BEST PRACTICE GUIDELINE

Measurement of carbon dioxide, methane and nitrous oxide fluxes between soil-vegetation-systems and the atmosphere using non-steady state chambers

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0. PREFACE

This Best Practice Guideline was been initiated by the Working Group Soil Gases (*AG Bodengase*) of the German Soil Science Society (*Deutsche Bodenkundliche Gesellschaft*). Our intention was to collect and aggregate the expertise of different working groups in our field. As a compendium, this guideline may help both beginners and experts to meet the practical and theoretical challenges of measuring soil gas fluxes with non-steady state chamber systems.

The guideline was written and assembled by a group of main authors with extensive field and laboratory experience in their respective field of research. The full draft of the guideline was discussed in an open feedback round within the Working Group Soil Gases. The final Best Practice Guideline therefore resulted and profited from a peer-based feedback process, during which far more people than the main authors contributed. We would like to thank all those who supported, discussed and contributed to this document.

1. INTRODUCTION

As a result of their relative inexpensiveness, high versatility and seemingly easy application, manual closed chamber measurements are a widely used and accepted technique for estimating the exchange of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) between soils, vegetation and the atmosphere. Flux measurements with chambers require a suite of decisions, each of them affecting the quality of the final flux data.

The choice of temporal measurement resolution, the nature, number and spatial layout of measurement plots, and the recorded ancillary data (see Chapter 3) as well as chamber design and handling (see Chapters 4 and 5) can have large effects on the quality of the resulting flux data and its suitability for meta-analyses or modelling. Chamber design varies widely and has been established as one major source of uncertainty with substantial consequences for upscaled emission estimates, derived emission factors, and the inter-comparability of published flux data (Pumpanen et al., 2004; Pihlatie et al., 2013). Following the classification of Livingston and Hutchinson (1995), most studies in which N_2O and CH_4 fluxes are determined employ non-flow-through, non-steady-state chambers, while CO_2 measurements typically rely on flow-through, non-steady-state chambers. If an on-site gas monitor is not available, gas samples taken in the field for later analysis in the laboratory are prone to uncertainty and errors resulting from gas sampling, sample storage and gas chromatographic analysis, and should be minimized (see Chapter 6). Although the increasingly common “fast analysers” offer many advantages regarding the temporal resolution of measurements, they are also associated with specific challenges (see Chapter 7). While flux estimation methods have been widely discussed with respect to suitability (Nakano et al., 2004, Livingston et al., 2006, Pedersen et al., 2010, Parkin et al., 2012), little attention is often paid to the storage, screening and handling of flux and ancillary data (see Chapter 8) as well as to practices of flux and error estimation (see Chapter 9). Finally, the usefulness of published high-quality flux data for the scientific community could be considerably improved by thorough and consistent data reporting and description (Rochette & Eriksen-Hamel 2008; see Chapter 10).

For each of the above-mentioned steps, this document provides recommendations on how sources of error and uncertainty can be minimized and how the quality and reporting of CO_2, CH_4 and N_2O flux data may be improved. With this guideline, the authors hope to contribute towards a standardized procedure for greenhouse gas (GHG) flux measurements in order to improve the validity and comparability of GHG studies and to make users more sensitive to potential error sources of GHG flux measurements from planning to data reporting and publishing.

This document originates from intensive discussions within soil science communities in several European countries regarding the comparability of closed chamber measurements of soil CO_2,

CH_4 and N_2O exchange with the atmosphere. The contents of this document have been widely distributed and discussed within the Working Group "*Soil Gases*" of the German Soil Science Society (*Deutsche Bodenkundliche Gesellschaft*; DBG), with participation from colleagues in Austria, Switzerland and Sweden.

However, the recommendations provided here are not meant to stand alone; rather, the authors wish to integrate them into existing standardisation processes at the international level for measurements of N_2O (de Klein & Harvey 2012; Global Research Alliance on Agricultural Greenhouse Gases), and CO_2, CH_4 and N_2O (Parkin & Venterea, 2010; Pavelka et al., 2018, ISO 20951, 2019). Acknowledging these existing standardisation efforts for GHG measurements, the authors nevertheless feel the need to address various gaps between these protocols, particularly regarding chamber-based CO_2 measurements and quality assurance for gas chromatography data. A single standard protocol covering the methodological details from chamber design to data reporting for all of the major three greenhouse gases (CO_2, CH_4 and N_2O) would be a consolidation of present knowledge and complementary to existing standardisation documents for manual GHG measurements.

To the possible extent, this document therefore draws upon and refers to existing guidelines regarding chamber measurements and explanations therein in order to minimize redundancies. More detailed reasoning will be provided wherever the authors disagree with existing recommendations, add additional recommendations, or address yet unmentioned aspects. The authors are aware that this guideline only represents a current snapshot of the respective ongoing scientific and methodological developments and therefore explicitly encourage its periodic revision and supplementation.

2. SCOPE

This guideline aims at providing standardized recommendations for manual and automated non-steady-state, i.e. closed chamber, measurements (Livingston & Hutchinson 1995) of CO_2, CH_4 and N_2O fluxes at variable temporal and spatial resolution at the interface between soils, vegetation, and the atmosphere

- in terrestrial and semi-terrestrial ecosystems (including wetlands and nearshore environments of inland water bodies), and for
- different land use types with varying management intensity such as agricultural fields, grasslands, managed and restored peatlands, forests, drainage ditches, etc.

Gas flux measurements in flowing water, lakes, and oceans and measurements of reactive gases (e.g., ammonia or biogenic volatile organic compounds) are not considered in this document.

3. STUDY DESIGN AND ANCILLARY DATA

3.1. Summary of recommendations

Considering the high investments associated with setting up a GHG measurement programme, a well-planned study design is essential to producing high-quality data and to achieving the desired research objectives. In general, chamber-based GHG measurements are employed to describe the release or uptake of one or several GHGs from one or several land cover types or treatments. However, the study objective is not always the accurate quantification of an absolute GHG flux at a certain site at a given time. Rather, the difference between GHG fluxes from different land cover types or treatments or the temporal dynamics of the GHG exchange may also be focused upon.

Apart from choosing a chamber design (see Chapter 4), the following issues must be addressed when designing a study involving GHG measurements:

- Spatial resolution and pattern: In addition to accurate information on the study location and design, an adequate spatial measurement replication should be ensured which depends on the studied system and its inherent variability.
- Temporal resolution: Considering the respective study aim, the temporal measurement resolution must account for the anticipated temporal variability of fluxes due to the major underlying biogeophysical drivers of gas exchange at different temporal scales. An adequate sampling has to monitor low background fluxes as well as high fluxes during critical events (hot moments).
- Ancillary data: Depending on the studied system and in line with the selected spatial and temporal resolution, a range of basic and specific ancillary data must be collected along with the gas flux data.

3.2. Rationale

3.2.1. Spatial resolution and pattern

The reader’s understanding of publications on GHG fluxes from ecosystems is often hampered by inconsistent terminology with regard to the location of gas flux measurements. We propose employing the following specification to accurately describe the location.

On the highest level, the “location” designates the area where sampling takes place. The location is generally a local topographical name that, ideally, already says something about the ecosystem type (“*Hütelmoor*” designating a mire; “*Bad Lauchstädt*” designating a city close to and associated with a well-known agricultural field trial; “*Höglwald*” describing a well-known experimental forest).

On the next level, the “site” describes a vegetation unit within the location (“sedge-fen”; “pine forest”) or the agricultural field where a field trial takes place. Further levels such as plot, treatment, level, etc. may be necessary and helpful, but we consider it impractical to suggest specific designations for these levels. However, regarding the lowest level, we propose naming the exact spot of GHG flux determination “chamber base position”.

The chamber base positions should be described as accurately as possible by exact geographical coordinates for their retrieval and representation in maps. In summary, an exemplary correct designation of three replicate chambers could be: “*The measurement location was the Hütelmoor fen close to Rostock, Germany. There, measurements were conducted in a reed stand with three chamber base positions (54.133455 N 12.12345 E; 54.123455 N 12.12345 E; 54.143455 N 12.12345 E).*” For the sake of improved readability, it is suggested to include a table with the measurement positions in the coordinates in a supplement file or another adequate location of the documentation.

Following the notion that the landscape and parts thereof are mosaics of discrete, more or less homogeneous units, the GHG flux from different sites can be compared based on replicate chamber measurements conducted on all studied sites. In theory, the number of the replicates per site should be determined by the sample size required to identify statistically significant differences between these sites, mainly depending on the (often unknown) within-site heterogeneity. Due to the large – and sometimes enormous – spatial and temporal variability of GHG emissions (e.g., Koch et al., 2014), this theoretical approach often results in replicate numbers impossible to implement in practice. For example, Herbst et al., (2009) report that 31 spatial replicates of chamber-based flux measurements are needed to estimate the mean value of heterotrophic soil respiration with a significance level of 0.125. Folorunso and Rolston (1984) state that 350 replicate N_2O flux measurements were required to estimate the "true" mean flux within 10% of the estimated mean and Velthof et al., (1996) report that 375 to 1240 replicates were required to achieve the same confidence from managed grasslands.

Despite the fact that such replicate numbers cannot be realized in long-term field studies, researchers should try to obtain an estimate of the degree of the spatio-temporal variability of GHG exchange in their studied ecosystem(s) by conducting some pre-study measurements (i.e., a pilot study). Ideally, these "test" measurements should be conducted at different times as spatial variability and patterns of GHG emissions can change over time (Chadwick et al., 2014). If test measurements are not possible it may be helpful to assess basic environmental variables to guide proper placement of measurement locations. Eventually, the number of replicate flux measurements is often determined by logistic limitations. Because basic statistical parameters such as arithmetic mean and median must be calculated from at least three independent values, at least three spatially independent replicates need to be realised. However, more independent replicates are preferable, as Chadwick et al., (2014) show the benefit in achieving more accurate N_2O emission estimates when moving from one to five replicate chamber base positions. The exact distance that can be considered "sufficient" needs to be determined by geostatistical analysis (e.g., semivariograms), but it should be at least a few meters to avoid too strong autocorrelation.

Spatial dependence of factors affecting gas fluxes may be considerable and may occur at different spatial scales. Using variograms, Velthof et al., (1996) observed that an in-between distance of about 6 m was needed to ensure spatial independence of N_2O fluxes measured on grassland. Obviously, this distance strongly depends on the measured GHG and the size of the chamber footprint in relation to the size of the studied ecosystem. In practice, the range of spatial dependence is difficult to determine since the number of available chamber base positions is usually insufficient to support geostatistical analyses. We therefore recommend either using a random block design, which allows controlling for spatial dependence during statistical analysis, or placing chamber frames as far apart as feasibly possible considering ecosystem disturbance and technical/logistic limitations. The pooling of gas samples as suggested by Arias-Navarro et al., (2013) should be avoided whenever possible because it doesn't allow for deriving estimates for uncertainty and heterogeneity.

Where the landscape is considered a continuum of gradually changing properties, i.e. of "ecotones" (Gosz, 1993), any design relying on clustered measurement locations is problematic. According to the "ecotone" concept, locations for GHG chamber measurements need to be either selected using a predetermined grid, transect, or by randomization (Fig. 1). However, such a design will likely result in decreased measurement frequency as the person carrying out the measurements will have to cover longer distances between chamber base positions, potentially causing more damage in sensitive ecosystems.

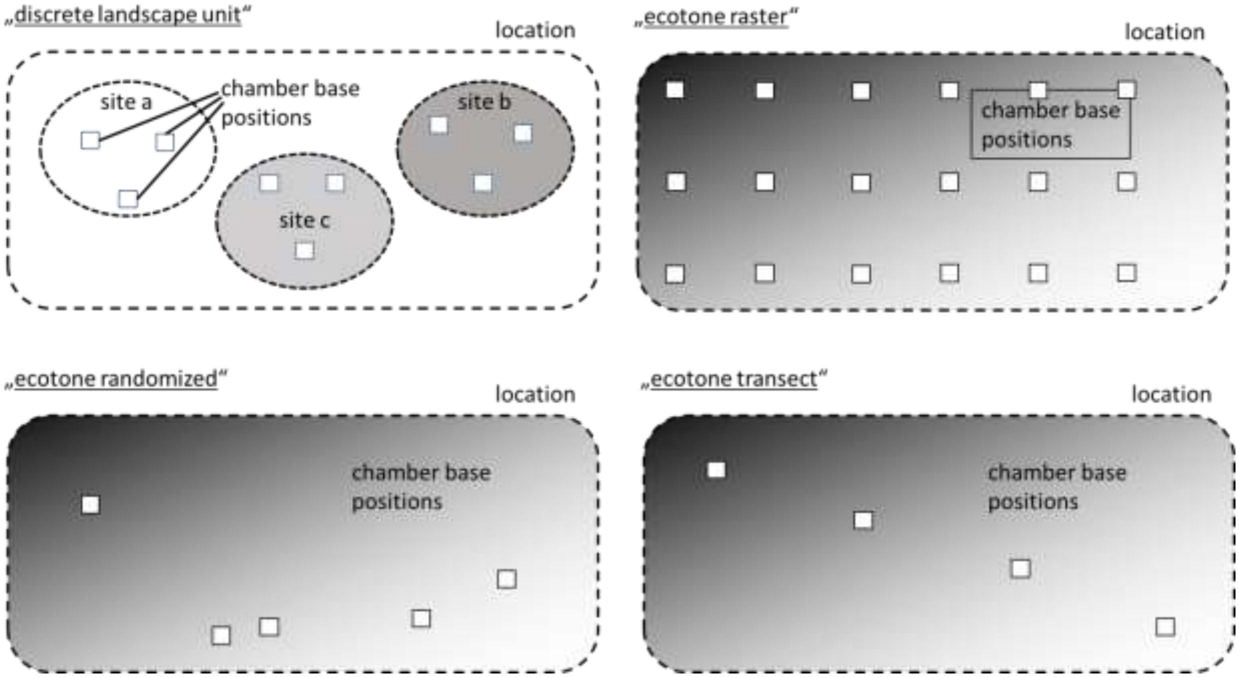

Fig. 1: Overview of different spatial layout types of chamber base positions within different landscape and ecotone contexts

3.2.2. Temporal resolution

Any chamber-based flux determination represents the GHG exchange at the exact moment of it being carried out. This is most evident when observing the highly transient nature of N_2O fluxes (Butterbach-Bahl et al., 2013), for CO_2 measurements of the vegetation-soil system under changing light conditions (Kaiser et al., 2015), or for soil respiration following tillage operations (Fiedler et al., 2015). Given the fact that automated chamber measurements outscore manual chambers in tackling temporal variability by far, we recommend using automated chambers whenever possible in order to minimize interpolation errors. The sampling schedule for manual measurements should be flexible and aim to account for hot moments such as land management measures (e.g. tillage, harvest), meteorological events (drought, strong frost, and heavy precipitation) and plant phenology.

However, since knowledge of background fluxes is essential for the identification of treatment effects and for GHG budgets, periods with small fluxes must be considered and are especially important considering a possible bias towards high fluxes, as occasions with fluxes around zero tend to be ignored in flux determination procedures. Regular measurement campaigns every 1-2 weeks will ensure that background flux periods are adequately captured.

Measurements should ideally not be interrupted for more than 1-2 weeks, while additionally accounting for critical events such as the above-mentioned hot moments, because the uncertainty of flux budgets is almost directly proportional to measurement gaps (Lucas-Moffat et al., 2018). Experiences from recent projects show that GHG flux data often not fulfil this standard of fine temporal resolution measurements due to insufficient funding. The authors therefore appeal to research funding organizations to support projects with higher measurement frequencies as projects with low measurement frequency result in disproportionately higher interpolation errors.

A thorough understanding of the factors controlling the temporal variability of the studied GHG fluxes is essential for developing an adequate study design. In terms of N_2O, these controls have been reviewed by Butterbach-Bahl et al., (2013), for CH_4 by Bridgham et al. (2013), for soil respiration by Vargas et al. (2011), and for gross primary production by Anav et al. (2015).

In summary, all GHG studies should account for the temporal variability of the following factors:

1. **Photosynthesis** not only influences CO_2 but also CH_4 and N_2O exchange via associated root exudation and thereby accelerates microbial activity. This results in short-term variability as well as diurnal, seasonal and inter-annual cycles. For instance, a study of tussock grass by Marinier et al. (2004) found a statistical relationship between CH_4 flux and growing biomass and a relation to photosynthesis. This can even affect the choice of chamber design, because some wetlands species have a gas-transport mechanism that is directly driven by the rate of photosynthesis (Günther et al., 2013).

   Irradiance is known to have an inhibitory effect on foliar respiration. This so-called Kok effect might lead to an overestimation of ecosystem respiration using opaque chambers covering soil areas including vegetation (Atkin et al., 1998, Heskel et al., 2013, Wehr et al., 2016). Air and soil temperatures are important controls of biological processes (e.g. denitrification, nitrification, methanogenesis, methane oxidation, decomposition, respiration) and also exhibit short-term, diurnal, seasonal and inter-annual variability.

2. **Soil moisture, the occurrence and depth and duration of frost, precipitation (incl. snow and ice cover), and (ground-)water table depth** control both microbial and plant processes almost as strongly as temperature, and in extreme cases even stronger. These factors also affect the transport of GHG from the soil to the atmosphere. Particularly N_2O fluxes are known to be associated with precipitation and thaw events (Mørkved et al., 2006), a classic example of the so-called “hot moments” of GHG release, which are often related to drastic changes in GHG transport through the soil. Moreover, rapid changes in soil volumetric water content caused by rain or groundwater table rise, induces GHG enriched soil air in the pore space to be purged by soil water.

3. **Management** can be an extremely powerful control of GHG fluxes depending on the studied ecosystem. Particularly relevant management measures are, for example, fertilization, pesticide application, tillage, harvest operations, crop choice, as well as grazing. Further, all manipulation measures affecting water table and soil moisture must be considered, including drainage of peatlands for peat harvesting, agricultural use, and forestry, as well as restoration measures like re-wetting. The timing, intensity and characteristics of such management measures must be recorded and GHG flux measurements should be ideally conducted directly before and with higher resolution immediately after these measures.

