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Measuring techniques for concentration and stable isotopologues of CO_2 in a terrestrial ecosystem: A review

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1. Introduction

With increasing emphasis on the carbon dioxide (CO_2) effect on climate dynamics (Pachauri et. al, 2014), monitoring the carbon exchange between the atmosphere and terrestrial ecosystems and carbon cycling in ecosystems is of essential importance for understanding climate change (Vaughn et al., 2010; Schimel et al., 2015). The stable isotopes of carbon ($\delta^{13}C$) track changes in photosynthesis, respiration, organic matter decomposition and anthropogenic fuel emission inputs (e.g., McDowell et al., 2008), while the oxygen isotopes of water ($\delta^{16}O$ and $\delta^{18}O$) contain information on the linkages between the carbon and water cycles (Dawson and Simonin, 2011). Analysis of both the concentrations and isotopic composition of CO_2 is a useful tool for tracing, characterizing and quantifying the CO_2 cycle on temporal and spatial scales. Concentration measurements of CO, NO_x, CO_2, etc. became widespread in the mid-1960s, when the first semiconductor diode lasers were developed to trace its cycle in different applications. Much of this instrumentation is based on near- and mid-infrared absorption spectroscopy, spanning wavelengths from 1 to >10 μm (McDonagh et al., 2008). The traditional spectroscopic technique has been non-dispersive infrared (NDIR), by which the transmission has been measured at two wavelength regions, one at absorbing and the other at non-absorbing wavelengths (Linnerud et al., 1998). Fourier transform infrared (FTIR) spectroscopy is an alternative to NDIR-based analysers and has advantages because of a high-throughput and being well-suited to multicomponent analysis of gases and other chemical elements/compounds.

Through continuous progress, the stable isotope techniques have become widespread in environmental sciences (Hoefs, 2009; Michener & Lajhta, 2008 and West et al., 2011) and, over recent decades, our understanding of environmental changes and, in

particular, of carbon fluxes and carbon-water relations, has considerably improved owing to the development (and employment) of precise and accurate isotope ratio mass spectrometry (IRMS) and laser-absorption spectroscopy (LAS) measurement techniques (e.g., Crosson et al., 2002; Erdelyi et al., 2002; Griffis, 2013; Kerstel et al., 1999; Mortazavi and Chanton, 2002; Muccio and Jackson, 2009; Saleska et al, 2006; Schauer et al., 2005; Schnyder et al., 2004; Theis et al., 2004; Wada et al., 2016; West et al., 2011; Wen et al., 2013; Wehr et al., 2013, Wehr et al., 2016 and Wehr et al., 2017). Stable isotope abundance measurements require highly precise mass spectrometers (defined generally as a standard deviation in the range of 4 to 6 significant figures, i.e., parts per thousand) (Brenna, 1997; Brenna et al., 1997), allowing the introduction of simple analytes. The samples for off-line IRMS must first be converted into a gaseous form (e.g., CO_2, N_2, SO_2, CO etc.) and later introduced for analyses. On-line sample inlet systems were introduced with the development of the continuous-flow IRMS measurement technique in the 1980s, which allowed a faster and higher throughput of samples. In the early 1990s, the first LAS techniques were employed for stable isotope ratio measurements in air samples and are nowadays widely used in the analysis of trace gases, including CO_2 isotopologues (Werle, 1998).

While LAS is readily field-deployable and widely implemented, the IRMS techniques are more oriented to laboratory usage (McAlexander et al., 2011). The choice of which technique to use highly depends on the research questions, remoteness of the study area and financial capacities. However, regardless of the study aims, the type of analytical instrument chosen should meet the required sensitivity and must be insensitive to vibrations and mechanical instabilities when used for measurements in the field. In this paper, we outline the strengths and weaknesses of both IRMS and LAS analytical

techniques for concentration and stable isotope ratio measurements of CO_2, highlighting some examples of ecological research campaigns.

2. Methodology

This review focused on papers that used IRMS and LAS analytical techniques for concentration and stable isotopologues of CO_2 measurement. To refine the pool of searched literature that met our criteria, Scopus and Web of Science, as two of the world's largest citation databases, were used. At each query, terms and keywords such as 'CO_2 isotopologues', 'laser-absorption spectroscopy', 'isotope ratio mass spectrometry', 'isotope analyser', 'CO_2', 'trace gas', 'stable isotopes', 'decision tree' and 'terrestrial ecosystem' were used individually to produce an extensive list of articles. Using Scopus and Web of Science, the body of literature was searched based on a fixed set of inclusion criteria: 1) The search was set from the date of the first relevant article until until early 2019, 2) The predefined keywords should exist as a whole in at least one of the fields: title, keywords or abstract, 3) The paper should be published in a scientific peer-reviewed journal and 4) The paper should be written in the English language. The outcome of this review is presented in Results and Discussion and Conclusions and Outlook sections.

3. Results and Discussion

3.1 CO_2 sample collection and treatment for stable isotope ratio measurements

Long-term measurements of CO_2 concentration and stable carbon and oxygen isotope ratio measurements based on hourly or minute scale (LAS) or periodic sampling (IRMS) are essential for understanding CO_2 dynamics in the environment.

Isotopologues of carbon dioxide (e.g. $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{17}O_2$, $^{12}C^{18}O_2$, $^{13}C^{17}O_2$ and $^{13}C^{18}O_2$) are key tools for investigating CO_2 gas exchanges and have been valuable in assessing the proportion of ecosystem respiration of CO_2 (Bowling et al, 2003) and investigating the dynamics of the atmospheric surface layer within forest canopies (Bowling et al. 1999). Stable isotopes of CO_2 have recently been used on a global scale to study the magnitude and nature of carbon exchange between terrestrial ecosystems and the atmosphere (Bowling et al., 2003; Ogée et al. 2003 and van Geldern et al. 2014), while Guillon et al. (2012) identified carbon sources by monitoring stable isotope changes in CO_2 degassing from an underground tunnel. Both IRMS and LAS techniques have great ability for the detection and monitoring of constituents in gas phases and enabling a complete understanding of terrestrial ecosystem dynamics in response to varying environmental conditions**.** The main limitation when using laboratory (off-line) IRMS facilities is the low frequency of sampling and relatively high analysis costs. The air or soil CO_2 samples are collected manually by employing syringes and vials for storage, although several automated devices for collection of air samples have been developed (Ribas-Carbo et al., 2002; Schauer et al., 2005; Schnyder et al., 2004 and Theis et al., 2004) and tested for their performance and precision (see decision tree diagram, section 3.5). Moreover, even portable gas sampling units connected to IRMS have been employed (Schnyder et al., 2004).

Commercially available gas sample preparation systems (e.g., Isoprime TraceGas preconcentrator, Thermo-Finnigan Precon and GasBench, Europa Anca TG-II) involve processing volumes of air of more than 100 mL (Zeeman et al., 2008) through a set of chemical traps that remove water and purify the analyte CO_2, which is later concentrated cryogenically with liquid N_2. For the estimation of the carbon net

ecosystem exchange, sources or respiration sources, CO_2 concentrations must also be measured (Keeling, 1958) and although IRMS instruments are not primarily devoted to gas concentration measurements, some studies have attempted to do so. Joos et al. (2008) determined CO_2 concentrations based on the peak areas of mass-to-charge ratios (*m/z*) 44, 45 and 46, with a precision of 3.5 to 13.1 ppm within a concentration range from 300 to 1000 ppm. Other reports coupling IRMS with an infra-red gas analyser (IRGA) (Feretti et al., 2000 and Schnyder et al., 2004) or NDIR (Schauer et al., 2005) gave measurement precisions below 1 ppm (see decision tree diagram, section 3.5).

