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

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Abstract. 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 collect and sampled in glass vials for greenhouse gas analysis.

The measurement setup for the sorbent tubes achieved analyte mass recovery rates of 63 % - 100 % (more favourable for lower chlorinated VOCs), when prepared from gaseous or liquid calibration standards, and reached a precision better than 0.7 ‰ for $\delta^{13}C$ in the molar ratio range of 0.35 – 4.45 nmol. The precision of triplicate CO_2 measurements from whole air sample replicates was < 7.3 mmol mol^{-1} and < 0.3 ‰ and < 0.03 µmol mol^{-1} and < 0.24‰ for CH_4 working gas standard replicates. 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 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

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 the atmospheric trace gas inventories, such as greenhouse gases (GHG) or volatile organic carbons (VOC). 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), 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

35 is particularly suitable for use in confined spaces, as they take off vertically, hover and have a high manoeuvrability (Burgués and Marco, 2020). 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.

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

40 implications for inventory estimates. In order to differentiate and identity sources and sinks, the application of stable isotope analysis of trace gas compounds has been proven to provide such additional information (Keeling, 1958; Keeling et al., 1979) which is of utmost importance, specifically when dealing with mitigation measures (Crotwell and Steinbacher, 2018) or law enforcement.

Sampling and analysing the atmosphere for the compound specific mole fractions of GHG or VOCs can be accomplished using

45 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, sample vessel tightness, avoidance of sample gas impurities, which are necessary for the sampling and measurement of low natural abundance, rare isotopic species of the GHG and VOC. For VOC, sampling efforts can be significantly eased using sorbent tubes rather than heavy-weight canisters or large volume sample bags

50 (Woolfenden, 1997). However, sampling methodology is attendant on the target 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). There are versatile approaches using small and light sampling vessels as alternatives for whole-air sampling (Górka and Lewicka-Szczebak, 2013). Nevertheless, above-ground surface sampling often relies on the availability and access to towers and buildings (Djuricin et al., 2010; Pataki et al., 2006; Takahashi et al., 2002). Such infrastructure is

55 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 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.

60 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-*

65   Dichloroethene (cDCE) and *trans*-Dichloroethene (tDCE)). All are commonly found in urban and industrial areas. (Ras-Mallorquí et al., 2007). CE 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 sample aliquots have to be transferred to measurement vessels, as is the case when

70   using gasbags for example (Chang et al., 2016; Greatwood et al., 2017). Moreover, the system described herein ensures detection limits are 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-board measurement (Khan et al., 2012; Martinez et al., 2020; Rohi et al., 2020) have

75   numerous advantages, 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.

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

80   site. (2) Spatially distributed air samples from a former domestic waste dump provided information on local GHG and CE inventories. 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

85   #### 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

90   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

95 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

100 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

105 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 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), 1999b). Gaseous aliquots were injected using a 100 µL gastight microliter syringe with a G26 side-port needle (SGE, BGB

110 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 Woolfenden (1997) the use of organic solvents such as methanol is not suitable for Tenax GR because methanol would also

115 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).

The gaseous calibration standard was prepared by injecting liquid aliquots of tDCE, cDCE, TCE and PCE to a molar ratio of

120 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 and syringe temperature of 60 °C. The calibration range was designed to the manufacturer's (Thermo Fisher Scientific)

125 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: 180x155x130 mm (LxWxH) with installed sorbent tubes). The sample gas inlet was adjusted with a manually adjustable pinch

130 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 (PBT) 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 ports of an electric four-port gas distribution manifold. The gas manifold enables switching between different sampling modes,

135 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 suction power of the pump a tee piece was installed prior to the pump feed to equalize the different flow rates set at the

140 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 sampler was connected via a quick release dovetail mount to the bottom of the UAV.

145 ## 2.2 Gas sampling with glass vials

2.2.1 Vial preparation and conditioning

20 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 12 glass vials and conditions the vials via flushing and evacuation. Flushing of closed vials was either done with synthetic air or helium

150 for 1 min at 200 mL min^{-1} using two G26 side-port needles 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). 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

155 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

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 vial's negative pressure to 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 (100 µL) and the residual flush-gas volume 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, 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 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 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 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 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 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: Sampling system overview comprising of the vial preparation device (B), the whole-air sampler (B), the gas sampler for
190 **adsorbent tubes (B), the sorbent tube conditioning device (TubeCon2, D) and the UAV applied in field test equipped with the whole-air sampler.**

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
195 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
200 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. 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
205 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
210 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 electronic 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
215 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 transferred with a Helium flow of 20 mL min^{-1}. Adsorbed

220 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, 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

225 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

230 (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.

