the opposite wells back to the starting point. Independent single samples were taken, which were analysed for the carbon isotope ratio and mole fraction of CO_2 and CH_4. Each compound was measured sequentially using a different measurement setup (Leitner et al., 2020), having been sampled using the same sample vessel and filled at the waste dump. First, CO_2 was analysed from triplicate injections of 300 µL each, before analysing the residual volume (~19.6 mL) for CH_4.

The sorption tube sampler was tested on a horizontal and vertical sampling profile at the ex-situ filter facility of the former

345 domestic waste dump. The filter facility surroundings had a noticeable odour that day. Sorbent tubes of the vertical sampling profile were loaded flushed with ambient air at a flow rate of 50 mL min^{-1} for an individual sampling time of 10 minutes. Discreet single samples were taken (sampling mode 4x1) at 7, 10 and 20 meters above ground level (the 4th sorption tube position was kept unloaded and used as a sample blank). The horizontal sampling flight took place over a covered observation well of the local funnel and gate system. An ambient air sample was taken at a fixed height of 3 m above the well, in

350 quadruplicate (sampling mode 1x4), with a pumping rate of 200 mL min^{-1}.

The second field campaign took place at the forest demonstration centre of the University of Natural Resources and Life Sciences, Vienna, located in Forchtenstein (Burgenland, Austria), to assess the positional accuracy of UAV-based whole air sampling. For vertical CO_2 profiling, manual samples were collected at six heights during the ascent to an observation tower with a final sample after the descent at the height of 0.4 m, similar to the position of the first sample. Subsequently, sampling was conducted with the air sampler in the immediate vicinity of the tower at six comparable and two additional heights. Prior to drone launch, additional samples were collected with the rotors turned on using the air sampler mounted to the UAV, which was not in flight mode. In addition, before the rotors were turned on, simultaneous manual and UAV-assisted sampling was carried out. All samples were taken in triplicate, with the exception of the sample at the descent from the tower, which was taken as a single sample.

The 36 m high tower is located in a mixed forest with a canopy height of about 20 m. Since the tower exceeds the canopy height by 16 m, it should be possible to capture the atmospheric CO_2 background in addition to the area strongly influenced by the soil and vegetation. The field sampling campaign took place in October 2021 with overcast weather conditions during sampling and temperatures around 8°C. Generated vertical profiles of CO_2 were carried out to draw conclusions whether the UAV-based sampling system meets the requirements for investigating net fluxes and identifying sources and sinks.

The second field campaign took place at the forest demonstration centre of the University of Natural Resources and Life Sciences, Vienna, located in Forchtenstein (Burgenland, Austria), to assess the positional accuracy of UAV-based whole air sampler. Vertical sample profiles were generated by manual sampling of triplicates at six different heights up the 36 m observation tower and followed by UAV-based sampling as close as possible to the tower at eight comparable heights. The tower is situated in a mixed forest with a vegetation crown height of approximately 20 m, a height which should enable a decoupling from the atmospheric CO_2-background. The field sampling campaign took place in October 2021 at temperatures around 8°C and was increasingly overcast. Manual sampling proceeded unmanned sampling. CO_2 vertical profiles generated should enable conclusions to be drawn as to whether the UAV-based sampling system presented meets the requirements for investigating greenhouse gas fluxes.

3 Results and Discussion

3.1 Calibration of chlorinated ethenes using sorbent tubes

Two calibration standards, one prepared by diluting pure liquid phase CE in an aqueous phase and a second using vaporized CE in a gas phase (He) were used for the calibration of the thermal desorption (TD) method. Their results were evaluated based on mass and $\delta^{13}C$-value recovery. The liquid phase calibration standard was first measured against other CE-containing laboratory working standards to check for the accuracy of assigned set values. This was accomplished by measuring liquid standard aliquots with a purge and trap GC-C-IRMS measurement setup described in Leitner et al. (2018). As with the latter, the TD method development was carried out using the same GC-C-IRMS instrumentation to enable the comparison of peak areas in order to check for the mass recovery of CE when loaded to sorbent tubes. A comparison of peak areas obtained from

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both measurement setups showed that, according to a Student-t-Test (Student, 1908), peak areas per injected mass of CE obtained by TD were not significantly lower (Table S2). In addition, incomplete loading of the sorbent tubes (compound breakthrough) would lead to a significant depletion in compound's $\delta^{13}C$ values (Klisch et al., 2012). Liquid standard aliquots were calibrated over a range of 0.35 – 4.45 nmol ~~injected~~ on GC-column (corresponding IRMS mass 44 intensity range: 100 to 8000 mV). ~~Injected amounts~~Set values of liquid standard aliquots showed a linear correlation with peak areas ($R^2 \geq 0.98$), valid for all CE, and on a 1:1 relationship.

Table 1. Comparison of $\delta^{13}C$ mean values ± ~~2~~ twice the standard deviation (2 σ)~~σ~~ and mass recovery rates, as means ± 2 σ, obtained from measurements of gaseous and liquid calibration standard aliquots at the given mass range (nmol) loaded to sorbent tubes.

Tschickardt et al. (2017) recommended to calibrate TD-methods with test gases, spiking liquid stock solutions to a gas stream~~.,~~ ~~while spiking~~The conducted approach of spiking ~~of~~ gaseous calibration standard aliquots to sorbent tubes was designed as a proxy for ambient sampling conditions. Gaseous calibration standard aliquots were loaded to the sorption tubes in similar mass quantity as for ~~the~~ liquid calibration standard aliquots. Sequences of measurements were carried out over a period of one month using gaseous calibration standards prepared at least every week and stored in between at 60°C (U.S. Environmental Protection Agency (EPA), 1999a). The raw data were adjusted for outliers using a 2-sided Grubbs outlier test (Grubbs, 1969) with a p-value criterion of < 0.05. Residual data ~~was~~ were filtered according to a two-sigma (2σ) criterion on the $\delta^{13}C$ and subsequently on the ~~determined~~ recovered compound ~~amounts~~masses. According to a Student-t-Test, means of ~~remaining~~ filtered $\delta^{13}C$ values obtained from both calibration standard types originated from the same population. Still, means of gaseous calibration standards showed a minor enrichment in ^{13}C when compared to liquid standards (Table 1). Volatilization of ~~the light isotopes~~ CE is reported to show a minor ^{12}C-enrichment in $\delta^{13}C$ values of the residual ~~fraction~~ phase with a magnitude similar to measurement uncertainties ~~of adsorbed compounds~~ (Huang et al., 1999; Jeannottat and Hunkeler, 2012; Poulson and Drever, 1999). Therefore, differences in $\delta^{13}C$ mean values of recovered CE were assigned to handling issues of the gaseous calibration standards, which indicated higher standard deviations when compared to the recovered CE obtained by the liquid calibration standard~~As the standard deviation (1σ) of $\delta^{13}C$ values of all CE obtained from measurement of gaseous standard aliquots were more pronounced than for liquid ones, enrichment due to volatilization was not evident~~ (Figure 2~~Figure 2~~). Compound breakthrough due to the loading procedure was discarded ~~as a reason for this~~, because it would have resulted in ~~even more pronounced~~ significant ^{13}C-depletion of the recovery CE (Klisch et al., 2012). ~~More likely, condensation due to transfer of especially small standard aliquots and/or leakage due to storage of the gaseous standard were assumed to cause the slight enrichment in $\delta^{13}C$ values.~~ Gaseous calibration standards were prepared and stored according to reported recommendations (U.S. Environmental Protection Agency (EPA), 1999a). A further ~~, while decreasing~~decrease in the recommended maximum operation time ~~of gaseous standards~~ to 48 h resulted in some improvement on the ~~improved later on~~subsequently mass recovery rates. Plotting mass recovery rate versus ~~injected~~ the spiked amounts of compounds, as shown in Figure 3~~Figure 3~~, revealed that recovery rates were lower ~~lower recovery rates~~ at smaller calibration standard aliquots. Nevertheless, poor recovery rates seemed to level-out above higher calibration standard aliquots of 2.2, 1.8, 1.3 and 1.3 nmol (PCE, TCE, cDCE and tDCE). The latter~~, which~~ was assigned as the minimum quantification limit (MQL) for mixing ratios and stable carbon isotope ratios of