3.2 Measuring stable isotope ratios of CO_2 with IRMS

In 1919, Francis W. Aston built an early double-focusing mass spectrometer in Cambridge (UK) (Fry, 2006) but the first accurate measurements of isotope abundances in gases were made by Alfred O. C. Nier (Nier, 1940) by placing a multi-collector into a mass spectrometer. Stable isotope ratios of substances are most commonly measured with a stable isotope ratio mass spectrometer (IRMS) that, in principal, separates charged atoms or molecules based on their *m/z*. The ratios of stable carbon and oxygen isotopes are always measured relative to a reference with known isotopic composition to eliminate any bias or systematic error in the measurements (Muccio and Jackson, 2009). There are five main components of an IRMS instrument: a sample inlet system, an ionization chamber, a magnetic sector for ion separation, a Faraday-collector for ion detection, and a computer-controlled data acquisition system (Brand, 2004 and Sulzman, 2007) (Fig. 1).

Once the sample (or reference) gas leaves the inlet system, it enters the ionization chamber, where is bombarded with electrons produced from heated wire of tungsten, rhenium or thoriated iridium (Brand, 2004). The electrons impact gas molecules,

forming positively charged ions that are gathered into an ion beam, which is further accelerated by an electrical field through a set of extraction and focusing plates towards the flight tube. The ion beam then enters the magnetic sector of the mass spectrometer, where it is bent by a strong magnetic field based on the mass of the ions, with the lighter isotope beams bending more than the heavier. Ions of identical mass are then captured by multiple Faraday cups, each positioned to capture specific masses (Fig. 1). The ion current flowing through the resistor of the cups producing a certain voltage serves as an output for the computer system, which converts relative signal strengths to a heavier isotope / lighter isotope ratio.

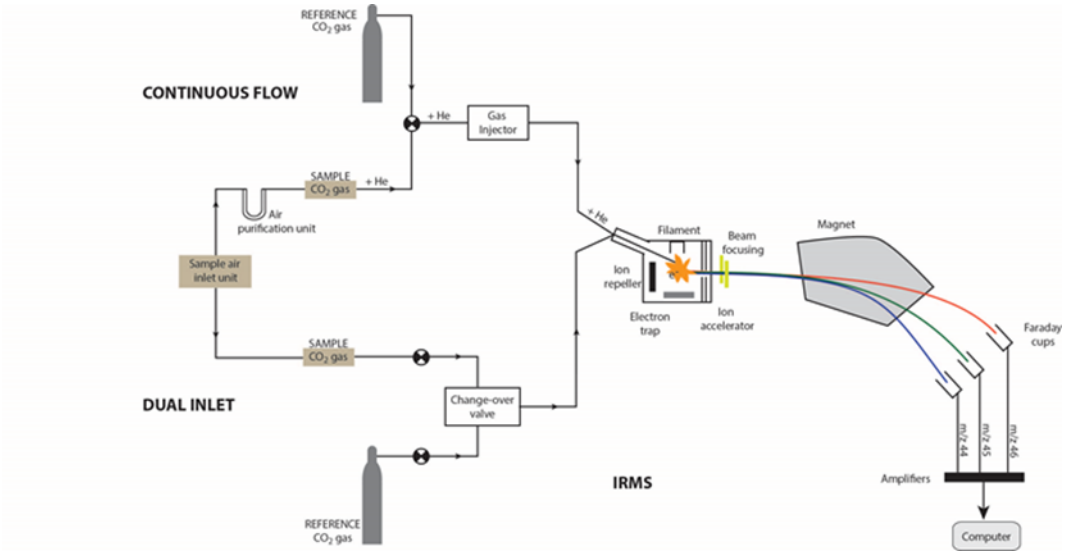

Fig. 1: Diagrammatic representation of dual inlet and continuous flow isotope ratio mass spectrometry (IRMS) analysis system.

There are two types of inlet system: dual-inlet (DI) and continuous-flow (CF) (Fig. 1). In either case, the inlet system introduces pure gases (e.g. CO_2, H_2, N_2, CH_4) into the IRMS via thin capillary tubes, which enable a constant viscous flow of gas molecules, ensuring no isotopic fractionation occurs prior to measurements. In a DI system, the

145 reference and sample gases are kept in separate bellows, keeping both gases under the
146 same pressure and from where they flow either into the ion source of a mass
147 spectrometer or to a waste line via a change-over valve (typically, 5 to 10 pairs of
148 sample and reference gas isotope ratio measurements are made for each sample) (Carter
149 and Barwick, 2011), allowing high precision isotope measurements of 0.01 ‰ for $\delta^{13}C$
150 and 0.03‰ for $\delta^{18}O$ in air for gaseous samples (Sulzman, 2007). In the CF inlet system,
151 the analyte CO_2 (sample or reference) is carried in a constant helium stream through a
152 gas chromatographic (GC) column or trap. Each sample gas is typically introduced only
153 once and followed (or preceded, depending on the analysis setting) by the introduction
154 of a reference CO_2 gas. Although, the CF-IRMS measurements can be less precise
155 (0.01-0.21 ‰ for $\delta^{13}C$ and 0.03-0.34 ‰ for $\delta^{18}O$; see decision tree diagram, section
156 3.5), its great advantage is on-line (automated) sample preparation. The CF-IRMS
157 instrumentation allows processing of a sample size from 100 up to 300 mL and enables
158 faster sample throughput, which can significantly reduce the analysis costs.

159 ***3.3 Measuring the stable isotope composition of CO_2 with LAS***

160 Laser-based spectroscopy (LAS) is the most convenient technique for *in-situ* trace gas
161 analysis, enabling CO_2 concentration and stable isotope analysis/measurements with
162 higher measuring frequency and reduced costs (Bahn et al., 2009 and Marron et al.,
163 2009).

164 In contrast to IRMS, LAS does not measure the isotope ratios but the mixing ratios of
165 individual isotopologues, e.g., $^{12}CO_2$ and $^{13}CO_2$. The working standards should
166 therefore bracket the expected mixing ratios of both isotopologues.

During the past 25 years, laser absorption spectroscopic techniques have become widely commercially available (Tittel et al., 2013) and are used by a growing number of isotope researchers for significant advances in their own field of research (Kerstel and Ginafrani, 2008). A combination of measurement techniques appropriate to a particular question will normally ensure the most robust results. In forest research, LAS instruments are most effectively used in combination with micrometeorological techniques, providing new tools for in depth investigation of the isotope exchange in ecosystems (Aouade et al., 2016; Griffis et al., 2007; Griffis et al., 2008; Griffis et al., 2010; Midwood and Millard, 2011; Munksgard et al., 2013; Santos et al., 2012; Sturm et al., 2012; Wada et al., 2016; Wehr and Saleska, 2015; Wehr et al., 2016; Wehr et al., 2017 and Wingate et al., 2010). CO_2 analysis in the field requires a compact, low power, portable, robust, cost-effective and easy to use analytical system that, in some cases, should enable sampling up to 10 times per second (Sturm et al., 2012). All these factors should thus be carefully considered when measuring the concentration and isotopic composition of CO_2 at remote locations.