235 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

240 atmospheric air components (e.g. N_2, CO_2 and N_2O) and 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 description

The gas-sampling system was tested at two field sites, which were representative for the application of the sorbent tube and/or

245 whole air sampling system. Target compounds using the sorbent tube sampler were VOC 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 had been identified as

250 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.

The whole air sampler was tested along a horizontal sampling profile above the interconnecting pipeline of two landfill gas
255 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 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
260 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 domestic waste dump. The filter facility surroundings had a noticeable odour that day. Sorbent tubes of the vertical sampling profile were loaded with ambient air at a flow rate of 50 mL min^{-1} for an individual sampling time of 10 minutes. Discreet
265 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 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
270 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
275 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

280 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 the latter the TD

285   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 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

290   over a range of 0.35 – 4.45 nmol injected (corresponding IRMS mass 44 intensity range: 100 to 8000 mV). Injected amounts 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 $\pm 2 \sigma$ 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.

Tschickardt et al. (2017) recommended to calibrate TD-methods with test gases, spiking liquid stock solutions to a gas stream,

295   while spiking of gaseous standard aliquots was designed as a proxy for ambient sampling conditions. Gaseous standard aliquots were loaded to the sorption tubes in similar mass quantity as for the liquid standard. 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 filtered according to a two-sigma (2σ) criterion on

300   the $\delta^{13}C$ and subsequently on the determined compound amounts. According to a Student-t-Test, means of remaining $\delta^{13}C$ values obtained from both calibration standard types originated from the same population. Still, means of gaseous standards showed a minor enrichment in ^{13}C when compared to liquid standards (Table 1). Volatilization of the light isotopes is reported to show enrichment in $\delta^{13}C$ values of the residual fraction of adsorbed compounds (Huang et al., 1999; Jeannottat and Hunkeler, 2012; Poulson and Drever, 1999). As the standard deviation (1σ) of $\delta^{13}C$ values of all CE obtained from measurement of

305   gaseous standard aliquots were more pronounced than for liquid ones, enrichment due to volatilization was not evident (Figure 2). Compound breakthrough due to the loading procedure was discarded as a reason for this, because it would result in significant ^{13}C-depletion (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 standards were prepared and stored according to reported recommendations (U.S. Environmental Protection Agency (EPA),

310   1999a), while decreasing the maximum operation time of gaseous standards to 48 h improved later-on mass recovery rates. Plotting mass recovery rate versus injected amounts of compounds, as shown in Figure 3, revealed lower recovery rates at smaller standard aliquots. Nevertheless, poor recovery seemed to level-out above higher aliquots of 2.2, 1.8, 1.3 and 1.3 nmol (PCE, TCE, cDCE and tDCE), which was assigned as the minimum quantification limit (MQL) of CE for the presented measurement setup and represents a compound molar ratio of 105, 84, 64 and 63 nmol mol^{-1}, when sorbent tubes were loaded

315   at a flow rate of 50 ml min^{-1} over a sampling time of 10 minutes. Such MQL render 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 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

320 from liquid standard aliquots showed more complete and reproducible mass recovery. Nevertheless, mass recovery rates suggested that using liquid calibrations standards is better compared 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 standard aliquots (nmol) for PCE, TCE, cDCE and tDCE.

325 **Figure 3: 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 of CO_2 and CH_4 were 0.13 ‰ and 0.23 ‰, 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:

330 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 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).

3.3   Field sampling campaigns

3.3.1   Former domestic waste dump

3.3.1.1   Whole air sampler

335 CO_2 molar ratios from measurement triplicates of whole air samples were found at 371 to 404 mmol mol^{-1} ($1\sigma \leq 5.6$ mmol mol^{-1}) with $\delta^{13}C$-values of -10.4 ‰ to -9.2 ‰ ($1\sigma \leq 0.21$ ‰) as shown in Figure 4. For CH_4, molar ratios of measurement singles were found between 2.05 to 4.34 mmol mol^{-1} with $\delta^{13}C$-values of -56.1 ‰ to 47.7 ‰.