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CE for the presented measurement setup and ~~represents~~ represented a compound molar ratio of 105, 84, 64 and 63 nmol mol^{-1}, ~~when~~ if sorbent tubes were loaded at a flow rate of 50 ml min^{-1} over a sampling time of 10 minutes. Such a MQL ~~render represents a~~ sufficient sensitivity for ambient air monitoring applications (Hartwig, 2017; Maceira et al., 2017; Ras-Mallorquí et al., 2007; Woolfenden, 1997).

The relative standard deviation for mass recovery of each compound and calibration standard agreed with previous recommendations of less than 10% (Bianchi and Varney, 1993). Influences due to humidity ~~was~~ were neglected, because (1) Tenax filled tubes did not show an influence in the presence of environmental humidity (Maceira et al., 2017) and (2) mass recovery from liquid standard aliquots showed more complete and reproducible mass recovery. Nevertheless, mass recovery rates suggested that using liquid calibrations standards ~~is~~ was better ~~compared than~~to using gaseous ones. To conclude, calibration using liquid standards is preferred, because of smaller uncertainties of mass recovery and less fluctuation in $\delta^{13}C$ values.

Figure 2: Comparison of $\delta^{13}C$ values obtained from sorption tubes loaded with either gaseous or dissolved calibration standard aliquots (nmol) for PCE, TCE, cDCE and tDCE. The dotted lines indicate the set values for $\delta^{13}C$.~~Comparison of $\delta^{13}C$ values obtained from sorption tubes loaded with either gaseous or dissolved standard aliquots (nmol) for PCE, TCE, cDCE and tDCE.~~

Figure 3~~3~~: Relative mass recovery rates of PCE, TCE, cDCE and tDCE when measured by the presented thermal desorption method after loading of gaseous or liquid calibration standard aliquots over the calibration range of chlorinated ethenes (nmol)..

~~Summary of the relative mass recovery rates of PCE, TCE, cDCE and tDCE when measured by the presented thermal desorption method after loading of gaseous or liquid standard aliquots over the calibration range of 0.5 to 4.5 nmol.~~

3.2   Calibration of carbon dioxide and methane using glass vials

Precisions~~-~~ of $\delta^{13}C$ values (1σ) ~~-~~of CO_2 and CH_4 were 0.13 ‰ and 0.23 ‰, respectively, when determined from working gas calibration standards (n=9, CO_2: 210 – 960 µmol mol^{-1}, CH_4: 550 – 2700 µmol mol^{-1}) extended over the atmospheric background levels (for 2021: CO_2 at 413.2 µmol mol^{-1} and CH_4 at 1889 µmol mol^{-1} (WMO - World Meteorological Organization, 2021)). The precision in molar ratio from the same measurements (1σ) ~~-~~was ±2 µmol mol^{-1} for CO_2 and 0.11 µmol mol^{-1} for CH_4. Detailed information is provided in Leitner et al. (2020).

~~3.2~~3.3 Field sampling campaigns

~~3.2.1~~3.3.1   Former domestic waste dump

~~3.2.1.1~~3.3.1.1   Whole air sampler

CO_2 molar ratios ~~from measurement triplicates~~ of whole air samples were found at 371 to 404 mmol mol^{-1} (1σ ≤ 5.6 mmol mol^{-1}) with $\delta^{13}C$-values of -10.4 ‰ to -9.2 ‰ (1σ ≤ 0.21 ‰) as shown in Figure 4~~Figure 4~~. For CH_4, molar ratios ~~of~~

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measurement singles were found between 2.05 to 4.34 mmol mol^{-1} with δ^{13}C-values of -56.1 ‰ to 47.7 ‰. Each whole air sample was first analysed for CO_2 via triplicate measurement of a 300 µL sample before being analysed for CH_4 using the residual whole air sample volume of approx. 20 mL.

Figure 4: Results for CO_2 and CH_4 molar ratios and δ^{13}C-values obtained from samples taken above an active (in operation) and non-active (in stand-by) landfill gas suction system unit.

Figure 4Figure 4 illustrates the results for CO_2 and CH_4 measurements from samples taken above the active and non-active landfill gas extraction system pipelines. A Welsh two-sample t-test could not confirm that means of the molar ratio or the δ^{13}C-values from active and non-active sampling spots were significantly different. Nevertheless, data points of the non-active pipeline incorporated three outliers (according to a Grubbs outlier test), , according to a Grubbs outlier test, three outliers, which were indicated in Figure 4Figure 4 as D6, D7, D14. It was hypothesized that those were biased by local emissions of CO_2 and CH_4 through the surface sealing originating from microbial degradation of organic waste materials. Estimates of global CH_4 emissions rank waste disposals in the top-5 of anthropogenic methane sources. (Fowler et al., 2009) Therefore, a Keeling Plot (Keeling, 1958) of the latter three points was used as a tentative proxy to link the outliers to the formation of methane at the landfill. The estimated source signals were -20.2 ‰ (R-squared: 0.999) and -60.2 ‰ (R-squared: 0.718) for CO_2 and CH_4 respectively. Both source signal values clearly did not reflect the atmospheric background (annual means CO_2: -8.7 ‰ ± 0.5 ‰ (2015) and 419 ± 8 mmol mol^{-1} (2021) at the NOAA Station Hegyhatsal, Hungary, which is the nearby NOAA station (White et al., 2015), and global annual mean CH_4: -47.3 ‰ and 1869 µmol mol^{-1} (WMO - World Meteorological Organization, 2021)). Despite this preliminary finding a more precise interpretation would require the δ^2H-CH_4 values to confirm, that the source values of the δ^{13}C-CH_4 pointed towards formation of CH_4 due to microbial activity, which was indicated by depleted values when compared to the atmospheric background (Whiticar, 1999). Nevertheless, the isotope ratio values for CO_2 and CH_4 in Figure 4 fell within the same characteristic range as previously shown for landfill gas emissions (Hackley et al., 1996). Methanogenesis from CO_2-H_2 was shown to yield a δ^{13}C-CH_4 value of ~ -60 ‰ (Krzycki et al., 1987), while the pathway via CO_2 reduction was less likely because the δ^{13}C-CO_2 source value would therefore have pointed to a more enriched value (~ -14‰) (Botz et al., 1996). Concomitant fermentation of the organic waste to supply the metabolic need of dissolved organic carbon and CO_2 respectively would need a δ^{13}C-value of ~ -22 ‰, which is close to previous observations (Mohammadzadeh and Clark, 2008). Although the former landfill is equipped with a landfill gas extraction system and surface sealing, minor landfill gas leakage of CH_4 could be identified due to the incorporated fraction of the locally emitted biogenic footprint of CH_4, as also shown in previous studies (Bakkaloglu et al., 2021).