Consequently, when designing the temporal sampling scheme, studies involving GHG flux measurements should consider the relevance of

- **Diurnal cycles** (i.e. day-night variability), which determine the frequency and timing of measurements within a 24-hour period, and may change throughout the season or year (especially important for CO_2 and CH_4, rarely studied for N_2O): Ideally, diurnal cycles are captured with automatic chambers, alternatively with intensive manual chamber campaigns. A pragmatic approach to characterize diurnal GHG cycles relies on ≥6 temporally equidistant measurements per 24 hours. The cumulative chamber deployment period per 24 hours should not be too high to avoid inhibition of plant growth due to shading.

- **Seasonal** (i.e. growing and non-growing season) **and inter-annual cycles** (i.e. year-to-year variability), resulting in the recommendation to conduct measurements in or throughout ≥2 years, although adequately capturing inter-annual variability requires ≥5 measurement years: CO_2, CH_4 and N_2O measurements should ideally be conducted at least every 1-2 weeks and should be continued throughout the winter (albeit with reduced frequency).

- **The timing of critical “events”** such as e.g. heavy precipitation (especially for CH_4 and N_2O), freeze-and-thaw cycles (especially N_2O), and management events like fertilization, tillage or harvest (especially for CO_2 and N_2O): in addition to the regular temporal measurement frequency, additional measurements should be conducted immediately before and after such events whenever possible, potentially continuing with higher frequency until the event-related effects subside (e.g. after fertilization). A fine measurement resolution of the entire evolution of events has great benefits for model-data integration.

Depending on the research question(s), knowledge about soil parameters like nutrient status, redox potential, or pH may also be important ancillary data, but are generally less relevant for the temporal variability of GHG exchange.

3.2.3. Ancillary data: type and resolution

The above-mentioned factors illustrate the need for recording the following parameters when conducting chamber-based GHG flux measurements; for which we give the following suggestions. Depending on study aim, many other parameters might additionally be relevant.

1. Within the chamber, air temperature, PAR (for transparent chambers when determining CO_2 and CH_4 volume concentrations) and air moisture content need to be logged during sampling
2. Air temperature and precipitation, photosynthetically active radiation (PAR), atmospheric pressure, wind speed (and optionally direction) at 2 m height, snow/ice cover and depth, and frost depth typically do not vary strongly within sites. So generally, one adequately equipped weather station per site can supply these data for the experiment.
3. Synoptic data (weather data) should ideally have a higher (but at least the same) resolution than the gas flux data. Particularly for empirical gap-filling procedures, half-hourly to hourly resolution of synoptic data is recommended.
4. Soil moisture or water table and topsoil temperature (5 to 10 cm depth) are preferably logged by affordable instruments directly at the chamber base (ideal) or in the plot in close proximity to the chamber base position. Additionally, these parameters should be manually measured at the time of GHG flux measurements.
5. Soil chemical variables, like nutrient concentrations or dissolved organic carbon (DOC) in the soil pore water can be of great value when modelling is intended or as explanatory variables. For instance, the availability of mineral nitrogen or other nitrogen species as substrate for N_2O production might improve the explanation of N_2O exchange.
6. In case of vegetated sites, information about dynamically changing plant properties such as species composition and abundance, ground coverage, plant functional types, leaf area, vegetation height (also within the chamber for calculations of chamber volume), phenological development, and rooting depth need to be determined several times a year and, if possible, when conducting gas flux measurements.
7. A regular photographic documentation of all sites and chamber base positions is recommended for data quality assurance. With the availability of cheap and easy-to-deploy camera traps, it may also be interesting to install such a camera and use it in regular interval mode to get a regular view on the measurement locations that later may help in interpreting the data.

3.2.4. Study site setup

The following questions may provide some help with the decision on the number of spatial replicates and their distribution according to the “plot” or the “ecotone” concept (Fig. 1):

1) What is the context of the planned study?
    a) “agronomy”, where the notion of homogeneous plots is rarely challenged (plot concept) and randomized block designs are common
    b) “ecology“, where the ecotone character of the landscape is highly appreciated (ecotone concept)

Does the studied landscape or landscape unit conform to the “plot” concept; i.e. can it be considered relatively homogenous over large distances?

Is the spatial or the temporal resolution of greater relevance to the study objective (i.e. what are the preferences regarding the trade-off between the representation of temporal and spatial variability?

All study sites should be set up to minimize inadvertent human disturbance of the studied ecosystem in general and particularly during sampling. A very common problem in GHG studies is the forcing of CH_4 ebullition (i.e. non-diffusive release of CH_4 bubbles) due to physical disturbance when sampling in wetlands (e.g. Weishampel & Kolka 2008; Forbrich et al., 2010; Winton & Richardson 2016), the gradual compaction of soils associated with a subsequent reduction in gas transport (e.g. Hansen et al., 1993; Ruser et al., 1998), and the damaging of plants. At least for sites on organic soils, water-logged soils and soils prone to compaction, it is therefore highly recommendable to install boardwalks several weeks before the first GHG measurement campaign. For flux measurements on mineral soils, prescribed standing areas for the sampling person also help to minimize soil disturbance and its possible effects on greenhouse gas release.

Further issues to be considered when choosing measurement locations are:

- A regular and close contact to the person managing a GHG study site (i.e. farmer, forester, etc.) is very important and crucial for obtaining both high-quality GHG fluxes and ancillary data.
- Availability of grid power, which is very helpful for operation and service of instruments. Often, grid power cannot be accessed. In this case, solar power may be a good alternative, if power supply is in line with demand especially in times of lowest solar radiation (e.g. at night, in winter). It is advisable to consult specialists for calculation of power supply and demand. A methanol-powered fuel cell may be another good alternative, especially in combination with solar panels, while gasoline-operated power generators are not advisable as they produce GHG and may thus cause artefacts. However, in some cases they may be needed nevertheless. In this case, special attention needs to be given to install generators downwind and in appropriate distance of the chamber base positions.
- It is very helpful to work on sites with GPS, cell phone and internet access for data transfer and easy access to help in case of problems arising in the field.
- The topographical position of the site deserves special attention. Factors to be considered include the diurnal and seasonal patterns of potential sunshine and shadow (especially in high latitude or mountain locations), wind direction and velocity and its temporal variation, exposition of chamber base positions and the associated boardwalks to ensure insolation of the chamber base position when handling the chamber.

4. CHAMBER DESIGN

4.1. Summary of recommendations

Many different non-steady-state chamber designs have been used for measurements of GHG fluxes between soils or soil-vegetation systems and the atmosphere. Although the principle of the method appears simple, some standardisation in chamber design and deployment is needed to reduce methodological uncertainty and achieve better comparability between studies in the future.

There is no chamber design which optimally and simultaneously addresses all requirements derived in Chapter 4.2. Hence, a compromise between the different requirements must be found depending on the study question and the properties of the soil-vegetation complex under investigation. However, a set of general recommendations can be given:

1. Typically, chambers are composed of two components: a base typically called collar or frame, which is permanently inserted in the soil, and a chamber top, which is put on the base only during flux measurements. Floating chambers for measurements in water only consist of a chamber top that can be installed in the centre of a life buoy (Jordan et al., 2016). As plants should not be cut or folded by the chamber, the chamber top may be composed of several parts (lid, extensions) in order to adjust for plant growth (e.g., extension + chamber top; extension + lid); also helpful in case of water table fluctuations. While chamber height should fully accommodate present vegetation, chamber should not be too large because the chamber volume-to-base area ratio must be small enough that the change of the volume concentration of the gas of interest is well quantifiable against the measurement noise of the gas analysis during reasonable chamber deployment periods (see Chapter 5).
2. The base area of the chamber should be as large as possible in consideration of practical handling and the desired spatial resolution of the study.
3. The chamber headspace volume must be accurately determined considering the micro-relief of the soil surface within the frame as well as snow or water located above the soil surface. As micro-relief can change throughout seasons and years, headspace volume determinations should be repeated regularly. Water and snow height above the soil surface must be measured on each flux measurement day.
4. Chamber materials must be composed of gas-tight and nonreactive materials.
5. If vegetation is present in the chamber and is expected to have a relevant effect on the flux rates of the gas of interest, day measurements must be conducted with chamber made from transparent material equipped with a PAR sensor. In this case, the deployment period must be shortened to minimize the greenhouse effect. Transparent chamber wall materials need to have high optical transmittance (> 90%) particularly in the visible light spectrum, but the transmittance in the UV and infrared range should also be considered. When using opaque chambers, walls with reflective outer sides are preferable to minimize chamber warming.
6. The seal between the frame and top of the chamber must be gas-tight. Air-tightness of the seal should be carefully checked under controlled laboratory and field (wind effects!) conditions at regular intervals prior to individual field campaigns, but at least prior to starting a GHG study (for other chamber functionality checks see Chapter 5).

7. The decision on the insertion depth of the frames should be based on careful consideration of soil properties, root distribution, and chamber deployment period. The higher the air-filled porosity of the soil and the longer the chamber deployment period, the deeper the chamber frame has to be inserted. However, disturbances of the root system should be minimized, and lateral water flow in the soil should not be impeded. If the installation of bases is not possible, it is important to at least ensure that any mass flow of air between the chamber headspace and the ambient air is prevented by airtight sealing. Bases are not needed in areas where water levels are always at or above the soil surface. At high water levels or for measurements in open water, floating chambers (buoys) can be used or the chamber walls may reach into the water to ensure airtightness.
8. Overpressurization of the chamber headspace during chamber placement needs to be carefully avoided. This can be done by closable vents with cross-sectional areas as large as possible, which are opened during chamber placement. The problem is also avoided if a topless chamber is used that is closed with a lid after chamber placement. Depending on the research question and environmental conditions, the deployment of a vent that is permanently open during chamber deployment may be reasonable to allow atmospheric pressure fluctuations affecting the soil-(vegetation)-atmosphere gas fluxes. However, the construction and arrangement of the vent needs to be carefully checked under controlled field conditions to avoid systematic flux artefacts caused by wind-induced pressure gradients (*Venturi effect*) leading to increased air advection from soil pore space to the chamber headspace.
9. Turbulent mixing of the chamber air is necessary to ensure near-homogenous properties of the chamber headspace air (gas volume concentrations, temperature). In small flow-through chambers, the air flow by the pump may be sufficient to induce turbulent mixing, particularly when combined with a properly designed sample intake manifold. However, most chamber types require fans to induce turbulent mixing. Fans should not be stronger than necessary for efficient headspace mixing and should not be directed towards the soil surface, in order to avoid advective flushing of the top soil pore space.
10. For the flux estimation of a gas of interest, not only the volume concentration of this gas in the chamber headspace should be analysed over the chamber deployment period, but ideally also the volume concentration of water vapour (mixing ratio) to allow for correcting the water dilution effect, which is particularly relevant for small GHG fluxes.
11. Air temperature and PAR (for transparent chambers only) should be measured inside the chamber. Ideally, mean atmospheric pressure during chamber closure should be measured at the study site. If such on-site measurements are not available, estimating pressure from altitude or from nearby weather stations is possible.
12. If a transparent chamber and/or long chamber deployment periods are necessary, the use of a cooling system might be appropriate. However, the installation of a cooling system should be considered as the last option if excessive warming during chamber closure cannot be avoided otherwise. The cooling system should only prevent excessive warming of the headspace air, but cooling of headspace air relative to ambient air and pronounced removal of water vapour due to condensation at the cooling surfaces should be avoided since this typically leads to considerably decreasing relative humidity which might affect stomatal closure of plants.

4.2. Rationale

4.2.1. Principle of the method – Derivation of requirements

The non-steady-state closed chamber method allows estimating the exchange flux of a gas of interest between soils or a soil-vegetation system and the atmosphere $\Phi_{\text{gas,s-v-a}}$ (t) by separating a part of the soil-vegetation-atmosphere system from its surroundings. The amount of gas molecules $n_{\text{gas}}(t)$ in the air-filled closed chamber headspace volume V_{h} increases or decreases over time as a result of the net molar gas flux $\Phi_{\text{gas,net}}(t)$ (with dimension NT^{-1}) into and/or out of the chamber headspace, respectively (Fig. 2).

$$\Phi_{\text{gas,net}}(t) = \Phi_{\text{gas,s-v-a}}(t) + \Phi_{\text{gas,wall}}(t) + \Phi_{\text{gas,leak}}(t) = \frac{dn_{\text{gas}}}{dt}\,(t)$$

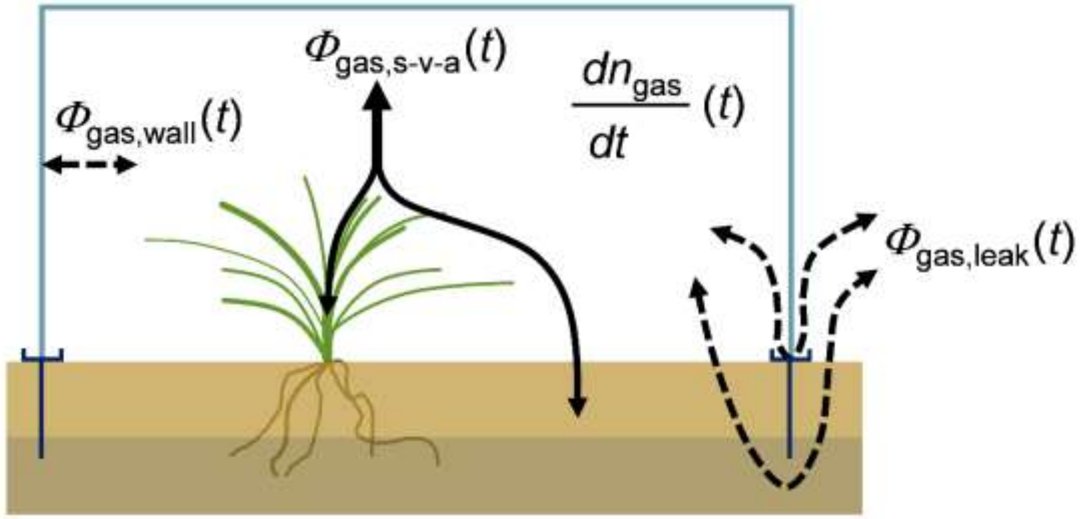

Fig. 2: Schematic of the general principle of the closed chamber method. The net gas flux at a given time t during chamber closure $\Phi_{gas,net}$ (t) (with dimension NT-1) can be expressed as the sum of the gas flux between the soil-vegetation system and the atmosphere $\Phi_{gas,s\text{-}v\text{-}a}$ (t), the gas flux between inside and outside of the chamber $\Phi_{gas,leak}$ (t) and the gas flux between the chamber materials and the chamber headspace $\Phi_{gas,wall}$ (t). The net gas flux $\Phi_{gas,net}$ (t) is reflected in changes of the amount of gas molecules n_{gas}(t) present in the chamber headspace over time t

To be able to approximately equate the chamber net gas flux into the chamber headspace $\Phi_{\text{gas,net}}$ (t) with the gas flux between the soil-vegetation system and the atmosphere $\Phi_{\text{gas,s-v-a}}$ (t), gas fluxes between inside and outside of the chamber $\Phi_{\text{gas,leak}}$ (t) as well as gas fluxes between chamber materials and the chamber headspace $\Phi_{\text{gas,wall}}$ (t) need to be minimized. Therefore, the chamber should

1. be composed of gas-tight and nonreactive materials, which neither transmit, absorb or emit the gas of interest nor react with it (e.g., stainless steel, aluminium, polyvinyl chloride, polycarbonate, polyethylene, or polymethyl methacrylate),
2. be constructed so that the headspace volume is not significantly altered during chamber closure,
3. effectively separate the air inside from the air outside the chamber not only in the atmosphere but also in the soil pore space, and
4. minimise water condensation at the inner chamber surface, particularly for flux measurements of CO_2, which has high solubility in liquid water.

Then, the gas flux between a soil-vegetation system and the atmosphere $\Phi_{\mathrm{gas,s\text{-}v\text{-}a}}(t)$ at a given time t_i can be approximated by:

$$\Phi_{gas,s-v-a}(t) \cong \frac{\partial n_{gas}}{\partial t}(t) * A^{-1} \qquad (4.1)$$

where:

A: base area of the chamber

The headspace volume V_h, the pressure $p_{air}(t)$ and temperature $T_{air}(t)$ of the headspace air as well as the volume concentration of the gas of interest $\sigma_{gas}(t)$ need to be known for the calculation of the amount of gas molecules $n_{gas}(t)$ in the headspace air at a given time t according to the ideal gas law is given by:

$$n_{gas}(t) = \frac{p_{air}(t)V_h}{RT_{air}(t)}\sigma_{gas}(t) \qquad (4.2)$$

where:

R: ideal molar gas constant

The headspace volume V_h is constant during the closure period of a single closed chamber measurement; however, it might change over longer time scales with changes in soil surface height or height of water or snow in the chamber. While headspace air pressure is typically assumed constant over the chamber closure time and equal to the ambient air pressure measured by a nearby meteorological station ($p_{air}(t) \cong p_{ambient}$ = constant), headspace air temperature has to be measured in the chamber headspace during closure.

The volume concentration of the gas of interest in the headspace air is measured by a gas analyser (e.g. a gas chromatograph, see Chapter 6) either off-site in discrete samples (via syringes, vials or other sampling container) taken from the headspace air or on-site in an air stream that is circulated in a closed loop from the chamber to the gas analyser (e.g. based on infrared absorption spectroscopy, see Chapter 7).

In many flux measurement situations, water vapour can be emitted into the chamber headspace during chamber closure due to evaporation of water from the soil-vegetation complex, which leads to expansion of the headspace air and dilution of the gas of interest (Welles et al., 2001; Rochette & Hutchinson 2005; Pérez-Priego et al., 2015). For a vented chamber, this dilution effect on the volume concentration of gas of interest can be approximately corrected for if the water vapour volume concentration $\sigma_{H2O}(t)$ over chamber deployment period t is monitored in the chamber headspace:

$$\sigma_{gas,corr}(t) = \sigma_{gas,uncorr}(t)\frac{1-\sigma_{H2O}(t_0=0)}{1-\sigma_{H2O}(t)} \qquad (4.3)$$

where:

$\sigma_{H2O}(t_0)$: water vapour volume concentration at the moment of chamber placement

Since the measurements of the volume concentrations of the gas of interest and water vapour as well as of air temperature must be representative for the entire headspace volume, it is necessary that

1. the concentrations of the gas of interest and water vapour as well as temperature are near-uniform throughout the chamber headspace, which requires turbulent mixing of the headspace air (Rochette & Hutchinson 2005; Christiansen et al., 2011).