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

340 Figure 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 $\delta^{13}C$-values from active and non-active sampling spots were significantly different. Nevertheless, data points of the non-active pipeline incorporated, according to a Grubbs outlier test, three outliers, which were indicated in Figure 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

345 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

350   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 to confirm, that the source values of the $\delta^{13}C$-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). Methanogenesis from CO_2-H_2 was shown to yield a $\delta^{13}C$-CH_4 value of ~ -60 ‰ (Krzycki et al., 1987), while the pathway via

355   CO_2 reduction was less likely because the $\delta^{13}C$-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 $\delta^{13}C$-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

360   CH_4, as also shown in previous studies (Bakkaloglu et al., 2021).

3.3.1.2   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 was found to be approx. 15 and 20 nmol mol^{-1} and toluene approx. 40 nmol mol^{-1}. Compounds were identified according to their MS spectra (Wallace, 2022) and

365   verified 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. $\delta^{13}C$-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.

3.3.2   Forest demonstration center

370   Results showed CO_2 molar ratios over a narrow range of 382 to 404 µmol mol^{-1} with $1\sigma \leq 7.3$ µmol mol^{-1} and $\delta^{13}C$ values of -7.5 ‰ to − 8.8 ‰ with a $1\sigma \leq 0.3$‰ (from triplicate measurement of whole-air sample triplicates). Measurement triplicates of singles showed $1\sigma \leq 6.6$ µmol mol^{-1} and ≤ 0.2 ‰ and there were no significant differences between manually and UAV-collected samples.

375   **Figure 5: Comparison of CO_2 molar ratios and $\delta^{13}C$ 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 $\delta^{13}C$ 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

380 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 illustrates the vertical profiles from manual and UAV-based sampling for molar ratios and $\delta^{13}C$-values of CO_2, indicating the consecutive sampling path by the dotted lines. Manual sampling at the tower was done around noon, approx. two hours prior to UAV-based sampling. The largest variations were

385 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 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

390 covers a range of < 30 mmol mol^{-1} only.

Although the sampling entrance point was located at the chilled centre of the UAV-rotor plane it was assumed, that the influence of 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). Observing results from manual sampling at the UAV and UAV-

395 based sampling with rotors on 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, 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

400 difference in sampling time as already pointed out on 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

405 for 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 be further applied to investigate the isotope ratios of hydrogen, oxygen and nitrogen in nitrous oxide.

410 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),

415 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.