A key optical component for LAS is the commercial availability of high-performance semiconductor lasers (Tittel et al, 2013). To put it simply, semiconductor lasers are devices in the form of a diode that emits light in a certain narrow band wavelength. Today, several LAS instruments are available, which differ in design, precision, accuracy and sensitivity (Fig. 7). However, the most useful commercially available LAS instruments for CO_2 concentration and stable isotopic measurements apply various techniques, such as tunable diode laser absorption (TDLAS), quantum cascade laser spectroscopy (QCLAS), cavity ring-down spectroscopy (CRDS) and off-axis cavity enhanced absorption spectroscopy (OA-CEAS)**.** The latter two are based on an external

191 cavity with high reflecting mirrors, with a reflectivity of ≥ 99.99%. This is also a
192 drawback of the technique (CRDS and OA-CEAS), since the highly reflective mirrors
193 can limit the usable wavelength range to some 10% of a central wavelength.
194 Furthermore, the laser beam quality is more critical than with other techniques (Sigrist
195 et al., 2008). Wen et al. (2012) provided a comprehensive comparison of the above-
196 mentioned LAS measurement techniques for water vapour isotope measurement. Their
197 work is the first systematic attempt to compare multiple LAS analytical instruments
198 (OA-CEAS, CRDS, QCLAS and TDLAS) to determine whether their calibration
199 methods are truly transferrable from one to another. Instruments based on these
200 techniques have been reported to operate with precisions of ± 0.04 to 0.25 ‰ for $\delta^{13}C$
201 and ± 0.05 to 2.0 ‰ for $\delta^{18}O$ (Barker et al., 2011; Wen et al., 2013; Xia et al. 2016) for
202 field measurements and thus approaching the ± 0.01 ‰ levels reported for IRMS in
203 several laboratories (Mortazavi and Chanton, 2002; Griffith et al., 2012 and van
204 Geldern et al., 2014)

205 *3.3.1 Fourier-transform infrared spectroscopy (FTIR)*

206 FTIR spectroscopy uses broadband infrared radiation from a blackbody light source that
207 covers the entire infrared spectrum simultaneously. In FTIR (Fig. 2) spectroscopy, the
208 source radiation is modulated by a Michelson interferometer (precisely measures the
209 wavelength of optical beams through the creation of interference patterns) and all
210 optical frequencies are recorded simultaneously in the measured interferogram (Griffith
211 et al., 2012). Fourier transform (a mathematical process) is required to convert the raw
212 data (intensity to frequency domain) into the actual spectrum. The method requires no
213 sample preparation other than optional drying of the sample and may be applied directly
214 to ambient air samples (Esler et al., 2000). Current FTIR spectrometers offer precise

quantification of a wide range of analytes for concentrations down to single-digit ppb levels and are now available as integrated and relatively compact units compared to the complex and bulky units offered in the past (Flores et al., 2017; Griffith et al., 2012; Griffith, 2018; Hammer et al., 2012 and McDonagh et al., 2008). Furthermore, in situ FTIR spectrometers record and store a broadband absorption spectrum, from 1800-5000 cm^{-1} for each measurement. The recorded spectra are analysed online by non-linear least squares fitting of sections of the measured spectrum with a modelled spectrum calculated from the HITRAN database (Gordon et al., 2017; Hill et al., 2016; Rothman et al., 2013) of absorption line parameters. The theoretical spectrum is calculated by MALT (multiple atmospheric layer transmission) as described elsewhere (Griffith et al., 2012).

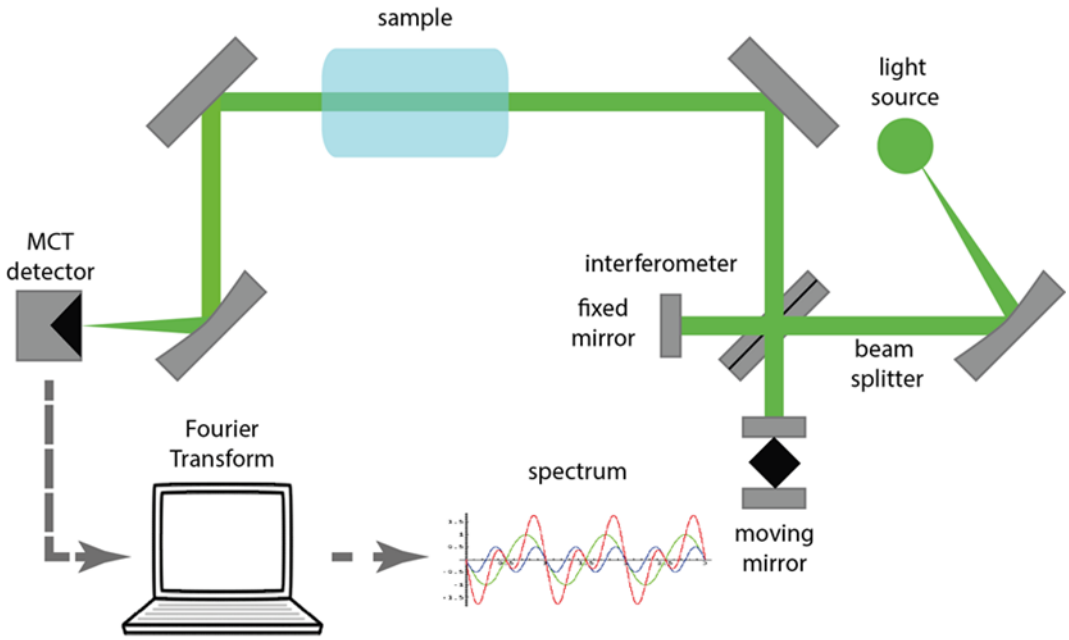

Fig. 2: Schematic illustration of fourier-transform infrared spectroscopy (FTIR) sketched following the example of Glewen (2007). In FTIR spectroscopy, IR radiation that has been

modulated is passed through the sampling area and is detected by a highly sensitive mercury cadmium telluride (MCT) detector.

3.3.2 Quantum cascade laser spectroscopy (QCLAS)

QCLAS are semiconductor lasers and were first demonstrated in the nineteen nineties by Faist et al. (1994). QCLAS (Fig. 3) offers real-time high-precision measurement of mixing ratios of the individual CO_2 isotopologues using infrared absorption spectroscopy with a pulsed, room-temperature quantum cascade laser (Nelson et al., 2008 and Tuzson et al., 2008). QCLAS systems do not require special sample preparation and are particularly attractive because of their stable single mode spectral output, high power and because they offer a significant advantage for field deployment du to real-time continuous in situ measurement (Saleska et al., 2006). With the progressive development of a specialized QCLAS in the late 2000s, researchers (Nelson et al., 2008 and Tuzson et al., 2008) have been able to do competent CO_2 isotope monitoring. Their QCLAS scanned across three spectral lines (near 2310 cm^{-1}), quantifying three CO_2 isotopologues: $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$. In another study, Saleska et al. (2006) used a pair of CO_2 spectral lines near 2311 cm^{-1} (2311.399 cm^{-1} for $^{13}C^{16}O_2$ and 2311.105 cm^{-1} for $^{12}C^{16}O_2$). Wehr et al. (2013) used cryogen-free, continuous-wave QCLAS for eddy covariance measurement of the net ecosystem exchange of CO_2 isotopologue molar mixing ratios ($^{13}C^{16}O_2$, $^{18}O^{12}C^{16}O$, and $^{12}C^{16}O_2$). They collected the data of real-time isotopic CO_2 measurements over the 2011 growing season (from May to October 2011) in a temperate deciduous forest dominated by trees such as red oak and red maple, located at the Harvard Forest in Petersham, Massachusetts, USA. Similarly, Sturm et al. (2012) used QCLAS and the eddy

covariance method to measure isotope fluxes of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{16}O^{12}C^{18}O$ above a forest canopy. The QCLAS system was established at the Swiss national air pollution monitoring site in the beech dominated forest in the Lägeren mountains (Switzerland).