3.2.1.23.3.1.2   Sorption tube sampler

Analysis of sorption tubes did not reveal any local emissions of CE. However, heptane and toluene could be detected in one or two sorbent tubes taken above the ex-situ filter facility. The molar ratio of heptane and toluene was found to beat approxat. 15 and 20 nmol mol^{-1} and toluene approx. 40 nmol mol^{-1}, respectively. Compounds were identified according to their MS spectra (Wallace, 2022) and verified and quantified by measurement of gaseous calibration standard aliquots (~1000 µmol

mol[-1]) of 20 to 50 µL, adding heptane and toluene before loading them to sorbent tubes similar as for CE. The measurement setup was also similar as for the CE. δ^{13}C-values of the compounds used in the calibration standard and obtained by field-derived samples agreed by less than 0.5 ‰ (-27 ‰ for toluene, -29 ‰ for heptane), which was an indication that both chemicals were once produced from similar resources like coal tar or crude oil.

485 **3.2.23.3.2   Forest demonstration center**

Results showed CO_2 molar ratios over a narrow range of 382 to 404 µmol mol^{-1} with 1 σ (single standard deviation) ≤ 7.3 µmol mol^{-1} and δ^{13}C values of -7.5 ‰ to – 8.8 ‰ with a 1 σ ≤ 0.3‰. Values were obtained (d from triplicate measurement of by successive analysis of three 300 µL whole-air sample aliquots from each sample vial ("measurement triplicate"), which were taken in triplicates at each sampling height and location during the field sampling campaign (n=9) triplicates).

490 Measurement triplicates of singles individual whole-air samples showed 1 a σ ≤ 6.6 µmol mol^{-1} and ≤ 0.2 ‰ and there were with no significant difference in σs between manually and UAV-collected samples.

Figure 5: Comparison of CO_2 molar ratios and δ^{13}C values obtained by UAV-based (black) and manual sampling (white, red) at the forest demonstration site. Dotted lines indicate consecutive sampling. Grey rectangles represent the sampling height (pointes were dogged to increase visibility of individual samples). Error bars were obtained from measurement triplicates (n=3). Comparison of
495 **CO_2 molar ratios and δ^{13}C values obtained by UAV-based and manual sampling at the forest demonstration site. Dotted lines indicate consecutive sampling. Grey rectangles represent the targeted sampling height, with points dodged within and points outside resulting from UAV-height oscillations.**

Factors, such as photosynthesis and soil respiration, usually maintain the δ^{13}C source signal below -22‰ (Cernusak et al., 2013; Hemming et al., 2005). The expected pattern of a vertical profile at the sample location, starting from the atmospheric
500 background level of CO_2 (δ^{13}C - -8.5‰ (Rubino et al., 2019)), must therefore follow continuous ^{13}C-CO_2 depletion approaching ground level. The diurnal variation in the CO_2 molar ratio has been shown to fluctuate more the closer to the ground level one gets and that diurnal changes have a higher magnitude closer to ground level than along the entire vertical profile (Bowling et al., 2005; Buchmann et al., 1998). Figure 5 Figure 5 illustrates the vertical profiles for molar ratios and δ^{13}C-values of CO_2 from obtained from manual and UAV-based sampling for molar ratios and δ^{13}C-values of CO_2, indicating
505 the consecutive sampling path of each group by the dotted lines. Initial Mmanual sampling at the tower ("manual at tower") was done around noon, starting approx. two hours prior to the UAV-based sampling procedure, which also included some manual sampling. The latter comprised of simultaneous manual ("manual at UAV") and UAV-based air sampling at a height of 0.4 m with the UAV-rotors not yet turned on ("UAV rotors off") and the UAV-based sampling with rotors turn on along the ascent of the vertical profile ("UAV rotors turned on"). With the exception of the final manual sample at 0.4 m during the
510 descent of the tower, all samples were collected in triplicate.

The largest variation in CO_2 molar ratios was observed for the sampling height of 0.4 m. Results showed a higher molar ratio of CO_2 for the final manual sample at 0.4 m at the tower (indicated by the red triangle in Figure 5) compared to the initial three samples, but similar values of δ^{13}C, which is why the increase in the molar ratio was reasoned by slightly elevated air temperatures (sample gas density) compared to the start of the manual sampling. The latter was also argued for the slight offset

515 of the manual and UAV-assisted vertical profile data. The variation of CO_2 molar ratios between simultaneous manual sampling at the UAV and sampling by the UAV itself could have been caused by the breath of the operators while walking around the UAV and/or by the operators walking over and disturbing forest floor vegetation and the moist soil layer. In conclusions, fluctuations in molar ratios and $\delta^{13}C$ values, were attributed to the diurnal variability in ecosystem respiration (Ehleringer and Cook, 1998), which for the presented data covered a range of < 30 µmol mol^{-1} and 2.5‰ and seemed to level

520 out with increasing sample height. Factors, such as photosynthesis and soil respiration, usually maintain the $\delta^{13}C$ source signal below -22‰ (Cernusak et al., 2013; Hemming et al., 2005). The expected pattern of a vertical profile at the sample location, starting from the ground level, must therefore follow continuous ^{13}C-CO_2-enrichment when approaching the atmospheric background level of CO_2 ($\delta^{13}C$ ~ -8.5‰ (Rubino et al., 2019)). The diurnal variation in the CO_2 molar ratio has been shown to be more pronounced closer to the ground level and that diurnal changes at ground level are of a higher magnitude than

525 variations along vertical profiles from forest floor to above the canopy (Bowling et al., 2005; Buchmann et al., 1998). ~~Factors, such as photosynthesis and soil respiration, usually maintain the $\delta^{13}C$ source signal below -22‰ (Cernusak et al., 2013; Hemming et al., 2005). The expected pattern of a vertical profile at the sample location, starting from the atmospheric background level of CO_2 ($\delta^{13}C$ ~ -8.5‰ (Rubino et al., 2019)), must therefore follow continuous ^{13}C-CO_2-depletion approaching ground level. The diurnal variation in the CO_2 molar ratio has been shown to fluctuate more the closer to the~~