Generally, a critical assumption of the method is that the gas flux between the soil-vegetation system and the atmosphere does not significantly change due to the closure of the chamber or, alternatively, that a chamber-induced change of the flux is theoretically correctable. As a theoretical correction is often difficult to apply in praxis, the ideal chamber system should be designed to minimize perturbations in factors that could affect the gas fluxes, such as

2. the radiation balance (incoming shortwave and longwave, outgoing shortwave and longwave)
3. the soil water status, i.e. closing the chamber should be avoided during significant precipitation; it is thus recommended to equip automated chambers with a rain sensor
4. the temperature of the soil, vegetation and air within the chamber
5. air humidity (increases due to evapotranspiration but also decreases due to too strong cooling and condensation)
6. the surface gas flux resistances of the soil-vegetation complex
7. air pressure fluctuations due to atmospheric turbulence (“good”) or setting of the chamber (“bad”)
8. air flow velocities in the chamber headspace strongly deviating from ambient wind speeds, resulting in instantaneous changes of the aerodynamic resistance of the headspace air (turbulent transport resistance) and the quasi-laminar boundary layer resistance (diffusive transport resistance)

Of course, it is also important that

9. mechanical disturbances of vegetation and soil, particularly at the edges of the chamber, are avoided as much as possible.

4.2.2. Dimensions of chamber (frame and top)

Typically, chambers are composed of two components: a base, which is permanently inserted in the soil, and a chamber top, which is put on the base only during the flux measurement. The chamber top may be composed of several parts, e.g. to adjust for plant growth and water table fluctuations. Using only a chamber top and pushing this into the soil for each measurement is not recommended since inserting the chamber walls into the soil can destroy fine roots, create coarse pores and decreased soil resistance to gas exchange (Matthias et al., 1980). Also, pushing the chamber walls into the soil can create pressure-induced mass flow out of the soil creating biased fluxes at the beginning of chamber closure. These effects are typically less critical if a frame is installed in the soil only once allowing for an equilibration phase between the time of disturbance and the first measurements.

Chambers can have different geometries and sizes depending on the research question, study design and the structure of the ecosystem under investigation. Most commonly, base areas are circular or quadratic, but also rectangular base areas have been used, e.g. in row-crop systems. A systematic testing of the performance of different chamber geometries appears useful, particularly for investigations of irradiation-dependent photosynthetic CO_2 fluxes.

The base area of the chamber should be as large as possible regarding the practical handling and the desired spatial resolution of the study (Kaiser et al., 1996). The smaller the base area, the smaller the base area-perimeter ratio of the chamber and thus the larger the potential relative effects of edge disturbances. Following Rochette and Eriksen-Hamel (2008) and de Klein and Harvey (2012), who based their reasoning on diffusion modelling results of Healy et al. (1996), a base area-perimeter ratio of ≥ 10 cm is considered as very good (e.g. a quadratic base area with 40 cm edge lengths or a circular base area with a diameter of 40 cm), whereas a base area-perimeter ratio of ≤2.5 cm is considered as very poor. Chambers designed for measurements between cereal crop rows (rectangular and narrow) might i.e. bias gas fluxes as a result of small base area-perimeter ratios. This theoretically derived recommendation is supported by the results of a chamber calibration campaign for CH_4 flux measurements (Pihlatie et al., 2013).

The chamber top must be high enough that plants are not mechanically disturbed by the chamber placement. Plants must not be folded or even clipped. Disturbance of the plants may not only have effects on their photosynthesis and respiration and thus the fluxes of CO_2, water (H_2O) and oxygen (O_2) but also on the transport of other trace gases. For example, it is well known that CH_4 is transported in aerenchyma of wetland plants from the water-saturated root zone to the stems and leaves, and from there to the atmosphere (e.g., Armstrong & Armstrong 1991, Kutzbach et al., 2004). Stressing of plants might result in stomata closure and perturbation of gas emissions.

On the other hand, the chamber volume-to-base area ratio must be small enough that the change of the concentration of the gas of interest is well quantifiable against the measurement noise of the gas analysis during reasonable chamber deployment periods (Fig. 3).

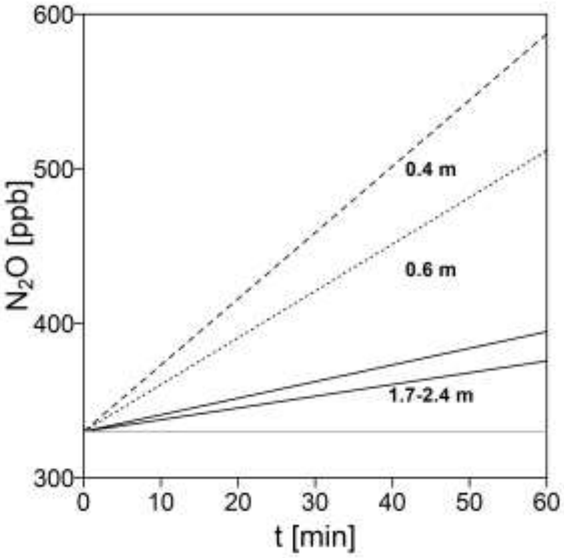

Fig. 3: Estimated N_2O volume concentration change during typical chamber-closure times at a fixed efflux of 200 µg m^{-2} h^{-1} for the differing V:A-ratios of 'small' (dashed line, V:A-ratio: 0.4 m), 'flexible' (black lines, V:A-ratios: 1.7–2.4 m), and 'box-shaped' chambers (dotted line: V:A-ratio 0.6 m). Grey line marks an ambient N_2O volume concentration of 330 ppb (Source: Huth 2016)

The seal between the base and top of the chamber must be gas-tight. In the past, many studies used water-filled groves to ensure airtight closure, but these may be of limited service under frost conditions. Other possibilities include gaskets made of rubber or closed cell foams. If the installation of bases is not possible, it is important to at least ensure that any mass flow of air between the chamber headspace and the ambient air is prevented by air-tight sealing.

Air-tightness of each chamber should be tested under laboratory and field conditions (wind effects!) at regular intervals prior to field campaigns, but at least prior to starting a GHG study. The strength of leakage and/or absorption on chamber materials can be checked by installing the chamber on an air-tight surface, injecting a known amount of the gas of interest and monitoring its volume concentration over time (e.g. Pérez-Priego et al., 2010, 2015, Hoffmann et al., 2018, Olfs et al., 2017). Air-tightness can also be checked in the field using smoke cartridges (Hoffmann et al., 2018). Other chamber functionality checks are described in Chapter 5.

The decision on the insertion depth of the frames should be based on careful consideration of soil properties, root distribution and chamber deployment period. The higher the air-filled porosity of the soil and the longer the chamber deployment period, the deeper the chamber base has to be inserted. However, unless trenching experiments are conducted, disturbances of the root system should be minimized, and lateral water flow within the soil should not be impeded. Following Rochette and Eriksen-Hamel (2008), who based their reasoning on diffusion modelling results of Hutchinson and Livingston (2001), a ratio of insertion depth to chamber deployment period of ≥ 12 cm h^{-1} is considered as very good, whereas a ratio of insertion depth to chamber deployment period of ≤ 5 cm h^{-1} is considered as very poor. If the installation of frames is not possible, it is important to at least ensure that no openings between the soil surface and the chamber top exist that allow mass flow of air between the chamber headspace and the ambient air. Frames are not needed in areas with water levels always at or above the soil surface. At high water levels or for measurements in open water, floating chambers (buoys) can be used.

Chamber headspace volume has to be accurately determined considering the micro-relief of the soil surface within the base as well as snow or water above the soil surface. To this end, measurements of base height on a regular grid within the base are recommended. Four to eight height measurements at different positions are often found in the literature as appropriate to determine the chamber height. Depending on the micro-topography and/or vegetation complexities inside the chamber base area, more measurements might be warranted. As micro-relief can change over seasonal to multi-annual scales, headspace volume determinations should be regularly repeated. Water and snow heights should be measured on each measurement day. Plant biomass volume needs only be considered for very dense plant canopies. The smaller the height-area ratio of the chamber, the more accurate the effective headspace height needs to be determined.

4.2.3. Pressure-related effects

During the placement of the chamber, short-time pressurization of the chamber headspace is likely to occur, which can lead to moderate to pronounced irregularities in gas fluxes at the beginning of the chamber deployment period (Davidson et al., 2002, Christiansen et al., 2011). This initial “pressure shock” has been observed even with a permanent vent installed (Davidson et al., 2002), because the cross-sectional areas of the permanent vents are too small for fast equilibration of the overpressure induced by chamber placement. Therefore, we recommend equipping the chamber with additional closable vents with cross-sectional areas as large as practicable, which are opened during chamber placement. The problem is also avoided by using a topless chamber that is closed with a lid. Although recommendations for such additional openings during chamber placement have been orally communicated in parts of the chamber flux community, but it appears that this practice has not yet been described in the literature and cannot yet be considered a standard. More systematic testing of this technical improvement is warranted.

Under ambient conditions, turbulent air movement in the atmospheric boundary layer leads to so-called pressure pumping. These pressure fluctuations at the soil surface lead to oscillating contraction and expansion of soil pore air, which can induce mass flow and significantly increase emission of gases produced in the soil compared to fluxes by diffusion alone (Hutchinson & Mosier 1981, Hutchinson & Livingston 2001, Maier et al., 2010, 2012).

Depending on the research question and environmental conditions, the deployment of a vent that is permanently open during chamber deployment may be reasonable to allow atmospheric pressure fluctuations affecting the soil-(vegetation)-atmosphere gas fluxes. However, excessive diffusional loss of the gas of interest through this vent opening should be minimized. Proper dimensions (length and diameter) of the vent tube can be obtained from the paper of Hutchinson and Mosier (1981). It is very important that the construction and arrangement of the vent is carefully checked under controlled field conditions to avoid systematic flux artefacts caused by wind-induced pressure gradients (*Venturi effect*) leading to increased air advection from soil pore space to the chamber headspace (Conen & Smith 1998, Bain et al., 2005, Maier et al.,2019; Xu et al., 2006). If permanent vent tubes are installed, their openings to the ambient atmosphere should be installed as close to the soil surface as possible since average wind speed can be assumed to decrease with proximity to the surface. Even more suitable may be the application of a vent tube design developed by LI-COR, Inc., which reduces negative pressure excursions under windy conditions by a special aerodynamic form of the vent opening, which counteracts the Venturi effect (Xu et al., 2006). However, the vent tube of LI-COR is a special development for their automated soil CO_2 flux system (LI-8100, LI-COR, Inc.), and this approach needs to be tested for other chamber types and dimensions.

4.2.4. Effects of turbulence and aerodynamic resistance

Several studies showed that the strength of turbulence inside the chamber headspace influences the flux estimate (e.g. Reicosky et al., 1997, Pumpanen et al., 2004, Rochette & Hutchinson 2005, Lai et al., 2012, Goerres et al., 2014). The gradients of gas volume concentrations inside the soil and vegetation as well as in the soil-near atmospheric boundary layer are adjusted to the gas source/sink strengths and the ambient flux resistances within soils, plants and the atmosphere. At the interfacial layers between vegetation, soils and the atmosphere, these flux resistances are mainly of diffusive nature. In the turbulent atmospheric boundary layer above the interfacial layer, aerodynamic resistances are predominant (Healy et al., 1996, Hutchinson et al., 2000). The lower the atmospheric turbulence, the thicker is the quasi-laminar boundary layer at the soil and vegetation surface, where diffusion still dominates the exchange fluxes. These quasi-laminar boundary layers are characterized by strong gas concentration gradients. If the aerodynamic resistance is increased by chamber placement due to lower turbulence in the chamber, the storage of a gas that is produced in the soil is increased in the interfacial layers and the soil pore space. At the same time, the observed flux into the well-mixed part of the chamber headspace is attenuated until the concentration gradients have re-adjusted to the new conditions.

By contrast, if the aerodynamic resistance is decreased by chamber placement due to strong fans, the storage of such a gas is decreased in the interfacial layers and the soil pore space by a strong initial “flushing” flux. Similar effects are expected at the interfacial layers between vegetation and the atmosphere and in the intercellular space of plant leaves when plants act as CO_2 source due to dominating respiration (in the dark), whereas inverse effect are expected when plants act as CO_2 sink due to dominating photosynthesis. Particularly strong artificially increased CO_2 fluxes have been observed under stable atmospheric stratification during night-time (Schneider et al., 2009, Lai et al., 2012), when chamber placement disrupts strong gas volume concentration gradients in the lowest meters of the atmospheric boundary layer.

No standard method is so far available to correct for the effects of artificial and abrupt changes of turbulence due to chamber placement on soil-vegetation-atmosphere gas fluxes. A control unit that adjusts the turbulence inside the chamber to outside levels would be an optimal solution; however, its implementation appears too complex to be realistic for standard gas flux monitoring campaigns. Lai et al. (2012) recommended longer chamber deployment periods to allow the gas volume concentration gradients and gas fluxes to re-adjust to pre-deployment levels. However, it must be considered that during this longer dead band period, gas volume concentrations as well as other environmental variables are already altered from ambient levels with respective potential for biased flux estimates. More research on the uncertainty introduced by these turbulence effects on gas fluxes appears necessary.

5. CHAMBER HANDLING AND GAS SAMPLING

5.1. Summary of recommendations

When applying a closed chamber for flux measurements, the following basic recommendations for chamber handling and gas sampling should be followed:

1. The duration of the chamber deployment period depends on the expected gas fluxes, the precision of the volume concentration analysis method, soil and vegetation canopy properties as well as on typical atmospheric boundary layer characteristics at the study site. The chamber deployment period should be as short as possible to minimize ecosystem disturbance due to changes in temperature, humidity, radiation, and headspace gas volume concentrations. At the same time, longer chamber deployment periods result in decreasing detection limits and thus flux uncertainty. Longer chamber deployment periods may also be advantageous if strong disturbances of concentration gradients between soils, vegetation and the atmosphere are expected due to abrupt changes of aerodynamic resistance. Typical chamber deployment periods are 20–60 min for gas chromatography-based measurements and 3–5 min for fast online analysers.
2. The functionality of all chambers should be carefully checked under controlled conditions at regular intervals prior to field campaigns, but at least once prior to starting a GHG study. In addition to an air-tight seal between chamber and frame (see Chapter 4), this includes testing for delay times due to tube length (see 8.), chamber headspace mixing and optical transmissivity.
3. The insertion of chamber bases biases real gas fluxes. Therefore, this installation-related disturbance effect should be considered thoroughly when determining the start of gas measurements after initial insertion of the base and with respect to the point in time from which on data are considered reliable.
4. Chambers need to be flushed before closure. The chamber top needs to be carefully and slowly lowered onto the frame in order to avoid initial pressure fluctuations during chamber placement.
5. Chambers, particularly if transparent, should be cleaned on a regular basis.
6. Manual gas sampling can be done with syringes, non-evacuated vials, or evacuated vials. Pumping with syringes prior to sampling is not recommended. It is advantageous to use a sampling method that allows creation of over-pressure in the sample containers for instance by sampling with syringe and then pushing the sample into an evacuated vial that has smaller volume than the syringe.
7. At least four (4) headspace air samples for air composition (volume concentration) analysis should be taken over the chamber deployment period to allow appropriate regression analysis of the increase of headspace gas amounts chamber deployment period; five are even better.
8. When using online gas analysers, the material of the tubes connecting the chamber to the analyser must be appropriate for the gas of interest. Tube lengths should be similar at the inlet and outlet, and be adequate for the pump flow. The time delay between the concentration change in the chamber and the detection of this change in the analyser is a function of tube length and pump flow and must be considered during flux estimation. Analysers should be protected from damage by using particle filters and water filters (or traps) at the inlet.

5.2. Rationale

5.2.1. Chamber closure

Short versus long chamber closure periods

There are good reasons for both short and long chamber closure periods. Short chamber closure periods minimize the disturbance of the studied ecosystem due to changes in temperature, humidity and gas concentrations of headspace air as well as in radiation and wind influence (de Klein & Harvey 2012; Rochette & Hutchinson 2005). On the other hand, longer closure periods allow for a lower detection limit for gas fluxes. The decision on closure periods should be based on the expected flux magnitude and the detection limit of the gas volume concentration determination method. However, it is widely accepted that chamber deployment periods should not exceed 60 min. Typical deployment periods are 20–60 min for gas chromatography-based measurements and 3–5 min for fast online analysers.

The gas exchange fluxes investigated by the closed chamber method are typically assumed to be mainly driven by diffusion although advective fluxes can be important under specific circumstances (e.g., pressure pumping, ebullition). A change of the analyte volume concentration (dimension NV^{-1}) gradient between soil, vegetation and the headspace air, which drives gas diffusion, is inevitable since the closed chamber method relies on analysing the gas amount change in the headspace. Thus, the flux within the chamber will not be constant during chamber closure, but will respond to the change in headspace gas concentrations.

There are different ways to account for this problem when estimating gas fluxes (see also Chapter 9):

Option 1 is to restrict the flux estimation to a short period at the beginning of the chamber closure period (but excluding a so-called dead band time period that is needed for complete headspace mixing and sample transport in tubes in case of through-flow systems) for which the headspace analyte amount change can be assumed approximately linear. This approach benefits from a large chamber volume-to-base area ratio.

Option 2 is to allow or even foster nonlinearity of the headspace analyte gas volume concentration change and to fit a nonlinear function to the data (excluding again initial data in the “dead band”) allowing for the approximation of the slope at the moment of chamber placement (Livingston et al., 2006, Lai et al., 2012, Pérez-Priego et al., 2015). This approach calls for longer closure periods and small chamber volume-to-base area ratios. Pérez-Priego et al. (2015) argue for moderately longer (3 min) chamber deployment periods to reduce uncertainty in nonlinear regression parameters used to calculate CO_2 fluxes from fast-analyser data. Lai et al. (2012) argue for longer deployment periods to allow re-adjustment of gas volume concentration gradients and fluxes after the abrupt perturbation of aerodynamic resistance by the chamber placement.

Functionality checking prior to field campaign

The functionality of the chamber should be thoroughly checked under controlled conditions in the laboratory and under field conditions (wind effects!) before the start of the field campaign. In addition to an air-tight seal between chamber and frame and/or absorption on chamber materials (see Chapter 4), this includes testing for delay times due to tube length, chamber headspace mixing and optical transmissivity.