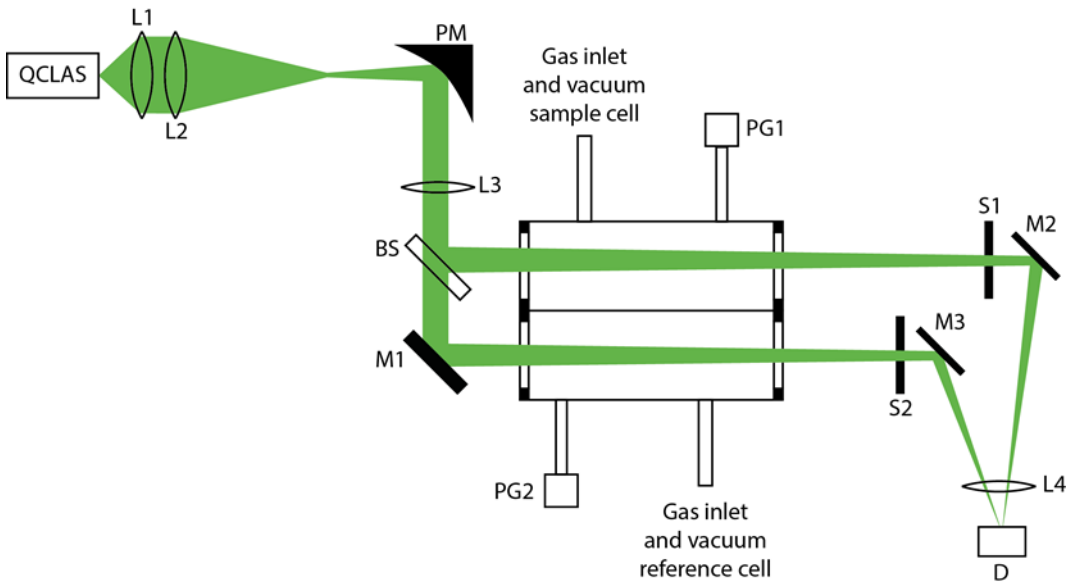

Fig. 3: Schematic illustration of quantum cascade laser spectroscopy (QCLAS) consisted of parabolic mirror (PM), beam splitter (BS), mirrors (M), shutter (S), pressure gauge (PG), detector (D) and lenses (L1 and L2). The QCLAS system was sketched following the example of Castrillo et al. (2007).

3.3.3 Tunable Diode Laser Absorption Spectroscopy (TDLAS)

TDLAS is a commonly used LAS instrument for quantitative measurements in gaseous media and is gaining in popularity for measuring the mole fraction and stable isotopic composition of CO_2 in air in studies of biosphere-atmosphere gas exchange (Schaeffer et al., 2008). TDLAS measures the absorption of infrared energy, which is proportional to molecular density, following Beer's law (Sulzman, 2007). The analytical instrument utilizes semiconductor lasers to detect a variety of different trace gases, from oxygen in

271 the near infrared range to carbon dioxide and carbon monoxide in the short-wavelength
272 infrared range. This measurement technique enables the miniaturization of transmission
273 and receiving units, providing highly sensitive, quantitative measurements with fast
274 response times without the need for frequent calibration (Shuk and Jantz, 2015).
275 TDLAS usually scans over an isolated absorption line of the chemical species under
276 investigation using a single narrow laser line. To achieve the highest selectivity,
277 analysis is done at low pressure, whereby the absorption lines are not substantially
278 broadened by pressure (Werle, 1998). One of the most important applications of
279 TDLAS in atmospheric measurements has turned out to be their use in combination
280 with a multi-pass cell with path lengths of 100 m or more (Werle et al., 2004).

281 TDLAS measures the mixing ratios of stable isotopes of carbon dioxide in the air (e.g.,
282 the isotopologues, $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{16}O^{12}C\ ^{18}O$) by comparing the infrared
283 absorption of sample and reference gases in a specific absorption line of the spectrum
284 (Santos et al., 2012). However, measuring the stable isotope composition with TDLAS
285 requires high mole fraction measurement accuracy for a single isotope, although
286 TDLAS has been shown to be capable of effective, accurate measurement even when
287 losing ~95% of the original signal in a dusty environment (Shuk and Jantz, 2015). The
288 majority of reported field campaigns applications (Bowling et al., 2003, Marron et al.,
289 2009, Santos et al., 2012 and Wingate et al., 2010) were conducted with the
290 instruments, TGA200 and TGA200A (Campbell Scientific, Inc., Logan, UT, USA) (Fig.
291 4), based on the original patented design developed by Edwards, Kidd, and Thurtell at
292 the University of Guelph (Edwards et al., 1994). For CO_2 isotopologue measurement the
293 TGA200 and TGA200A analytical instruments can be tuned to adsorption lines between
294 2293 and 2311 cm^{-1}. Common to all is a combination of the LAS measurement

technique with the use of micrometeorological instruments such as temperature and moisture sensors. A successful use of a TDLAS field campaign for ecosystem-atmosphere CO_2 exchange studies was conducted by Bowling et al. in 2003. They measured the carbon isotope content of CO_2 at atmospheric mole fractions and isotopic abundance of $\delta^{13}C$. The ability of the instrument to measure isotope ratios of $\delta^{13}C$ was tested outdoors in a grassland and compared to standard laboratory based IRMS. In addition, Wingate et al. (2010) carried out a comprehensive field campaign in a nearly homogenous maritime pine forest, while designing a multi-inlet sampling system automatically to select and measure the CO_2 isotope composition and environmental conditions in the vertical atmospheric profile below, within and above the canopy, in open soil chambers and a closed branch chamber. In a similar experimental setup, Santos et al. (2012) used a TDLAS instrument in near-continuous measurement to study the CO_2 stable isotopic exchange near the floor of a temperate deciduous forest. Marron et al. (2009) recorded the temporal variability of $\delta^{13}C$ composition of CO_2 efflux released by forest soil at different time scales and showed that TDLS can also be useful at an ecosystem level. In another study, Schaeffer et al. (2008) conducted the first multi-year analysis of TDLAS instrument performance for measuring CO_2 isotopes in the field (high-altitude subalpine coniferous forest at Niwot Ridge AmeriFlux). Air was sampled from five to nine vertical locations in and above the forest canopy every ten minutes for 2.4 years. Von Sperber et al. (2015) researched the influence of soil moisture, soil particle size, litter layer and carbonic anhydrase on the isotopic composition of soil□released CO_2 and H_2O in soil column experiments under laboratory conditions. They used a TGA200 instrument in their research, which was

tuned to adsorption lines at 2308.171 cm^{-1} for $^{13}C^{16}O_2$, 2308.225 cm^{-1} for $^{12}C^{16}O_2$ and 2308.416 cm^{-1} for $^{16}O^{12}C^{18}O$.

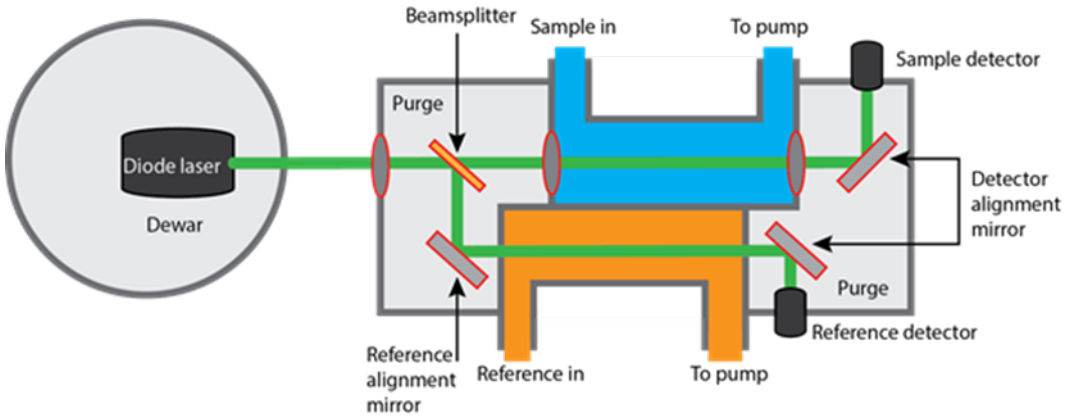

Fig. 4: Schematic illustration of tunable diode laser absorption spectroscopy (TDLAS). Sketched following the example of Campbell Scientific, Inc., Logan, UT, USA.