530 ~~ground level one gets and that diurnal changes have a higher magnitude closer to ground level than along the entire vertical profile (Bowling et al., 2005; Buchmann et al., 1998).~~
~~The largest variations were observed at the height of 0.4 m. Manual sampling at the tower started and ended with sampling at 0.4 m with 120 minutes in between (start: sample triplicates, end: single sample). The forth sample of height 0.4 m showed a higher molar ratio of CO_2 when compared to the lower initial three samples. Consecutive manual samples taken from a similar~~

535 ~~height, but at the time of the launch of the UAV ("manual at UAV" in Figure 5) together with the successive UAV-based samples ("UAV rotors off") were all attributed to the diurnal variability in ecosystem respiration (Ehleringer and Cook, 1998), which for the presented data covers a range of < 30 mmol mol^{-1} only.~~
~~Although the~~The sampling entrance point was located at the ~~chilled~~ centre of the UAV-rotor plane, which was reported as the location with the minimal impact due to the rotation of the rotors (Zhou et al., 2018). It ~~it~~ was assumed~~,~~ that the influence of

540 the UAV rotors, due to the downwash generated by the propellers and the resulting disturbed air flow field, was the factor most influencing the vertical falsification of the actual sampling point, especially when the UAV operated close to ground level (Burgués and Marco, 2020; Zhou et al., 2018). UAV-sampling took place during the ascent with a dwell time at a constant altitude of about 1.5 minutes, which is needed to take triplicate samples. According to ~~(~~Brosy et al.~~(~~ 2017) sampling during the ascent ensures that the air is not mixed by the UAV before sampling is initiated. ~~(~~Andersen et al.~~.(~~ 2018) compared UAV-

545 based whole- air taken during the ascent and descent and relative to a tower and reported a variation of <13 µmol mol^{-1} comparing UAV-based samples and tower measurements and similar standard deviations for the ascent as for the descent.
Observing results from manual sampling at the UAV and UAV-based sampling with rotors on (Figure 5) showed that $\delta^{13}C$-values of manual sampling pointed towards the impact of soil respiration while UAV-based samples indicated continuous

$\delta^{13}C$-enrichment of residual CO_2, which was linked to photosynthetic activity of the overlying layers pursued by the consecutive UAV-based samples at the height of 5 and 13 meters. The impact of downwash seemed to level-out with the last sample of height 13 m, thereafter showing similar $\delta^{13}C$-values from manual and UAV-based sampling. The apparent offset in molar ratios between manual and UAV-based samples was attributed to difference in sampling time as already pointed out ~~on~~ for the example of manual sampling at the tower with 120 minutes in between.

4   Conclusions

The most demanding step, as for most analytical systems, is the implementation and testing of the initial workflow of the sampling procedure. Here we present a sampling system coupled to an off-line measurement setup to measure ~~the atmosphere for~~atmospheric CO_2, CH_4, and VOC molar ratios and $\delta^{13}C$-value at ambient conditions. Two samplers and a whole-air sample vessel preparation device were developed and evaluated at field conditions, while the measurement setup was evaluated in prior experiments (Leitner et al., 2020). That measurement setup enabled the determination of the mole fraction and stable isotope ratio of carbon of the target compounds detailed herein and ~~can~~ could be further applied to investigate the isotope ratios of hydrogen, oxygen and nitrogen in nitrous oxide.

The samplers can be easily mounted to any unmanned aerial vehicle with sufficient payload capacity, making it simple to sample at remote places or conduct automated sampling missions. The sampling system was tested at two field sites. A comparison with manual sampling revealed reasonable compatibility with the UAV-based sampling method. The results also showed that the system sensitivity is sufficient to detect CH_4 emissions and stable isotope signatures close to atmospheric background molar ratios, for which otherwise extensive and expensive sampling flights are required (Bayat et al., 2017), thereby providing an alternative to traditional approaches (Mønster et al., 2019).

Although we have proven the functionality of this system, location-specific sampling especially for vertical sampling profiles due to the impact of UAV-rotor downwash needs further investigation. Such impact to the air field surrounding the UAV is thought to be dependent on the applied UAV-specifications (Shukla and Komerath, 2018), thereby limiting the scope for general recommendations.

5   Acknowledgements

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References

Alvarado, M., Gonzalez, F., Erskine, P., Cliff, D. and Heuff, D.: A methodology to monitor airborne PM10 dust particles using a small unmanned aerial vehicle, Sensors (Switzerland), 17(2), doi:10.3390/s17020343, 2017.

Andersen, T., Scheeren, B., Peters, W. and Chen, H.: A UAV-based active AirCore system for measurements of greenhouse gases, Atmos. Meas. Tech., 11(5), 2683–2699, doi:10.5194/amt-11-2683-2018, 2018.

Aurell, J., Mitchell, W., Chirayath, V., Jonsson, J., Tabor, D. and Gullett, B.: Field determination of multipollutant, open area combustion source emission factors with a hexacopter unmanned aerial vehicle, Atmos. Environ., 166, 433–440, doi:10.1016/j.atmosenv.2017.07.046, 2017.

Bakkaloglu, S., Lowry, D., Fisher, R. E., France, J. L. and Nisbet, E. G.: Carbon isotopic characterisation and oxidation of UK landfill methane emissions by atmospheric measurements, Waste Manag., 132(July), 162–175, doi:10.1016/j.wasman.2021.07.012, 2021.

Barbieri, L., Kral, S. T., Bailey, S. C. C., Frazier, A. E., Jacob, J. D., Reuder, J., Brus, D., Chilson, P. B., Crick, C., Detweiler, C., Doddi, A., Elston, J., Foroutan, H., González-Rocha, J., Greene, B. R., Guzman, M. I., Houston, A. L., Islam, A., Kemppinen, O., Lawrence, D., Pillar-Little, E. A., Ross, S. D., Sama, M. P., Schmale, D. G., Schuyler, T. J., Shankar, A., Smith, S. W., Waugh, S., Dixon, C., Borenstein, S. and Boer, G. De: Intercomparison of small unmanned aircraft system (sUAS) measurements for atmospheric science during the LAPSE-RATE campaign, Sensors (Switzerland), 19(9), doi:10.3390/s19092179, 2019.

Bayat, B., Crasta, N., Crespi, A., Pascoal, A. M. and Ijspeert, A.: Environmental monitoring using autonomous vehicles: a survey of recent searching techniques, Curr. Opin. Biotechnol., 45(645141), 76–84, doi:10.1016/j.copbio.2017.01.009, 2017.

Bergmaschi, P. and Harris, G. W.: Measurements of stable isotope ratios (13CH4/12CH4; 12CH3D/12CH4), Global Biogeochem. Cycles, 9(4), 439–447, 1995.

Bianchi, A. P. and Varney, M. S.: Sampling and analysis of volatile organic compounds in estuarine air by gas chromatography and mass spectrometry, J. Chromatogr. A, 643(1–2), 11–23, doi:10.1016/0021-9673(93)80536-H, 1993.

Botz, R., Pokojski, H. D., Schmitt, M. and Thomm, M.: Carbon isotope fractionation during bacterial methanogenesis by CO2 reduction, Org. Geochem., 25(3–4), 255–262, doi:10.1016/S0146-6380(96)00129-5, 1996.