For flow-through chambers in combination with online measurements, it is recommended to determine the delay time due to the sample transport through the inlet tube and the analyser’s optical cell by monitoring the response of the system to a step change of the concentration of the gas of interest. This experimentally determined delay time can be used to define the duration of the “dead band” at the beginning of the chamber closure.

Optical transmittance of chamber wall materials should be tested, ideally across the whole spectrum from ultraviolet to near-infrared light (Pérez-Priego et al., 2015). It should also be assured that the concentration of the analyte in the sampled headspace air is representative for the composition of the total headspace air. In general, the representability is achieved by headspace air mixing (fan) or by through-flow sampling in closed dynamic chambers.

Chamber handling considerations during field campaign

Chamber bases should be installed so that their upper edge is as close to the surface as is practical to avoid alteration of the micro-climate (shadowing, wind shielding) in the bases. The installation of chamber bases disturbs the soil structure and may cut roots, thus biasing the natural gas flux (Heinemeyer et al., 2011). To minimize this effect in agricultural settings, it is strongly recommended to insert bases into bare soil (e.g. shortly after seeding) since the disturbance usually lasts for no more than one hour in coarse-textured soils to a few days in clay soils (de Klein & Harvey 2012). If the installation of bases in vegetated areas (e.g. permanent grassland) is unavoidable, damaged roots need to regrow over the course of weeks to even months (de Klein & Harvey 2012) until the natural gas flux has been re-established. Nevertheless, we recommend starting chamber and ancillary measurements directly after base insertion. This allows for (i) the monitoring of the disturbance period as well as (ii) the identification of the disturbance period by using a modelling approach.

Walking and stamping next to the chamber during the actual measurement must be avoided as it may cause a pumping effect, especially in ecosystems with thick humus layers. For measurements in wetlands, boardwalks need to be installed and bases should be located as far from the poles supporting the boardwalk as possible to minimise soil disturbances and ebullition due to movements of the boardwalk. If transparent chambers are used, boardwalks, measurement equipment and the person taking the measurement should be located on the north side of the chamber (south side for southern hemisphere) to avoid shading of the chamber during measurements.

Before using the chamber for a new flux measurement, the chamber must be flushed with ambient air since chamber deployment should start with (near-) ambient conditions. When closing the chamber, it is important to carefully and slowly lower the chamber top onto the base to avoid excessive pressure shocks. It is recommended to first set one edge or side of the chamber top onto the frame and then slowly lower the rest of the chamber top so that most of the air below the chamber top can escape before chamber closure.

Calm conditions and atmospheric stratification can pose a challenge for the chamber measurements, as the air near the ground is then less mixed than in unstable conditions, and stronger local gas concentration gradients near the ground must be expected (see Chapter 4.2.4.). Measurements with flow-through and online gas analysers lead to a significant change in the local stable atmospheric stratification within and near the chamber, which can lead to an artefact in the flux estimation. Although there is evidence that this effect might be very important, no thorough assessment of the practical relevance or solutions to this problem have been presented so far.

Chambers should be regularly cleaned. This is especially important for transparent chambers to ensure optimal radiation transmissivity.

5.2.2. Manual gas sampling for lab analysis

Closed chamber measurements are typically carried out with manual sampling from the chamber headspace with low frequency (< 0.005 Hz), i.e. few gas samples (4 to 5+) are taken from the closed chamber headspace after defined intervals of typically 5 min, 10 min, 20 min, 30 min.

A number of methods exist for collecting gas samples from closed chambers, which must be compatible with the autosampler of the off-site gas analyser (e.g. gas chromatograph).

- Syringes may be used as sample containers if samples are manually injected into the GC. This limits the maximum number of samples that can be stored and is associated with higher transport risks. When taking air samples with syringes, prior pumping of headspace air in and out of the syringe is not recommended since this can induce pressure fluctuations that lead to irregular gas flux fluctuations (Christiansen et al., 2011).
- Gas samples are taken with a syringe and transferred into evacuated vials, which should be evacuated shortly before sampling. Under adverse weather conditions, this method can be somewhat difficult, and the cannulas present some safety risk. The method is suitable to create over-pressure, which may increase the reliability of the air sample analysis.
- Non-evacuated vials are flushed forwards and backwards with chamber air using a syringe. The method is suitable to create over-pressure.
- Evacuated vials are simply connected directly to the chamber air. Vials should be relatively big and should be evacuated shortly before sampling. No over-pressure can be created.
- Chamber air is pumped into evacuated vials, which should be evacuated shortly before sampling. The method is suitable to create over-pressure.
- Chamber air is pumped through the vial and back into the chamber. By first closing the outflow connection, over-pressure is created. It must be ensured that the vial volume is sufficiently often exchanged, i.e., more than 10 times.

Three types of vials are typically used for sample collection: Labco (Lampeter, Wales, UK) Exetainers® (with rubber septum), glass vials with crimp top and rubber septum, and glass vials with stopcock. While not all of these are equally suited for all sampling methods, in principle all of these may be used. Labco Exetainers® and vials with crimp top are more convenient for transport and storage. As vials with stopcock are quite large and expensive, the storage of large sample numbers is hardly possible, which can become an issue if the GC is not operational and field sample collection must be continued.

Reliability generally increases with increasing number of data points. Hence, it is highly advisable to consider the trade-off between sampling cost, statistical accuracy, and study design. Generally, the frequency and quality of the volume concentration measurements have important implications for the reliability of regression modelling approaches used during flux estimation. Long-term experience tells us that at least four (4) chamber air samples are recommended to ensure reliable estimation of fluxes and flux uncertainty. However, Jungkunst et al. (2018) have shown that also two-point flux estimates may be justified when – in turn – the number of flux measurements can be increased accordingly, thereby reducing the overall uncertainty while allowing for higher uncertainty of individual flux estimates. The planning of the number of gas samples should also account for chamber deployment period, chamber volume, vial volume and the detection limit of the subsequent composition analysis.

The first gas sample (t_1) from the chamber headspace should be taken as soon as possible after chamber placement at time $t_0 = 0$, because it cannot be assumed that the headspace air composition at t_0 is similar to that of ambient air (Rochette et al., 2011). For flux estimation, the elapsed time since chamber placement must be recorded.

5.2.3. Gas sampling with online gas analysers

During the last 15 years, technological advancements allow for continuous gas measurements in the field, thus enabling *in situ* monitoring of gas volume concentration change. These online gas analysers have many advantages over other systems, but also create new challenges.

To perform chamber measurements with online gas analysers, gas is sampled from the chamber headspace, analysed (frequency of ~0.5 to 1 Hz), and pumped back to the chamber in a closed loop. Depending on the tube length and the pump rate of the analyser, a time delay between the change of the gas concentration in the chamber and the analyser has to be accounted for. An additional pump can also be used to support or replace the analyser's internal pump thus decreasing the time delay. However, positive or – even worse – negative pressure fluctuations in the chamber headspace due to high pump air flow should be avoided since this can lead to the suppression or enhancement of soil-(vegetation)-atmosphere gas fluxes, respectively.

The length of the connecting tubes should be similar at the inlet and outlet of the analyser, in order to account for the flow resistance of the tubes and to avoid pressure imbalances. The material of the tubes should be appropriate for the gas of interest; hence, silicone must not be used (highly permeable for CO_2), and special tubing is recommended for studying the isotopic composition of gases (e.g. PTFE, Tedlar©, aluminium-coated tubes).

To ensure representative sampling from the chamber headspace, we recommend closed-loop sampling or the use of manifolds in addition to the mixing provided by a within-chamber fan.

The use of particle filters at the analyser inlet is recommended for all analysers.

In addition, a water filter or trap should be installed in front of the analyser inlet to protect the analyser from water condensing inside the tubes. An insulation particularly of longer tubes might be necessary when condensation of water inside the tube is expected (recommended for all automatic systems). Some analysers require further conditioning (e.g. a dew point controller) and drying of the sampled air (by cooling, trapping and re-heating the water, or Nafion®-dryer) to avoid problems with condensing water and to avoid interferences.

For further recommendations regarding online gas analysers, please refer to Chapter 7.

6. GAS CHROMATOGRAPHIC (GC) ANALYSIS AND GAS SAMPLE STORAGE

6.1. Summary of recommendations

Infrastructure

- Ensure stable temperature using air conditioning.
- Ensure stable electricity supply using an uninterruptible power supply.
- Minimize length of gas pipes. Install purifiers if gas pipes get longer.
- Ensure proper safety installations and procedures for gas supply.

GC system

- Consider a laser-based GHG analyser as an alternative to purchasing a GC.
- For new systems, an HID is the recommended detector since it avoids common problems and safety considerations of an ECD.
- Install a backflush system.

Standard gases and calibration

- Use at least four standards with gas volume concentrations distributed equidistantly over calibration range or concentrated at lower end of calibration range in combination with weighted regression.
- Calibration range should span from below ambient to 5 or 10 times ambient.
- Volume concentration should be on x-axis, peak area on y-axis for regression.
- Choose calibration model based on statistical parameters, stability and accuracy at the lower end of the calibration range.
- Calibrate for each run.
- Do not extrapolate. Avoid combining two calibrations (based on different ranges) in a sample campaign.

Quality control

- Record basic system parameters such as the baseline weekly.
- Check the autosampler for sample carry over.
- Check coefficient of variation (CV) of the peak area of the lowest standard, by measuring 10 standards consecutively. CV > 3 % indicates problems. Record these values.
- Include control samples in all runs.
- Do not use drift correction routinely. Fix the underlying problem instead.
- Measure samples from one flux measurement in direct succession.

Auto-sampler

- Use an autosampler that can easily be integrated with your GC model.
- A closed sample transfer system is preferable to open sample transfer (with a syringe). If you have to transfer the sample with a syringe, extra care must be taken to avoid carry-

over effects, for instance by issuing extra flushes (ambient) after each chamber measurement is completed.

- Use a system that can get standard gases directly from supply pipes.

Sample storage

- Use exetainers or crimp top vials since they are cheaper and easier to store and transport.
- When ordering new types of septa always check for interactions with analytes and tightness.
- Conduct storage tests regularly. Store at lab temperature out of direct sunlight.
- If sample containers are filled with overpressure, check the pressure before GC-measurement. If they are evacuated, check that they hold the vacuum.

6.2. Rationale

Many aspects of gas chromatographic (GC) analysis strongly depend on the available instrumental setup. This protocol strives to give general recommendations where possible, but instrument-specific considerations should also be taken into account. The recommendations are mostly based on extensive personal experience since such details are usually not part of scientific publications.

6.2.1. GC vs. online GHG analysers

In recent years, online GHG analysers (e.g. Cavity Ring-Down Spectroscopy) have become available at reasonable prices. The price of such analysers is now comparable to that of a GC, but their operation does not rely on an expensive laboratory infrastructure and requires fewer consumables and technical staff. In the long run, investing in an online analyser will likely be cheaper than installing and maintaining a GC laboratory. Moreover, online analysers are more precise. Although, currently, no auto-samplers for online GHG analysers are available on the market, in principle it should be possible to use such analysers equipped with available small sample modules also for air samples. Until then, they have to be connected directly to the flux chambers, which allows for considerably shorter chamber deployment periods and improved flux precision (Brümmer et al., 2017).

6.2.2. Laboratory infrastructure

A GC laboratory requires a range of infrastructure, which can be expensive to install and maintain. Most essential is a good gas supply system, with gas pipes of minimal length. To ensure a high gas quality, the use of simple purifiers (installed directly at the GC gas inlets), which (at least) remove traces of water and oxygen, is advisable. To comply with safety regulations, sensors for flammable gases in indoor air (e.g., H_2, CH_4) may be installed (depending on local rules) and maintained if such gases are used in the laboratory. The pressure of the gas pipes should be continuously monitored by a system that can cut the gas supply in case of a sudden pressure drop. To protect the instrument from damage, it is preferable that it shuts down automatically in case the gas supply is interrupted, but safety considerations must be a priority. The necessity of an O_2 sensor for indoor air has to be assessed by the local safety officer. Since a cut of the gas supply interrupts the operation of the instrument and can even damage the columns and detectors of the GC if it does not shut down automatically in such a case, it is recommended to install gas supply stations that change automatically from an empty to a full bottle and allow exchanging gas bottles without interrupting the gas supply.

A GC should be operated in a laboratory with controlled and stable temperature and a ventilation system that does not cause sudden atmospheric pressure changes in order to ensure a high measurement quality. Air conditioning is generally advisable since GCs generate a lot of heat.

A GC can be seriously damaged by a power outage and some sensors are also sensitive to power fluctuations. Thus, an uninterruptible power supply (UPS) stabilizing voltage and current should be installed.

6.2.3. GHG GC systems

To measure GHG volume concentrations, GC systems from all major manufacturers can be used. The market has changed a lot in recent years, ranging from dedicated GHG GCs from major manufacturers to GC systems customized by small specialized companies. One should not expect a newly delivered GC system to be ready for routine measurements immediately after delivery. According to common experience, even with large established companies, it can take from about three months to more than a year until a new GHG GC system is operating reliably. Any promises with respect to shorter installation time periods should be regarded critically.

The most important decision one faces is the choice of detectors used for the three gases N_2O, CO_2, and CH_4 (Table 1). N_2O is commonly detected using an electron capture detector (ECD). An ECD usually offers a good detection limit for N_2O, but it typically also presents the most trouble for laboratories. ECDs are notorious for being “individuals” and each detector has somewhat specific characteristics. After installation, it can take a long time (sometimes months) until the detector is stable and ready for measurements. Furthermore, since the detector contains a radioactive nickel foil, compliance with national radiation protection regulations is required, i.e., a trained and certified radiation protection officer might be on site and yearly inspections may be mandatory (depending on local rules).

An ECD requires make-up gas, with best performance achieved when using a mixture of 90% argon (Ar) and 10% CH_4. However, for gas concentrations typical of samples from chamber measurements, it is often sufficient to use N_2 instead, at least if a packed column is used. If N_2 is used as make-up gas, it should not be extremely pure, i.e., contain traces of oxygen as is the case for N_2 5.0 quality; otherwise ECD sensitivity is reduced. For that reason, make-up gas purifiers that remove oxygen, sometimes recommended by the GC manufacturers to protect the ECD from oxidation, should not be used. The ECD’s sensitivity may fluctuate due to the individual bottle’s N_2 make-up gas purity. Care should be taken regarding a good separation of N_2O and CO_2 to make sure that no CO_2 from the sample reaches the ECD because otherwise CO_2 influences the N_2O signal. Alternatively, a make-up gas containing a substantial CO_2 concentration can be used (Wang et al., 2010).

A good alternative to an ECD is a (pulse discharge) helium ionization detector (HID). This detector can measure not only N_2O, but a broad range of compounds, including CO_2, CH_4, N_2, and O_2. The HID requires helium (He) of extremely high purity as a carrier gas. In practice, this can usually only be achieved by means of a gas purifier, which is available for reasonable prices. A system with an HID used for detection of N_2O participated in a recent Germany-wide intercomparison test for GHG-GCs and achieved a precision comparable to systems equipped with an ECD.

An additional possibility for N_2O detection is a mass spectrometer coupled with the GC. CH_4 is usually detected using a flame ionization detector (FID), which is a very reliable detector for a wide concentration range and requires a gas supply of hydrogen (H_2) and synthetic air (for the flame). The routine operation of an FID typically offers no serious challenges. If the GC system includes a (more expensive) HID for the detection of other analytes, it may also be used for detecting CH_4. A thermal conductivity detector (TCD) is a third alternative for CH_4 detection, although usually only for higher concentrations than in the atmosphere.

CO_2 is most commonly detected after catalytic reduction to CH_4 (using a “methaniser”) with H_2 reconditioning the reducing agent. This method can be used for concentrations common in chamber measurements, but the catalyser may be overloaded by very high concentrations.

CO_2 can also be detected with an ECD (Loftfield, 1997). However, this can exacerbate difficulties of N_2O detection because the ECD configuration needs to be optimized for both gases simultaneously. If a modern ECD is operated with N_2 as make-up gas, CO_2 detection might necessitate adding a trace concentration of O_2 to it. TCD or HID are also alternative CO_2 detectors.

Table 1: Detectors that can be used for measurement of GHG

Analyte	**Common detector**	**Alternatives**
N_2O	ECD	HID, mass spectrometer
CH_4	FID	HID, TCD
CO_2	FID + Methaniser	ECD, TCD, HID

The separation of the three analytes is uncomplicated. Usually, a Porapak Q column maintained at constant temperature is used in combination with N_2 (quality 5.0) as a carrier gas. Alternatively, a PLOT Q column may be used. An HID requires purified He and should be used with other columns (e.g., a ShinCarbon column and a mole sieve) in order to be able to separate and measure O_2 and N_2.

Air samples generally contain substantial amounts of water and other minor components. Thus, the GC system must include a backflush system (which may use a pre-column) to separate the analytes from undesired components, which would quickly deteriorate the system’s performance. The flow direction of the column or pre-column is reversed after the analytes have been passed thereby removing all contaminations from the system.

6.2.4. Autosamplers

Given adequate spatial and temporal sampling resolution, manual and particularly automated chamber measurements can produce relatively large numbers of gas samples. Hence, autosamplers are typically required to facilitate GC measurement. Unfortunately, autosamplers for measuring the GHG concentration of low-volume gas samples are a niche market. Autosamplers available on the market have usually been developed for a diverse set of applications or for other applications, thus sometimes customization is required.

Four different methods can be employed to transfer gas samples to the GC:

- Sample transfer with a syringe and injection into an injection port. This requires over-pressurized gas samples and risks gas exchange with ambient laboratory air. However, the advantage is that standard autosamplers and standard injection ports can be used.

- Injection of carrier gas into the gas sample and subsequent release of the over-pressurized gas sample into the carrier gas supply of the GC system. This requires a defined pressure of the gas sample; and a defined temperature is ensured by heating. Closed sample transfer.
- The gas sample is connected to an evacuated sample loop connected to a long capillary (i.e., a relaxation loop; Loftfield 1997). Thereafter, the pressure is adjusted to ambient pressure by opening the relaxation loop to the atmosphere. The sample loop is subsequently connected to the column. This system needs a sufficient sample volume, but no defined pressure (as long as the pressure is not too low). Closed sample transfer.
- Carrier gas is flushed through the gas sample. This approach requires a defined gas sample pressure. Closed sample transfer.