420 **5   Acknowledgements**

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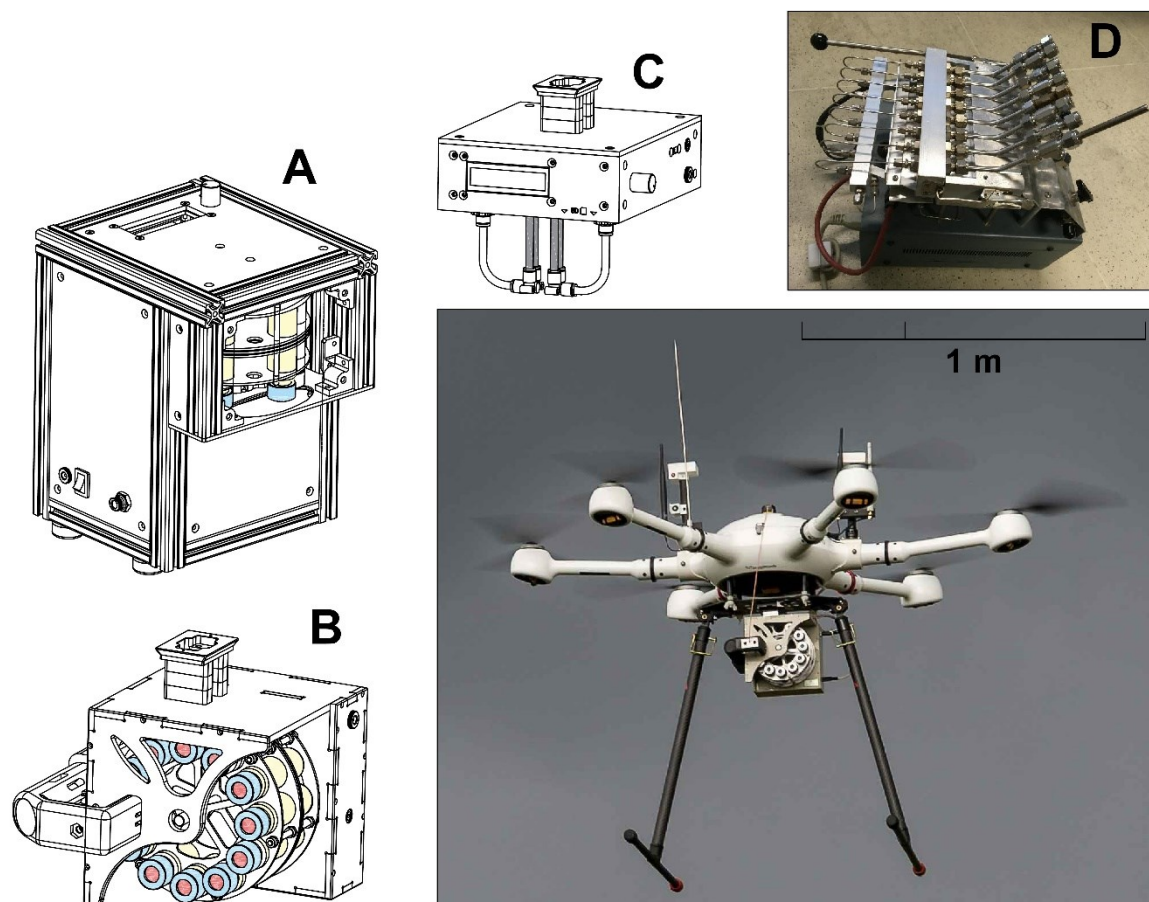
Figure 1: Sampling system overview comprising of the vial preparation device (B), the whole-air sampler (B), the gas sampler for adsorbent tubes (B), the sorbent tube conditioning device (TubeCon2, D) and the UAV applied in field test equipped with the whole-air sampler.

Table 1. Comparison of $\delta^{13}C$ mean values $\pm$ 2 σ and mass recovery rates, as means $\pm$ 2 σ, 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 σ)	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

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liquid	cDCE	-26.0 ± 0.08	1.00 ± 0.04	1.3 - 4.4	26
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