Bowling, D. R., Burns, S. P., Conway, T. J., Monson, R. K. and White, J. W. C.: Extensive observations of CO2 carbon isotope content in and above a high-elevation subalpine forest, Global Biogeochem. Cycles, 19(3), 1–15, doi:10.1029/2004GB002394, 2005.

Brewer, P. J., Kim, J. S., Lee, S., Tarasova, O. A., Viallon, J., Flores, E., Wielgosz, R. I., Shimosaka, T., Assonov, S., Allison, C. E., van der Veen, A. M. H., Hall, B., Crotwell, A. M., Rhoderick, G. C., Hodges, J. T., Mohn, J., Zellweger, C., Moossen, H., Ebert, V. and Griffith, D. W. T.: Advances in reference materials and measurement techniques for greenhouse gas atmospheric observations, Metrologia, 56(3), 034006, doi:10.1088/1681-7575/ab1506, 2019.

Brosy, C., Krampf, K., Zeeman, M., Wolf, B., Junkermann, W., Schäfer, K., Emeis, S. and Kunstmann, H.: Simultaneous

19

multicopter-based air sampling and sensing of meteorological variables, Atmos. Meas. Tech., 10(8), 2773–2784, doi:10.5194/amt-10-2773-2017, 2017.

Brown, R. H. and Purnell, C. J.: Collection and analysis of trace organic vapour pollutants in ambient atmospheres : The performace of a Tenax-GC adsorbent tube, J. Chromatogr. A, 178(1), 79–90, doi:10.1016/S0021-9673(00)89698-3, 1979.

615   Buchmann, N., Hinckley, T. M. and Ehleringer, J. R.: Carbon isotope dynamics in Abies amabilis stands in the Cascades, Can. J. For. Res., 28(6), 808–819, doi:10.1139/cjfr-28-6-808, 1998.

Burgués, J. and Marco, S.: Environmental chemical sensing using small drones: A review, Sci. Total Environ., 748, 141172, doi:10.1016/j.scitotenv.2020.141172, 2020.

Cernusak, L. A., Ubierna, N., Winter, K., Holtum, J. A. M., Marshall, J. D. and Farquhar, G. D.: Environmental and
620   physiological determinants of carbon isotope discrimination in terrestrial plants, New Phytol., 200(4), 950–965, doi:10.1111/nph.12423, 2013.

Chang, C. C. Y., Wang, J. L., Chang, C. C. Y., Liang, M. C. and Lin, M. R.: Development of a multicopter-carried whole air sampling apparatus and its applications in environmental studies, Chemosphere, 144, 484–492, doi:10.1016/j.chemosphere.2015.08.028, 2016.

625   Chang, C. C. Y., Chang, C. C. Y., Wang, J. L., Lin, M. R., Ou-Yang, C. F., Pan, H. H. and Chen, Y. C.: A study of atmospheric mixing of trace gases by aerial sampling with a multi-rotor drone, Atmos. Environ., 184(September 2017), 254–261, doi:10.1016/j.atmosenv.2018.04.032, 2018.

Coplen, T. B.: Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results, Rapid Commun. Mass Spectrom., 25(17), 2538–2560, doi:10.1002/rcm.5129, 2011.

630   Crotwell, A. and Steinbacher, M.: 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2017), GAW Rep., (242), 1–136, doi:10.1016/j.yhbeh.2013.09.005, 2018.

Djuricin, S., Pataki, D. E. and Xu, X.: A comparison of tracer methods for quantifying CO2 sources in an urban region, J. Geophys. Res. Atmos., 115(11), 1–13, doi:10.1029/2009JD012236, 2010.

Ehleringer, J. R. and Cook, C. S.: Carbon and oxygen isotope ratios of ecosystem respiration along an Oregon conifer transect:
635   preliminary observations based on small-flask sampling, Tree Physiol., 18(8–9), 513–519, doi:10.1093/treephys/18.8-9.513, 1998.

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S. A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir,
640   N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Ro-Poulsen, H., Cellier, P., Cape, J. N., Horváth, L., Loreto, F., Niinemets, Ü., Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N. and Erisman, J. W.: Atmospheric composition change: Ecosystems-Atmosphere interactions, Atmos. Environ., 43(33), 5193–5267, doi:10.1016/j.atmosenv.2009.07.068, 2009.

645 Górka, M. and Lewicka-Szczebak, D.: One-year spatial and temporal monitoring of concentration and carbon isotopic composition of atmospheric CO2 in a Wrocław (SW Poland) city area, Appl. Geochemistry, 35, 7–13, doi:10.1016/j.apgeochem.2013.05.010, 2013.

Greatwood, C., Richardson, T. S., Freer, J., Thomas, R. M., Rob Mackenzie, A., Brownlow, R., Lowry, D., Fisher, R. E. and Nisbet, E. G.: Atmospheric sampling on ascension island using multirotor UAVs, Sensors (Switzerland), 17(6), 1–24,

650 doi:10.3390/s17061189, 2017.

Grubbs, F. E.: Procedures for Detecting Outlying Observations in Samples, Technometrics, 11(1), 1, doi:10.1080/00401706.1969.10490657, 1969.

Hackley, K. C., Liu, C. L. and Coleman, D. D.: Environmental Isotope Characteristics of Landfill Leachates and Gases, Ground Water, 34(5), 827–836, doi:10.1111/j.1745-6584.1996.tb02077.x, 1996.

655 Hartwig, A.: Tetrachlorethen [MAK Value Documentation in German language, 2017], in The MAK-Collection for Occupational Health and Safety, vol. 1, pp. 878–985, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany., 2017.

Hemming, D., Yakir, D., Ambus, P., Aurela, M., Besson, C. K., Black, K., Buchmann, N., Burlett, R., Cescatti, A., Clement, R., Gross, P., Granier, A., Grünwald, T., Havrankova, K., Janous, D., Janssens, I. A., Knohl, A., Östner, B. K., Kowalski, A., Laurila, T., Mata, C., Marcolla, B., Matteucci, G., Moncrieff, J., Moors, E. J., Osborne, B., Pereira, J. S., Pihlatie, M., Pilegaard,

660 K., Ponti, F., Rosova, Z., Rossi, F., Scartazza, A. and Vesala, T.: Pan-European δ13 C values of air and organic matter from forest ecosystems, Glob. Chang. Biol., 11(7), 1065–1093, doi:10.1111/j.1365-2486.2005.00971.x, 2005.

Huang, L., Sturchio, N. C., Abrajano, T., Heraty, L. J. and Holt, B. D.: Carbon and chlorine isotope fractionation of chlorinated aliphatic hydrocarbons by evaporation, Org. Geochem., 30(8 A), 777–785, 1999.

International Atomic Energy Agency: IAEA-TECDOC-1268 Stable isotope measurement techniques for atmospheric

665 greenhouse gases. [online] Available from: http://www-naweb.iaea.org/napc/ih/documents/TECDOCS/TECDOC 1268 Atmospheric greenhouse gases 2002.pdf (Accessed 22 June 2020), 2002.