Obviously, the autosampler needs to be integrated with the GC system, which may result in design restrictions either for the GC or the autosampler. Some autosamplers can be connected to pipes supplying gas standards, which eliminates the need to fill gas standards into vials for calibration.

6.2.5. Standard gases and calibration

Standard gases should be mixtures of trace concentrations of the three GHGs in synthetic air. The quality of these standards is crucial for overall measurement quality. In an inter-lab comparison, Lemke et al. (2002) found standard quality to be a major source of variability. Volume concentrations of standard gases of the best available quality in Germany are certified with ±1% analytical tolerance (or even better). It is strongly recommended to use this quality.

Generally, standard concentrations should be representative of and typically distributed equidistantly over the range of typical gas samples. Although practical and financial considerations often limit the number of standards, a minimum of four standards is recommended. For samples from chamber measurements, standard concentrations should range from slightly below ambient concentration to 5-10 times ambient concentration. Note that many GC systems cannot quantify concentrations considerably below ambient. Also, as GHG fluxes are often small, most measurements will be close to the lower end of the calibration curve, which unfortunately is the range of lowest precision. This effect can be partly mitigated by having standards closer together at the lower end of the calibration range, but that necessitates using weighted regression or transformations to avoid the effect of influential values (for this calibration strategy see e.g. Doerffel (1990) and Miller & Miller (2010)).

Calibration models should be selected according to the detector characteristics in the measurement range. Common available alternatives include “linear through zero”, “linear with intercept”, “quadratic through zero”, and “quadratic with intercept”. The choice should not only be based on statistical metrics (e.g., Akaike’s information criterion corrected for finite sample size, AIC), but also on stability over time and accuracy at the lower end of the calibration curve. Note that for the regression the certified volume concentrations should be on the x-axis and the instrument response on the y-axis. The resulting model then needs to be inverted to calculate sample volume concentrations. In general, calibration models must not be extrapolated. If calibrations over two different ranges are used during a sample campaign, there will be a break and an offset between samples in the vicinity of the transition of the two calibration models – which should be avoided.

The calibration curve should not be strongly nonlinear since typical chamber air concentrations are expected to be in the linear range of common detectors. Strong nonlinearity is therefore an indicator of problems.

It is highly recommended to calibrate the GC before each run. For long runs, a full set of calibration standards in the middle of the run may also be useful if problems occur.

Detection limits can be estimated following the procedures given in ISO 11843-2 (2000) or 11843-5 (2008). Most GC software programs provide options for calculating uncertainty of sample concentrations.

6.2.6. Quality control of GC measurements

Basic diagnostic values such as the baseline (uncorrected, called “zero free” by some GC systems) or calibration parameters should be monitored and recorded weekly (i.e., laboratory documentation). The GC and autosampler systems should also be checked regularly for problems associated with sample carryover by measuring the lowest standard several times directly after the highest standards. No carryover effects should be visible in this test.

The stability of the system should be assessed weekly. We recommend measuring a close-to-ambient standard 10 times in succession and checking the coefficient of variation (CV). There are several publications that report CV values below 0.5 % (Kelliher et al., 2015), but we found this difficult to maintain in practice, with CV values between 1 and 2 % being more realistic. A CV value above 3% usually indicates problems and routine measurements must be stopped until the source of the problem has been identified and fixed. For these routine tests, we recommend checking the CV of the peak areas instead of the volume concentrations, because the test will then be independent of calibration. However, assuming a precise calibration, the CV of volume concentrations and peak areas should be very similar.

Sample runs must always include control samples. Ideally, those would differ from the calibration standards, but this cannot always be implemented due to financial or practical reasons. Some laboratories use control samples analysed before, during and after a sample run for drift correction. However, such a drift correction only combats the symptom of a problem underneath. It is therefore recommended to determine and remove the source of the sensitivity drift. A stable GHG GC system does not require drift correction. Nevertheless, it is recommended to measure gas samples from the same flux measurement in direct succession in order to further mitigate drift effects.

Regardless of the GC setup and instrument specifications, general rules of good laboratory practice (OECD 1998) must be followed, which includes maintaining an instrument journal and archiving raw data from all measurements.

6.2.7. Gas sample storage

Samples should be stored at laboratory temperature, in dry conditions, and away from direct sunlight. For this purpose, a cupboard in the laboratory is absolutely sufficient.

When establishing a new vial system, it should be thoroughly tested. This includes testing how well it maintains over-pressure and gas composition over time. Such storage tests would typically be conducted by filling vials with gas standards at a defined over-pressure, followed by periodic measurements of pressure and gas volume concentrations at several time points up to some maximum storage time. Since these measurements are destructive or at least can alter the sample, a sufficient number of samples need to be prepared. Exemplary results from such a storage test are shown in Fig. 3. Such tests should be repeated regularly, but especially if septa are ordered from a new supplier. Even if septa are ordered from the same supplier, the manufacturer might have changed the rubber recipe. Since septa are generally not produced specifically for GHG samples, such changes may not always be communicated and may present problems due to chemical reactions with the desired analytes. For example, there are septa on the market that absorb CO_2. For an additional short-term storage test, the change of isotopic composition can be checked with an isotopic mass spectrometer.

If vials are evacuated for sampling, a test should be conducted to assess how well they preserve vacuum. It is recommended to use each septum only once to avoid problems due to repeated perforations. Since stopcocks are always reused, they need to be checked for tightness at regular intervals (preferably before each use). If samples are filled with over-pressure, the pressure should be measured and recorded before GC measurements.

A comparison by Glatzel and Well (2008) found some slight advantages of Exetainers over crimp top vials, but, to our knowledge, no further comparisons have been published. It has been reported that more than 90% of the analyte can be recovered from vials with butyl-rubber septa even after storage up to one year (Kelliher et al., 2015). However, this depends on the analyte volume concentration relative to ambient air.

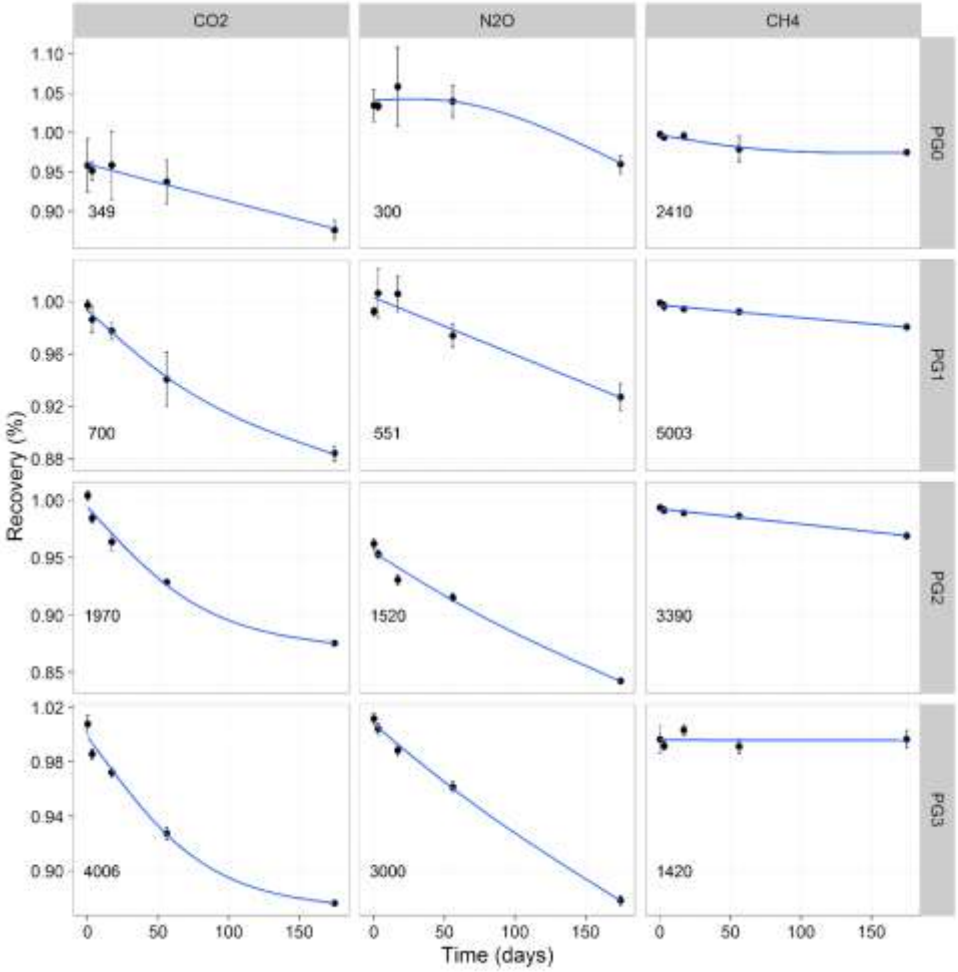

Fig. 4: Example results from a storage test. Number of replicates was n = 4 and samples were filled to 1700 mbar absolute pressure. Recovery was calculated relative to certified volume concentrations of the standard gasses. Samples were discarded after measurement. Numbers give volume concentrations of the standard gases (CO_2: ppm, N_2O: ppb, CH_4: ppb). Recovery of less than 90% was observed for higher concentrations after two months, which indicates that such long storage times should be avoided for these sample containers. PG0 to PG3 are lab-internal IDs of the standard gases

7. ONLINE GAS MEASUREMENTS WITH FAST ANALYSERS

7.1. Summary of recommendations

During the last 15 years, technologies have been developed that allow for continuous gas measurement in the field so that it became possible to monitor the change of gas concentrations inside a measurement chamber in-situ. Fast gas analysers have many advantages but there are also details that must be considered carefully.

1. Choose the right system: The utility of fast analysers depends on the research question and the usage scenario. Mobility can be a limiting factor for fast analysers because most of them are still heavy, need a constant electrical power supply, and often do not work properly in harsh environments. The most important manufacturers offer “lightweight” variations of their systems to facilitate mobility, which is usually traded for precision. It is essential to consider the technical requirements of your project (e.g. detection limits, precision, minimum detectable fluxes, mobility, temporal resolution) and the available resources (e.g. manpower, time, money) when deciding whether to work with fast analysers or not.
2. Check your system regularly and check your data directly in the field: Checking your equipment on a regular basis is essential to obtain reliable data. A good routine should always include a regular validation of the calibration and testing of leakage of the system (especially important if the analyser cell is operated at low pressure). In the field, it is important to avoid vibrations and protect your system against contamination by particles and especially against damage by water. Working with fast analysers allows monitoring the concentration change in a closed chamber and, thus, adapt (i.e. shorten or prolong) the deployment period of the chamber. Detecting nonlinearities in concentration change can help to identify irregularities and solve problems in the measuring method. The risk of data loss and power blackouts is never zero, back up your data regularly and use external storage to do so.

7.2. Rationale

Infrared gas analysers (IRGA) have been available for decades now and have facilitated CO_2 measurements substantially including automated systems. New technologies have evolved quite recently that allowed the development of fast gas analysers for measuring CH_4, N_2O, as well as their isotopes and isotopologues. In this chapter we will cover technical issues that are associated with the application of such GHG analysers that can be used for online chamber measurements.

7.2.1. Online gas analysers for gases other than CO_2

Advantages

A big advantage of online gas analysers is the possibility to check and optimize chamber measurements directly in the field, which can lead to better quality of flux measurements. For instance, it is much easier to choose the optimal chamber deployment period, which can lead to better quality and efficiency in manual chamber measurements. Further, the much higher sampling frequency (compared to sampling with vials) yields much more data points, which allows for much short chamber deployment periods and minimum detection limits at the same time (Brümmer et al., 2017). It also allows for an easier identification of the linearity of the initial concentration change in the closed chamber. Checking the linearity can also help to identify ebullition and treat artefacts like unsteady installed chamber bases (Hoffmann et al., 2017). Another advantage is the reduction of possible errors of the vial sampling procedure from field measurement to GC analysis, because there are plenty of possible handling errors such as missing evacuation, mixing up of vials in the field, during transport or when placing them in the auto sampler array, improper recording, and/or reporting of irregularities. The usually low maintenance requirements of online gas analysers also make them suitable for automated measurements. The first manufacturers started to produce modules that allow introducing small discrete volumes of gas samples (e.g. 20 ml gas vials), what allows using the analysers in a way similar to the traditional laboratory GC.

Disadvantages

Online gas analysers are expensive and rather heavy (compared to gas sampling with vials). Some of the available analysers are not yet ready yet for truly mobile applications, although backpack solutions become more and more common. Sufficient power supply can still be an issue, because some analysers can only be applied for < 2 hours before the rechargeable battery packs are drained, which may be feasible if the battery packs are hot-swappable. Sometimes, the truly mobile analysers available on the market may also have issues when applied in harsh environments (i.e. in heavy rain, temperatures outside the operating temperature range, etc.).

Analyser types and manufacturers

Fast gas analysers are available from several manufacturers using different technologies. The analysers currently on the market differ in many features, e.g. number and types of gases that can be measured, concentration ranges and precision, measurement frequency, minimum sampling volume and air flow, drift and temperature or matrix sensitivity, size, weight and power consumption. The majority of analysers currently in use is, in principle, based on the absorption of laser beams and differs in how the laser is implemented and the absorption is detected. Also, other technologies are used (Warlo et al., 2018).

Laser based gas analysers

Most mobile gas analysers are based on laser technology that allows for precise gas volume concentration measurements by measuring the absorption in narrow and precise bandwidths of radiation. They are usually operated in a continuous flow-through mode and allow for a high measurement frequency (> 1 Hz) and precision. Many of the analysers available today allow for the measurement of several gas species at once. Only very few, however, allow for the combined analyses of the three major well-mixed GHG and none of these is truly portable.

Gas analysers of *Picarro* (Picarro, Inc., Santa Clara, USA) and *Los Gatos* (Los Gatos Research, San Jose, USA) are probably the most widely used analysers in soil gas research. They are based on similar technologies. Whereas *Picarro* analysers use Cavity Ringdown Spectroscopy (CRDS), *Los Gatos* claims to have further developed the approach to the so called Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS). A beam from a single-frequency laser diode enters a cavity defined by high reflectivity mirrors in which the beam is “trapped”. The laser frequency fits a specific absorption spectral line of the gas of interest. When the laser is abruptly turned off, the strength of the laser signal decays (“*ringdown*”) according to the absorbance that corresponds to the gas volume concentration. Both companies offer analysers for CO_2, CH_4, N_2O, different isotopes in these GHG, and other gases. *Aerodyne* (Aerodyne Research Inc., Billerica, USA) and *Campbell* (Campbell Scientific, Inc., Logan, USA) offer a similar spectrum of analysers, which are based on tunable infrared laser direct absorption spectroscopy (TILDAS) at mid-IR wavelengths

(*Aerodyne*) and tunable-diode laser absorption spectroscopy (TDLAS, *Campbell*). Both provide very high precision and accuracy but at the cost of mobility, power needs, and rigidity.

Laser technology is advancing rapidly and further manufacturers are developing analysers that might become interesting for GHG measurements in the future: e.g., *Mirico* (Mirico, Chilton, UK) building tunable diode laser spectroscopy analysers that rely on laser dispersion sensing (compared to absorption that is used in all other analysers reported above), and *AERIS* (AERIS Technologies, Redwood City, USA) building miniature mid-infrared absorption spectroscopy analysers. An interesting new player in the field of analysers simultaneously measuring CO_2 and CH_4 is the LI-7810 of Licor, Inc.

Multiple species gas analysers (other technologies)

Lumasense (Lumasense, Ballerup, DK) recently bought technology from INNOVA and produces field gas analysers that based on photoacoustic spectroscopy, that is also used for highly sensitive laboratory analysers. The absorption of electromagnetic energy by different gas species is measured by means of acoustic detection. Pulsed electromagnetic energy with a specific bandwidth (either laser or infrared source and optical filters in case of Lumasense) causes thermal expansion and sound that is proportional to the volume concentration of the gas species.

Gasmet (Gasmet, Helsinki, FI) analysers use Fourier Transform Infrared Spectroscopy (FTIR) and can be configured to measure up to 25 gases simultaneously. Unlike the other technologies mentioned above that use monochromatic sources of electromagnetic energy to identify the absorption in very specific wavelength, FTIR measures the full spectrum of absorption. An interferometer allows for scanning the spectrum of absorption of the gas sample, which then allows deducing the gas sample composition and volume concentrations. However, to report volume concentration values with high precision and accuracy this technology needs relatively many spectra that are averaged over time. Integration periods of at least 1 min or more are needed for measuring CH_4 volume concentrations with a precision and accuracy comparable to the above-mentioned laser-based analysers, likely because the CH_4 band is small and strongly interferes with the water bands. In contrast, for CO_2, the system can reach a precision that is similar to the devices of *Los Gatos* and *Picarro* with integration periods of 5 s. The precision of N_2O was between ±10 and ±30 ppb at 5-s intervals. It has to be noted, though, that long integration periods for single volume concentration values are problematic in a non-steady-state system.

In short, both technologies, FTIR and photoacoustic spectroscopy, allow for the measurement of multiple gas components at once, but also require a sequential gas sampling, which therefore limits the sampling and measurement frequency (< 0.05 Hz).

7.2.2. Gas analysis: accuracy, precision and sampling frequency

The scientific question, experimental design, and chamber system determine the gas concentration range and the accuracy and precision needed for the gas analysis, i.e. the specifications that must be met by the gas analyser. In most cases, chambers are operated at ambient concentrations, and the concentration in the chamber at the end of a measurement does not deviate more than ± 25% from the initial concentration. Meeting the required precision is essential for any method of gas analysis including online gas analysers.

Interference with other gases can result in a loss of precision or even drifting measurement values, which was observed for instance with CO_2 affecting δH_2O measurement values (Gralher et al., 2019) or water vapour affecting N_2O concentration measurements (Warlo et al., 2018). Temperature can affect the measurement precision and accuracy. Some manufacturers offer analysers with enhanced precision that include sophisticated temperature stabilization (and usually heavy) casings. Temperature change can also instigate drift and, thus, affect the accuracy of the measurements. Although some analysers are much less prone to temperature issues and drift, it is important to warm up the analyser before and to maintain stable conditions while measuring, and to keep conditions as stable as possible at least during the period of an individual chamber measurement.