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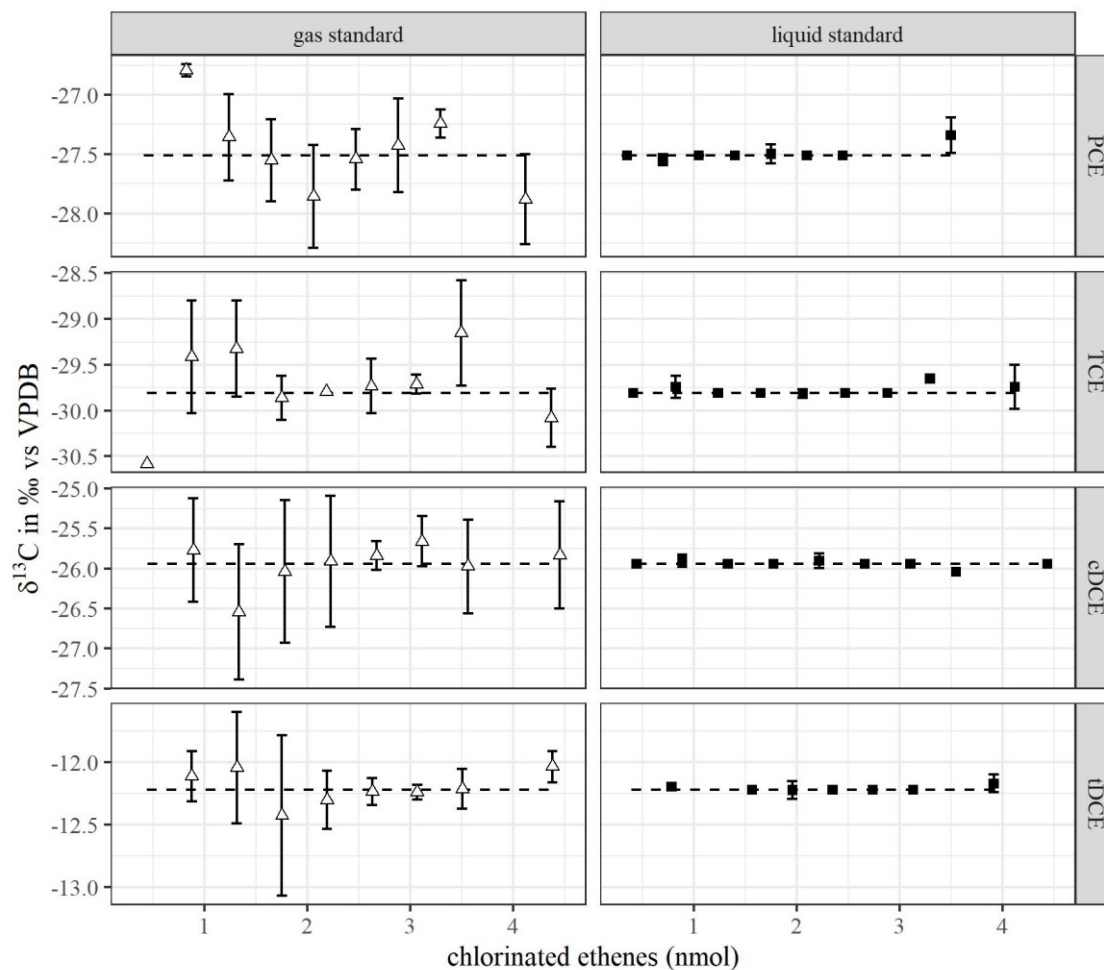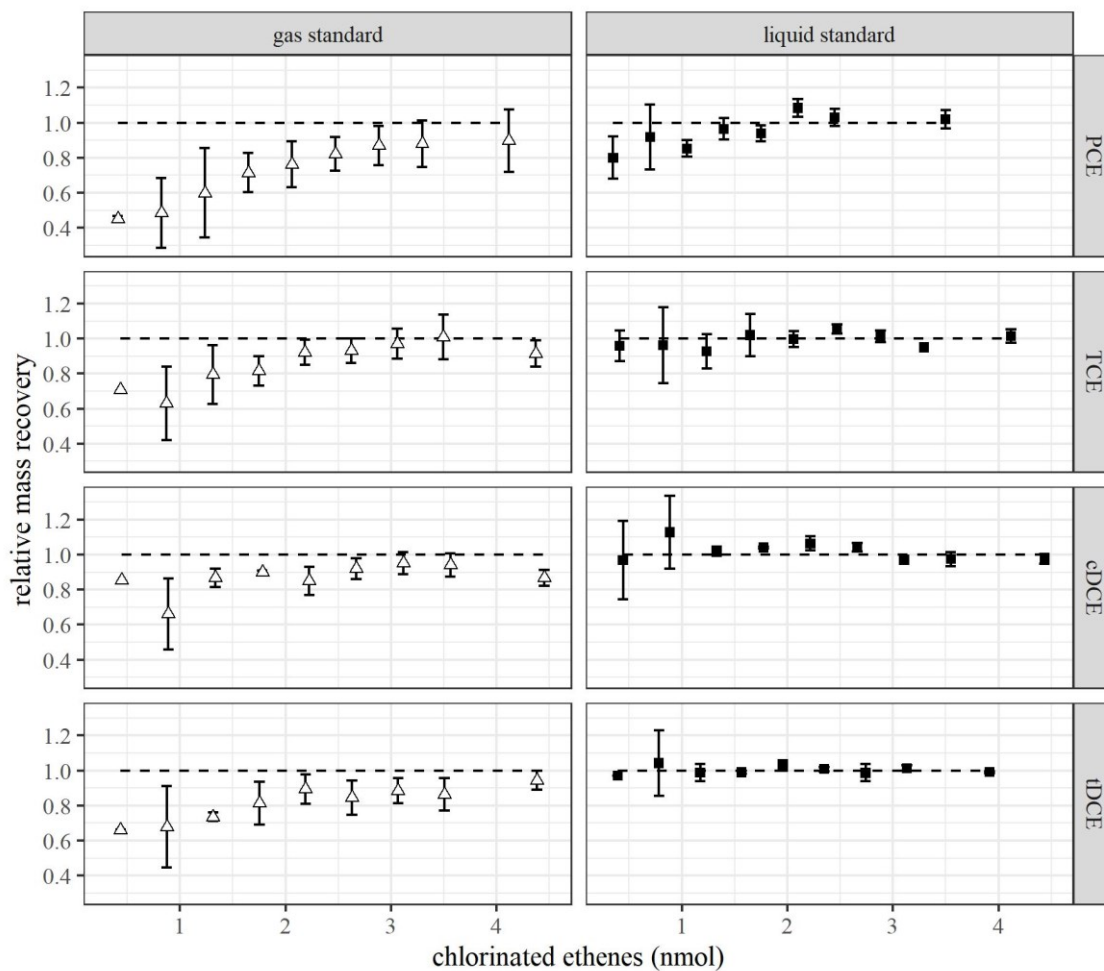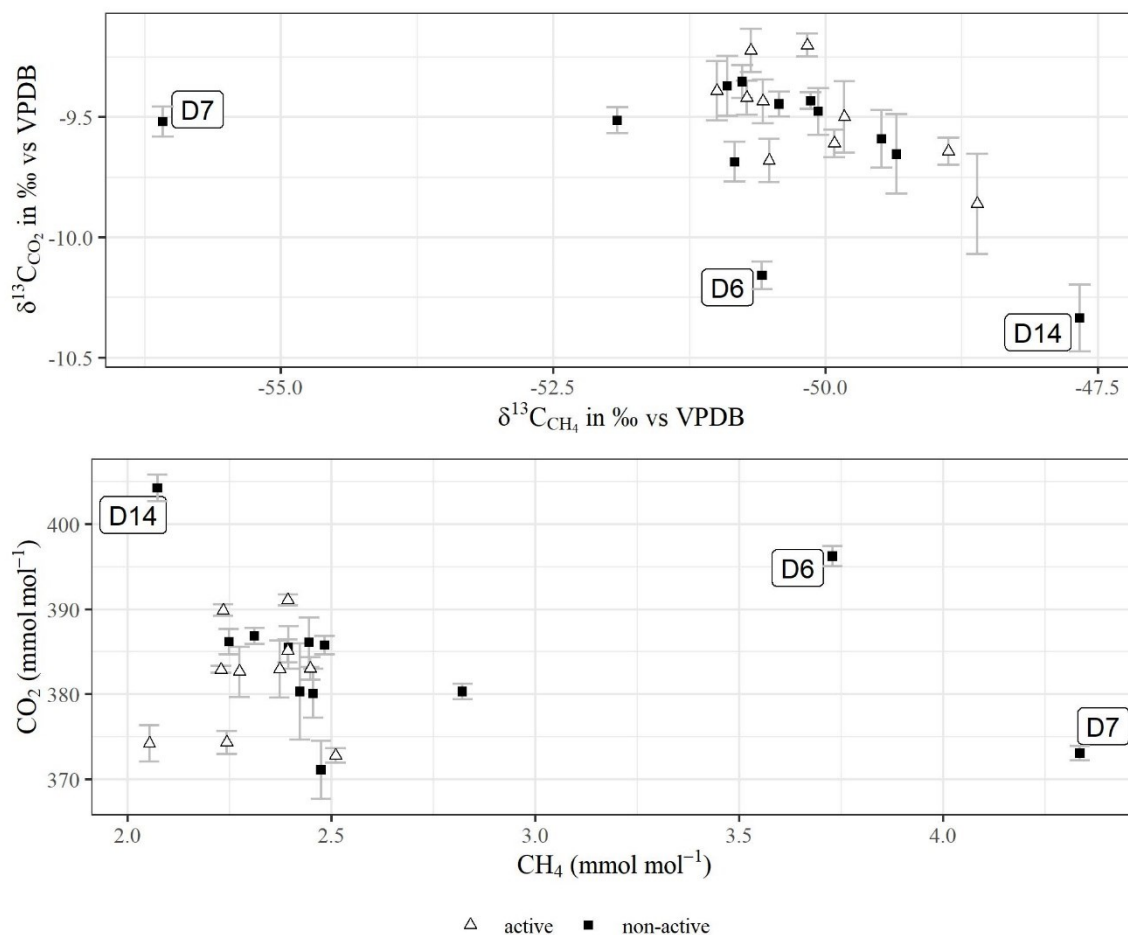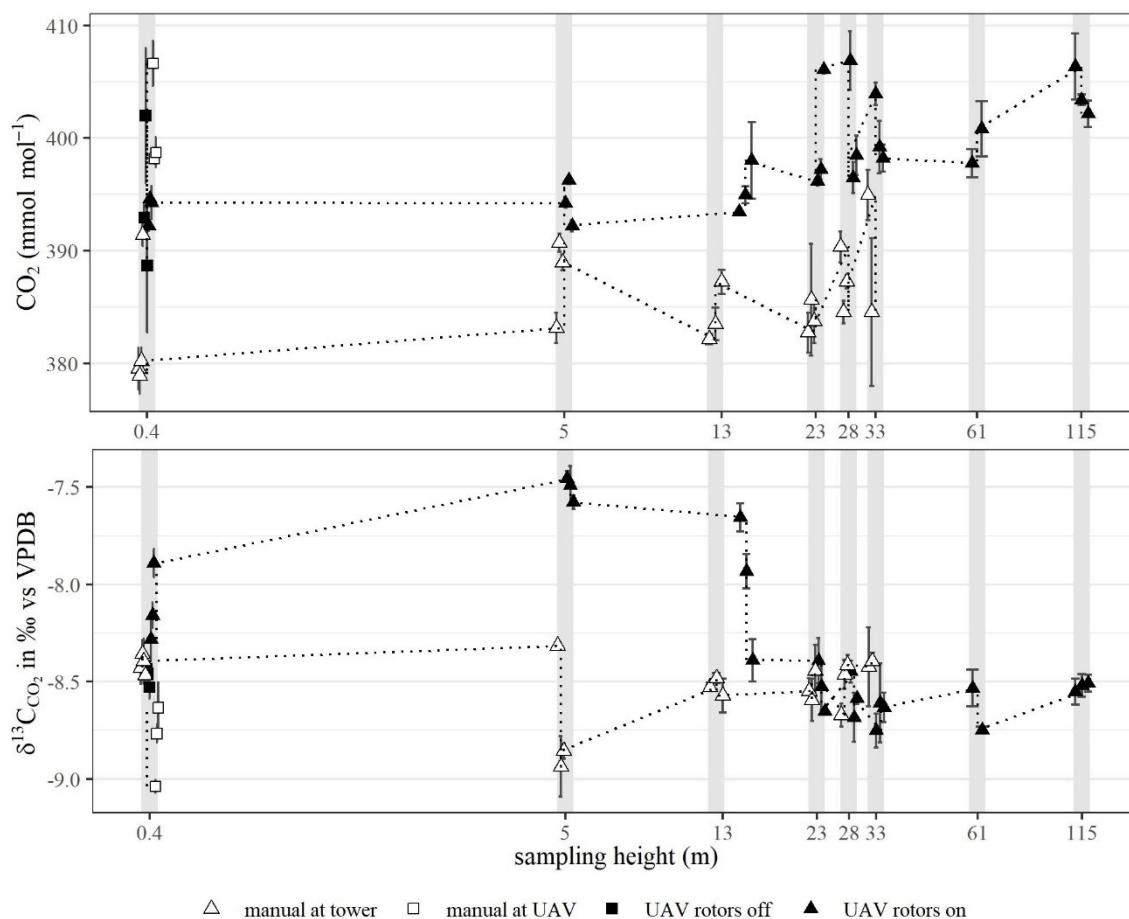

Figure 2: Comparison of $\delta^{13}C$ values obtained from sorption tubes loaded with either gaseous or dissolved standard aliquots (nmol) for PCE, TCE, cDCE and tDCE.

605 **Figure 3: 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.**

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.

Figure 5: Comparison of CO₂ molar ratios and δ¹³C 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 points outside resulting from UAV-height oscillations.