Jeannottat, S. and Hunkeler, D.: Chlorine and carbon isotopes fractionation during volatilization and diffusive transport of trichloroethene in the unsaturated zone, Environ. Sci. Technol., 46(6), 3169–3176, doi:10.1021/es203547p, 2012.

Keeling, C. D.: The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas, Geochim.

670 Cosmochim. Acta, 13(4), 322–334, doi:10.1016/0016-7037(58)90033-4, 1958.

Keeling, C. D., Mook, W. G. and Tans, P. P.: Recent trends in the 13C/12C ratio of atmospheric carbon dioxide, Nature, 277(5692), 121–123, doi:10.1038/277121a0, 1979.

Khan, A., Schaefer, D., Tao, L., Miller, D. J., Sun, K., Zondlo, M. A., Harrison, W. A., Roscoe, B. and Lary, D. J.: Low power greenhouse gas sensors for unmanned aerial vehicles, Remote Sens., 4(5), 1355–1368, doi:10.3390/rs4051355, 2012.

675 Klisch, M., Kuder, T., Philp, R. P. and McHugh, T. E.: Validation of adsorbents for sample preconcentration in compound-specific isotope analysis of common vapor intrusion pollutants, J. Chromatogr. A, 1270, 20–27, doi:10.1016/j.chroma.2012.10.050, 2012.

Krzycki, J. A., Kenealy, W. R., DeNiro, M. J. and Zeikus, J. G.: Stable Carbon Isotope Fractionation by Methanosarcina

barkeri during Methanogenesis from Acetate, Methanol, or Carbon Dioxide-Hydrogen, Appl. Environ. Microbiol., 53(10), 2597–2599, doi:10.1128/AEM.53.10.2597-2599.1987, 1987.

Leitner, S., Reichenauer, T. G. and Watzinger, A.: Impact of sorption processes on PCE concentrations in organohalide-respiring aquifer sediment samples, Sci. Total Environ., 615, 1061–1069, doi:10.1016/j.scitotenv.2017.09.225, 2018.

Leitner, S., Hood-Nowotny, R. and Watzinger, A.: Successive and automated stable isotope analysis of CO 2 , CH 4 and N 2 O paving the way for unmanned aerial vehicle-based sampling, Rapid Commun. Mass Spectrom., 34(24), 1–11, doi:10.1002/rcm.8929, 2020.

Maceira, A., Vallecillos, L., Borrull, F. and Maria, R.: Science of the Total Environment New approach to resolve the humidity problem in VOC determination in outdoor air samples using solid adsorbent tubes followed by TD-GC – MS, , 600, 1718–1727, doi:10.1016/j.scitotenv.2017.05.141, 2017.

Martinez, B., Miller, T. W. and Yalin, A. P.: Cavity ring-down methane sensor for small unmanned aerial systems, Sensors (Switzerland), 20(2), doi:10.3390/s20020454, 2020.

Mohammadzadeh, H. and Clark, I.: Degradation pathways of dissolved carbon in landfill leachate traced with compound-specific 13C analysis of DOC, Isotopes Environ. Health Stud., 44(3), 267–294, doi:10.1080/10256010802309814, 2008.

Mønster, J., Kjeldsen, P. and Scheutz, C.: Methodologies for measuring fugitive methane emissions from landfills – A review, Waste Manag., 87, 835–859, doi:10.1016/j.wasman.2018.12.047, 2019.

Palomaki, R. T., Rose, N. T., van den Bossche, M., Sherman, T. J. and De Wekker, S. F. J.: Wind estimation in the lower atmosphere using multirotor aircraft, J. Atmos. Ocean. Technol., 34(5), 1183–1191, doi:10.1175/JTECH-D-16-0177.1, 2017.

Pataki, D. E., Bowling, D. R., Ehleringer, J. R. and Zobitz, J. M.: High resolution atmospheric monitoring of urban carbon dioxide sources, Geophys. Res. Lett., 33(3), 1–5, doi:10.1029/2005GL024822, 2006.

Paul, D. and Skrzypek, G.: Normalization of measured stable isotopic compositions to isotope reference scales – a review, , 3006–3014, doi:10.1002/rcm, 2007.

Poulson, S. R. and Drever, J. I.: Stable Isotope (C, Cl, and H) Fractionation during Vaporization of Trichloroethylene, Environ. Sci. Technol., 33(20), 3689–3694, doi:10.1021/es990406f, 1999.

Poyi, G., Bousbaine, A. and Wu, M.: Computational fluid dynamics model of a quad-rotor helicopter for dynamic analysis, Int. J. Res. Eng. Adv. Technol., 4(3) [online] Available from: http://hdl.handle.net/10545/618421,%0Ahdl:10545/618421%0A, 2016.

Randazzo, A., Asensio-Ramos, M., Melián, G. V., Venturi, S., Padrón, E., Hernández, P. A., Pérez, N. M. and Tassi, F.: Volatile organic compounds (VOCs) in solid waste landfill cover soil: Chemical and isotopic composition vs. degradation processes, Sci. Total Environ., 726, 138326, doi:10.1016/j.scitotenv.2020.138326, 2020.

Ras-Mallorquí, M. R., Marcé-Recasens, R. M. and Borrull-Ballarín, F.: Determination of volatile organic compounds in urban and industrial air from Tarragona by thermal desorption and gas chromatography-mass spectrometry, Talanta, 72(3), 941–950, doi:10.1016/j.talanta.2006.12.025, 2007.

Ras, M. R., Borrull, F. and Marcé, R. M.: Sampling and preconcentration techniques for determination of volatile organic

22

compounds in air samples, TrAC - Trends Anal. Chem., 28(3), 347–361, doi:10.1016/j.trac.2008.10.009, 2009.

Restek Corporation: Optimizing the Analysis of Volatile Organic Compounds. [online] Available from: 715 https://d1lqgfmy9cwjff.cloudfront.net/csi/pdf/e/rk08.pdf (Accessed 24 August 2022), 2003.

Rohi, G., Ejofodomi, O. and Ofualagba, G.: Autonomous monitoring, analysis, and countering of air pollution using environmental drones, Heliyon, 6(1), e03252, doi:10.1016/j.heliyon.2020.e03252, 2020.

Rubino, M., Etheridge, D. M., Thornton, D. P., Howden, R., Allison, C. E., Francey, R. J., Langenfelds, R. L., Paul Steele, L., Trudinger, C. M., Spencer, D. A., Curran, M. A. J., Van Ommen, T. D. and Smith, A. M.: Revised records of atmospheric 720 trace gases CO_2 , CH_4 , N_2O, and $\delta 13 C$ -CO_2 over the last 2000 years from Law Dome, Antarctica, Earth Syst. Sci. Data, 11(2), 473–492, doi:10.5194/essd-11-473-2019, 2019.

Shaw, J. T., Shah, A., Yong, H. and Allen, G.: Methods for quantifying methane emissions using unmanned aerial vehicles: A review, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci., 379(2210), doi:10.1098/rsta.2020.0450, 2021.

Shirey, C. B.: Technical Report A Tool for Selecting an Adsorbent for Thermal Desorption Applications, n.d.