3.3.4 Cavity Ring-Down Spectroscopy (CRDS)

CRDS is a spectroscopic measurement technique for detecting atmospheric trace gases and was pioneered by O'Keefe and Deacon (1988). A typical CRDS setup involves an optical cavity made from two (O'Keefe and Deacon, 1988) or three (Fig. 5) (Morville et al., 2005 and Paldus et al., 1998) highly reflective mirrors (reflectance >99.999 %), in which photons propagate for a prolonged time (Rao, 2012). However, a three-mirror cavity provides superior signal to noise compared to a two-mirror cavity that supports a standing wave (Picarro, Inc., Santa Clara, CA, USA). CRDS spectroscopy is a direct absorption technique, which can be performed with pulsed or continuous light sources and has a significantly higher sensitivity than obtainable in conventional absorption spectroscopy (Berden et al., 2000). Light is coupled into the cavity through one of the mirrors and light leaking out of the cavity is detected, i.e., the technique is based on

measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined in a closed optical cavity with a high-quality factor. The advantage over normal absorption spectroscopy is a result of the intrinsic insensitivity to light source intensity fluctuations, the extremely long effective path lengths (> 10 km) that can be realized in stable optical cavities and time-based measurements (Berden et al., 2000). Like other analysers, CRDS instruments are designed for very sensitive gas absorption measurements and have volumes of tens to hundreds of millilitres (Crosson, 2008 and Waechter et al., 2010).

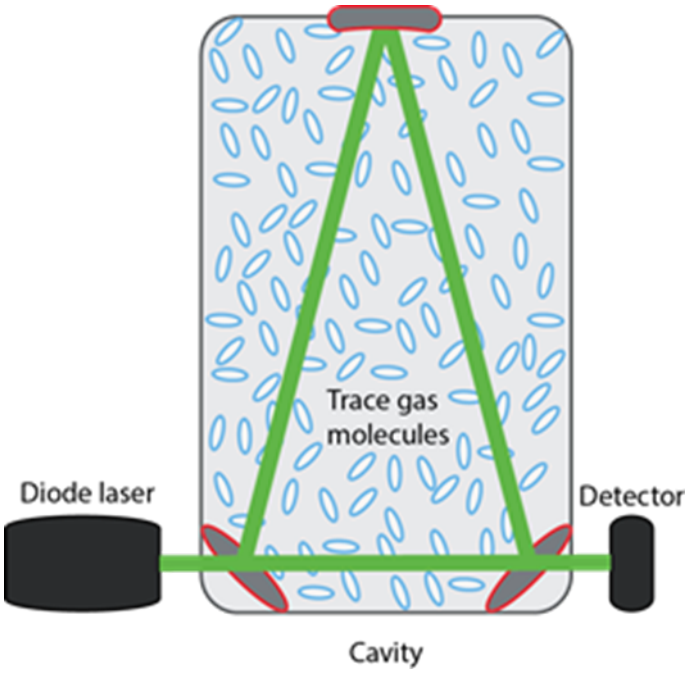

Fig. 5: Schematic illustration of a cavity ring-down spectroscopy (CRDS) analyser cavity showing how a ring down measurement is carried out in a three-mirror cavity (sketched following the example of Picarro, Inc., Santa Clara, CA, USA). The gas sample is led into in a three highly reflective mirror (R~0,9999) cavity, shown in the figure above, to support a continuous traveling light wave.

CRDS instruments have been commercially available for decades. Recently, cavity ring-down spectroscopy has been successfully employed in carbon dioxide detection. Munksgaard et al. (2013) described in detail the method and application of field-based CRDS measurement techniques of $\delta^{13}C$ in soil respired CO_2, while comparing the instrument precision with that of continuous flow–isotope ratio mass spectrometry (CF-IRMS). They used a CRDS analyser (model G2012-i; Picarro, Inc.) in two modes, firstly for continuous analysis of soil-respired CO_2 drawn directly from a soil chamber into the analyser at a controlled rate and, secondly, for batch analysis of carbon dioxide in sequentially sampled gas bags from a soil chamber. CRDS measurements of $\delta^{13}C$ and CO_2 were performed at 1 Hz. The instrumental precision of individual $\delta^{13}C$ determinations was <0.3 ‰ for a 5-min integration time (1-Sigma Standard Deviation, 1SD), drift was <2 ‰ over 24 h. According to Picarro, Inc., 5-minute averaged precision is often used in industry and is a useful averaging time for many types of measurements in scientific applications. The precision is the 1SD of 5-minutes averages, obtained over at least 60 minutes of measurement. This means that it obtains at least 12 average values of five minutes length. A 1SD of 0.3‰ means that 67% of these 5-minute averages are scattered around the mean value M +/- 0.3‰. To have a higher confidence, you would need to take the 2-Sigma Standard Deviation, in this case 95% of the 5-min averages will fall within a band of M +/- 0.6‰. The drift specification is based on peak-to-peak differences over a measurement period of at least 24 hours. The analytical technique developed in their study demonstrated an acceptable accuracy and precision for the determination of $\delta^{13}C$ values in soil-respired CO_2 in field campaigns. The CRDS analyser (model G2131-i; Picarro Inc.) can measure the $^{13}CO_2$ stable isotope abundance by measuring two independent spectral absorption lines in the

near-infrared region of the spectrum, including one for $^{12}C^{16}O_2$ at 6251.760 cm^{-1} and one for $^{13}C^{16}O_2$ at 6251.315 cm^{-1} (Dickinson et al., 2017). The precision of the system has been reported to be better than 200 ppb for $^{12}C^{16}O_2$ and 10 ppb for $^{13}C^{16}O_2$ for a 30-s measurement as the measuring time increases (Maher et al., 2014). In another field campaign Albanito et al. (2012) deployed a CRDS analyser (model G1101-i; Picarro, Inc.) for continuous measurement of two CO_2 isotopologue mixing ratios ($^{12}C^{16}O_2$ and $^{13}C^{16}O_2$) and isotopic signature ($\delta^{13}C\text{-}CO_2$) by connecting the CRDS analyser with dual-chambers inserted into the soil to a depth of approximately 2-3 cm in semi-managed Mediterranean pine forest. Samples were collected and analysed throughout daylight hours and separated into those collected in the morning and afternoon to detect any short-term temporal changes in CO_2 flux (from roots, litter/humus and old soil organic matter) and isotopic signature ($\delta^{13}C\text{-}CO_2$). They used a multichannel gas sampling control system programmed to perform routine analysis. In a different survey, Dubbert et al. (2014) presented the first data set on daytime cycles (morning and afternoon measurements) of direct estimates of the isotopic composition of transpired water vapour in key environmental periods in a Mediterranean climate: spring wetness, summer drought and the beginning of a wet and cold autumn in cork-oak trees (*Quercus suber*). Fluxes and the isotopic composition of cork-oak transpiration were measured using a CRDS instrument (model L2120-i; Picarro, Inc.) in combination with custom-built branch chambers in an open gas exchange system. In another field campaign Jochheim et al. (2017) deployed an isotopic analyser based on wave-length-scanned cavity ring-down spectroscopy (model G1101-i; Picarro, Inc.). The CRDS instrument was used to detect seasonal dynamics in beech and pine forest soils at different soil depths, while connected via a 16-position valve (VALCO STF) for the detection of

401 $\delta^{13}C\text{-}CO_2$, consecutively for each channel. The precision of the isotopic analyser for
402 $\delta^{13}C$ was < 0.3‰. In such a layout - a sequence of 16 channels was achieved within 80
403 minutes, resulting in 18 measurement cycles per 24 h.