7.2.3. From chambers to fluxes

The volume concentration change over time and the volume of the chamber system is needed to estimate the soil-(vegetation)-atmosphere flux in a chamber (see Chapters 4 and 9). The volume of the system includes the inner volumes of the closed chamber, all tubes and filters and the internal volume of the analyser. Since the measuring cell of the analyser might be operated at a different pressure, the effective volume (corrected by the pressure) must be used. Some analysers measure all surrounding parameters needed for volume concentration determination, others require the input of atmospheric pressure, sample air temperature and humidity. It is important to be aware which physical unit of concentration the output of the analyser is in, and which parameter it was corrected for.

7.2.4. Limiting factors

- **Power consumption** of online gas analysers can be a limiting factor for automatic measurement and campaigns in remote areas without power connection, as most online gas analysers are designed to be operated on grid power. The technologies of the online analysers originate from laboratory devices that were designed for constant electrical power supply. To facilitate mobility weight and power consumption of some models have been reduced. Typical power consumption of mobile gas analysers ranges from 25 W to > 100 W with the latter requiring strong (and heavy) batteries which can be laborious on extended field campaigns and limit a day`s workload. The market is highly dynamic and manufacturers are working on solutions to this challenge. The more promising analysers in the market offer lightweight, hot-swappable Li-Ion Power Packs that allow up to 8 h of operation under field conditions.
- **Data safety and data economy** can be crucial. The above analysers are often operated with data loggers where economic data handling can be crucial. An appropriate trade-off between sampling frequency, internal data aggregation, and limited data storage must be found. Laser analysers are run by their own computer systems that can store large volumes of data, which means data storage is often not limited. Yet, power blackouts can result in data loss and can even damage the operating system; therefore, routine backups and regular storage of data on external devices is highly recommended.
- The **minimum detectable flux** (MDF) depends on chamber height, chamber deployment period, as well as the precision and frequency of the measurements. Higher flux rates allow for shorter deployment periods and faster measurements. Setting a pre-defined minimum detectable flux according to the research question allows for effectively allocating the time available for the individual measurements. Flux rates of the different gas species and the respective measurement precision are very different. Measuring N_2O fluxes (and GHG isotopes) is usually the most challenging task. Using a laser analyser can improve the

minimum detectable flux and the chamber deployment period at the same time (Brümmer et al., 2017).

7.2.5. Typical problems and challenges

- It is important to check the analyser and the connectors for **airtightness**. Since the measurement cavities of some of the laser analysers operate at a very low pressure, any leakage results in a constant intrusion of ambient air into the system, inflating the system slowly. This can affect the flux measurement substantially, especially in highly porous soils. This effect cannot be identified in the time series of the volume concentration measurements. Airtightness can be easily checked by connecting the system to a closed volume (e.g. a glass) and monitoring the pressure inside the glass over time.
- **Power blackouts** can result in **data loss** and can even damage the operating system, so that routine backups and regular storage of data on external devices is highly recommended.
- **Vibrations** can be very problematic for most gas analysers and should be avoided during measurements. Analysers should be transported carefully, and massive shocks should be avoided.
- **Particles and water** can severely damage the gas analysers. Condensation of water inside the tubing is especially dangerous and common in automatic measurements systems during the night. Insulation or heating of the tubes can solve this problem. Working in harsh and wet environments like peatland should be done only with a water filter at the inlet of the analyser. Using humidity sensors within the tubing that switches of the (external) pump can provide additional safety.
- Sensitivity to **abrupt pressure changes** can influence the performance of some online analysers. Such pressure changes may occur, for example, during the placement or lifting of the chambers or when air-flow is interrupted.

8. DATA STORAGE, SCREENING AND HANDLING

8.1. Summary of recommendations

GHG projects are typically associated with the collection of a wealth of variables and parameters, resulting from field sampling, laboratory analysis, GHG concentration analysis and flux estimation. Due to the large data volume and the complexity of such datasets, storage of all data in a database is strongly recommended. Raw data should always be stored alongside any derived or aggregated data, in order to allow for re-analysis of the data with novel methodologies. For example, the storage of GC base data (chromatograms and peak areas) would allow for calibration on the fly (given appropriate intervals of calibration gas measurements). Data with limited quality should be flagged rather than deleted.

Given adequate data structure and documentation, the storage of all raw data, aggregated data and metadata required for flux estimation and subsequent data analysis ensures transparency and repeatability, and thus better science. This requires the long-term availability of all raw data without any inappropriate editing.

Table 2: Summary of chamber and ancillary data recommended for a GHG study database.

Required data on	**Data parameter(s)**	**Temporal data resolution**
Campaign objective	Study design, location, spatial resolution and pattern, temporal resolution, ancillary data	
Study site	Geographical data, topography, pilot study results	Prior to sampling campaigns
Chamber design	Construction data: dimensions, material, mechanical details, sampling or online gas concentration measurement details (type of tube, length of tube etc.), vent characteristics, results of air-tightness tests, etc.	Once per chamber or chamber redesign
Chamber set-up	Geographical data of each chamber location, frame insertion date(s) and depth, handling of plants, geographical data of chamber distribution	Once per chamber set-up
Chamber handling	Details of installation and operation: opening and placement dates and times, within-chamber conditions (temperature, RH, PAR, etc.)	Every chamber placement and opening
Sampling procedure	Type of sampling instrumentation, dates and times	Every sampling
Sample storage	Transport and storage room conditions (temperature etc.), duration, and results of storage tests	Each sample
Online gas concentration measurements	Type of gas concentration measurement instrument (gases, water vapour, measurement frequency, detection limit, calibration data, precision etc.), retardation time of gas sampling tube, raw data corrections, error estimations	Corresponding to measurement frequency

GC gas concentration measurements	Peak areas of chromatograms, gas volume concentrations (gases, water vapour, measurement frequency, detection limit, calibration data, precision etc.), raw data corrections, error estimations	Corresponding to sampling
Weather characteristics	Temperature, pressure, RH, atmospheric stability, wind speed, wind direction, PAR, precipitation; raw data and temporal averaged data, error estimations	Half-hourly
Soil characteristics	Soil moisture, topsoil temperature, snow and ice cover and depth, frost depth, groundwater table, nutrient status, redox potential, pH; raw data and temporal averaged data, error estimations	Diurnal or during chamber operation
Vegetation characteristics	Leaf area, vegetation height, species abundance, ground coverage and rooting depth, error estimations	During chamber operation
Management	Documentation of all events (e.g., fertilization, harvesting, irrigation, etc.)	During chamber operation
Photo documentation	Photographic documentation of vegetation development, soil disturbances, etc.	During chamber operation
Method of flux estimation	Type of method, data handling, estimated flux data, error estimations	

8.2. Rationale

8.2.1. Data handling and screening

As a best practice measure, discarding any data should be avoided.

Information on chamber design and deployment period (Chapters 4 and 5), study site setup (Chapter 3.2.4), ancillary data (Chapter 3.2.3, Table 2), as well as GC results (chromatograms, peak areas, mixing ratios etc.) required for flux estimation (Chapter 9) should be completely collected to enable other researchers to comprehend and potentially replicate the study or experiment later on.

It is generally recommendable to analyse gas samples as soon as possible after field collection, since sample containers may leak (Fig. 3) and the risk of gas sample contamination increases with storage duration (Rochette & Erikson-Hamel 2008; cf. Chapter 6.2.7). Moreover, rapid analysis following field collection allows for the screening of the concentration data prior to the next sampling campaign, which will help to identify and resolve potential problems associated with field sampling, gas sample collection and/or transport.

It is well known that GC data obtained from one chamber measurement may be “noisy”, particularly when fluxes are small (Kroon et al., 2008). However, the arbitrary removal of single gas volume concentrations prior to flux estimation should be strictly avoided, since this procedure is subjective and compromises the comparability of data sets handled by different operators. The rejection of individual volume concentrations is only appropriate if there is specific evidence indicating problems during the respective sampling (e.g., based on evidence from reliable field documentation) or during transport and analysis (e.g., contamination of a sample with ambient air due to a leaking sample container). In all other cases, simply flag data that seems out of the ordinary. Data screening must not compensate for problems associated with chamber design, closure, field sampling or transport. In no case should this procedure be used to “improve” or “facilitate” flux estimation.

As described for the GC data, volume concentration data from field-analysers should be collected and stored together with raw data and parameters of instrument operation. Data should be marked when certain parameter limits are exceeded. Depending on the amount of field data collected in individual campaigns, internal storage devices of field analysers may be insufficient and additional external storage devices may be required.

8.2.2. Data storage

Given the fact that a huge amount of gas concentration and ancillary data is gathered during a single project involving GHG measurements, adequate data storage and management procedures are essential to ensure thoroughness, transparency, and thus the overall quality of a dataset. Therefore, we strongly recommend using a simple, self-explanatory relational database for storage and documentation of study design, measurement methods, and other meta-data. This database should also include ancillary data like chamber, meteorological or environmental parameters, soil and vegetation characteristics and ambient air concentration data (see also Chapter 9). Alternatively, data could be stored as CSV files (TIDY data) in an organized folder system together with comprehensive metadata and a ReadMe file. In any case, rules for creating “tidy datasets” (e.g., Wickham 2014) should be respected. In collaborative research, GHG flux determination may only be one element of much larger measurement campaigns. All the more, consistent management of the GHG flux data, integrating it into data management frameworks is strongly encouraged (Finkel et al., 2020).

Always store raw data together with any derived or aggregated data. Transparency, i.e. the inclusion of raw data, is particularly vital to enable later re-analyses of gas concentration data using (new) alternative flux estimation methods. We therefore strongly recommend storage and publication of all concentration data used for GHG flux estimation, ideally in combination with procedures of error and uncertainty estimation used during analysis. If available, also store data from pilot studies.

All data should be regularly saved on a durable storage medium in order to ensure an appropriate backup practice. We further encourage researchers to archive their data sets for at least ten years as recommended by the Safeguarding Good Scientific Practice in the Memorandum of the *Deutsche Forschungsgemeinschaft*[1]. Ideally, all data should be published open-access alongside the respective publications. This will improve the availability of GHG flux data for meta-analysis, data interpretation, and thus the overall value for the scientific community.

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[1] http://www.dfg.de/download/pdf/dfg_im_profil/reden_stellungnahmen/download/empfehlung_wiss_praxis_1310.pdf

9. FLUX ESTIMATION

9.1. Summary of recommendations

1. Transparency and reproducibility are basic necessities when deriving flux estimates from gas measurements. We recommend running tests of several flux estimation approaches (Table 3) choosing the most suitable method for a given measurement based on objective and sound selection criteria. Since comparability should also be ensured, it is recommended to use one of the available approaches, discuss your choice and use standard protocols.
2. If unsure whether a nonlinear approach is really suitable for describing the data, linear regression should be used instead. Robust estimators should be used in order to mitigate the impact of outlier samples and other artefacts (Weber et al., 2018) which are common problems when only a limited number of volume concentration measurements are available (e.g. from GC analysis).
3. For manual gas sampling, we recommend using at least four, better five, concentration measurements to allow assessing the quality of flux estimates. Alternatively, two-point fluxes may be an option when larger spatial and temporal coverage can thus be realised (Jungkunst et al., 2018).
4. For online gas measurements, data should be checked for possible chamber placement artefacts in the first seconds after chamber closure and cut off. After that, appropriate regression methods should be used to approximate the initial slope of $\partial c/\partial t$. The initial approximately linear change becomes quickly nonlinear in smaller chambers.
5. Be aware of the minimum detectable flux that can be measured with your system.

9.2. Rationale

9.2.1. Overall uncertainties in flux measurements

The uncertainty associated with choosing a model for estimating the slope of the volume concentration increase at t_0 in the chamber headspace is only one source of uncertainty, yet it is the most important one for gas flux estimation based on manual gas sampling from the chamber headspace. Using data from field measurements and a Monte Carlo approach, Levy et al.(2011) found that, for fluxes based on air sampling with subsequent GC measurements, the choice of model and the model lack-of-fit were the largest sources of uncertainty; followed by, in this order, outlier filtering, temporal resolution of volume concentration samples, range of the used GC standards, and repeatability of the GC measurement as well as further minor uncertainties due to temperature measurements in the chamber headspace, chamber volume, measured air pressure, water vapour dilution effects, and the accuracy of GC standards.

9.2.2. Method description and theoretical background

Since the chamber is closed during the measurement, the gas volume concentration change in the chamber system volume must correspond to the flux in or out of the chamber via the bottom. The majority of approaches to estimate GHG fluxes from closed chamber data rely on the assumption that diffusion is the prevailing process of gas transport between soils and atmosphere (Lundegårdh 1927). This means that gas volume concentration gradients in the soil are the driving force of the measured fluxes at the soil-vegetation-atmosphere interface. The basic principle to estimate the surface flux is very simple as described in Chapter 4 in detail.

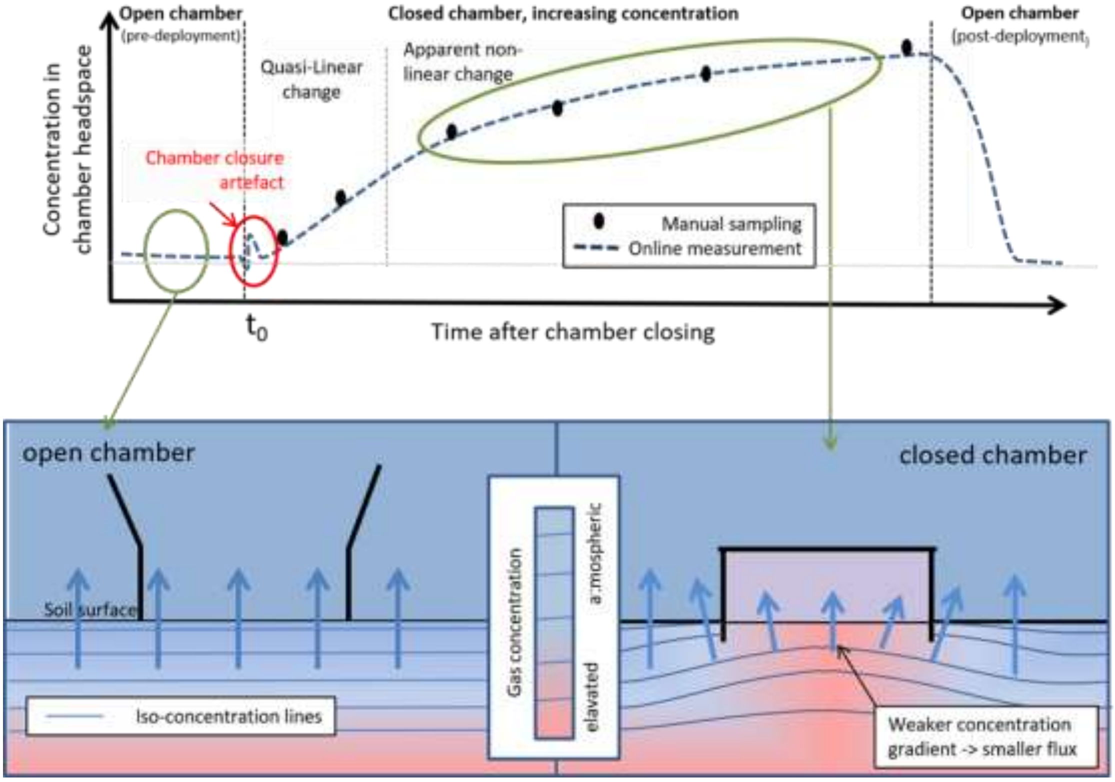

Fig. 5: Schematic idealised evolution of the gas volume concentration, e.g. CO_2 in a non-steady-state gas flux chamber (top), displayed as online measurement (dashed line) and measurements of manual samples (points). Cross section through a gas flux chamber before (bottom left) and during (bottom right) a flux measurement. Areas with atmospheric gas volume concentration are indicated in blue, areas of elevated gas volume concentration in red. Gas flux vectors crossing the soil-atmosphere interface are indicated as blue arrows. As soon as the chamber closes (t_0) the gas volume concentration in the closed chamber increases apparently linearly (linear flux estimation possible). As soon as the chamber volume concentration starts to increase, the volume concentration gradient at the soil-atmosphere interface and thus the flux into the chamber starts to decline slightly. The higher the volume concentration within the chamber, the more the gradient and the flux decline, and the nonlinearity becomes obvious after a certain time

Assuming constant soil gas production (or consumption) during the measurement, we can expect an (almost) linear increase (or decrease) in volume concentration in the chamber during the early stages of the measurement (Fig. 4). After a certain time, however, the gradient between the gas volume concentration in the chamber and in the soil decreases as the respective gas accumulates (or is depleted) within the closed chamber (Hutchinson et al., 2000). As a consequence, the flux decreases and the change in the chamber volume concentration becomes weaker with time. The change in gas volume concentrations in the chamber, thus, becomes nonlinear with increasing measurement time. In addition, lateral fluxes in the soil below the chamber walls may play a role (Well et al., 2019). Whether this effect is relevant for a certain measurement is mainly influenced by the effective chamber height (Livingston et al., 2006), flux rate and porosity of soil.

9.2.3. Estimating diffusive fluxes – Linear or nonlinear?

When soil gas fluxes are measured using closed chambers, we aim for an estimate of the gas flux unaffected by the chamber measurement. A simple linear regression model (LM; Table 1) can be used to estimate the flux (Lundegårdh, 1927) if the change in gas volume concentration in the closed chamber is linear. Since volume concentration measurements can include substantial errors due to sampling and detection problems, robust linear regression (Yu & Yao, 2017) is recommended to identify and exclude outliers. The soil gas flux might decline more or less strongly during the chamber measurement if the gradient in gas volume concentrations between soil and the chamber decreases during the measurement (Livingston et al., 2006). In all cases, we want to estimate the so-called pre-deployment flux which can be achieved with the linear model if the change in volume concentration gradient is negligible.