725 Shukla, D. and Komerath, N.: Multirotor Drone Aerodynamic Interaction Investigation, Drones, 2(4), 43, doi:10.3390/drones2040043, 2018.

Sikora, A.: European Green Deal – legal and financial challenges of the climate change, ERA Forum, 21(4), 681–697, doi:10.1007/s12027-020-00637-3, 2021.

Student: The Probable Error of a Mean, Biometrika, 6(1), 1, doi:10.2307/2331554, 1908.

730 Takahashi, H. A., Konohira, E., Hiyama, T., Minami, M., Nakamura, T. and Yoshida, N.: Diurnal variation of CO_2 concentration, $\Delta 14 C$ and $\delta 13 C$ in an urban forest: estimate of the anthropogenic and biogenic CO_2 contributions , Tellus B Chem. Phys. Meteorol., 54(2), 97–109, doi:10.3402/tellusb.v54i2.16651, 2002.

U.S. Environmental Protection Agency (EPA): Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in U.S. Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography-Mass Spectrometry 735 (GC-MS), [online] Available from: https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf, 1999a.

U.S. Environmental Protection Agency (EPA): Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes, Compend. Methods Determ. Toxic Org. Compd. Ambient Air, (January), 1–53 [online] Available from: https://www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf, 1999b.

U.S. Environmental Protection Agency (EPA): Air Sensor Guide, Washington, DC. [online] Available from: 740 https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=519616 (Accessed 22 June 2020), 2014.

Wallace, W. E. (Director): Mass Spectra, edited by P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899., 2022.

Werner, R. A., Brand, W. A., Biogeochemistry, M. and Box, P. O.: Referencing strategies and techniques in stable isotope ratio analysis, , 501–519, doi:10.1002/rcm.258, 2001.

745 White, J. W. C., Vaughn, B. H. and Michel, S. E.: Stable Isotopic Composition of Atmospheric Carbon Dioxide (13C and 18O) from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1990-2014, Univ. Color. Inst. Arct.

Alp. Res., (Version: 2015-10-26) [online] Available from: ftp://aftp.cmdl.noaa.gov/data/trace_gases/co2c13/flask/, 2015.

Whiticar, M. J.: Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, Chem. Geol., 161(1–3), 291–314, doi:10.1016/S0009-2541(99)00092-3, 1999.

750   Widory, D., Proust, E., Bellenfant, G. and Bour, O.: Assessing methane oxidation under landfill covers and its contribution to the above atmospheric CO2 levels: The added value of the isotope (δ13C and δ18O CO2; δ13C and δD CH4) approach, Waste Manag., 32(9), 1685–1692, doi:10.1016/j.wasman.2012.04.008, 2012.

WMO - World Meteorological Organization: WMO Greenhouse Gas Bulletin (GHG Bulletin) - No. 17, WMO Greenh. Gas Bull., 17, 1–10 [online] Available from: https://library.wmo.int/doc_num.php?explnum_id=10904 (Accessed 16 April 2020),

755   2021.

Woolfenden, E.: Monitoring vocs in air using sorbent tubes followed by thermal desorption-capillary gc analysis: Summary of data and practical guidelines, J. Air Waste Manag. Assoc., 47(1), 20–36, doi:10.1080/10473289.1997.10464411, 1997.

Zazzeri, G., Lowry, D., Fisher, R. E., France, J. L., Lanoisellé, M., Grimmond, C. S. B. and Nisbet, E. G.: Evaluating methane inventories by isotopic analysis in the London region, Sci. Rep., 7(1), 4854, doi:10.1038/s41598-017-04802-6, 2017.

760   Zhou, S., Peng, S., Wang, M., Shen, A. and Liu, Z.: The characteristics and contributing factors of air pollution in Nanjing: A case study based on an unmanned aerial vehicle experiment and multiple datasets, Atmosphere (Basel)., 9(9), doi:10.3390/atmos9090343, 2018.
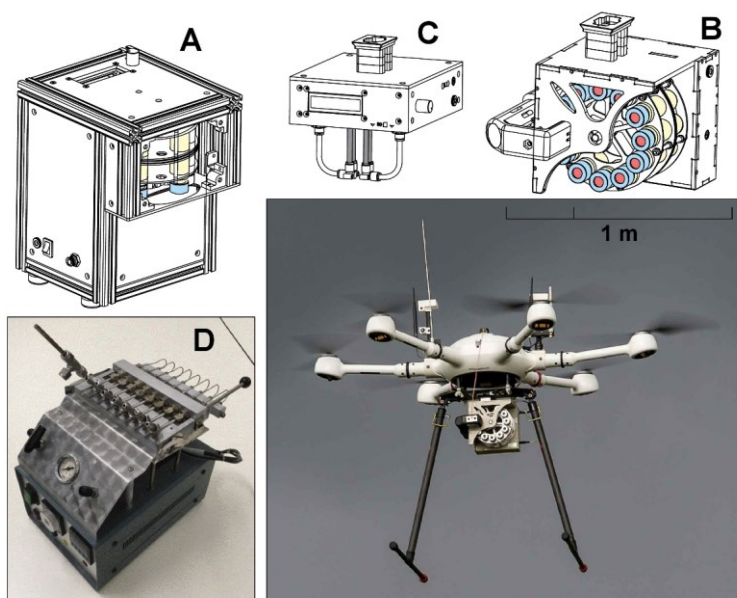
765 **Figure 1:** <u>Overview of the S</u>s̶ampling system ~~overview~~ comprising of the vial preparation device (A), the whole-air sampler (B), the gas sampler for adsorbent tubes (C), the sorbent tube conditioning device (TubeCon2, D) <u>with one sorbent tube attached</u> and the UAV applied in field test equipped with the whole-air sampler.

770 **Table 1.** Comparison of $\delta^{13}C$ mean values $\pm 2\ \sigma$ and mass recovery rates, as means $\pm 2\ \sigma$, obtained from measurements of gaseous and liquid calibration standard aliquots at the given mass range (nmol) loaded to sorbent tubes.

calibration standard	compound	$\delta^{13}C_{mean} \pm 2\ \sigma$	mass recovery (mean $\pm 2\ \sigma$)	nmol (min – max)	n
gaseous	PCE	-27.3 ± 0.5	0.63 ± 0.22	2.2 - 4.4	34
liquid	PCE	-27.5 ± 0.1	1.00 ± 0.06	2.1 - 3.5	12
gaseous	TCE	-29.5 ± 0.4	0.81 ± 0.17	1.8 - 4.4	29
liquid	TCE	-29.8 ± 0.1	1.00 ± 0.05	1.6 - 4.1	31
gaseous	cDCE	-25.9 ± 0.7	0.82 ± 0.11	1.3 - 4.4	39
liquid	cDCE	-26.0 ± 0.08	1.00 ± 0.04	1.3 - 4.4	26

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gaseous	tDCE	-12.2 ± 0.4	0.77 ± 0.13	1.3 - 4.4	43
liquid	tDCE	-12.2 ± 0.05	1.00 ± 0.03	1.6 - 3.9	32