3.3.5 Off-axis Cavity Enhanced Absorption Spectroscopy (OA-CEAS)

The off-axis design eliminates optical feedback from the cavity to the light source. Such an arrangement causes the light to be many times reflected by the mirrors and it fills the whole volume of the cavity (Nowakowski et al., 2009). For example, for a cell composed of two 99.99% reflectivity mirrors spaced at 25 cm, the effective optical path length is 2500 meters (ABB - Los Gatos Research, San Jose, CA, USA). The use of OA-CEAS, which utilizes a high-finesse optical cavity as an absorption cell, is shown in Fig. 6.

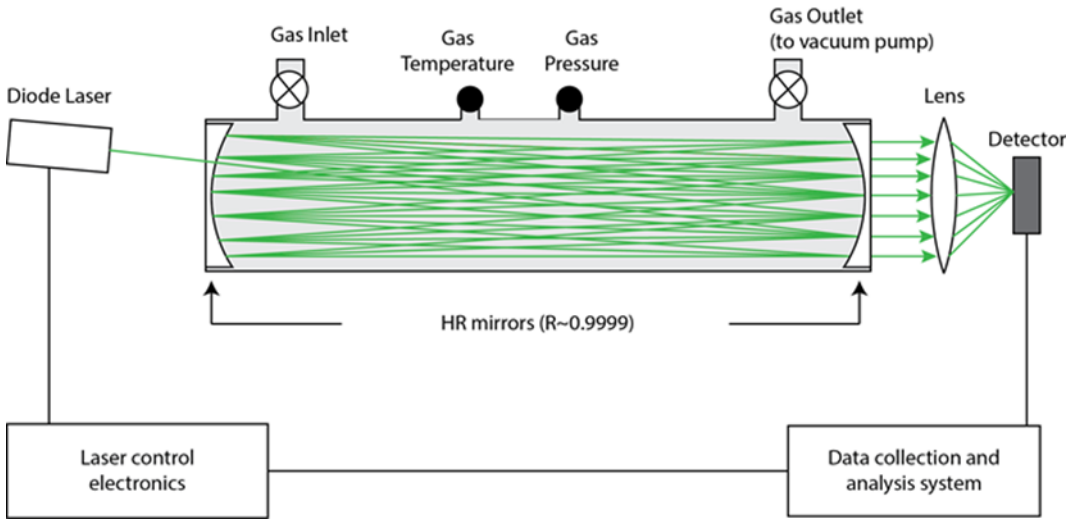

Fig. 6: Schematic diagram of an instrument based on OA-CEAS (sketched following the example of ABB - Los Gatos Research, San Jose, CA, USA). The gas sample is passed continuously through the cavity while the off-axis laser beam bounces multiple times between the highly reflective (HR) (R~0.9999) mirrors.

The method was introduced by Paul et al. (2001) and their paper clearly explains the basic principles. However, a fundamental problem with this technique is that the higher the finesse resonant optical cavity, the narrower the transmission mode envelope of the

cavity, and the more difficult it becomes to inject light into the cavity. OA-CEAS has advantages due to its enhanced sensitivity, high mechanical robustness and relatively simple optical configuration, which make it suitable for long-term measurements in the field (Gupta, 2012). Sprenger et al. (2017) reported that OA-CEAS analytical instruments use the absorption of a near-infrared laser beam by molecules (i.e., isotopologues) in a gaseous sample in a high-finesse optical cavity (Crosson, 2008; Baer et al., 2002). Directing the laser beam off-axis allows spatial separation of the multiple reflections within the cavity, (Paul et al., 2001), which results in fully resolved OA-CEAS absorption spectra (ABB - Los Gatos Research). Other associated LAS measurement techniques, such as CRDS, have a disadvantage when it comes to obtaining data in high temporal resolution. The mentioned constraints of CRDS favour OA-CEAS instruments when performing high-quality measurements of relevant trace gases (e.g., carbon dioxide, carbon monoxide) in different ecosystems (forest, caves, sea etc.) (Arévalo-Martínez et al., 2013). While OA-CEAS instruments are now being routinely used in terrestrial ecosystems continuously to measure, e.g., for analysis of the stable isotopes of water (δ^2H and $\delta^{18}O$) in different soil types (Orlowski et al., 2016), there are not many published research papers using OA-CEAS instruments for carbon dioxide isotope composition measurements in forest field campaigns. However, here we present two examples of successful monitoring of carbon dioxide using OA-CEAS instruments. In an effort to monitor leakage from underground CO_2 storage, (McAlexander et al., 2011) tested a field-deployable analyser capable of rapidly measuring the CO_2 mixing ratio and carbon isotope $\delta^{13}C$ values. The analyser was interfaced with a multiport inlet unit to allow autonomous sampling from multiple locations. In the mentioned study, they used an OA-CEAS isotope analyser from ABB -

Los Gatos Research to measure simultaneously both CO_2 concentration and carbon isotope composition. In another study, (Mahesh et al., 2015) tested a greenhouse gas analyser instrument (model GGA-24EP, ABB - Los Gatos Research), which used an OA-CEAS analyser with the objective of generating a long-term record of measurements of CO_2 and CH_4 concentrations conforming to standards set by the World Meteorological Organization. A research campaign using corrected observations over 12 months revealed the role of wind velocity and anthropogenic emissions, as well as seasonal variations in the ambient concentrations of CO_2 and CH_4 gases near the surface.

3.4 Combination of micrometeorological techniques and stable isotope analysis

Several different measuring techniques for stable isotope and concentration analysis of CO_2 in forest ecosystem are available. Researchers usually choose the methods that most reliably deliver the results researchers are seeking. Many researchers (Aouade et al., 2016; Wada et al., 2016, 2017; Stropes, 2017; Wen et al., 2016) combine micrometeorological measurements and advanced stable isotope analysis. Field-scale applications of this combined technology are now under development. IRMS and LAS analysers can be used in combination with micrometeorological techniques in chamber measurements, eddy covariance measurements or for vertical profile measurements of trace gas (e.g., CO_2) concentrations measured from tall and flux towers monitoring boundary layer mixing processes and trace gas exchange between the atmosphere, surface and plant/forest communities (Griffith et al., 2012). This combination of techniques allows very precise and frequent/continuous measurements of CO_2 components at the ecosystem scale and brings new insights into the mechanisms