To consider the effect of a changing volume concentration gradient over time, already in the beginning of the 1980s, a nonlinear regression model (HM; Table 3) was published (Hutchinson & Mosier 1981), which was later modified by Pedersen et al., (2010) (HMR; Table 3). Further detailed physical consideration of the soil-chamber-atmosphere environment led to the development of the Non-steady state Diffusive Flux Estimator (NDFE; Table 3) (Livingston et al., 2005, 2006). Sahoo & Mayya (2010) further developed this approach and proposed a two-dimensional non-steady state theory by considering both lateral and vertical diffusion in the soil-chamber-atmosphere environment. These approaches may provide an accurate framework for interpreting the set-up; however, they are not always easy-to-use, particularly for cases where not all required details are known (soil structure, porosity, diffusivity, moisture content, and homogeneity; vegetation). Even though these approaches are theoretically highly sophisticated and e.g. NDFE may produce very small errors when applied to uniform homogenous profiles of bare soil, they can fail when not all assumptions are met (Kutzbach et al., 2000; Venterea & Baker 2008) which is often the case in practice. Especially regression techniques which can converge to multiple solutions (e.g. NDFE) need to be interpreted carefully. Knowledge of the expected flux values based on soil properties could be useful in eliminating unrealistic solutions. However, in practice, this can be challenging because fluxes may range across more than one order of magnitude.

In contrast to these physics-based estimation approaches, there are also empirical nonlinear approaches, such as the exponential model (EM; Table 3) of Kutzbach et al., (2007) and the quadratic model (QM; Table 3) of Wagner et al. (1997). These approaches simply fit regression models to the chamber data in order to derive $\frac{\partial n_{gas}}{\partial t}$ during the early stages of the measurement.

Table 3: Regression methods used for flux estimations using non steady state chambers.

	Method	**Reference**
LM	Linear regression model	Lundegårdh (1927)
LMR	Robust linear regression	Yu & Yao (2017)
HM	Nonlinear model of Hutchinson & Mosier	Hutchinson and Mosier (1981)
HMR	HMR implementation by Pedersen	Pedersen et al. (2010)
QM	Quadratic model	Wagner et al. (1997)
EM	Exponential model	Kutzbach et al. (2007)
NDFE*	Non-steady-state diffusive flux estimator	Livingston et al. (2006)

** only for bare soil*

9.2.4. Linear or nonlinear: effect of chamber dimensions, flux magnitude and deployment period

When GHG volume concentration measurements are carried out with online analysers, the nonlinearity in the volume concentration change over time often becomes clearly apparent (Kutzbach et al., 2007, Kroon et al., 2008), especially when the effective chamber height is small. Pihlatie et al. (2013) tested different chamber designs and flux estimation approaches using known flux densities. Linear regression underestimated reference fluxes by 33%, while chamber fluxes estimated with the exponential model did not significantly differ from the reference fluxes ($p < 0.05$). Similarly, Kutzbach et al. (2007) found that linear regression-based flux estimates amounted to only 40% of the exponential regression-based estimates. They also observed that the amount of underestimation increased with increasing flux rates. Comparing different chamber systems at the same flux rates, Pihlatie et al. (2013) showed that increasing chamber height, area and volume significantly reduced flux underestimation by reducing the nonlinearity in the volume concentration change.

Nakano et al. (2004*)* tested the effect of chamber deployment period on different flux estimation approaches using online gas analyser data. For a deployment period of 10 minutes, significant differences between linear regression, exponential regression, and HMR were found. A reduction of the chamber deployment period improved the linearity of the curve. Reducing the chamber deployment period to only 15 s, Steduto et al. (2002*)* were able to eliminate differences between linear and quadratic flux estimation approaches suggesting to measure as short as possible and long enough considering the effect on the minimum detectable flux.

Inappropriate used of linear regression and R^2 as criterion to evaluate flux estimates can be problematic (Kutzbach et al., 2007). While nonlinear models often yield better fits (e.g. *RMSE)* for the individual time series of the flux measurement than linear regression, it should be considered that this is mainly due to the higher number of fitted parameters, and not necessarily indicates a lower uncertainty of the flux (Levy et al., 2011*).* One strategy to improve the quality of flux estimation is to reduce nonlinearity in chamber volume concentration data by means of higher chambers and shorter chamber deployment periods, if this is possible regarding the precision of the volume concentration measurements and, thus, also depends on the fluxes themselves.

9.2.5. Chamber closure artefacts

Using online volume concentration measurements in chambers additionally allows identifying artefacts during the first few seconds after chamber placement, which may result from pressure changes induced by chamber closure (Fig. 4). It is recommended to discard data points during an initial time period at the beginning of each online chamber measurement. The duration of this time period to be discarded can vary across chamber types and analysers*.* The function *flux* in package flux for R automatically detects this period and discards the data (Jurasinski et al. 2014).

9.2.6. Number of sampling points

Regression analysis should not be conducted on less than four volume concentration measurements to get a reliable flux and corresponding uncertainty estimate. More data points reduce the uncertainty of the flux estimate. Thus, whenever possible, online measurements should be preferred. If it is not feasible, though, manually sampled gas from the chamber headspace immediately after chamber placement should be included in analysis and regression because the accuracy of the volume concentration at this initial sampling time is crucial for flux accuracy (Rochette 2011).

9.2.7. Minimum detectable flux

When fluxes are small, the quality of the regression of the concentration change deteriorates and eventually fails. It is important to know the sensitivity of your experimental set-up and to know the minimum detectable flux. Fluxes below the MDF value are not necessarily zero, but they cannot be detected with the required statistical confidence, and this information should be considered during data analysis.

Christiansen et al. (2015) developed a concept of MDF, which was modified by Nickerson (2016) to include online measurements. MDF depends mainly on the analytical precision of the instrument, $P_{Instrument}$, the deployment duration of the chamber, D_{closed}, and the sampling periodicity $p_{sampling}$, but also on the dimensions of the applied chamber system and further physical parameters, such as the molecular mass of the respective gas, M, the mean chamber headspace air pressure, P_{air}, and temperature during deployment, T_{air}, as well as the chamber headspace volume V_h and basal area A (Eq.9.1).

$$MDF = \left(\frac{P_{Instrument}}{D_{closed}\sqrt{\frac{D_{closed}}{p_{sampling}}}} \right) \left(\frac{V_h P_{air}}{ART_{air}} \right) M \qquad (9.1)$$

Thus, rounding significant digits of the volume concentration may result in a larger MDF and should be avoided. Hüppi et al. (2019) developed an app that allows for calculating the MDF while also accounting for the applied flux estimation approach (Available online at https://sae-interactive-data.ethz.ch/minflxlim/).

9.2.8. Estimating ebullitive fluxes

Ebullitive fluxes may contribute a considerable share to the overall ecosystem exchange of CH_4 (Bastviken et al., 2010), especially in flooded peatland ecosystems (Green & Baird 2013). However, they have been largely neglected in the past due to their steady, periodical and episodic character and the associated difficulty to measure them. Diffusive and ebullitive fluxes may be driven by different environmental factors. Gas bubbles trapped below the water or peat surface may be artificially mobilized by vibration or pressure fluctuations during chamber positioning and deployment, so that extreme care is required when fluxes are measured. Separating diffusive and ebullitive fluxes and analysing the respective drivers may allow for a better prediction of total fluxes.

Different methodologies to quantify ebullition have been proposed during the last years, either by modifications to the technical design of the set-ups in order to quantify ebullitive fluxes or by detection of irregularities in the concentration increase in regular chambers. Bastviken et al. (2010) calculated ebullition as difference between fluxes measured by regular open bottom chambers and measured by chambers with extensions that mechanically exclude gas bubbles on their way from the ground. Others used acoustic measurements and other technical approaches (Ostrovsky et al., 2008; Vagle et al., 2010). As CH_4-enriched bubbles may result in sudden increases of the chamber headspace CH_4 volume concentration, online measurements can be used to detect such irregularities (Hoffmann et al., 2017). In case of concentration determination with vials, ebullition can often be recognized by typical volume concentration time series patterns (Jordan et al., 2016, 2020), but hardly be quantified by ordinary regression analyses (Hoffmann et al., 2017).

9.2.9. Choosing a suitable flux estimation approach

Above all, it is essential to use a reproducible methodology to calculate fluxes. We recommend using routines that test several or all of the available flux estimation approaches (Table 3) and determine the most suitable method for a given flux measurement based on objective and sound selection criteria. Several research groups developed their own scripts featuring different approaches and addressing different flux types (Table 4). These packages facilitate the reproducible estimation of large numbers of fluxes, and some also include selection algorithms to choose automatically linear or nonlinear flux estimates (e.g. Pedersen et al., 2010; Forbrich et al., 2010; Görres et al, 2014; Hüppi et al., 2018) suggested approaches to automatically select between linear and nonlinear estimates, and there is a still ongoing development. They offer a reliable approach to allow for non-linear estimates while not forcing nonlinear estimates on clearly linear volume concentration evolutions in the same dataset. This can strongly decrease the uncertainty associated with using nonlinear fits on essentially linear fluxes.

Table 4: Methods for flux estimations based on non-steady state chamber data.

R package name	**Reference**	**Methods** *(for abbreviations see Table 3)*
R-Script-CH4_version_1.0.R*	Hoffmann et al. (2017)	LM
flux	Jurasinski et al. (2014)	LM, LMR**
gasfluxes	Fuß (2017), Hüppi et al. (2018)#	LM, LMR, HMR, with automatic decision function
HMR	Pedersen et al. (2010)	LM, HMR, with semi-automatic decision
FluxCalR	Zhao (2019)	LM
chamberflux	Kutzbach et al. (2007), Eckhardt and Kutzbach (2016)	LM, EM, polynomial models; ordinary least-squares regression, many model selection criteria

** detects ebullition, ** uses median-based linear regression, #https://sae-interactive-data.ethz.ch/gasflxvis*

If datasets include flux measurements with nonlinear behaviour, a selection algorithm needs to be applied, that ideally uses well defined thresholds (RMSE, R^2) to choose between the calculation methods. The exact value of these thresholds however cannot be predefined and are in a certain sense study-specific, or arbitrary, should be reported. The definition of these thresholds may largely affect the calculated fluxes and are thus a major source of uncertainty regarding the estimation of annual sums and GHG balances.

As a standard, information on how the fluxes were determined should be reported along with basic statistics like the percentage of fluxes derived with which method, the median, mean, and range of fluxes, as well as the distribution of standard errors. The selected approaches will likely differ for small and large fluxes. If unsure whether a nonlinear approach really fits to the data, linear regression should be used instead. Robust estimators should be used for linear regression, especially for low-frequency data, i.e. fluxes based on manual air sampling with subsequent GC analyses, in order to mitigate the impact of outlier samples, which are a common problem due to propagated errors from sampling, storage and measurement of GC samples.

9.3. Concluding remarks

To date, there is no general consensus regarding the most appropriate method for estimating fluxes based on closed chamber data.

A good option is to adjust the measurement conditions to promote increased linearity in chamber volume concentration time-series data in order to minimize errors (Venterea & Baker 2008). Larger chamber height (or ratio volume/surface), shorter chamber deployment periods and smaller fluxes result in lower maximum volume concentrations in the chamber, and thus create less nonlinearity in chamber volume concentration change. Since physical factors like chamber height are usually predefined, the chamber deployment period should be kept as short as possible and be adapted to the expected flux magnitude (if known). If a large number of data points is available from online analysers, using only data from the initial minutes of a measurement is a good option.

The approach to promote increased linearity, however, requires a sufficient precision and temporal resolution in the concentration measurement. If these requirements are not given, or e.g. the gas measurements are affected by artefacts at the beginning, longer chamber closure times can be an option to promote and quantify nonlinearity in the concentration increase (Lai et al., 2012).

Practically, it is often necessary to find compromises in the sampling scheme when several gases are studied (CO_2, CH_4, and N_2O), as the respective gases have different flux rates and thus different accumulation behaviour in the chamber. While small fluxes of the same chamber measurement (e.g. N_2O) might result in a quasi-linear increase, larger fluxes (e.g. CO_2) may require nonlinear flux estimation, or using only the volume concentration measurements of the first minutes The dynamic kappa routine of Hüppi (2019) that is implemented in the package *gasfluxes* (Fuß et al., 2020) allows to select fluxes from the same dataset that are best fitted nonlinearly and linearly, respectively, in an automated way and could, thus, develop into a new standard.

10. ANALYSING FLUXES/WORKING WITH FLUX ESTIMATES

10.1. Summary of recommendations

1. Flux estimates should not be discarded, unless there is a good reason. If there is a reason, they should then be discarded.
2. It is important to estimate and know the Minimum Detectable Flux (MDF) of the measurement system used. Fluxes below MDF are not necessarily zero, which must be considered when annual balances are estimated.
3. Propagation of measurement errors and uncertainties in the flux estimates should be considered, quantified and reported to improve the communication of the quality the measurements.
4. Depending on the major research question, different aspects of the flux measurements and data may play a role, and which should be properly addressed.

10.2. Rationale

Data originating from GHG measurements can be analysed in many ways and each study is driven by its own scientific questions. It is therefore hardly possible to standardize the subsequent analyses of chamber flux data. However, there are general considerations that apply to any approach, which we try to carve out below.

In many cases, annual GHG balances are derived from time series of chamber air measurements. Annual estimates are often fed into meta-analyses and, thus, form the basis for regionalization and GHG reporting. Hence, standardized budgeting approaches would be helpful. High inter-annual variability and uncertainties of annual GHG balances further illustrate the need to ensure the quality of later meta-analyses and GHG reporting. However, there is nothing like an a priori standardized best solution for all studies since the specific challenges to each study vary widely. Chamber flux measurements can also be used for shorter studies where the objective of the data evaluation might be even more diverse, complicating the challenge of giving general recommendations.

10.2.1. Dealing with uncertainty in flux estimations

All flux estimates include some uncertainty that must be considered when balances are calculated. Therefore, the significance level of the applied regression model is not a good indicator to decide whether or not an estimated flux is to be discarded. We recommend using all calculated fluxes regardless of their respective magnitude or uncertainty in further analyses. Instead, it may be worth considering approaches using weights with fluxes of low uncertainty getting higher weights. An exception to this rule is when you have very good reasons to assume that the flux estimates are erroneous, such as documented problems during sampling or measurement in the laboratory.

Small absolute uncertainty in low fluxes e.g. during winter may represent a high relative uncertainty. The importance of such a small absolute uncertainty depends largely on the study objective, e.g when annual sums of GHG Fluxes are calculated, or when differences between treatments are evaluated.

We recommend estimating fluxes as soon as possible after the measurement in order to check flux uncertainties and plausibility, and to compare them to fluxes and uncertainties of prior campaigns. This allows recognizing and fixing problems in a timely manner. A well-developed scripted workflow including these points allows enhancing the quality of the data.

We do not recommend setting fluxes to zero (e.g., because the volume concentration change is below the GC precision or the flux is below the MDF). Regardless if small or large, significant or non-significant – all fluxes should be considered and systematically and reproducibly handled**.** The use of different acceptance or discarding criteria depending on the intensity of fluxes is not recommended. Special attention should be given to fluxes below MDF if these low fluxes occur over longer periods e.g in frozen soils. The standard error of the regression model should be reported for all fluxes. Propagation of errors from the flux measurement to the final evaluation must be considered. A relatively new idea is to use this error to model heteroscedasticity during statistical analysis thereby assigning less weight to more uncertain fluxes. Hence, fluxes with a large error will have less influence on calculated means (i.e. across replicates) and cumulative fluxes over particular time periods (i.e. calculated via linear interpolation or using an empirical model).

10.2.2. Greenhouse gas balancing and treatment evaluation/comparison

Working with flux time series

Flux estimates based on manual chamber measurements often result in time series with very sparse data. When using automated chambers, time series are typically much denser but still may contain considerable gaps between measurements. Therefore, the gaps between measurements have to be filled in a meaningful way to derive seasonal or annual balances. It has been shown that the uncertainty of balances may increase strongly when they are derived from too few measurements (Gana et al., 2018; Lucas-Moffat et al., 2018). According to the latter, manual chamber studies always have too few measurements to obtain annual balances with low uncertainty since the uncertainty of annual balances is almost directly proportional to temporal data coverage.

Strategies to fill the gaps reach from physiologically grounded empirical models to pure statistical models like neural networks. These approaches heavily depend on additional variables such as environmental factors (e.g. soil or air temperature, soil moisture) that are available as complete time series including all times of measurement. Such data might be measured by permanently installed sensors and loggers or weather stations or can be derived from remote sensing data. In some cases, when either there are no or not enough ancillary variables or the measured ones have not enough explanatory power, the only option is to fall back to simple linear interpolation.

Estimating balances using statistical modelling

It is impossible to cover all possible options of using statistical modelling to fill gaps in flux time series. In the past researchers most often used physiologically grounded separate models for gross primary production (GPP) (photosynthesis) and ecosystem respiration (R_{ECO}) because both processes are fairly well understood. GPP of vegetation at a given site is mainly controlled by the availability of photosynthetic active radiation (PAR) and by the amount of photosynthetically active tissue (Chapin et al., 2002) if no limitations by temperature or drought occur, whereas R_{ECO} is mainly driven by temperature and soil moisture (Janssens et al., 2001). Several models for both have been proposed in the literature (see *flux* package for an overview) and there is no consensus on one best suited model. It is advisable to test several with your data. In addition to choosing a model to fit the data to, you have to decide about a general modelling approach.

Huth et al. (2017) distinguished between two main approaches found in the literature that differ at three major methodological levels: the CO_2 flux measurements, the pooling of data, and direct or indirect modelling of NEE. The first approach can be described as global statistical modelling, where seasonal dynamics are represented using vegetation and other proxies to include the change in important forcing variables over the seasons (Günther et al., 2017, Karki et al., 2014, Wilson et al., 2007). Often these studies measure CO_2 exchange at different light conditions using shading (Whiting et al., 1992, Elsgaard et al., 2012, Karki et al., 2014) and model NEE directly by subtracting opaque chamber fluxes from transparent chamber fluxes (Whiting et al., 1992, Burrows et al., 2005, Elsgaard et al., 2012). The second approach can be categorized as local statistical modelling, where single-campaign measurements are used to derive local empirical models that reflect seasonal dynamics through changing model parameters during the study period (Beetz et al., 2013, Pohl et al., 2015, Günther et al., 2015, Leiber-Sauheitl et al., 2014). Both global and local models are then used to interpolate missing data and fill gaps. More recently, neural networks have been used to fill gaps in flux time series derived from chamber measurements and seem to perform quite well (Delon et al., 2007, Lucas-Moffat et al., 2018, Ebrahimi et al., 2019, Huth et al., 2020) especially when good ancillary data are available. Good ancillary data is an important prerequisite for all empirical modelling approaches.