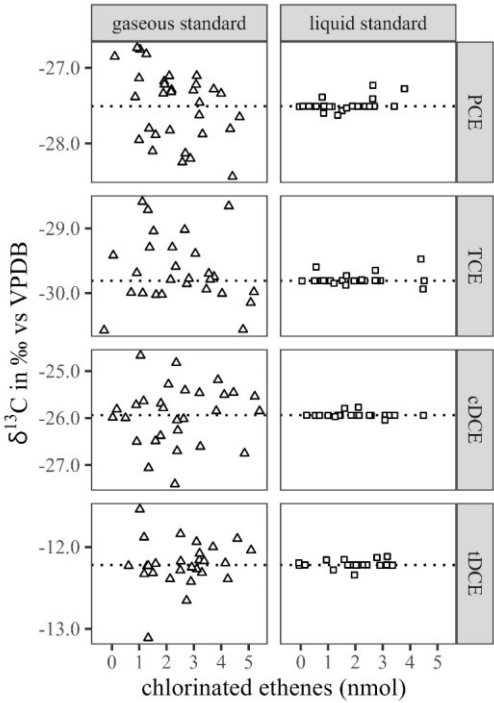**Figure 2: Comparison of δ¹³C values obtained from sorption tubes loaded with either gaseous or dissolved calibration standard aliquots (nmol) for PCE, TCE, cDCE and tDCE. The dotted lines indicate the set values for δ¹³C.**

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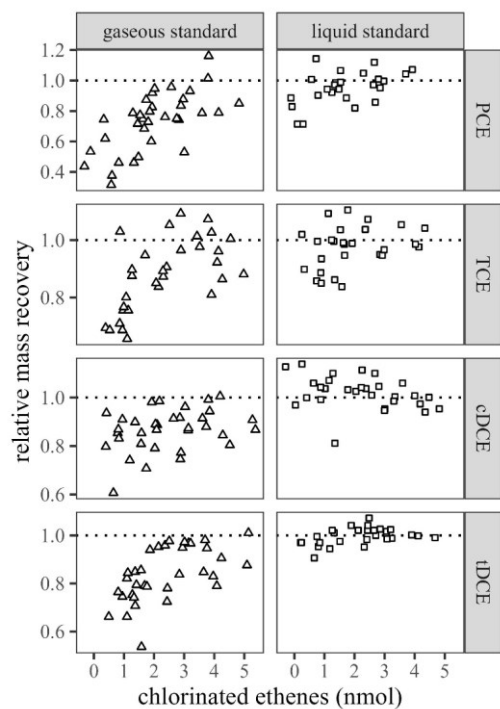**Figure 3:** ~~SRummary of the~~ relative mass recovery rates of PCE, TCE, cDCE and tDCE when measured by the presented thermal desorption method after loading of gaseous or liquid <u>calibration</u> standard aliquots over the calibration range <u>of chlorinated ethenes (nmol).</u> ~~of 0.5 to 4.5 nmol~~.
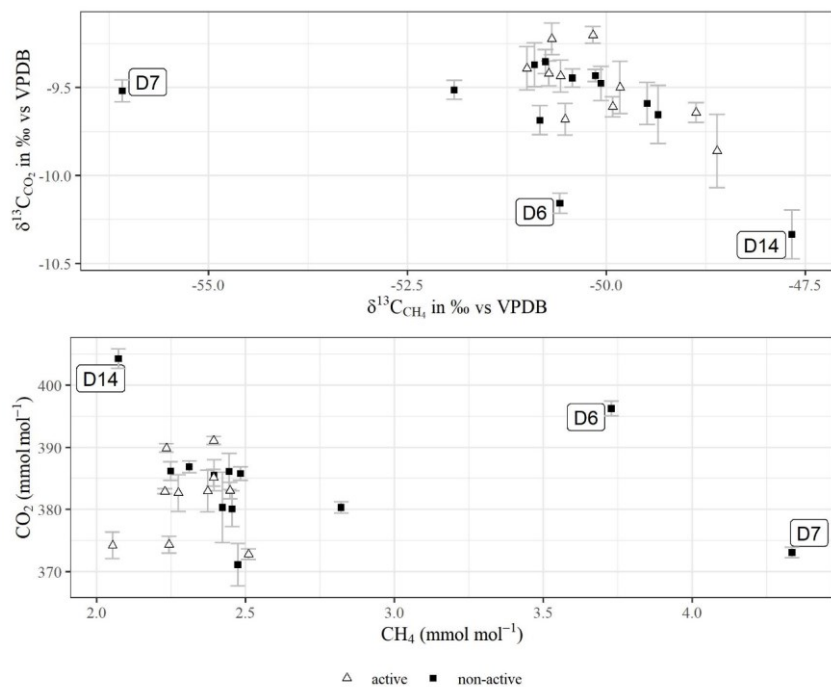
780

Figure 4: Results for CO₂ and CH₄ molar ratios and δ¹³C-values obtained from samples taken above an active (in operation) and non-active (in stand-by) landfill gas suction system unit.
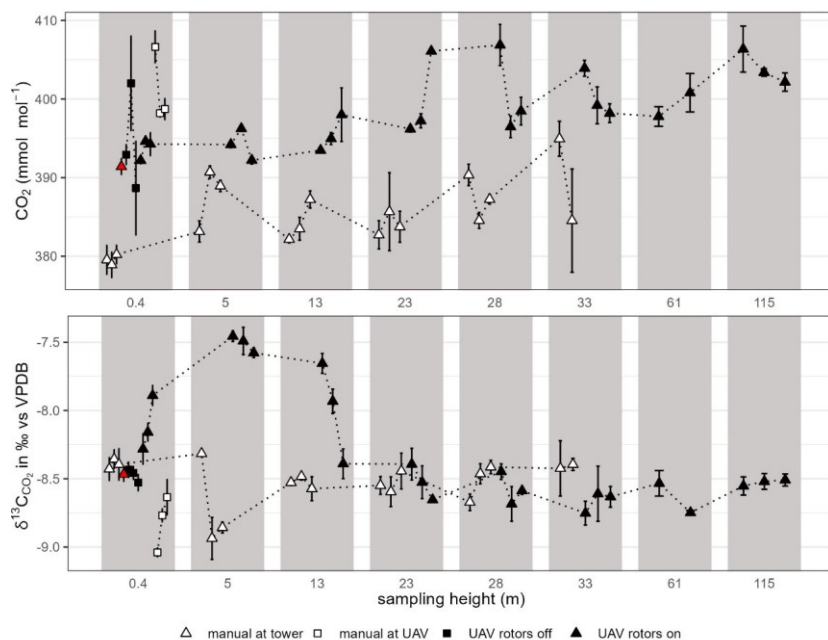
785 **Figure 5: Comparison of CO₂ molar ratios and δ¹³C values obtained by UAV-based (black) and manual sampling (white, red) at the forest demonstration site. Dotted lines indicate consecutive sampling. Grey rectangles represent the ~~targeted~~ sampling height (pointes were dogged to increase visibility of individual samples). Error bars were obtained from measurement triplicates (n=3). ~~, with points dodged within points outside resulting from UAV-height oscillations~~.**