469 governing biochemical cycles in ecosystems (Stropes, 2017). The choice of instrument
470 for a particular experiment depends not only on cost and measurement stability but also
471 on the time to get the advantage of the required precision. For example, if used for eddy
472 covariance measurements, then sampling rates higher than 5 Hz are required, while
473 random noise is not so much of a problem and can be filtered. If measuring sample bags
474 of CO_2 isotopologues, then high precision may be required in less than 30 s and an
475 analytical instrument with the same precision that takes 5 minutes may not be
476 appropriate. Furthermore, researchers should consider that sample storage in sample
477 bags provides acceptable results only for a short time (up to 10 days of storage),
478 because evaporitic isotopic enrichment might occur with samples stored for up to 6
479 months (Hendry et al., 2015). Power consumption is another important requirement that
480 might necessitate a particular choice of instrument. When reviewing the power
481 consumption of the analytical instruments, we found that, in most cases, recently
482 published research studies do not provide this information. Nevertheless, by comparing
483 a number of studies considered in our paper, we can assume that there are significant
484 differences between the instruments in power consumption. For example, the whole
485 QCLAS system (including the pumps) would need as much as 2000 W of power to
486 operate (Sturm et al., 2012), which is approximately 600W more than OA-CEAS or CF-
487 IRMS systems. By contrast, IRGA instruments require only about 20-35 W of power to
488 operate, while providing robust data sets. These analytical systems provide the lowest
489 power costs and smallest carbon footprint of all gas systems available. However, their
490 scope of analysis is consequently smaller and less demanding. Another important
491 consideration for making reliable field measurements is the ease of calibration of the
492 analytical instruments, which is a requirement that impacts on the quality/accuracy of

493 analysis. Assume that there is a selection of instruments (one or several) individually
494 measuring each of the most abundant CO_2 isotopologues. Each isotopologue is usually
495 calibrated independently after decomposing the standard's total CO_2 into its component
496 isotopologue mole fractions using the methods discussed by Flores et al. (2017), Griffis
497 (2013), Griffith (2018), Tans et al. (2017) and several others. How frequently such
498 calibrations need to be repeated depends on the individual instrument. In summary, it
499 can be said that each approach has its advantages, disadvantages and logistical
500 challenges. Hence, even though experimental approaches may differ from each other,
501 most of the described combinations can be considered reliable for carbon isotope
502 fractionation investigations.

3.5 Decision tree classifier: decision making process

CO_2 is a crucial element of interest in ecosystems. Analytical instruments and application techniques for CO_2 (concentration and stable isotopologues of CO_2) are discussed in detail. To ease the decision on selection of the suitable application for the desired ecosystem scale (leaf, tree, soil or whole ecosystem level), we prepared a decision tree (Fig. 7) on up-to-date and relevant application/measuring techniques. Each application option is supported by selected research campaigns and references.

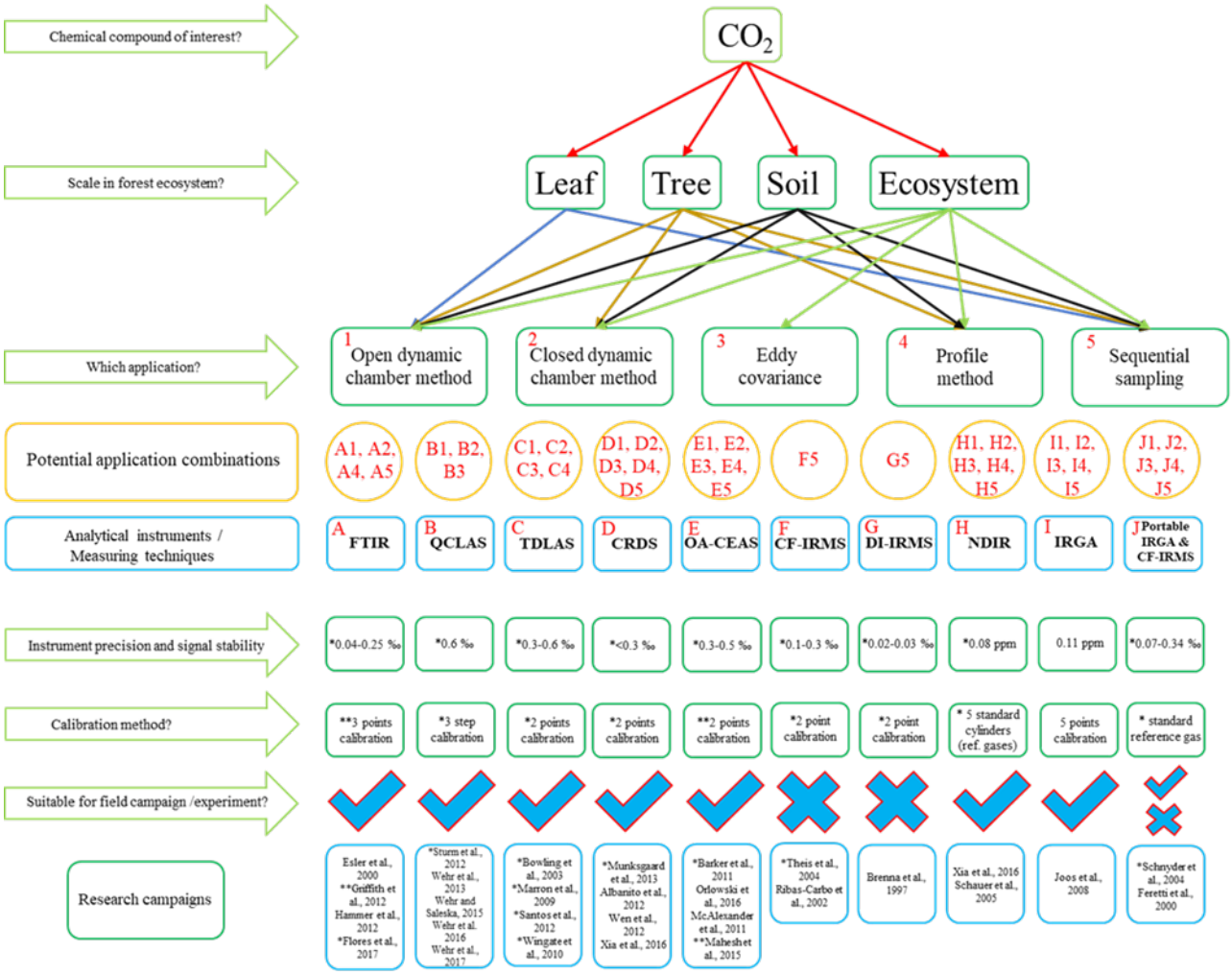

Fig. 7: Schematic diagram of decision tree (DT). The result of a DT is a set of potential application combinations, which are presented with an alphanumeric combination shown in

514 circles above. For example, alphanumeric combination (A1) indicates that an FTIR analytical
515 instrument can be used in combination with an open dynamic chamber method.

516 **4. Conclusions and Outlook**

517 The need to meet increasingly stringent research, environmental and legislative
518 requirements has led to the development of IRMS and LAS analytical techniques to
519 measure concentrations and stable isotopologues of carbon dioxide. There are many
520 reasons why carbon dioxide isotopologues offer great added value in studies on the
521 carbon cycle in a natural environment. One is that they enable insight into the origins of
522 the chemical species/elements (C, N…), as well as their uses as tracers. The other is that
523 high-frequency measurements may ambiguously explain a particular ecosystem process
524 (Aelion et al., 2009). IRMS and LAS analytical systems offer high precision for
525 measuring very small changes in isotope concentrations in selected natural
526 environments. van Geldern et al. (2014) noted that the monitoring data set would not
527 have been as complete if only IRMS analyses had been used. LAS data revealed a much
528 more intense dynamic, with fast changing $\delta^{13}C$ values. In the past, researchers relied on
529 measurements of concentrations of the chemical elements/compounds of interest in the
530 specific environment. This was not always successful and often led to uncertainty
531 because determination of stable isotopologues of carbon dioxide constitutes a challenge
532 in several ways, since the application/measurement technique needs to be sufficiently
533 sensitive and specific to detect the chemical species. It is important to highlight that
534 instrument noise can limit the instrument's ability to detect small changes in the
535 concentration of isotopes in ecosystems over a given time period. One option is to use
536 longer averaging periods, which can reduce some instrument noise. Furthermore,
537 Stropes (2017) stressed that statistical approaches, such as Allan deviation analysis, can

be used to evaluate instrument precision and its relationship with the averaging time. This approach has successfully been used in some previous studies to evaluate the precision of isotope ratio measuring systems (Tuzson et al., 2011 and Sturm et al., 2012). This analysis could provide means to find the optimum averaging time interval with the least deviation, and therefore most precision, in concentration signals for a sampling system.