Estimating balances when statistical models fail

Typically, it is best to base the estimation of annual GHG emissions on statistical modelling. However, in the absence of significant relationships between fluxes and available environmental parameters, one can either average the measured fluxes and multiply the average with the covered time period, or integrate over time (Koebsch et al., 2013). The averaging approach was used for many early GHG studies but today it is not recommended in most cases. Integration over time may be better than simple averaging when there is pronounced seasonality, but it does not provide an estimate of the interpolation error of the annual emission estimate.

The statistical procedure of resampling or repeated sampling of the actually measured data allows for deriving a measure of uncertainty for annual or seasonal fluxes based on the temporal variability of the measured fluxes (e.g. implemented in *auc.mc* in Jurasinski et al., 2014). The uncertainty of the individual flux estimate, however, is not considered in this approach. The uncertainty of the flux estimation can be included by a resampling approach that uses multiple flux data sets that are randomly generated from the flux estimates and an added random deviation which is based on the observed standard error of the flux estimate.

Annual fluxes should be calculated for each collar first, and then be averaged in a second step. This allows for calculating an estimate for the uncertainty originating from the flux estimation and/or from linear interpolation between measurement dates. Error terms for reporting can be calculated from the standard deviation of the mean and the standard deviations of the annual estimates per collar following the law of error propagation. Since there is no standard procedure to obtain uncertainties for annual or seasonal flux estimates, it is of utmost importance to clearly describe the methodology used. Steps towards a structured evaluation of the different methods (Liu et al., 2022) are valuable and should be further developed.

10.2.3. Studying processes and patterns

Most gas flux studies focus on time series which include temporal periodicity (diurnal, seasonal, wet-dry cycles) and erratic behaviour. Similar to this temporal scale, gas fluxes also vary on the spatial scale. This variability is often addressed by using replicates to calculate spatially representative average values for which it is not always easy to untangle whether the variance in pooled measurements comes from measurement uncertainties or spatial variability.

Instead of simple average values, regionalization methods (e.g., kriging which requires stationarity) can be used if spatial patterns can be detected. Understanding the spatial variability and the interdependence of GHG can help to understand the underlying processes (Maier et al., 2017, Warner et al., 2017). If spatial patterns are to be analysed, this already must be considered in the experimental design.

Chamber measurements can also be used to study transport, transformation and allocation in the soil-vegetation-atmosphere system. Manipulation experiments such as trenching (Subke et al., 2006) or the use of isotopically labelled material or natural isotope abundance allows separating different contributing processes (Brüggemann et al., 2011, Goffin et al., 2014). Chamber measurements are even used to quantify gas fluxes from tree stem surfaces (Barba et al., 2019, Maier et al., 2018). Even though the focus of such studies might be very different, recommendations generally remain the same: to consider the uncertainty in flux estimates and the importance of a proper standardisation and documentation of how the flux estimates were aggregated.

11. DOCUMENTATION AND DATA REPORTING

11.1. Documentation in field and laboratory

The internal documentation about field and laboratory work to determine GHG emission fluxes must contain all of the information that ensures the reproducibility of the emission investigation. All data from sampling and measurement indicated in Chapters 5 to 9 as well as any special features observed must be recorded.

11.2. Data reporting for publication

The report about the determination of emission fluxes must contain all of the information that ensures the reproducibility of the emission flux estimation results. Minimum requirements on this information, likewise for CO_2, CH_4 and N_2O, are:

Location

- name of location
- position (latitude, longitude, altitude)
- number of investigated sites

Site information

- site position (map or latitude, longitude, altitude)
- substrate and soil type (referred to soil classification)
- ecotope, plant community or dominating plant species
- previous and current land use (land use and land use history)
- previous and current site or soil management, land improvement, used fertilizers and poisons
- starting date and time of measurements

Measurement planning

- beginning and end of the measurement period(s)
- scope (i.e., process study or emission balance estimation)
- recorded measurement components and parameters
- used measurement and sampling methods
- required surrounding conditions for measurements or sampling, e. g. required states of soil, vegetation, weather or weather situation or weather type
- statistical design:
    - number, description, and exact location of all chamber base positions at a site
    - number of replicate chamber measurements at the same chamber base position within a site
    - time elapsed between replicate chamber measurements at the same chamber base position within a site
    - any additional information regarding blocking or pooling

Chamber design and chamber measurement

- design of chamber (type, material, shape)
- chamber characteristics:
    - chamber height

  - chamber base area
  - chamber air volume
  - chamber base area-to-perimeter ratio or chamber volume-to-base area ratio
  - range of chamber collar height and insertion depth
  - air mixing
  - pressure regulation, vents
  - sample port(s)
  - radiation shielding and heat insulation
- duration of chamber deployment period
- time offset between chamber placement (t_0) and first GHG volume concentration measurement or sampling (t_1)
- duration of a single chamber air measurement (signal sampling rate, internal averaging and recording intervals of IRGA instrument) or duration of a single chamber air sampling
- number of samples and time offset between these samples taken to estimate the composition change in chamber air during a single chamber measurement

Gas sampling methods

- for vial sampling:
  - vial types (material, volume, type of lock)
  - dimensions and materials of septa
  - sample handling (esp. vial flushing, number of air changes)
  - duration and conditions of air sample storage
  - vial tightness, analyte loss at maximum storage time
- for syringe sampling:
  - syringe types (material, volume)
  - sample handling (esp. flushing, chamber air mixing)
  - duration and conditions of air sample storage
  - syringe tightness, analyte loss at maximum storage time
- for sample air circuit:
  - sample air flow rate and duration of circulation

Gas analysis methods

- used determination method
- details of gas analysis equipment
- for GC: details of auto sampler and injection method
- detection limit of gas volume concentration
- repeatability or measurement uncertainty of gas volume concentration determination
- quality control information for gas analysis
- description about any internal automatic data treatment of the gas analysis devices

Calibration of the measurement devices

- used standards (volume concentration, mixture and uncertainty)
- used calibration method (number of standards, estimation method of calibration function)

Surrounding conditions

- soil temperature (at given depth) for each site and measurement or sampling date
- soil moisture content (at given depth) for each site and measurement or sampling date

- ambient air temperature, humidity, pressure, precipitation, atmospheric stability, wind speed and direction
- for CO_2 and CH_4 flux measurements: global radiation or photosynthetically active radiation for each site and measurement or sampling date

Method of flux calculation and data analysis

- used regression method (determination of slope at t_0)
- used statistical tests and filters with related confidence levels
- used method to estimate the diffusive emission fluxes
- used flux estimation software (with version number)
- minimum detectable flux (flux detection limits)
- used method to estimate the minimum detectable flux

Results

- emission fluxes for each site and date with number of replicates, distribution of replicate values and uncertainties of measurement
- information about the methods to estimate uncertainties of flux measurement
- If data falls below the MDF (or between the flux detection limits), report the actual measured value and add the note “below minimum detectable flux”. If a Q_{10} correction is performed, the original non-corrected fluxes must be reported as well.

11.3. Reporting of experimental data in a data repository

For GHG emission modelling, it is often required to use measurement data from literature. To provide useful and reliable data and information for modelling and to ensure its correct use, we recommend publishing experimental data (additional to data reported in a publication) in a data repository available as an online supplement or the like. Beside the information listed in Chapter 10.2, the following information is required for a data repository:

Site information

- soil profile (number and depth of soil horizons)
- initial soil physical characteristics in specified depths or horizons:
  - soil texture
  - bulk density
- initial soil chemical conditions in specified depths or horizons:
  - pH (determination in situ or in standard solution)
  - for N_2O flux measurements: total nitrogen content
  - for CO_2 and CH_4 flux measurements: total carbon content (or: loss on ignition)

Chamber air measurement or sampling information

- date, time and chamber base position of each chamber closure
- chamber collar height or chamber volume for each chamber base position
- measured analyte volume concentrations in chamber air for each chamber measurement
- chamber air temperature (mean or minimum and maximum) for each chamber measurement

Surrounding conditions and synoptic data

- soil temperature (at given depth) for each measurement position and chamber measurement
- soil moisture content (at given depth) for each measurement position and chamber measurement
- for hydromorphic and semi-terrestric soils: ground water level for each site and measurement or sampling date
- ambient air temperature (mean or minimum and maximum temperature at given height) for each site and measurement or sampling date
- ambient air humidity (mean or minimum and maximum moisture at given height) for each site and measurement or sampling date
- mean and maximal wind speed as well as wind direction (at given height) for each site and measurement or sampling date
- atmospheric pressure (mean or minimum and maximum pressure) for each site and measurement or sampling date and atmospheric stability
- precipitation sum of the 24 hours foregoing the flux measurement for each site and measurement or sampling date

Gas analysis and flux estimation data

- emission fluxes for each chamber measurement
- analysis scripts with applied parameters

12. TERMS AND DEFINITIONS, SYMBOLS AND ABBREVIATIONS

12.1. Terms and definitions

AIC

Akaike information criterion, a measure of the relative quality of statistical models for a given data set, used for model selection.

Amount fraction (less common: Mole fraction), y

Amount of a constituent divided by the total amount of all constituents in the mixture [according to IUPAC 2019].

Note 1: For real gases under ambient conditions, a volume concentration of 1 ppmn almost corresponds to a →volume concentration of 1 ppmv.

Note 2: Volume concentration is equal to the number fraction: the number of entities of one constituent divided by the total number of entities in the mixture.

Automated chamber

→Chamber system where the →chamber top is placed on and lifted from the →chamber frame by means of an automated system (e. g. electric motor, pneumatics, hydraulics).

Note: An automated chamber is typically combined with an →onsite gas monitor and controlled by a computer.

Baseline at zero free

Raw detector signal of a gas chromatograph measuring carrier gas only.

Chamber

Open-bottomed vessel suitable to tightly enclose air above a soil surface or a soil-vegetation complex.

Note: In general, a chamber consists of a →chamber top and a →chamber frame with air-tight fitting.

Chamber air (also: Headspace air)

Air above a soil surface or a soil-vegetation complex surface enclosed by a →chamber.

Chamber base (also: frame or collar)

Bottom part (rectangular, square or round) permanently inserted into the soil, with an air-tight fit to the →chamber top.

Chamber base area, A

Area of the soil surface or soil-vegetation complex surface a →chamber is placed on.

Note: The chamber base area is typically surrounded by a permanent →chamber frame.

Chamber base area-to-perimeter ratio

Ratio of the →chamber base area to the perimeter of the →chamber or →chamber frame.

Chamber base position

Soil surface or soil-vegetation complex surface within a →site on that a →chamber is placed for sampling or measurement.

Note: The chamber base position is marked out by a permanent →chamber frame.

Chamber deployment period (also: Chamber closure period/duration)

Time period during which the →chamber is kept closed for →chamber air sampling or on-line volume concentration measurements in the chamber air [according to ISO 20951, 2019; Lai et al., 2012; Pihlatie et al., 2013]

Chamber lid

Flat, almost two-dimensional cover with an air-tight fit to a →chamber top or →extension.

Chamber measurement

The procedure of →chamber air sampling or on-line determination of analyte volume concentration in chamber air for the estimation of a GHG →flux or various GHG fluxes.

Chamber placement (also: Chamber closure; chamber closing)

The procedure of placing the →chamber top on the →chamber base and closing the chamber with an air-tight fit [according to Pihlatie et al., 2013].

Chamber placement time (also: Chamber closure time), t_0)

Moment at which the →chamber is closed with an air-tight fit.

Chamber top

Open-bottomed vessel with an air-tight fit to a →chamber frame.

Chamber volume (also: Chamber headspace volume), V_h

Total air volume enclosed by the →chamber and the →chamber base.

Note: The chamber headspace volume should not be mistaken for the headspace volume of a vial in a gas chromatograph's headspace sampler used to transfer an air sample from the vial to the GC column.

Chamber volume-to-base area ratio

Ratio between the →chamber volume and the →chamber base area.

Note: The chamber volume-to-base area ratio must be small enough that the change of the →volume concentration of the gas of interest is well quantifiable against the measurement →noise of the gas analysis during reasonable chamber deployment periods.

Closed chamber / Non-steady-state chamber

→Chamber that allows no exchange between ambient air and →chamber air / headspace air, except for pressure balance by means of a laminar flow through a pressure vent.

Note: An air exchange between →chamber air and atmospheric air by means of a vial sampling system may take place in a very small extent in ratio to the →chamber air volume.

Crossflow sampling

Sampling with a →sample air circuit that leads the →sample air flow across the →chamber to obtain a →chamber air sample with an analyte volume concentration that is representative for the chamber air's volume concentration.

Dead band

Time period immediately after →chamber placement which is needed for complete →chamber air mixing and, where applicable, for sample air transport in tubes.

Note: Sample air transport in tubes only in case of →flow-through chambers.

Dynamic chamber / Flow-through chamber

→Closed chamber in which the sample air flow is led across the →chamber air.

Note: This kind of chamber is typically used when measuring with an →onsite gas monitor or when the chamber air is sampled with a →sample air circuit.

Emission flux

Mass (or other physical quality) of substance transferred into the atmosphere per unit time and area of the appropriate surface of an emitting source [according to ISO 4225, 1994].

Flushing

Before using a →chamber for a new →flux measurement, the chamber must be flushed with ambient air since conditions within the chamber should be (near-)ambient at the beginning of the →chamber deployment period.

Flux

Quantity (e. g. amount, mass, volume, etc.) transferred in a time interval through a cross-section perpendicular to the flow divided by the cross-sectional area and by that time interval [according to IUPAC2019].

Flux measurement

Determination of a GHG →flux by time series measurements of the respective gas →volume concentration in →chamber air, followed by regression analyses to estimate the volume concentration change per unit time and to estimate the flux out of it.

Location (also: Measurement location)

Area where sampling takes place.

Note 1: A location includes one →site or several sites investigated for their →emission fluxes.

Note 2: A location generally is a topographic name that, ideally, also indicates the ecosystem type.

Manual chamber

→Chamber system where the →chamber top is manually placed on and lifted from the →chamber frame.

Measurement period (also: Measurement duration)

Period between the first and the last →sampling date at a →location within a GHG emission investigation [according to ISO 4225, 1994].

Noise

Inherent variability of a gas analyser (signal variance) resulting in variability of the measured volume concentrations

Note: Measurement noise is particularly problematic during periods with small GHG fluxes, as occasions with fluxes around zero cannot be distinguished from the noise in flux determination procedures and are thus often ignored.

Online gas monitor (also: Fast analyser)

Portable or on-site instruments which allow for medium to high-frequency →flux measurements and thus direct determination of the volume concentration of GHG in the →chamber air. Depending on the setup, online gas monitors can be combined with →manual chambers or →automatic chambers.

Note: The instruments rely on varying technologies ranging from infrared analysis to laser-based technologies.

Open chamber (also: Steady-state chamber)

→Chamber that allows an exchange between ambient air and →chamber air.

Note: The air exchange between →chamber air and atmospheric air might be regulated by a fan.

Plots

Optional subunits of a →site which may be different independent replicates of →treatments.

Pre-deployment flux

GHG flux through the →chamber base at the moment before the →chamber top is placed on the →chamber frame.

Pre-deployment time

Moment before the →chamber top is placed on the →chamber frame.

Pseudo-replicates

Non-independent samples of GHG flux data (vs. → replicates), i.e. replicates of samples (subsamples) rather than of treatments.

Replicates

Independent samples of GHG flux data, i.e. flux data from spatially independent →chamber base positions of the same →site or →treatment (true statistical replicates).

Robust estimators

Statistics developed for data with non-normal probability distributions that are insensitive to moderate to large deviations from the assumptions underlying a statistical method.

Sample air

Part of the →chamber air / headspace air that is filled in a vial or measured in an →online gas monitor.

Sample air circuit

System of pump and tubing that leads a part of the →chamber air from the chamber through an →onsite gas monitor or a sampling vial and back into the chamber.

Sample air flow

Part of the →chamber air that is pumped through a tubing to supply an →onsite gas monitor or a sampling vial.

Sampling date

Short time period with sufficiently homogeneous atmospheric properties within 24 hours.

Note: A sampling date will typically consist of a couple of hours related to sunrise, daytime, sunset and night time as well as to weather changes.

Signal sampling rate

The time interval a continuous signal is reduced to a discrete signal in signal processing of an →onsite gas monitor.

Site

Unit within a →location with sufficiently homogeneous properties and with several →chamber base positions.

Note: →Replicates, →pseudo-replicates or →treatments may occur within a site. A sub-level of a site may be necessary for those purposes, e.g. the subdivision of a site to various subareas ("plots", "sectors", etc.).

Static chamber (also: Non-flow-through chamber)

→Closed chamber in which the →sample air is taken out at a sample port.

Note 1: This kind of chamber is typically used when chamber / headspace air is sampled or transferred with a syringe.

Note 2: The volume of sample air is replaced by ambient air streaming through the pressure vent.

t_0

→Chamber placement time

t_1

Moment at which the first chamber air sample is taken or, in case of an →onsite gas monitor, measured.

Treatments

Optional subunits of a →site which show clearly distinct levels or level combinations of one or more factors (explanatory variable manipulated by the experimenter).

Note: With respect to GHG measurements, treatments often include different vegetation types, crops, fertilization levels or other anthropogenic management measures.

Tube delay time / Delay time

Time period that is needed for sample air transport in tubes from the chamber to an →onsite gas monitor or to a sampling vial.

Vial with stopcock

Gas sampling bottle made of glass, with 2 stopcocks and without septum.

Note: Other commonly used terms are gas collecting tube, gas sampling bulb, or separatory flask.

Volume concentration, σ

Volume of a constituent divided by the volume of the mixture. [according to IUPAC 2019; DIN 1310].

Note 1: For real gases under ambient conditions, a volume concentration of 1 ppmv almost corresponds to an →amount fraction of 1 ppmn.

Wetland

A wetland is an area that is inundated or saturated by water at a frequency and for a period sufficient to support a prevalence of vegetation typically adapted for life in saturated soil conditions (Joosten & Clarke 2002). Wetlands can consist of mineral soils but they also form organic soils such as peat in mires and peatlands.

13. LITERATURE

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