CO_2 analysers are not equally sensitive to the isotopologues of CO_2. For example, LAS measurement techniques, which measure an absorption line from the most abundant CO_2 isotopologue $^{12}C^{16}O_2$, are blind to all the minor isotopologues of CO_2 (Tans et al., (2017). Furthermore, NDIR instruments are much more complicated in their response to the various minor isotopologues of CO_2. Most NDIR analysers use an optical band-pass filter to limit the wavelengths of light reaching the detectors. These filters often exclude part of the absorption bands of the minor isotopologues (e.g., Tohjima et al., 2009) but are more sensitive to the $^{13}C^{16}O_2$ lines within the passband because absorption of the much stronger $^{12}C^{16}O_2$ lines is partially saturated. The width and shape of the transmission window of the filter are generally not identical between analytical instruments. Tohjima et al. (2009) found significant differences in sensitivity to the minor isotopologues between different NDIR analysers. Karlovets et al. (2018) reported that, in spite of their low natural abundances, the ^{13}C minor isotopologues (in particular $^{16}O^{13}C^{18}O$, with a natural abundance less than 4.5×10^{-5}) contribute importantly to small residual opacity. Multiple minor isotopologues of CO_2 have very low terrestrial abundances according to the spectroscopic database HITRAN (10^{-6} and 10^{-7} for $^{16}O^{13}C^{17}O$ and $^{12}C^{17}O_2$, respectively) so their contribution to the m/z 46 signal is considered negligible. This is not the case for m/z 45 signal or the ^{13}C analysis, in which

562 the $^{16}O^{12}C^{17}O$ makes up about 7.27% (=0.0008/0.011) of the total intensities. In order to
563 determine how much of the m/z 45 signal is due to ^{13}C, we need to know how much of
564 it is due to ^{17}O. This is done by assuming that the ratio of ^{18}O to ^{17}O is constant in all
565 mass-dependent processes that result in isotope fractionation. (W. M. Keck Foundation
566 Laboratory for Environmental Biogeochemistry, https://www.kfleb.org/introduction-to-
567 isotope-analyses; last access: 01 August 2019).

568 The accuracy of this calculation of concentrations (LAS analysis results) depends on
569 knowledge of the instrumental laser line width and shape, and the molecular line
570 parameters, including line strength, pressure and temperature dependence. For most
571 trace gases of interest, the positions, strengths, widths and temperature dependences of
572 relevant absorption lines are available in the HITRAN database (Gordon et al., 2017;
573 Hill et al., 2016; Rothman et al., 2013) and in CDSD databank (Tashkun et al., 2015;
574 Tashkun et al., 2019). HITRAN is an acronym for high-resolution transmission
575 molecular absorption database and is available on the website of HITRANonline:
576 https://hitran.org/ or HITRAN on the Web: http://hitran.iao.ru/home (last access: 01
577 August 2019). CDSD is an acronym for Carbon Dioxide Spectroscopic Databank and is
578 available in HITRAN format as a single zipped ASCII file in the website of V.E. Zuev
579 Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of
580 Science: ftp://ftp.iao.ru/pub/CDSD-296 (last access: 01 August 2019). Comparisons of
581 new versions of the CDSD with HITRAN line lists are published in a paper by Tashkun
582 et al. (2019). The basic underlying principles of a number of commercially available
583 measurement systems, together with some of their key characteristics, which may help
584 to inform their use in future research campaigns are reviewed in papers by Bowling et
585 al. (2003), Saleska et al. (2006), McAlexander et al. (2011), Guillon et al. (2012), Wen

et al. (2012), Griffis (2013), Rothman et al. (2013), Elliott et al. (2014), Tashkun et al. (2015), Dickinson et al. (2017), Gordon et al. (2017), Tans et al. (2017), Griffith (2018), Tashkun et al. (2019), and others.

As mentioned earlier, spectroscopic databases are partly devoted to use in atmospheric retrieval models. These databases contain mainly, but not only, line-by-line spectra with quantum number assignments and a number of other spectroscopic parameters, which together are called a line list (Żak, 2017). For a successful measurement of isotopologues of CO_2, all absorption lines in a given spectral region have to be characterized, requiring high-resolution supporting data. There have been extensive efforts by several research groups (Gordon et al. (2017); Tashkun et al. (2019); Huang et al. (2017) and Jacquinet-Husson et al. (2016)) to expand the characterization of CO_2 isotopologues, from both experimental and theoretical standpoints, while using/comparing different spectroscopic databases (e.g. HITRAN, CDSD, AMES and GEISA). However, the LAS analysis uncertainty resulting from inconsistency hidden among these spectroscopic databases for CO_2 isotopologues, is still a question (Pogány et al., 2013). This question is well justified, since the intensity of most CO_2 IR transitions in spectroscopic databases have >1% uncertainty. More importantly, for the minor isotopologues, the uncertainty in the sample abundance is the result of intensity uncertainties, which range from 1.5% for the more abundant species ($^{13}C^{16}O_2$) to 5% for the less abundant ones (Toth et al., 2008). This is caused by inconsistency between the intrinsic models used, namely the different effective dipole models (EDM) individually fitted from different isotopologue experimental data. For example, Hovorka et al. (2017) highlighted two main phenomena that perturb LAS measurements while optimizing the data retrieval process for spectroscopic CO_2 isotopologue ratio

610 measurements: a.) interference between different molecular transitions (not necessarily
611 from the same molecule) b.) the different intensity temperature dependence of the two
612 transitions used for R (the ratio of the heavier over the lighter isotopologue) retrieval.
613 For a detailed review of potential LAS analysis uncertainty for isotopologues of CO_2,
614 see Ref. (Żak, 2017) and references therein.

615 The further development of analysers will surely help advance the ability to study plant,
616 canopy and ecosystem responses to climate change (Griffis, 2013). Advanced high
617 frequency stable isotope measurements provide great improvements over traditional
618 approaches and, in combination with micrometeorological measurements (see decision
619 tree diagram, Fig. 7), can trace the movement of CO_2 in ecosystems and the magnitude
620 of transportation in processes that exchange CO_2 (Griffis, 2013, Flanagan & Farquhar,
621 2014 and Riederer et al, 2015). For example, Wehr et al. (2017) combined these
622 approaches better to estimate stomatal conductance, transpiration and evaporation in a
623 temperate deciduous forest. Such approaches improve our understanding of carbon and
624 water cycling. Furthermore, the success of trace gas measuring techniques crucially
625 depends on the availability, sensitivity and performance of the analyser, combined with
626 appropriate detection schemes and spectroscopic databases. We have tried to highlight
627 the advantages and disadvantages of isotope measurement techniques throughout this
628 manuscript. Many technical aspects discussed in this review paper deserve deeper or
629 more thorough investigation. In other words, several topics could easily be extended to
630 full-length, independent papers. However, the core value of our review is to provide a
631 list of selected analytical instruments in a wide range of applications deployed in
632 terrestrial ecosystems, which we hope will be useful for the scientific community,
633 including IRMS and LAS laboratories. We believe that the new analytical instruments,

634 together with the challenges that remain, make this an exciting and rapidly developing
635 research field for years to come.

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